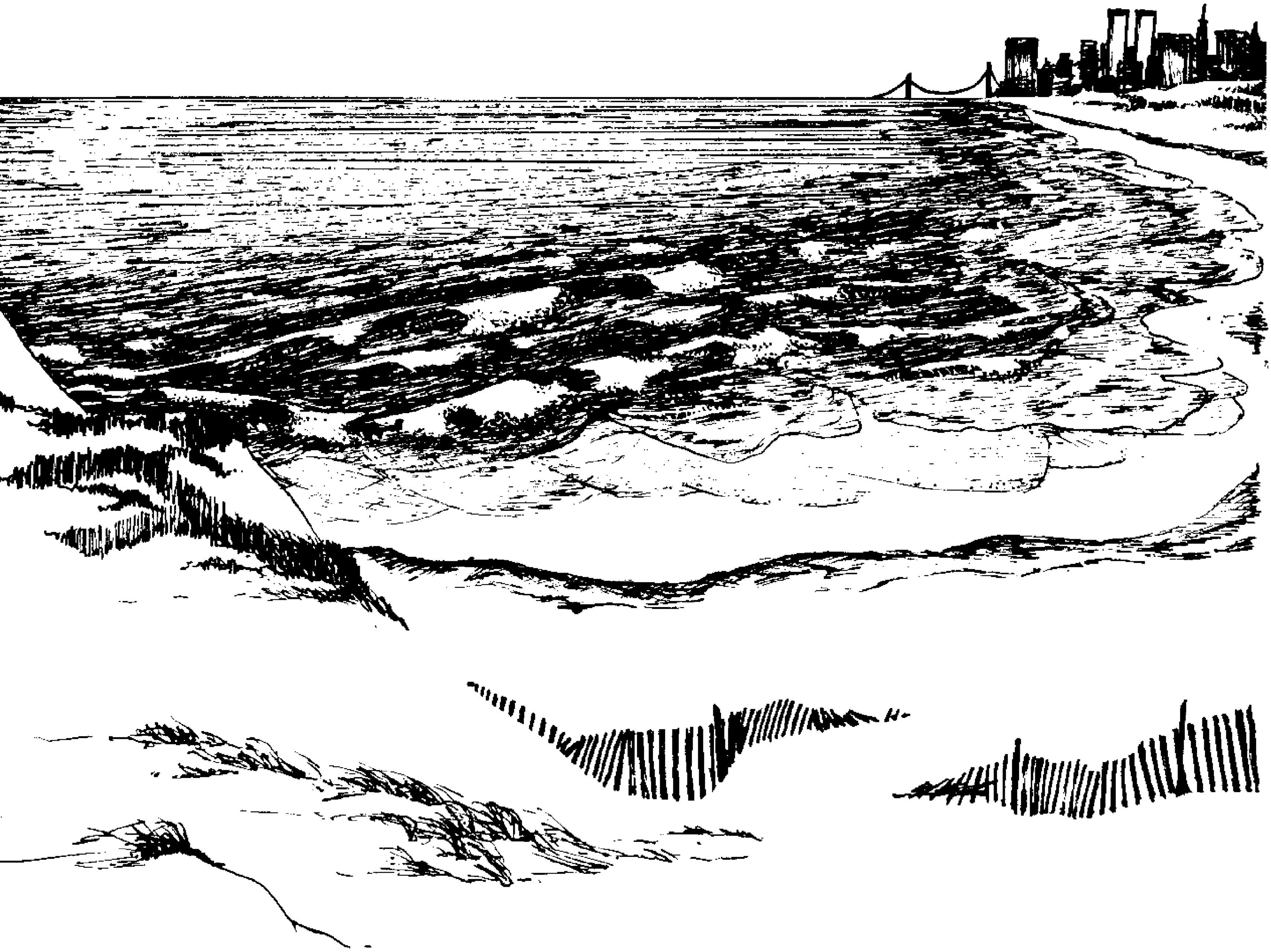
Air Quality

Volker A. Mohnen



MESA NEW YORK BIGHT ATLAS MONOGRAPH 28

The offshore water in the bend of the Atlantic coastline from Long Island on one side to New Jersey on the other is known as New York Bight. This 15,000 square miles of the Atlantic coastal ocean reaches seaward to the edge of the continental shelf, 80 to 120 miles offshore. It's the front doorstep of New York City, one of the world's most intensively used coastal areas—for recreation, shipping, fishing and shellfishing, and for dumping sewage sludge, construction rubble, and industrial wastes. Its potential is being closely eyed for resources like sand and gravel—and oil and gas.

This is one of a series of technical monographs on the Bight, summarizing what is known and identifying what is unknown. Those making critical management decisions affecting the Bight region are acutely aware that they need more data than are now available on the complex interplay among processes in the Bight, and about the human impact on those processes. The monographs provide a jumping-off place for further research.

The series is a cooperative effort between the National Oceanic and Atmospheric Administration (NOAA) and the New York Sea Grant Institute. NOAA's Marine EcoSystems Analysis (MESA) program is responsible for identifying and measuring the impact of man on the marine environment and its resources. The Sea Grant Institute (of State University of New York and Cornell University, and an affiliate of NOAA's Sea Grant program) conducts a variety of research and educational activities on the sea and Great Lakes. Together, Sea Grant and MESA are preparing an atlas of New York Bight that will supply urgently needed environmental information to policy-makers, industries, educational institutions, and to interested people.

ATLAS MONOGRAPH 28 presents what we know about the air quality of New York Bight—it is governed mainly by man-induced emission sources located inland of the Bight shoreline. Natural emissions of particulate and gaseous material from the continent and the ocean, and atmospheric chemical and physical processes also help determine the air quality of the Bight. Mohnen describes the basic processes and essential background for air pollution and estimates ambient levels of pollutant materials and their deposition rates.

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MESA NEW YORK BIGHT ATLAS MONOGRAPH **28**

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Abstract

The air quality of New York Bight is determined by anthropogenic and natural emissions of particulate and gaseous material from the continent and the ocean, and by chemical and physical processes that occur in the atmosphere. The concept of natural cycles for water, sulfur, and nitrogen containing molecules, and for suspended particulates is introduced. These highly interactive cycles (emissions—transport and chemical/physical processes—sinks) are first discussed on a global basis where assumptions can be made that they proceed until completion. Anthropogenic emissions are then treated as a perturbation in the natural cycles.

Air quality in the Bight is governed mainly by anthropogenic emission sources located inland of the Bight shorelines. Estimates are derived, using transport models, for the ambient level of pollutant material (mainly suspended particulate matter and sulfur dioxide) and for the deposition rate of pollutant material in New York Bight. While reasonably good air quality data exist from measuring stations located on land, similar data over the Bight are nonexistent.

Introduction

Air pollution is generally thought of as man-induced changes (not necessarily increases) in the atmospheric gas or particle content. Changes can occur in the concentration level of already present gases and particles, or new gaseous species or particles with different chemical composition or sizes can be introduced into the atmosphere. How to distinguish clearly between natural fluctuations and changes caused by man is a problem.

Before looking at air pollution over the New York Bight area, a brief review of what happens to natural gases and particles—focusing on the variable ones (see Table 1)—is useful. The atmospheric concentration level of variable gases and particles is governed by their source strength, their dispersion rate (transport), and their removal rate. At a given location the variation with time of any atmospheric species (gas or particle) is described by a simple "budget equation": variation of concentration with time = production rate (source strength) ± transport rate through horizontal and vertical atmospheric motions—removal rate through bacteriological, physical, or chemical processes.

Most species' sources and final *sinks* (a body or process that acts as a disposal mechanism) are the continents and the oceans. The atmosphere is a temporary holding reservoir and transport medium in which chemical or physical transformations occur, such as atmospheric cycles—the water cycle, the particle cycle, and the trace gas cycles. Each gaseous or particulate species is characterized by an average atmospheric residence time which is inversely proportional to the sum of all atmospheric removal processes acting on the particular species. It is convenient to discuss these cycles on a global scale; it can then be assumed that all cycles must proceed until completion within a finite time. Knowledge of the complete cycles is a prerequisite to understanding the physical and chemical processes that occur in New York Bight.

Water Cycle

Most fundamental is the water cycle: evaporation-condensation-precipitation. The water cycle is one determining factor in weather (short-range effect—about two weeks) and climate (long-range effect), and controls some very important trace gas cycles and the particle cycle. Furthermore, it best illustrates the significance of atmospheric transport processes on the micro-, meso-, and macroscale.

Critical in the atmospheric water cycle is condensation, the phase transition from vapor to droplets or ice crystals. Whenever the relative humidity reaches 100%, water vapor condenses on a flat surface. On the curved surfaces of suspended particles a higher relative humidity (supersaturation of water vapor) is needed to maintain a net gain of water on the particle's surface. Hence, particles in the atmosphere are important in the phase transition of water, providing either a center for condensation (cloud condensation nuclei) or a surface for sublimation (ice nuclei).

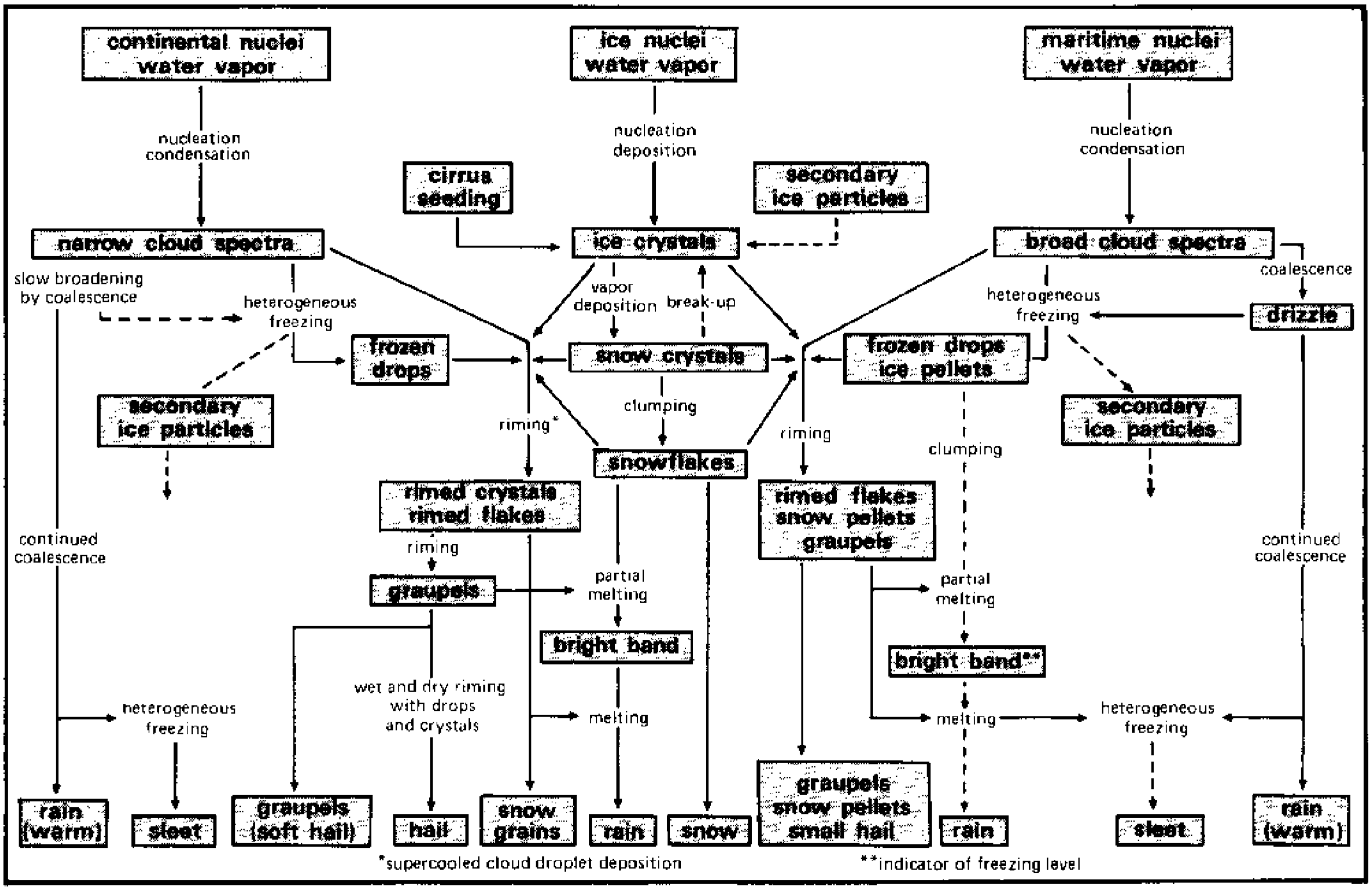
Cloud condensation nuclei are generally larger than 0.1 micron in diameter. Almost any particle can act as a condensation center, but *hygroscopic particles* (those with an affinity for water), such as sea salt, are preferred over *hydrophobic particles* (those with no affinity for water).

Only a very few particles in the undisturbed atmosphere can act as ice nuclei—on the order of 1/1,000 cm^3 (1/61 in^3) of air. The main determining factor is the chemical composition and crystal structure of the particle's surface rather than its size.

Cloud and precipitation elements provide the major, final removal process for many trace gases and for suspended particles. Figure 1 summarizes most precipitation elements and how they originate and grow; Figure 2 presents the size spectrum for various cloud and precipitation elements.

The two main processes by which cloud droplets grow into raindrops or snow crystals are:

1. collision of cloud droplets (*coalescence*) until a raindrop evolves that is large enough to overcome the updraft within a cloud and fall to the ground;



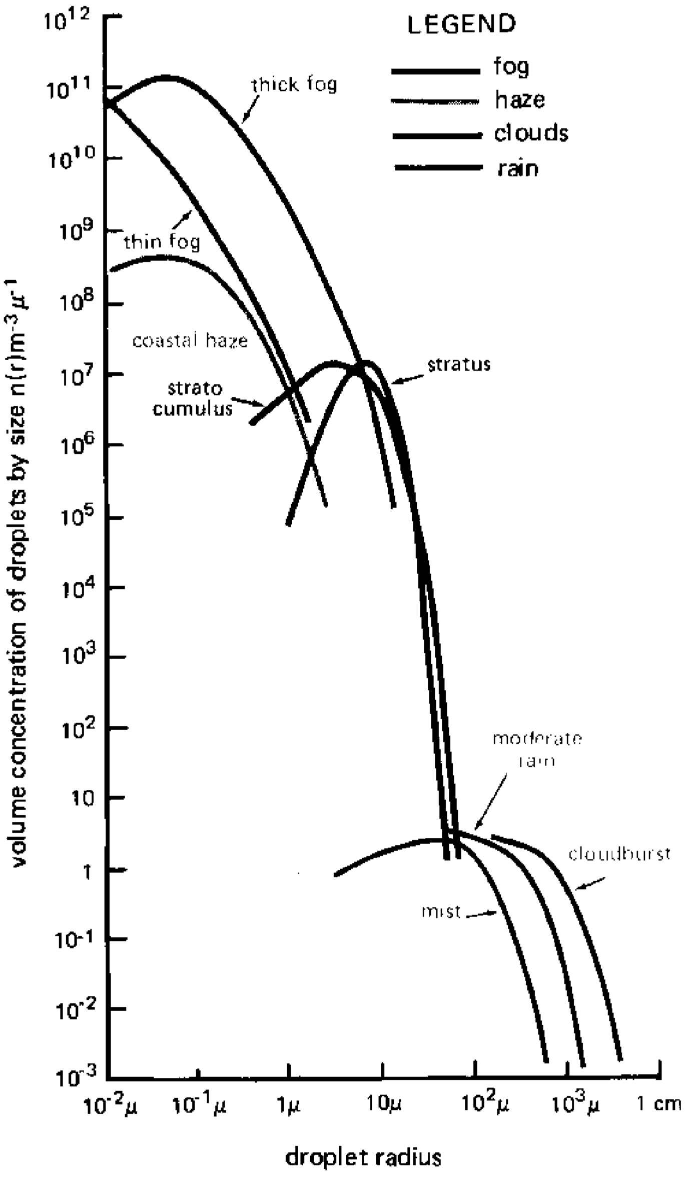
Source: Braham and Squires 1974

Figure 1. Major precipitation elements and processes

2. supercooled cloud droplets (ambient temperature is below 0°C or 32°F) become ice crystals; since the vapor pressure over ice is lower than the vapor pressure over supercooled liquid water, the ice crystal continues to grow by water vapor transfer from neighboring supercooled cloud droplets or by direct collision with supercooled cloud droplets.

Particle Cycle

Intimately connected with the water cycle is the particle cycle. The global source strength for particles introduced into the atmosphere has been estimated at 3 x 10^{10} metric tons/yr. Natural sources of particles with diameters larger than about 0.1 micron are the continents and the oceans. Therefore the *continental aerosol* and the *maritime aerosol* are generally spoken of. An aerosol is a suspension of fine solid or liquid particles in gas. Soil particles carried aloft by atmospheric motions are dispersed over a wide geographical area. Prospero (1972) found that in huge "dust clouds," that apparently originated from the Sahara, the mass transport of dust originating from the African continent through the longitude of Barbados in the trade wind belt, is between 20 and 40 million metric tons annually.



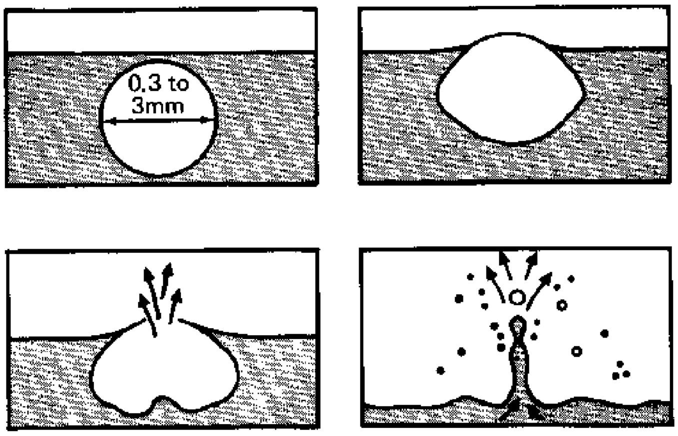
Source: Edwin Berry, personal communication

Figure 2. Water droplets: volume concentration by size

The elemental composition of the continental aerosol is, in decreasing order of abundance: silicon, aluminum, iron, sodium, potassium, and calcium. The maritime aerosol (Figure 3) is formed when tiny air bubbles breaking at the ocean surface produce water jets that inject water droplets into the air above the ocean, and after evaporation, create salt particles (seawater contains about 3% sodium chloride). Chlorine, sodium, sulfate, magnesium, and calcium are the main constituents of the maritime aerosol. There is considerable overlap of the aerosols near coastal areas.

Particles smaller than 0.1 micron in diameter generally originate from *nucleation processes* (a phase transition not requiring the presence of any surfaces) involving low *volatility* (vapor pressure) gases. This gas-to-particle conversion will be discussed later in conjunction with the trace gas cycles.

The atmospheric aerosol, ranging in size from 0.002 micron to 100 microns in diameter, is constantly moving and changing, governed by physical and chemical laws. First, *Brownian diffusion* (random motions of small particles suspended in air) causes a spatial displacement of particles. Since the diffusion coefficient is inversely proportional to the radius, particles smaller than 0.5 micron radius have an increasingly larger displacement, and particles larger



Source: Williamson 1973

Figure 3. Sea salt aerosol formation

than 0.5 micron radius have a negligibly small displacement. Small particles interact with large particles in a process known as *thermal coagulation.* Every collision of two particles creates one new and larger particle.

The coagulation process in general has a time constant; that is, in an aerosol containing particles of all sizes but equal concentrations per size interval, the small ones coagulate rapidly with the big ones. In time, the small-size fraction completely disappears if there is no replenishment of the small particles. The number density decreases, but the atmospheric mass-loading remains unchanged.

Second, gravitational sedimentation causes a constant downward flux of particles to the earth's surface. The sedimentation velocity is proportional to the radius; hence, only particles much larger than 0.5 micron are depleted from the atmospheric aerosol by this process. The larger the particle, the higher its sedimentation velocity, and, as a rule, the shorter its residence time in the atmosphere. This process decreases the atmospheric mass-loading, constituting a true sink.

Third, cloud and precipitation elements act as scavengers for particles. The air moves around cloud droplets and keeps them in suspension in spite of their high sedimentation velocity. Large particles cannot follow the streamlines around the cloud droplet due to their high inertia, and so collide with it. Small particles have enough Brownian motion to cause them to be intercepted by and incorporated into cloud droplets. Clouds, therefore, act like giant vacuum cleaners removing particles from the air. A nonprecipitating cloud, however, provides only a pseudosink. After evaporation (the average lifetime of a cloud droplet is about one hour), all collected particles remain as one single particle, larger in size and probably chemically altered. This single particle can be more easily activated as cloud condensation nuclei, or, at least, it will have a higher sedimentation velocity.

A precipitating cloud effectively returns collected particles to the earth's surface. As raindrops fall, they continue to collect particles that cannot escape collision because of high inertia. Rain does not consist of pure water but reflects the chemistry of the atmospheric aerosol. World-wide, 75% of the atmospheric particle mass is returned to the earth's surface by precipitation and only 25% by dry deposition. Precipitation also constitutes a significant sink process for pollutant material deposited within the Bight area. However, since detailed knowledge of precipitation quality is missing for the Bight area, the percentage of dry versus wet deposition cannot be stated at this time.

Table 1. Composition of undisturbed atmosphere near sea level

Constituent	Chemical Formula	Percent by Volume	Parts per Million by Volume
Permanent gases			
Nitrogen	N_2	78.084	780,900
Oxygen	O_2	20.946	209,400
Argon	Ar	0.934	9,300
Neon	Ne		18.2
Helium	He		5.2
Krypton	Kr		1.1
Hydrogen	H_2		0.5
Nitrous oxide	N_2O		0.3
Xenon	Xe		0.09
Variable gases			
Water vapor	H_2O	0-7	
Carbon dioxide	CO_2	0.032	315
Methane	CH_4		$\sim$1.5
Hydrocarbons other than Methane			$<$0.010
Carbon monoxide	CO		$\sim$0.1
Ozone	(stratospheric source) O_3		$\sim$0.02 up to 0.1
Ammonia	NH_3		$\sim$0.01
Nitrogen dioxide	NO_2		$\sim$0.001
Sulfur dioxide	SO_2		$\sim$0.0002
Hydrogen sulfide	H_2S		$\sim$0.0002

Particles

all sizes from 0.002-100 micron diameter

$\sim$500 particles/cm^3 over oceans

$\sim$1000 particles/cm^3 over land

The various size discriminatory processes for pseudo- or true sinks govern *atmospheric particle size distribution* (number of particles per size interval): the larger the particle, the lower the number concentration. Above 0.5 micron diameter, the particle number concentration decreases roughly by three to four orders of magnitude for each increase in particle diameter by one order of magnitude. This relationship between particle size and number concentration holds for both the continental and maritime aerosols, although the total number of all particles in the two aerosol types is different (see Table 1). In general, the atmospheric particle size distribution on a graph shows a peak around 0.1 micron (continental) and 0.5 micron (maritime) diameter. Particles smaller than 0.1 micron are efficiently removed by their diffusion, particles larger than 1 micron by their sedimentation: this indicates that the various removal processes do not efficiently affect the particles between 0.1 and 1 micron diameter. About one-half of all particles in the atmosphere are sufficiently large (greater than 0.1 micron) to act as cloud condensation nuclei. There are enough of these particles to provide a smooth transition from water vapor to liquid.

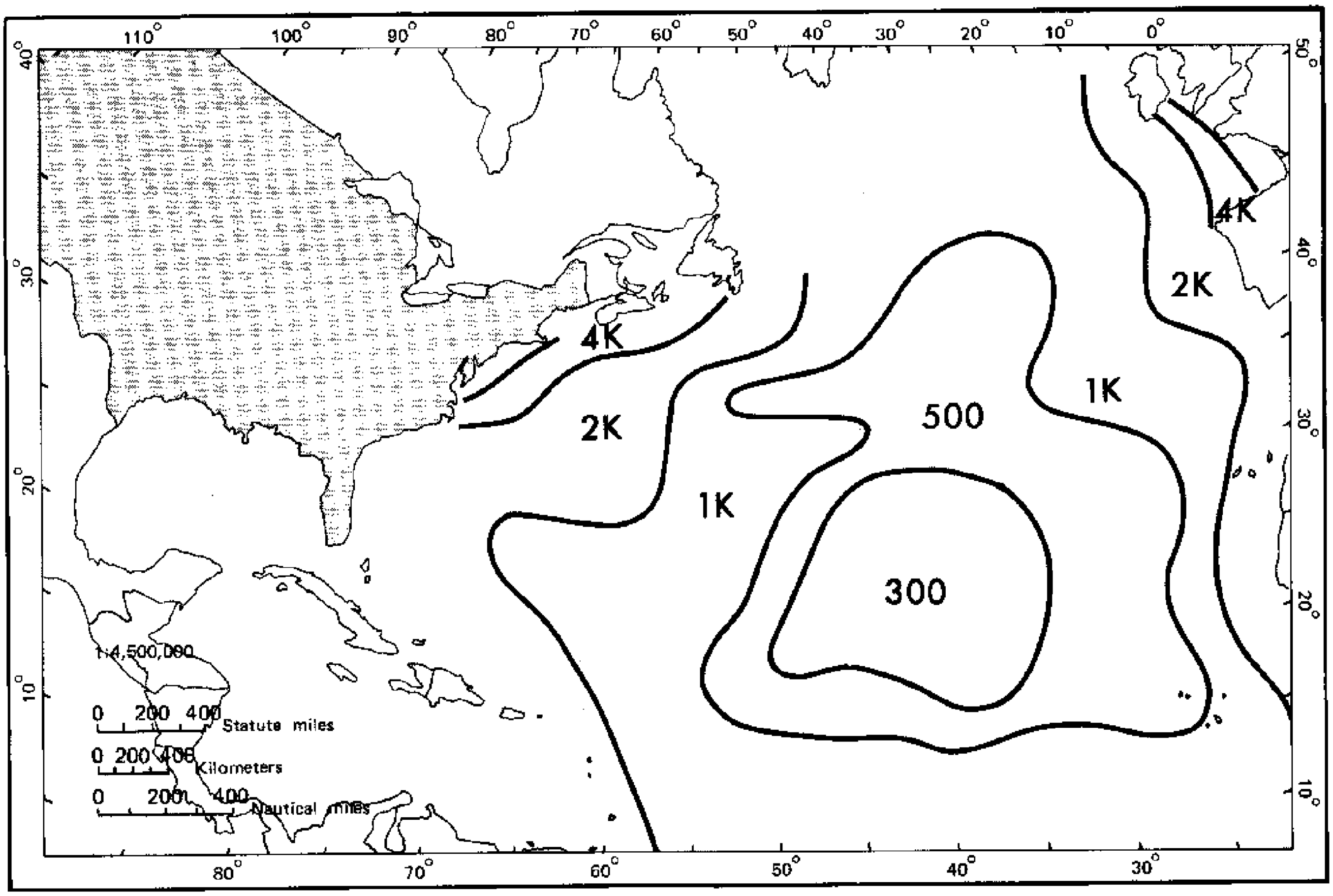
Because the removal rate of aerosols is so closely controlled by weather phenomena, considerable fluctuations in atmospheric particle concentrations are expected. One particle concentration measurement from one particular region is as meaningless for establishing a representative value as a set of weather observations taken on one particular day is for describing a region's climate. Years of observational data must be obtained and properly analyzed to establish an aerosol climatology. Map 1 shows the first results of such an aerosol climatology, from six years of daily observations over the North Atlantic. The greater source strength of the continents is quite pronounced.

Trace Gas Cycles

Atmospheric trace gases form three main cycles: the carbon cycle—methane to carbon monoxide to carbon dioxide; the nitrogen cycle—ammonia to nitrogen dioxide to nitrous oxide; and the sulfur cycle—hydrogen sulfide to sulfur dioxide and/or dimethyl sulfide.

One source of trace gases is bacteriological decay. For methane, ammonia, nitrogen dioxide, nitrous oxide, hydrogen sulfide, and dimethyl sulfide,

Map 1. Mean Aitken nuclei concentrations, 1966-71



Note: Mean Aitken nuclei concentrations, 1966-1971. Observations most frequent along 40° N and along major great circle trade routes; highest mean values found in regions generally characterized by persistent high pressure systems, lowest in mid-ocean.

Transverse Mercator Projection

Source: Hogan, Mohnen, and Schaefer 1973 bacteriological decay represents the only natural source. After these gases are emitted into the atmosphere, dispersed, and redeposited at the soil surface, decomposition proceeds through many types of soil bacteria. However, the bulk of emitted trace gases participate in numerous complex atmospheric chemical reactions, generating a host of new intermediate chemical species. In the atmosphere all these reactions are competitive. Such a chemical ecosystem is very sensitive to changes in concentration of any reactant gas as far as the products formed are concerned.

The carbon cycle does not interact directly with the water cycle. The gas-phase oxidation of methane eventually leads to carbon monoxide and water. Scientists today believe that this oxidation process represents a major natural source of carbon monoxide (Wolfsy, McConnell, and McElroy 1972), with minor contributions from oceans. Further oxidation transforms carbon monoxide into carbon dioxide, the end product. Some carbon monoxide is also consumed by soil bacteria after absorption at the surface. The atmospheric oxidation of carbon-containing molecules moves very slowly, limited by the extremely low concentration of the "oxidation agent," identified as the hydroxyl radical OH. This results in a rather long residence time (at least five months) in the atmosphere for methane and carbon monoxide.

Carbon dioxide is chemically rather inert and thus does not participate in any gas-phase chemical reactions. Its major source is the warm oceans of the world; its major sink is the cold parts of the oceans. The atmospheric concentration of carbon dioxide is on the order of 315 parts per million (ppm). With a sea surface pH of 8.1 (slightly alkaline) and a temperature of 10°C (50°F), the partial pressure of carbon dioxide above the surface in equilibrium with dissolved carbon dioxide corresponds to a concentration of only 230 ppm. Hence, the atmosphere is supersaturated, and carbon dioxide is continuously absorbed and dissolved in the ocean. On the other hand, if the ocean temperature is 25°C (77°F), the partial pressure of carbon dioxide above the ocean surface in equilibrium with dissolved carbon dioxide corresponds to a concentration of 415 ppm. Thus, there is a continuous flux of carbon dioxide from the ocean into the atmosphere. Atmospheric transport replenishes or removes the dissolved or released carbon dioxide; the much slower ocean currents transport the dissolved carbon dioxide in the hydrosphere. An estimated 14.8 x 10^{10} metric tons/yr of carbon dioxide are released by tropical oceans; an estimated 5.5 x 10^{10} metric tons/yr are dissolved in the northern hemisphere oceans; and 9.1 x 10^{10} metric tons/yr in the southern hemisphere oceans.

Plant decay, with a global source strength of 6.3 x 10^{10} metric tons/yr, is another major source of atmospheric carbon dioxide; plant growth represents a sink, removing an estimated 6.5 x 10^{10} metric tons/yr. The resulting atmospheric residence time for carbon dioxide is uncertain—roughly two to eight years.

The nitrogen and sulfur cycles involve liquid-phase reactions, gas-phase chemical reactions, and gas-solid chemical interactions. The complex system is summarized below.

Liquid-phase reactions are represented by cloud and precipitation elements. Gases dissolve in clouds and raindrops and eventually dissociate: gases such as carbon dioxide and ammonia form ions in solution; their solubility is strongly dependent on pH value.

In the absence of any other trace gas but carbon dioxide, cloud or rain droplets would have these characteristics at 10°C (50°F):

pH = 5.6
CO_2 x H_2O = 0.71 μg/cm^3 of water
(calculated as dissolved carbon dioxide)
HCO_3^- = 0.14 μg/cm^3 of water
$CO_3^=$ = 0.19 x 10^{-5} μg/cm^3 of water.

An ammonia concentration of 3 μg/cm^3 in the atmospheric system will alter the above chemical composition to:

pH = 7
NH_3 x H_2O = 1.2 x 10^{-3} μg/cm^3 of water
(dissolved ammonia)
NH_4^+ = 2.6 μg/cm^3 of water
CO_2 x H_2O = 0.71 μg/cm^3 of water
HCO_3^- = 3.3 μg/cm^3 of water
$CO_3^=$ = 1 x 10^{-3} μg/cm^3 of water.

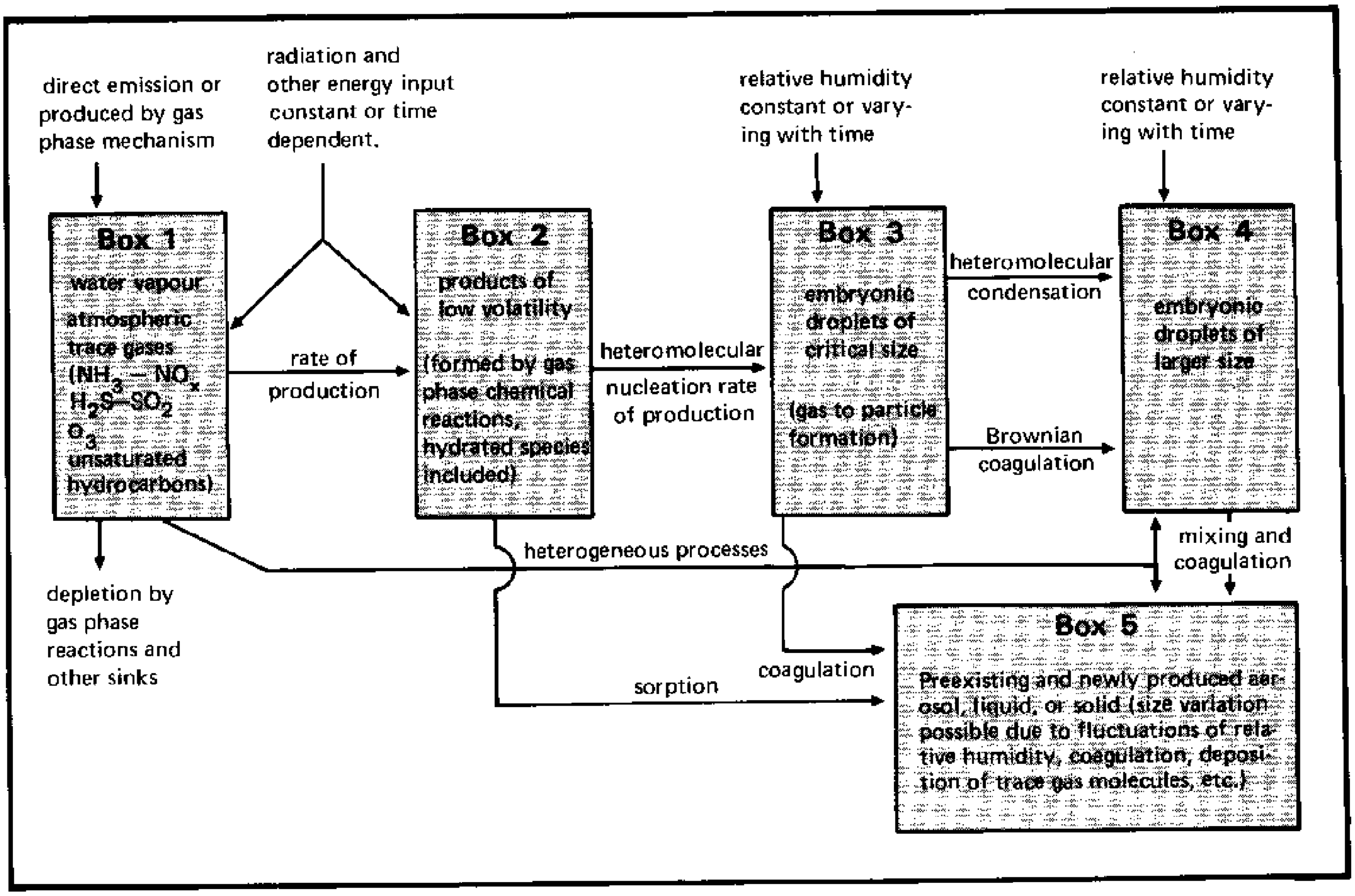
In this system of carbon dioxide, ammonia, and suspended cloud droplets with a liquid water content of 1 g/m^3 (typical for a well-developed cloud), the gaseous concentration of ammonia is reduced by about 90%; the gaseous carbon dioxide equilibrium concentration of 315 ppm hardly changes at all. Since pH values of 5 to 6 (slightly acid) are typical for precipitation in the unperturbed atmosphere, other trace gases in the atmosphere must, after solution in the cloud droplets, interact chemically with the already dissolved gases and ions to reduce the pH from 7 to 5 or 6. There is strong experimental proof that atmospheric sulfur dioxide and nitrogen dioxide are responsible for this pH reduction (Likens and Bormann 1974). These gases are dissolved and then irreversibly react with other materials in cloud water.

The liquid-phase oxidation of sulfur dioxide is also very pH sensitive. In pure water, the oxidation rate is negligible. However, ammonia ions act like a catalyst and enhance the chemical transformation to sulfate ions; thus, ammonia is the controlling factor. Other known catalysts, such as dissolved metal ions of manganese or iron, can considerably enhance the sulfur dioxide oxidation rate in cloud and precipitation elements. These catalysts are present in the natural continental aerosol collected by cloud droplets.

Ammonium sulfate and ammonium nitrate are formed from this liquid-phase removal process. The detailed chemistry, however, is not yet fully understood.

Gas-phase reactions. Ozone plays an important role in the overall chemical transformation of atmospheric trace gases. Low volatility gases produced in the transformation process can nucleate and form minute particles called *Aitken nuclei* (Figure 4). There is evidence that nucleation takes place in the atmosphere and is responsible for the existence of most particles less than 0.1 micron diameter. If there are cloud droplets or preexisting aerosols, then the low volatility products can condense on those surfaces. Once Aitken nuclei are formed, they are scavenged by larger aerosol particles and cloud droplets.

The overall effect of nucleation and condensation is that about 75% of the total atmospheric sulfur and nitrogen compounds are returned to the ground by precipitation. As a global (unperturbed) average, sulfates in rainwater amount to about 1 to 2 $\mu g/cm^3$ of water over oceans and about 3 $\mu g/cm^3$ of water over continents. The average global concentrations of ammonium ion and nitrogen trioxide ion vary considerably—0.001 to 1 $\mu g/cm^3$ and 0.1 to 1 $\mu g/cm^3$ respectively.



Source: Kiang et al 1973

Figure 4. Transition of gaseous products into solid or liquid particles

The nonmethane hydrocarbon cycle (mainly turpenes) is believed to initially involve gas-phase chemical reactions. The resulting low volatility products then follow the reaction scheme shown in Figure 4. It is estimated that 60% of the total nonmethane hydrocarbon emissions from vegetation (about 10^9 metric tons/yr) undergo this phase transition—preceded by complex chemical reactions—and form minute particles (Rasmussen 1972). The phase transition is enhanced in the presence of sulfur dioxide and nitrogen dioxide. Once in the particulate state, the removal processes are the same as those discussed earlier.

Urban Atmospheres

Numerous complex and competitive processes establish a pseudo-equilibrium for every atmospheric constituent—a chemical balance between sources and sinks. This balance is reflected in the concentration level and the chemical and physical nature of particular constituents. Any disturbance, natural or man-made, will propagate through the physical and chemical system and cause alteration in observable parameters, such as precipitation rate and chemistry, particle concentration and chemistry. The tolerable degree of disturbances caused by increased man-made emissions (gaseous and solid material, heat) into the atmosphere is still strongly debated. Historically, the problem of "How much is too much?" has been attacked primarily by establishing maximum atmospheric concentration levels for a few species (suspended particulates, sulfur dioxide, carbon monoxide, oxides of nitrogen, and total oxidants) known to impair human health.

For example, the New York State ambient air quality standards applicable to the shoreline of New York Bight for sulfur dioxide are (New York State Department of Environmental Conservation 1976):

1. during any 12 consecutive months, 99% of the 1-hr average concentration shall not exceed 0.25 ppm (650 $\mu g/m^3$) and no 1-hr average concentration shall exceed 0.50 ppm (1,300 $\mu g/m^3$);
2. during any 12 consecutive months, 99% of the 24-hr average concentrations shall not exceed 0.10 ppm (260 $\mu g/m^3$) and no 24-hr average concentration shall exceed 0.14 ppm (365 $\mu g/m^3$); and
3. during any 12 consecutive months, the annual average of the 24-hr average concentrations shall not exceed 0.03 ppm (80 $\mu g/m^3$).

There are, however, increasing efforts to broaden the criteria to include *anthropogenic effects* (influenced by man's impact on nature) on the total environment.

Understanding of cause-effect relationships for the perturbed atmospheric interacting system is essential before formulating any meaningful management plan or air quality strategy. Figure 5 shows possible propagation paths among atmospheric constituents. For example, cloud properties can be influenced by particles in several ways. Additional cloud condensation nuclei (Box 6) raise the cloud drop concentration (Box 8) and therefore, other things being equal, reduce the average size of the cloud drops. This bears directly on the efficiency of coalescence and thus on rain formation. Addition of ice nuclei (Box 7) increases the concentration of ice crystals (Box 9) in a cloud at temperatures below zero. Addition of trace gases (Box 1), such as sulphur dioxide, alters the chemistry of cloud droplets and ultimately the chemistry of rain. Particle properties can be modified by addition of reactive atmospheric trace gases (Box 1). After gas-phase reactions (Box 2), they either nucleate and increase the population of particles (Box 5) and through coagulation change the bulk or surface chemistry of larger particles (Box 6), or the gaseous products of low volatility (Box 2) can condense on preexisting aerosols.

A closer look at the atmospheric aerosol system (Figure 6) reveals characteristics typical of urban aerosols. The three "modes" in the aerosol size distribution—transient nuclei or Aitken nuclei range, accumulation range, and mechanically generated aerosol range—are a result of the different origin of particles and the interaction between particles. In contrast to this trimodal distribution, "pure" ocean air has a unimodal size distribution.

Incomplete knowledge of physical or chemical parameters for the individual transformation processes in Figure 6 prevents us at this time from performing a complete systems analysis that would predict the output (sink) for any given input data (source). Thus, the question "How much is too much?" remains unanswered. However, anthropogenic effects are clearly observable in almost any "polluted" area. For example, Table 2 shows average changes in climatic elements caused by increased emissions.

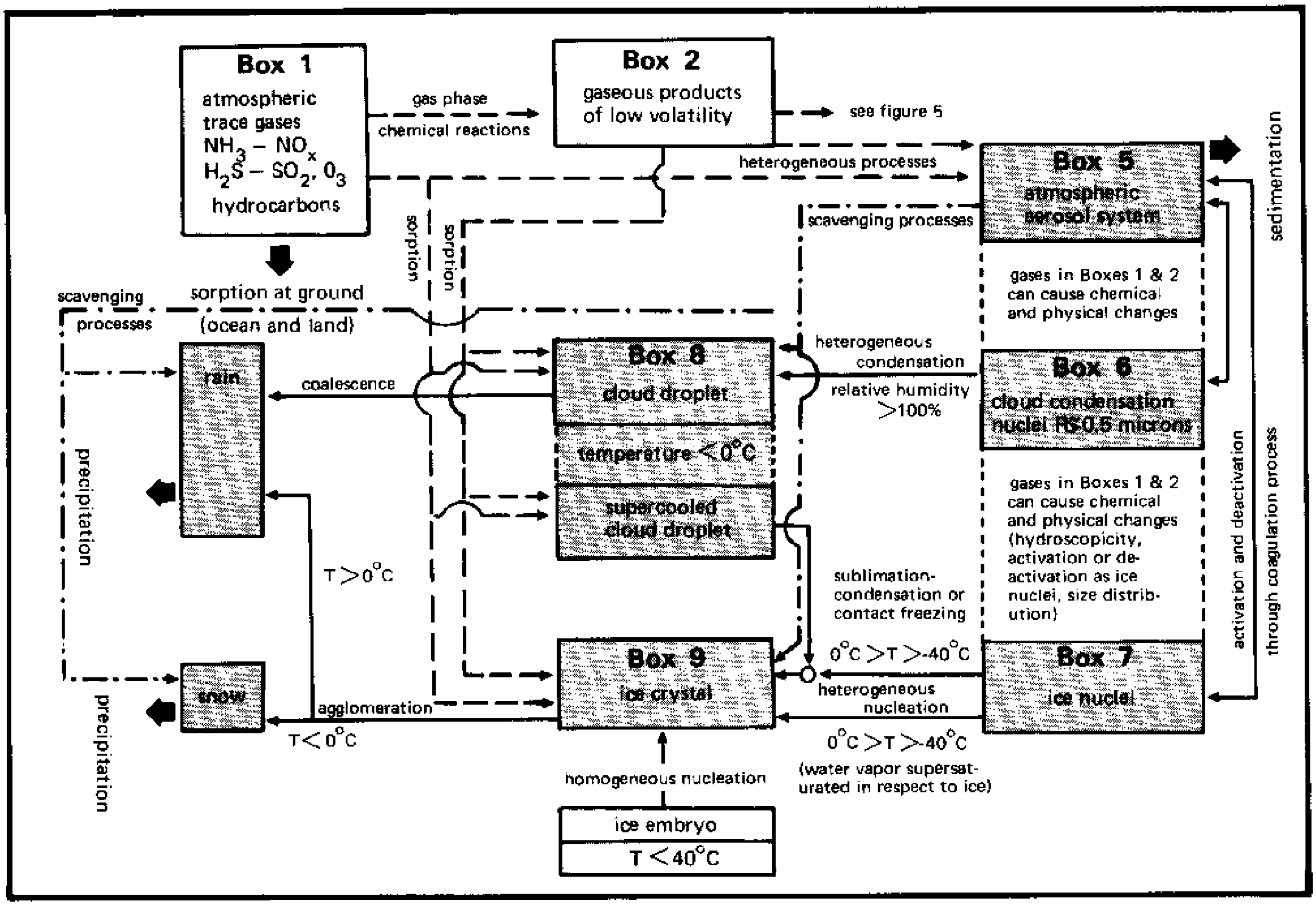
Primary Emissions

Most anthropogenic emissions result from fossil fuel combustion (coal and oil). The local source strength of particulate matter, carbon dioxide, carbon monoxide, sulfur dioxide, oxides of nitrogen, and nonmethane hydrocarbons is substantially increased. On a world-wide average, however, natural emissions are still dominating man-made contributions (Table 3).

New York Bight coastal areas are heavily industrialized and represent one of the largest emission sources in the United States. For instance, the total 1970 emissions for the Cape May, NJ, to Connecticut area (Table 4)—roughly 80 km (50 mi) deep and 320 km (200 mi) long—were:

carbon monoxide	8,053,428 metric tons
hydrocarbons	1,679,292 metric tons
oxides of nitrogen	1,505,782 metric tons
sulfur dioxide	1,214,014 metric tons
particulate matter	351,887 metric tons

After release into the atmosphere from point and area sources, these constituents are dispersed horizontally and vertically by air currents and winds. The resulting ambient concentration depends upon distance from the source, wind speed and direction, and dispersion capability. From emissions, meteorological processes (such as dilution, transport, scavenging), and redeposition at the sea and land surface evolves a particular ambient gas or particle concentration.

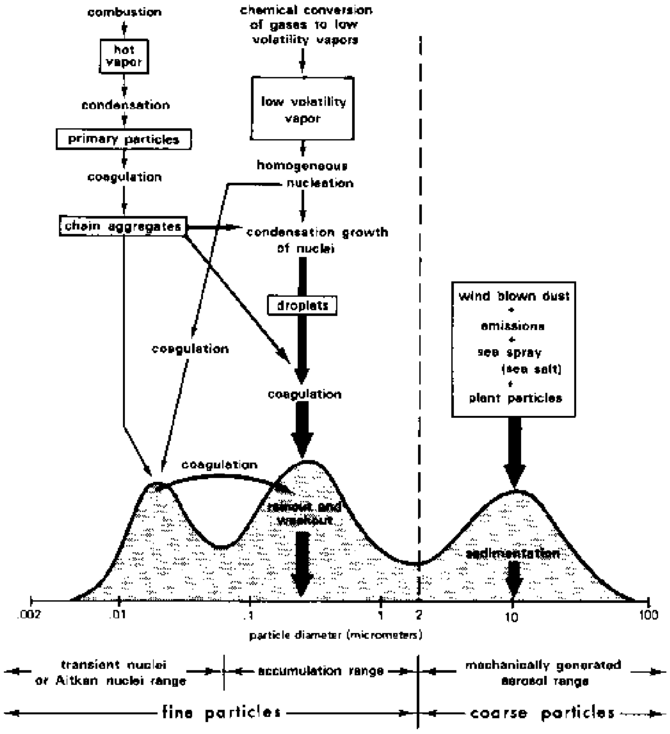


Source: Mohnen 1973

Figure 5. Water cycle block diagram

The 1973 ground-level concentrations for suspended particulates and sulfur dioxide measured from all stations within an 129 km (80 mi) strip inland of the Bight are presented in Maps 2 and 3. No measurements have been made over any water area. As expected, highest ground-level concentrations are found in areas of highest emission. Because of limited stations, *isolines* (lines of equal concentrations) in Maps 2 and 3 are estimates only. The 50 $\mu g/m^3$ isoline in both maps follows the Bight shoreline, except in the vicinity of New York City.

Air quality trends for total suspended particulates at New York State stations are shown in Figure 7. The statistically significant downward trend for particulates in the atmosphere over the past decade reflects the reduction in emission levels. Similar downward trends for suspended particulates presumably exist in New Jersey since their emission control efforts parallel those of New York State. Most astonishing is the increase in nitrates in the aerosol (Figure 8), despite controls to reduce nitrogen oxide emissions. This phenomenon has been confirmed for all stations in New York State. No satisfactory explanation for this trend is available at present. However, it shows the extreme complexity of atmospheric chemical reactions (nitrates are formed in the atmosphere) that can result from an increase in a reaction product's concentration while the precursor concentration (oxides of nitrogen) and the concentration of some other gases remain constant or even decrease. Unfortunately, there is little information on the elemental composition of the suspended aerosol. From long-term measurements taken at other US locations (National Academy of Sciences 1972), however, we can safely conclude that this anthropogenic aerosol (Table 5) contains lead as well as bromine, zinc (mainly from car exhaust), traces of vanadium, cadmium, manganese, iron (from oil and coal combustion), and sodium (from sea salt). As mentioned earlier, some of these elements can act as catalyzers for enhancing sulfur dioxide oxidation into liquid-phase sulfates.



Source: Whitby 1975

Figure 6. Atmospheric aerosol surface area distribution

Table 2. Average changes in climatic elements, caused by urbanization

Element	Comparison with Rural Environment
Contaminants	
condensation nuclei and particles	10 times more
gaseous admixtures	5 to 25 times more
Cloudiness	
cover	5 to 10 times more
fog—winter	100% more
fog—summer	30% more
Precipitation	
totals	5% to 10% more
days with less than 5 mm	10% more
snowfall	5% more
Relative humidity	
winter	2% less
summer	8% less
Radiation	
global	15% to 20% less
ultraviolet—winter	30% less
ultraviolet—summer	5% less
sunshine duration	5% to 15% less
Temperature	
annual mean	0.5° to 1.0° C more
winter minima (average)	1° to 2° C more
heating degree days	10% less
Wind speed	
annual mean	20% to 30% less
extreme gusts	10% to 20% less
calms	5% to 20% more

Source: Landsberg 1970

Air quality trends for sulfur dioxide, nitrogen dioxide, nitric oxide, total hydrocarbons, and carbon monoxide at Roosevelt Island and Eisenhower Park are presented in Figure 9. Though the trend from these two urban stations may be representative for the Bight coastal area, the actual values are, of course, different (and probably lower) at other locations. Control measures have certainly had a visible impact on the ambient concentration level of sulfur dioxide, nitrogen dioxide, and possibly nitric oxide and carbon monoxide, however, the number of automobiles has increased over the past four years. Since car emissions contribute mostly to the carbon monoxide burden of the atmosphere, there seems to exist an obvious explanation for the upward trend in ambient carbon monoxide levels.

A slight upward shift in sulfur dioxide concentrations since November 1973 is noticeable. The impact of the energy crisis on air quality in the New York metropolitan area—that is, the use of high sulfur content fuel and reconversion of oil-fired to coal-fired plants—seems real. An Environmental Protection Agency (EPA) study (1974) showed that the use of high sulfur content fuels caused higher concentrations at sites where sulfur dioxide levels are most frequently influenced by power plant emissions. Roosevelt Island, for example, showed an increase of 18% in sulfur dioxide concentration between winter 1972-73 (0.038 ppm annual concentration) and winter 1973-74 (0.045 ppm). The overall concentration levels for the Bight coastal area did not change significantly, however.

At this point some simplified conclusions can be drawn from our assessment of air quality in the Bight coastal region. First, the ambient annual ground-level concentration for total particulate matter (measured as mass per unit volume) reflects proximity to fixed and mobile emission sources. Emissions, meteorological processes (such as transport, dilution, removal by cloud and precipitation elements), and redeposition establish a complex annual concentration pattern. An isoline could be drawn every year, roughly following the Bight shore, as on Map 2 for 1973. For 1975, an estimated 10% reduction in particulate matter emissions translates directly into a 10% reduction in the ambient air quality (all other meteorological factors remaining constant). This means that along the Bight shores an annual ground-level concentration between 45 and 50 $\mu g/m^3$ can be expected.

Second, the ambient annual ground-level concentration for sulfur dioxide reflects the proximity to fixed point sources (major oil- or coal-fired power plants) and fixed area sources (oil heating of houses). Emissions, meteorological processes (such as transport, dilution, and atmospheric chemical transformations), and deposition establish another complex concentration pattern. Again, an isoline could be drawn each year, roughly following the Bight shores, as on Map 3 for 1973. An estimated reduction by at least a factor of two in ambient concentration has been documented between 1970 and 1973, but virtually no change took place between 1973 and 1975. This means that along the Bight shores an annual ground-level sulfur dioxide concentration of 0.006 ppm or 8 to 16 $\mu g/m^3$ can be expected.

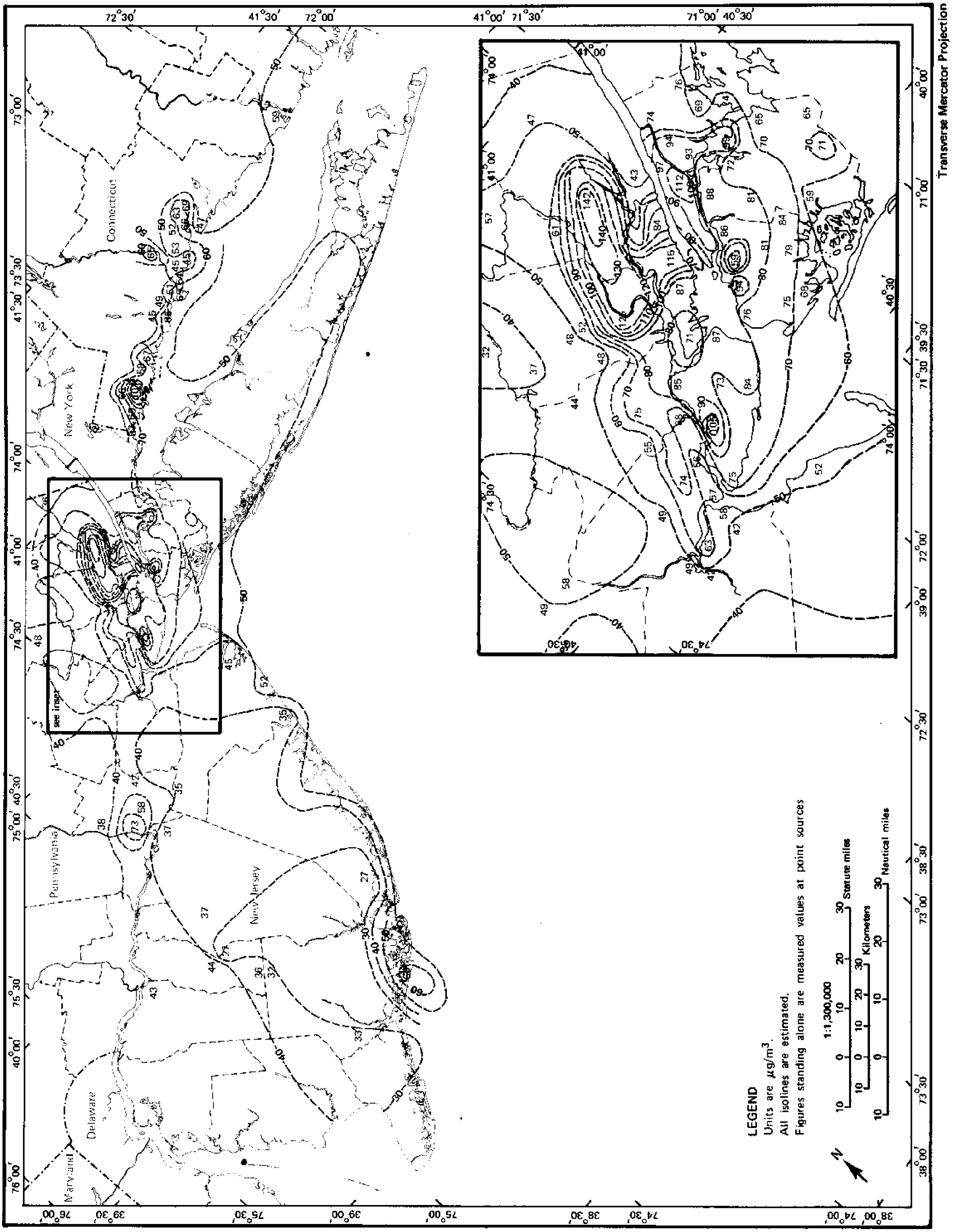
Table 3. Global summary of source strengths for atmospheric particulate matter

Source	Strength (Tg*/yr) Natural	 Anthropogenic
Primary particle production	**1,207**	**92**
Fly ash from coal	–	36
Iron and steel industry emissions	–	9
Nonfossil fuels (wood, mill wastes)	–	8
Petroleum combustion	–	2
Incineration	–	4
Agricultural emission	–	10
Cement manufacture	–	7
Miscellaneous	–	16
Sea salt	$\sim$1000	
Soil dust	200	
Volcanic particles	4	
Forest fires	3	
Gas-to-particle conversion	**1,105**	**204**
Sulfate from hydrogen sulfide	204	–
Sulfate from sulfur dioxide	–	147
Nitrate from oxides of nitrogen	432	30
Ammonium from gaseous ammonia	269	–
Organic aerosol from turpenes, hydrocarbons, and others	200	27
TOTAL	**2,312**	**296**

*Tg—terra grams
= 10^{12}grams
= 10^6 metric tons

Source: Charlson 1973

Map 2. Suspended particulates: ambient ground-level concentration, 1973



Map 3. Sulfur dioxide: ambient ground-level concentration, 1973

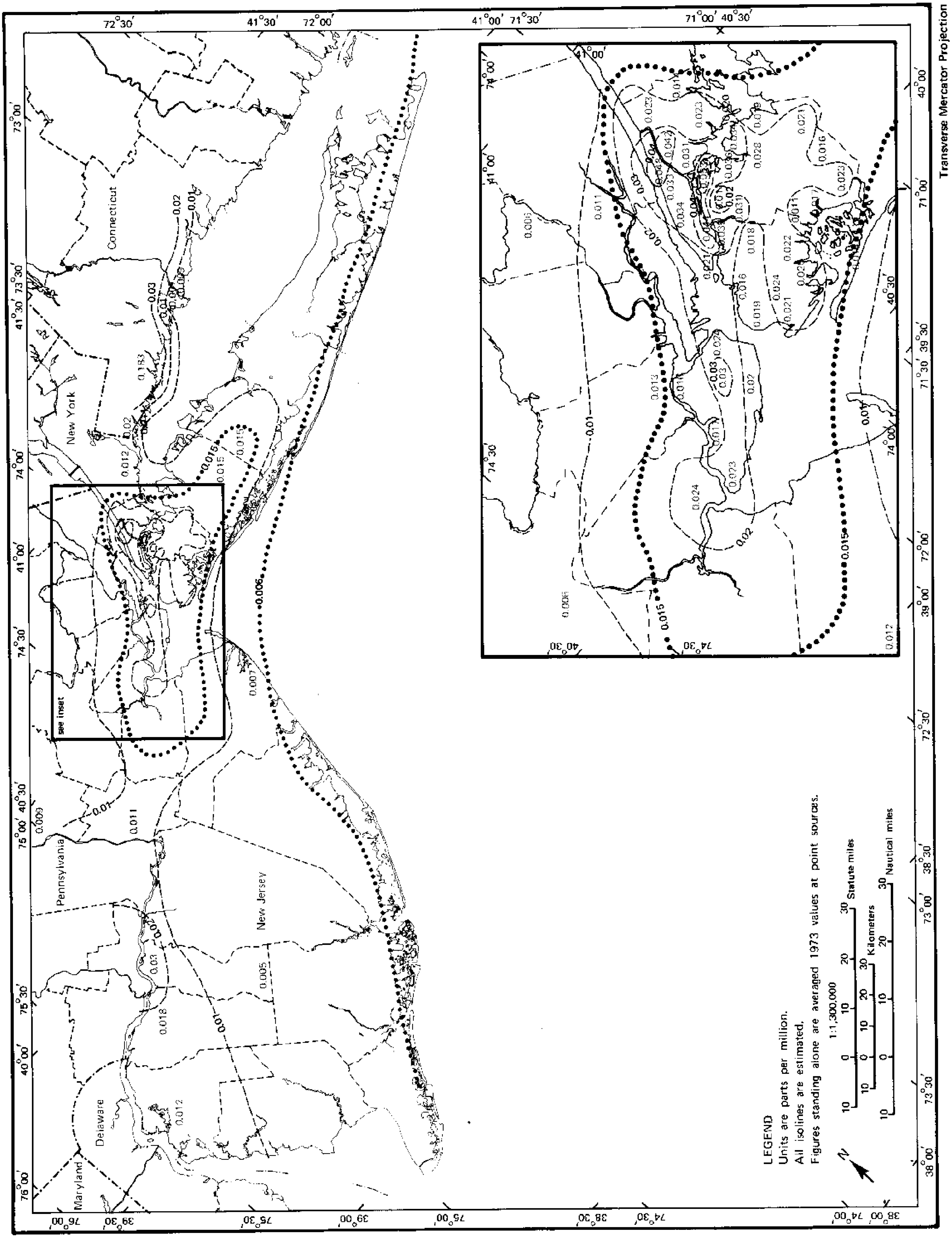


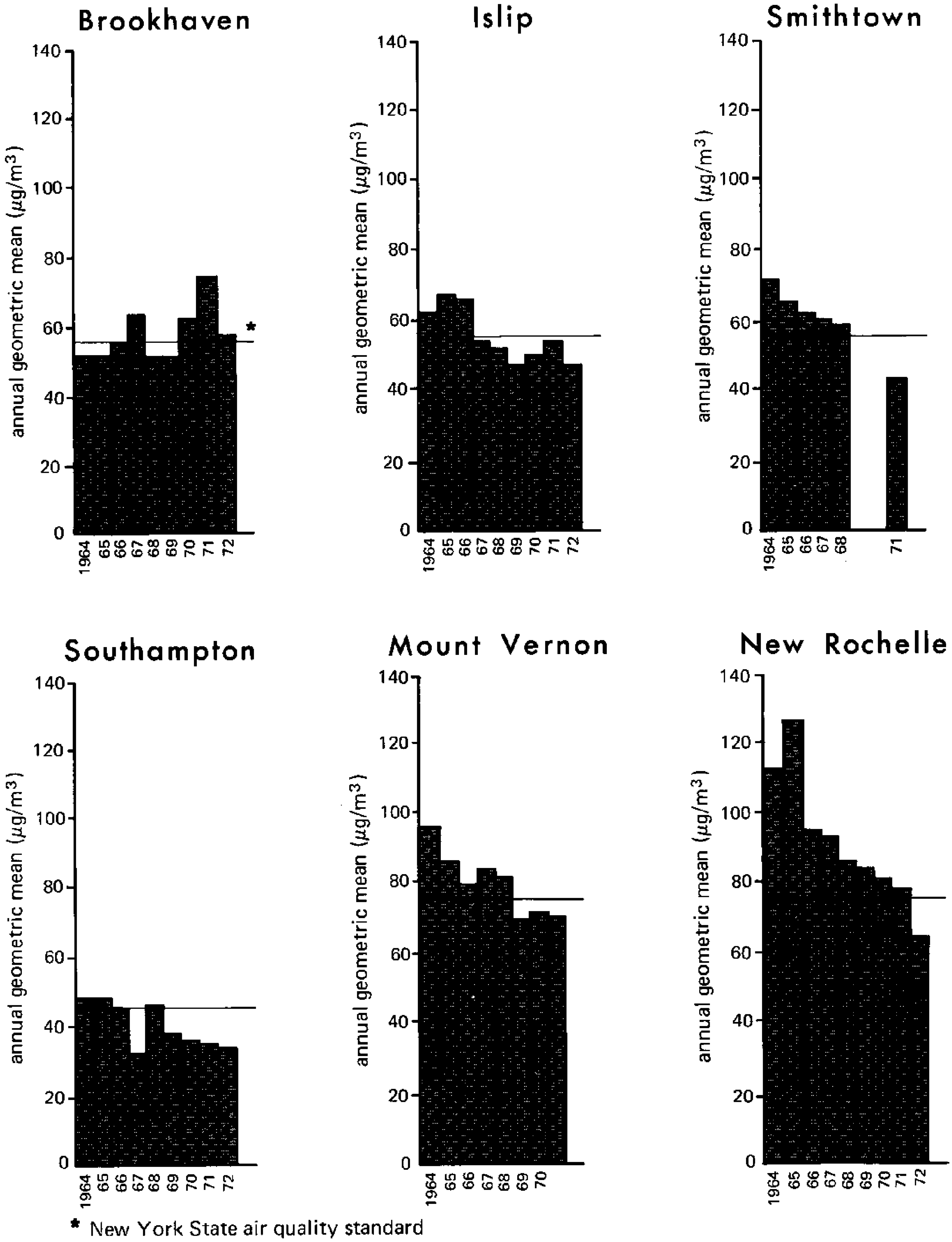
Table 4. Emissions, 1970
(metric tons)

Counties	Suspended Particulates	Sulfur Dioxide	Carbon Monoxide	Hydrocarbons	Nitrogen Oxides
NEW YORK[a]	**177,400**	**640,413**	**4,207,500**	**831,200**	**741,400**
Bronx	13,500	47,570	273,200	45,700	49,000
Kings	36,500	90,700	443,000	146,000	92,000
Nassau	26,500	98,743	1,040,000	180,800	163,900
New York	29,500	91,300	393,800	60,300	90,900
Queens	30,000	118,400	666,400	141,800	135,100
Richmond	4,500	36,600	137,000	42,400	32,000
Rockland	3,800	8,200	126,300	21,500	18,500
Suffolk	19,600	126,500	592,300	101,700	91,000
Westchester	13,500	22,400	535,500	91,000	69,000
NEW JERSEY[a]	**166,237**	**534,469**	**3,838,281**	**842,611**	**720,600**
Atlantic	7,307	41,983	72,888	17,878	37,504
Bergen	14,592	57,396	522,114	74,797	79,444
Burlington	7,723	23,548	205,689	29,631	41,890
Camden	12,777	12,421	247,877	49,804	35,006
Cape May	1,966	5,284	23,758	6,649	7,123
Cumberland	15,356	16,542	45,472	11,200	10,980
Essex	13,409	43,764	370,145	52,014	57,683
Gloucester	5,833	18,549	99,819	20,268	28,372
Hudson	10,707	74,507	238,062	237,700	71,125
Hunterdon	2,055	8,097	32,637	7,177	10,377
Mercer	15,110	45,693	172,187	32,683	43,492
Middlesex	21,906	66,940	491,342	67,504	85,052
Monmouth	5,733	10,821	312,182	50,057	40,668
Morris	4,126	11,422	232,785	42,640	32,224
Ocean	4,299	6,882	80,765	22,544	16,209
Passaic	4,441	12,849	216,101	38,767	29,480
Salem	4,432	27,633	34,372	11,935	19,490
Somerset	6,068	5,235	129,269	24,111	18,964
Union	8,397	44,903	310,817	45,252	55,517
CONNECTICUT[b]	**8,250**	**39,132**	**7,647**	**5,481**	**43,782**
Fairfield	3,192	18,533	1,429	3,306	22,003
New Haven	4,202	17,030	5,890	2,060	19,510
Middlesex		10			
New London	856	3,559	328	115	2,269
TOTAL	**351,887**	**1,214,014**	**8,053,428**	**1,679,292**	**1,505,782**

[a] Area and point sources

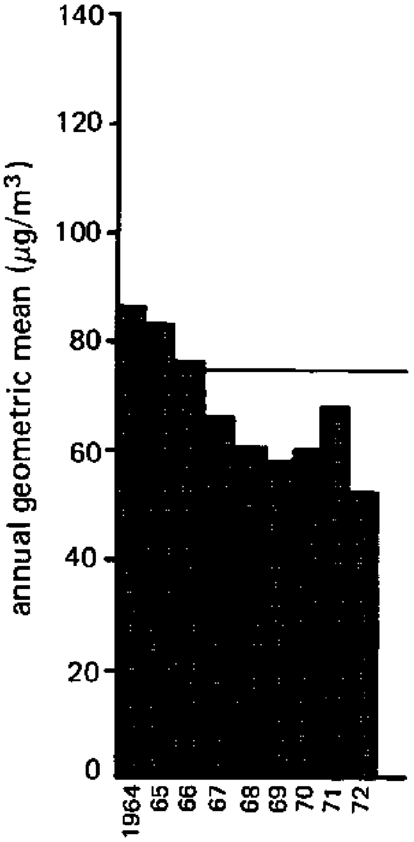
[b] Point sources only

Sources: New York City Department of Air Resources 1973*a*
New York State Department of Environmental Conservation 1974*b*
New Jersey Department of Environmental Protection 1971*a*, 1971*b*
Connecticut Department of Environmental Protection 1972

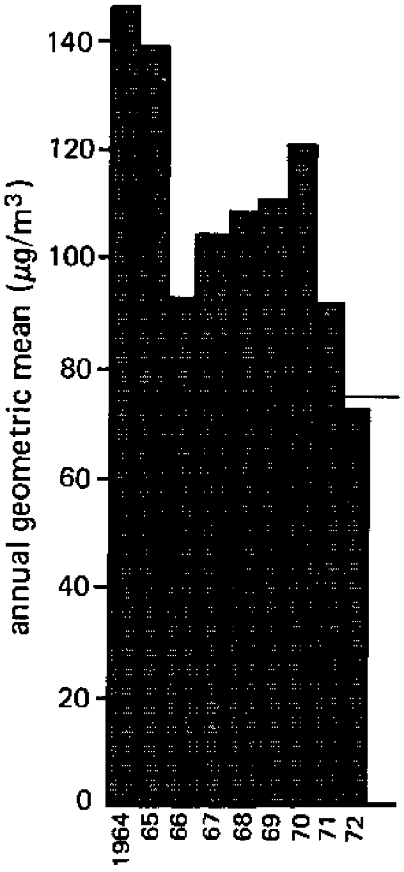


Source: New York State Department of Environmental Conservation 1974a

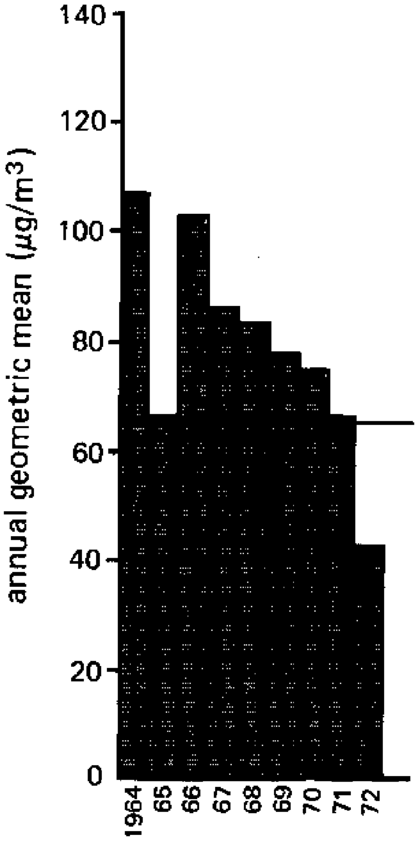
Figure 7. Trend-total suspended particulates, New York, 1964-72



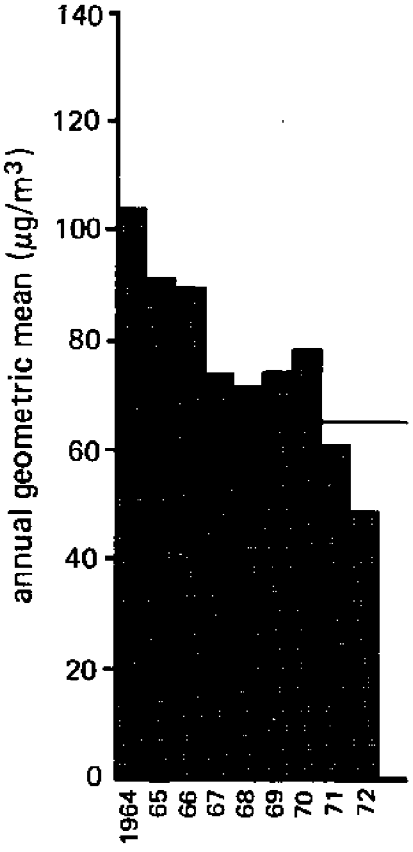
Garden City



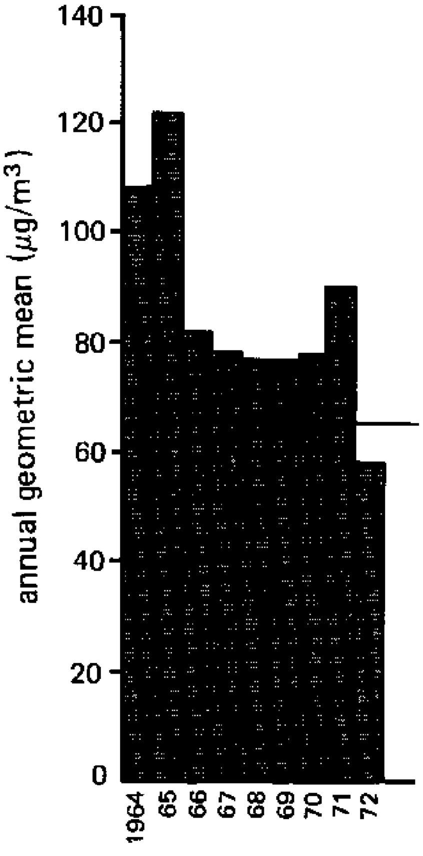
Rockville Ctr.



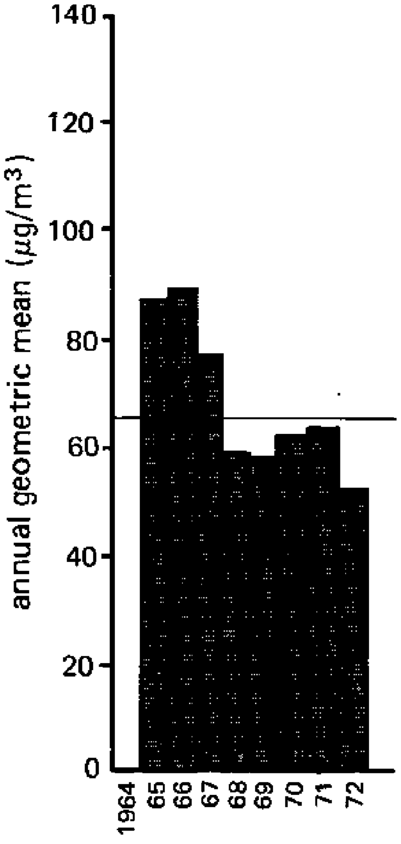
Kings Point



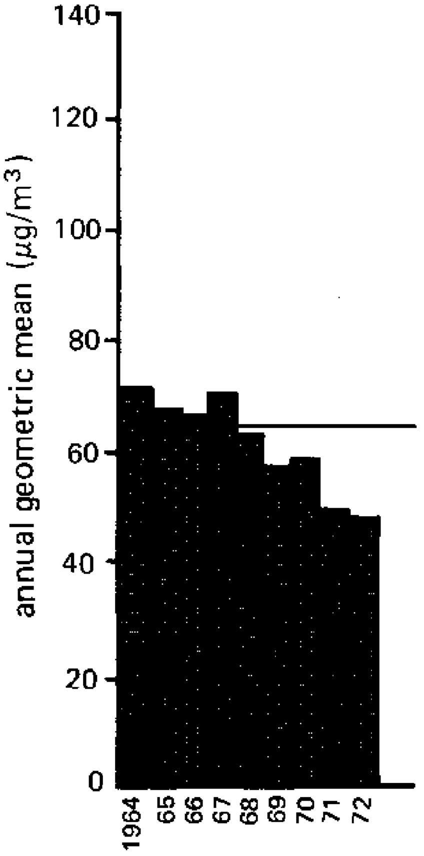
No. Hempstead



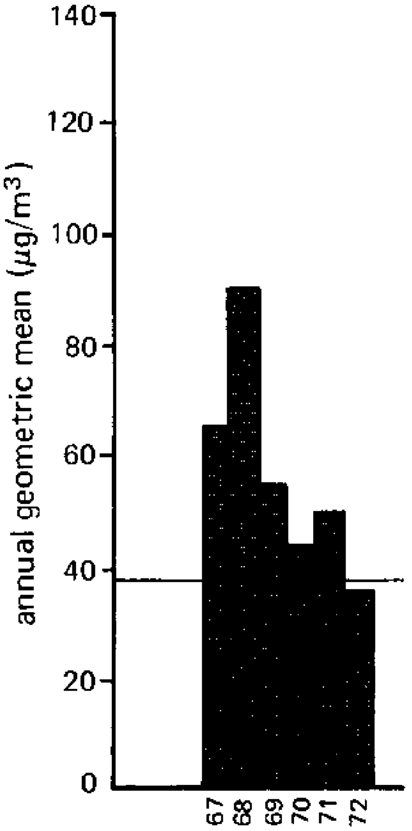
Oyster Bay



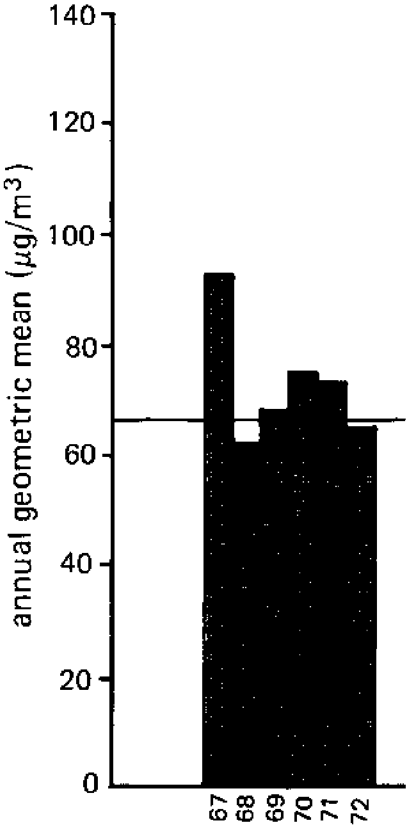
Babylon



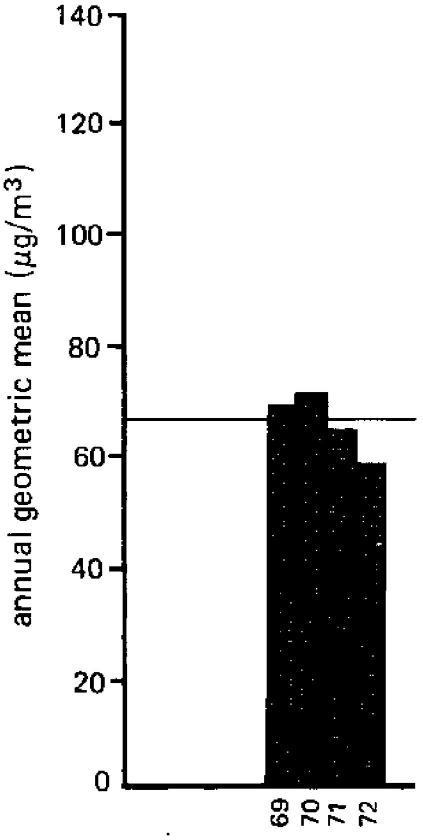
Ossining



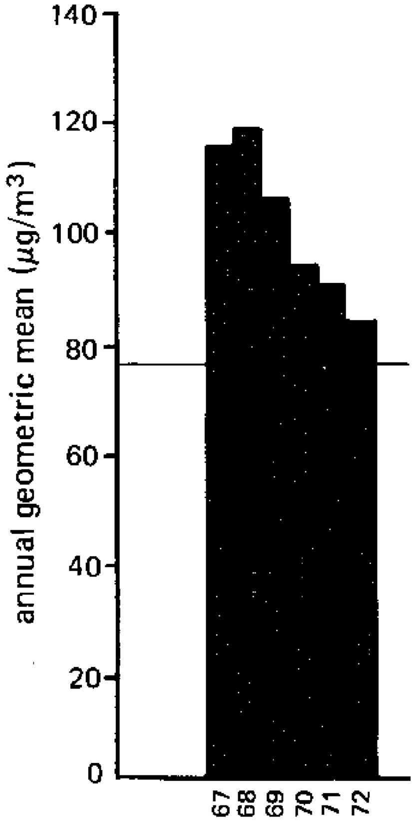
Yonkers



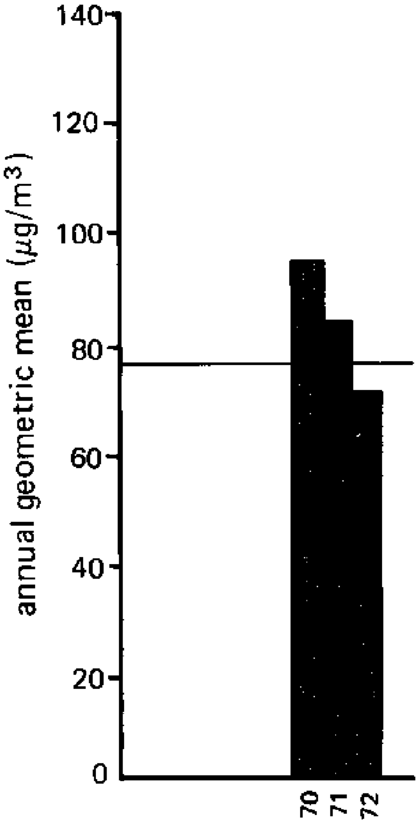
Rye



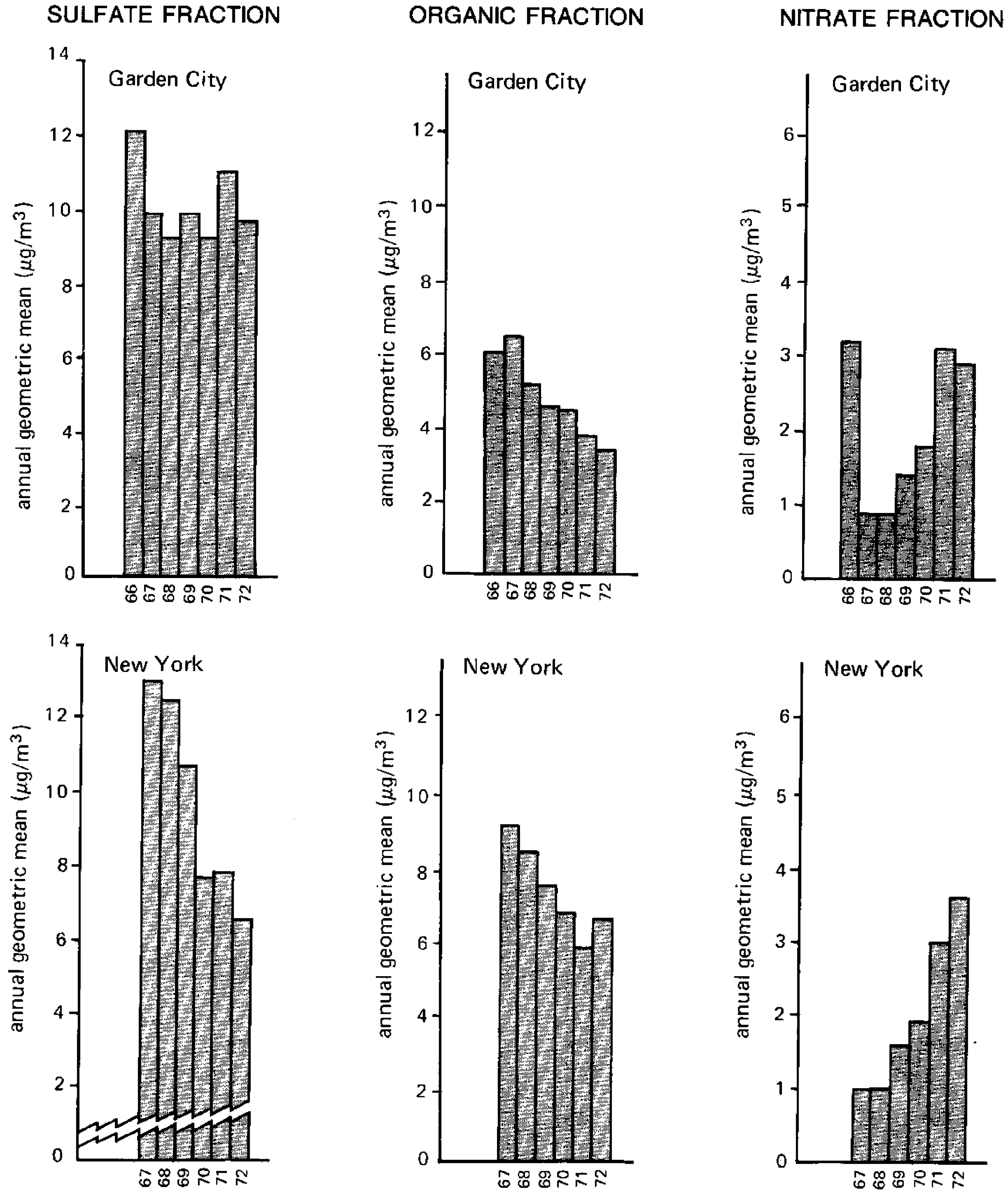
Mamaroneck



Manhattan



Roosevelt Island



Source: New York State Department of Environmental Conservation 1974*b*

Figure 8. Suspended particulate fractions at two New York stations, 1964-72

Third, there are no measuring stations along the Bight shores or measuring platforms in the Bight to verify any ambient air quality level.

Fourth, there are not sufficient measuring stations for nitrogen oxides, carbon monoxide, or total hydrocarbons from which to deduce concentration patterns like those for sulfur dioxide and suspended particulates.

Secondary Emissions

This discussion of urban atmospheres has concentrated mainly on particulate matter and gases, such as sulfur dioxide, oxides of nitrogen, and hydrocarbons—products emitted directly into the atmosphere. Homogeneous and heterogeneous gas-phase reactions transform these primary emissions into other chemical species (*secondary products*), some with a low enough volatility to either inititate a nucleation process and form new aerosols or condense out on preexisting particles.

Of particular interest is the sulfate aerosol for which an ambient air quality standard has to be defined by 1980 and which is thought to be responsible for the increased acidity of rain. Also well-documented is ozone, found in urban atmospheres under unfavorable atmospheric conditions such as high incident solar radiation and high atmospheric nitrogen dioxide concentrations (*Federal Register* 1971).

Ozone. A federal ambient air quality standard exists for the secondary product ozone (*Federal Register* 1971). The 1-hr average ozone concentration must not exceed 80 parts per billion (or 0.080 ppm) more than once a year. Typical for all (urban or remote) measurement stations is ozone's rise in the spring and decline in fall and winter (Figure 10). Ozone has a natural source in the stratosphere. The general global circulation pattern enhances the intrusion of stratospheric, ozone-rich air from January through August, yielding high ground-level ozone concentration. Solar intensity is higher in summer than in winter; hence the photochemical production of ozone is also enhanced during summer. This combination results in elevated ground-level ozone concentrations far above the federal ambient air quality standard. In 1974, for instance, violations of the 1-hr standard of 0.080 ppm were numerous throughout the entire Bight region: Roosevelt Island had 217 violations and an hourly peak of 0.185 ppm; Eisenhower Park showed 35 violations and an hourly peak of 0.154 ppm; a background station (far from any emission sources) had 52 violations and a maximum hourly value of 0.107 ppm.

Ozone constitutes a regional problem. The analysis of ground-level ozone data from New Jersey, New York, Connecticut, and Massachusetts (Cleveland et al 1975) revealed that "photochemical pollution" from primary emissions in the New York City

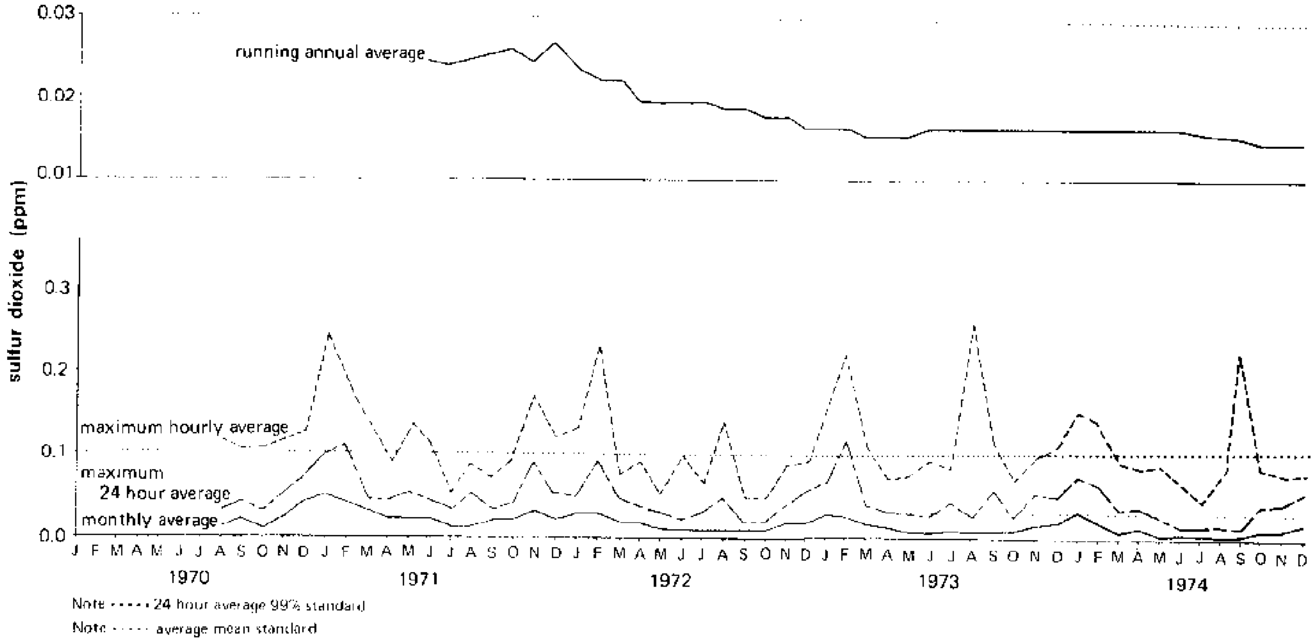
Table 5. Urban aerosol elements: possible origins

Element	Remarks and Possible Origins
carbon (total and organics)	primary—natural and anthropogenic sources secondary—photochemicals[a]
nitrogen (NO_3^-, NH_4^+, ammino and pyridino)	sources—oxidation of NO_x, NH_3, fuel additives
sodium	mainly sea salt
aluminum	mainly soil—some possible anthropogenic
silicon	mainly soil
sulfur ($SO_4^=$, $SO_{3m}^=$ S . . .)	mainly secondary production from SO_3 oxidation
chlorine	mainly sea salt, but some man-made
potassium	mainly natural[a]
calcium	cement production
titanium	anthropogenic and natural
vanadium	power plant—fuel oil
chromium	anthropogenic
manganese	anthropogenic, smoke suppressant
iron	anthropogenic and natural
nickel	anthropogenic
copper	anthropogenic
zinc	tire dust, smelting, field additives
arsenic	combustion, metal production and processing
selenium	combustion
bromine	auto exhaust
cadmium	metal production and processing
iodine	sea salt[a]
barium	diesel exhaust and lub oil atomization
lead	auto exhaust, industrial processing
water	liquid water content is a potentially important inert ingredient in visibility question

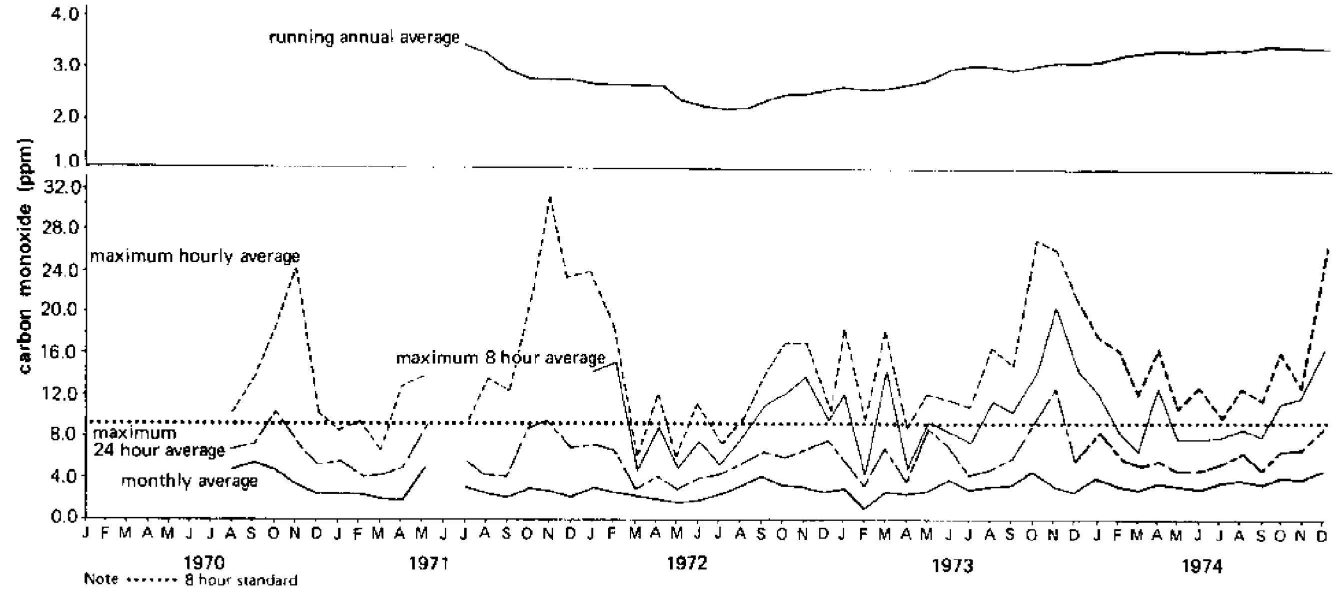
[a] possibly other sources

Source: Hidy 1975

Eisenhower Park



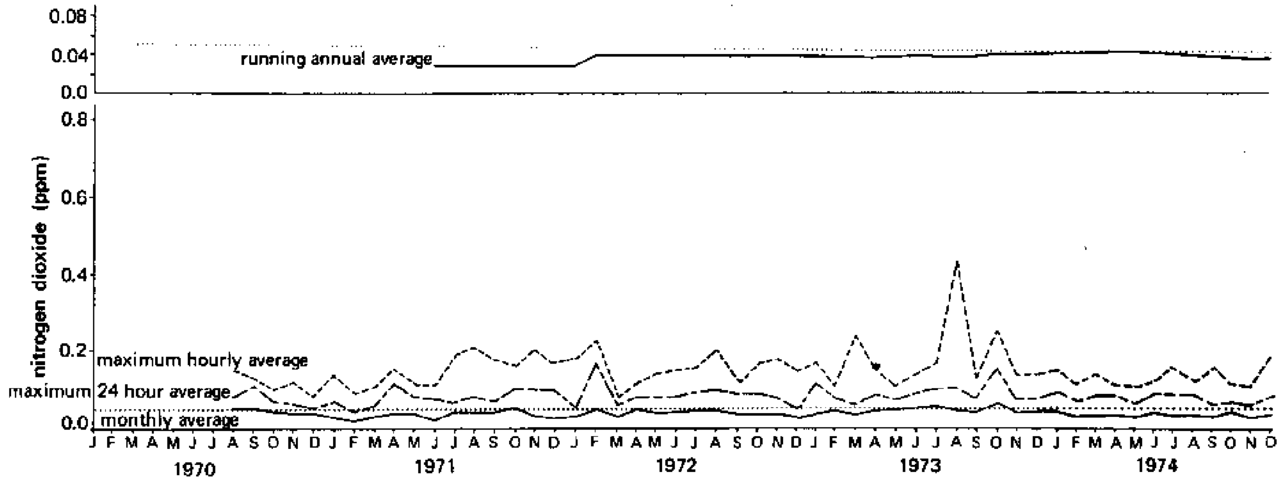
Eisenhower Park



Source: New York State Department of Environmental Conservation 1975

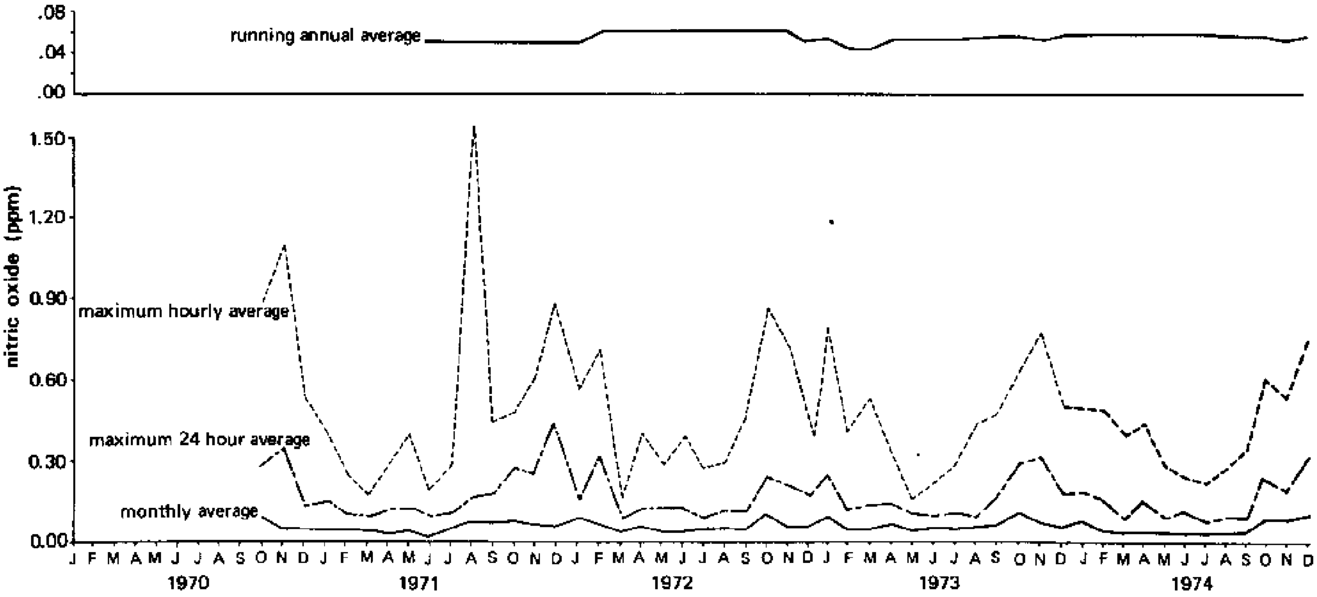
Figure 9. Air quality trends at two New York stations, 1970-74

Eisenhower Park

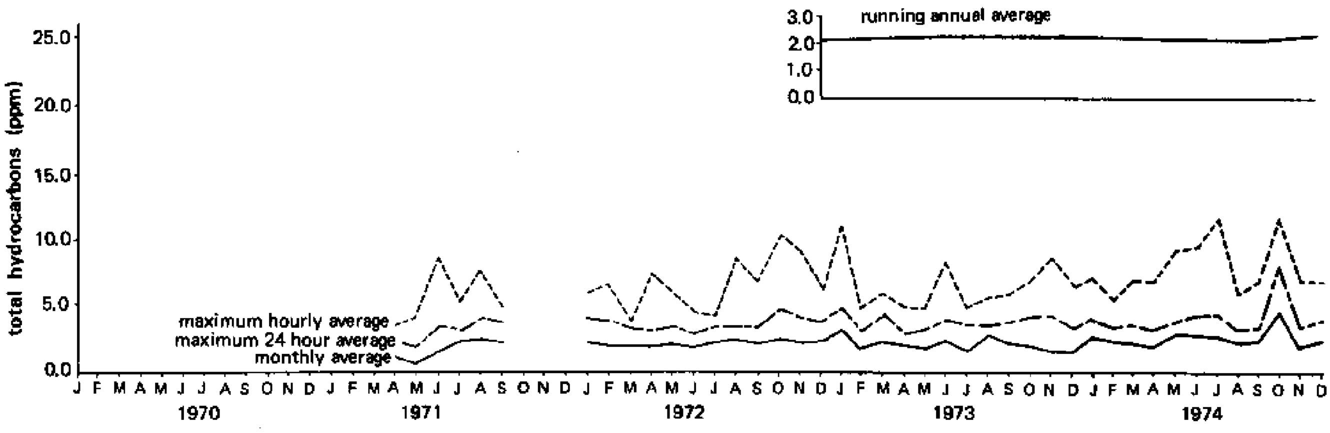


Note······· annual mean standard·······

Eisenhower Park

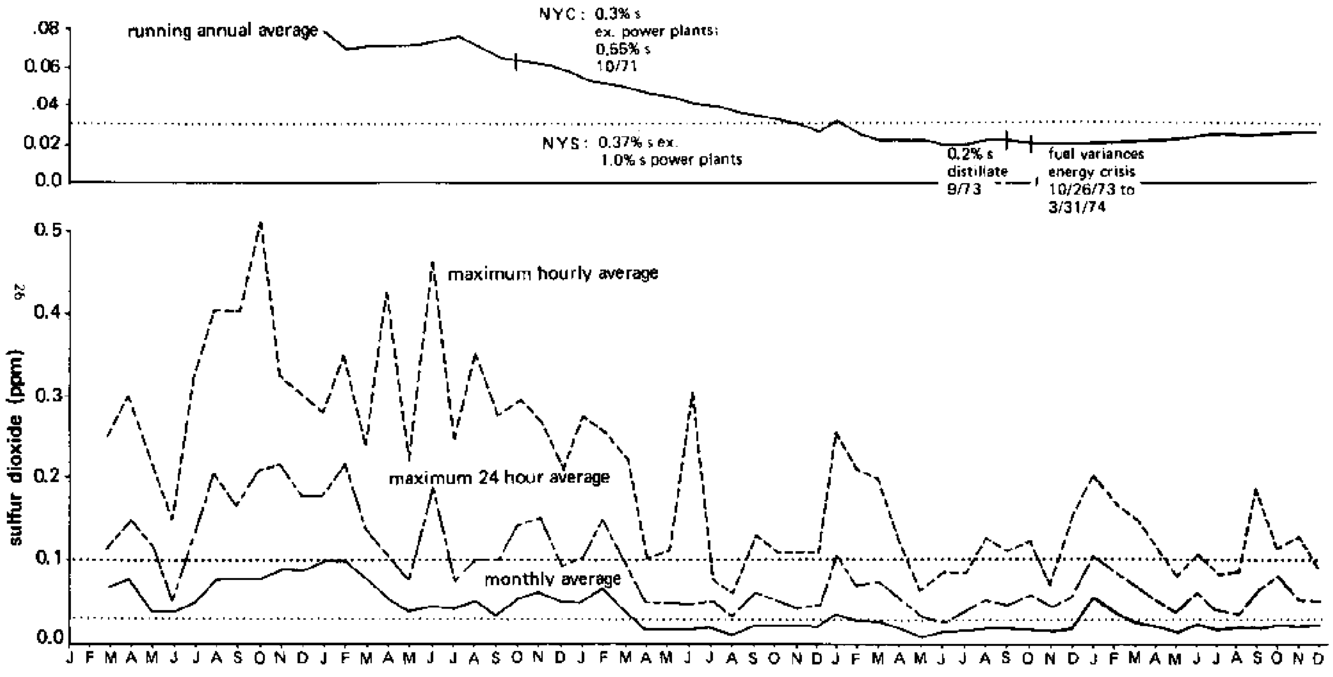


Eisenhower Park



Roosevelt Park

(formerly Welfare Island)

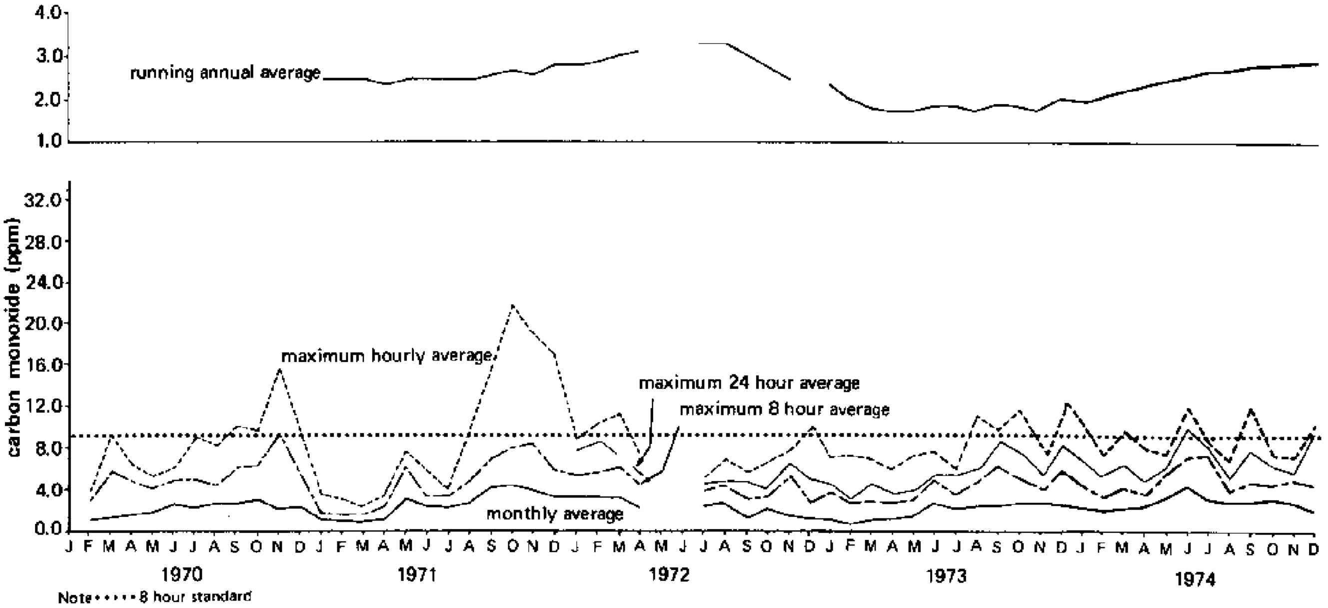


Note •••••• 24 hour average 99% standard

Note ------- annual mean standard

Roosevelt Park

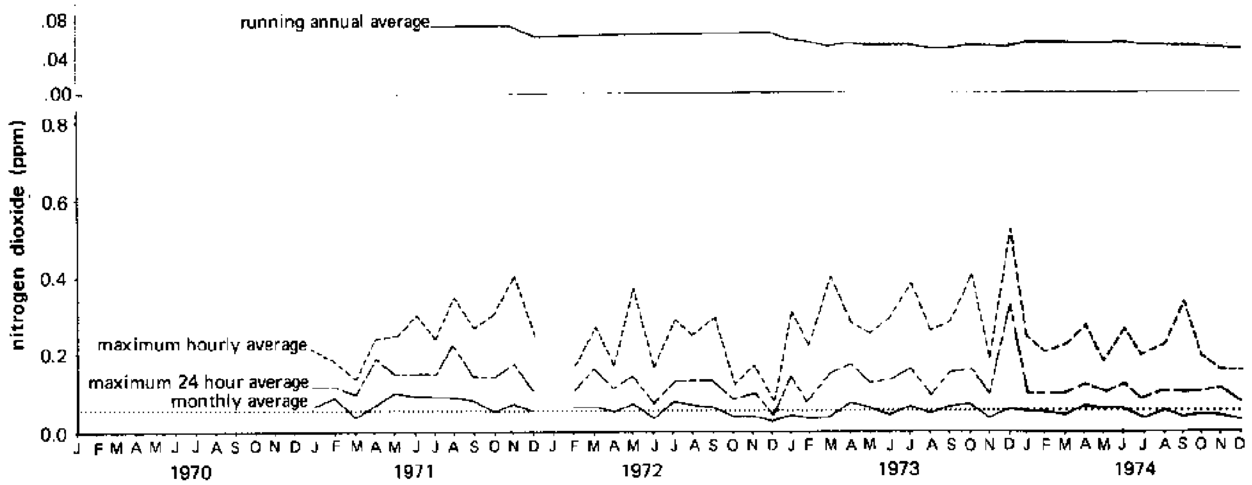
(formerly Welfare Island)



Note••••• 8 hour standard

Roosevelt Island

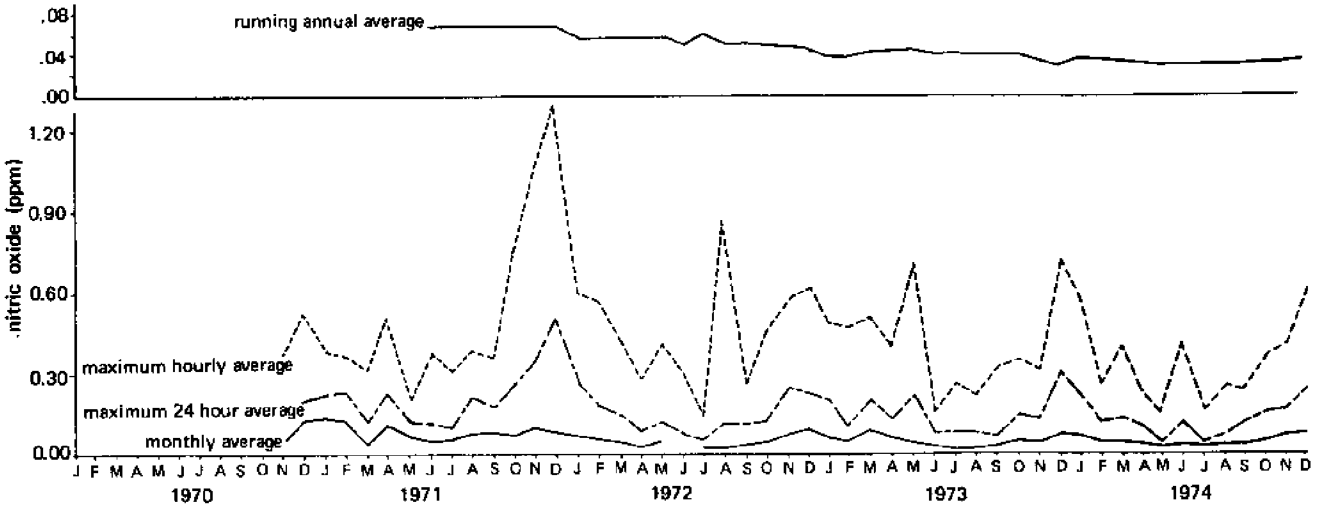
(formerly Welfare Island)



Note······ annual mean standard······

Roosevelt Island

(formerly Welfare Island)



Roosevelt Island

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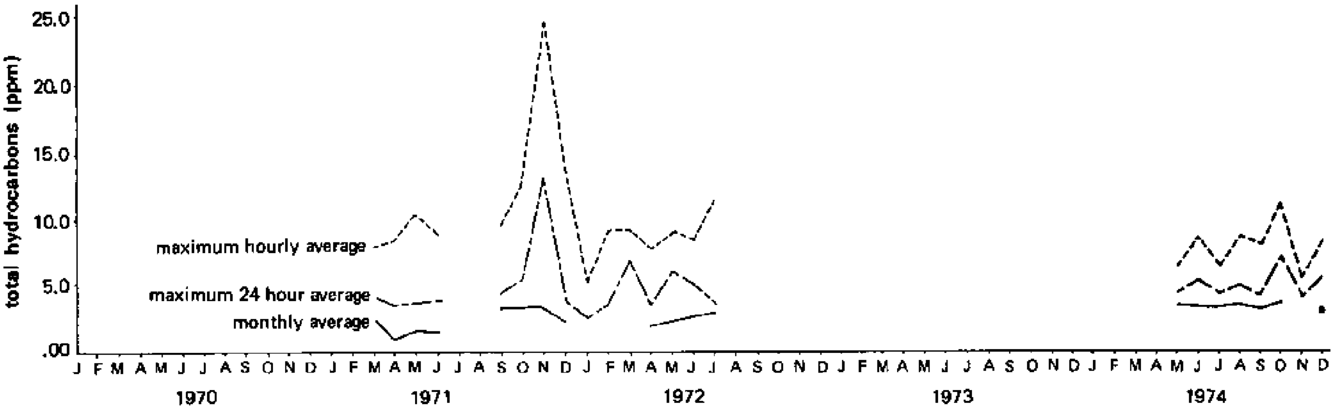
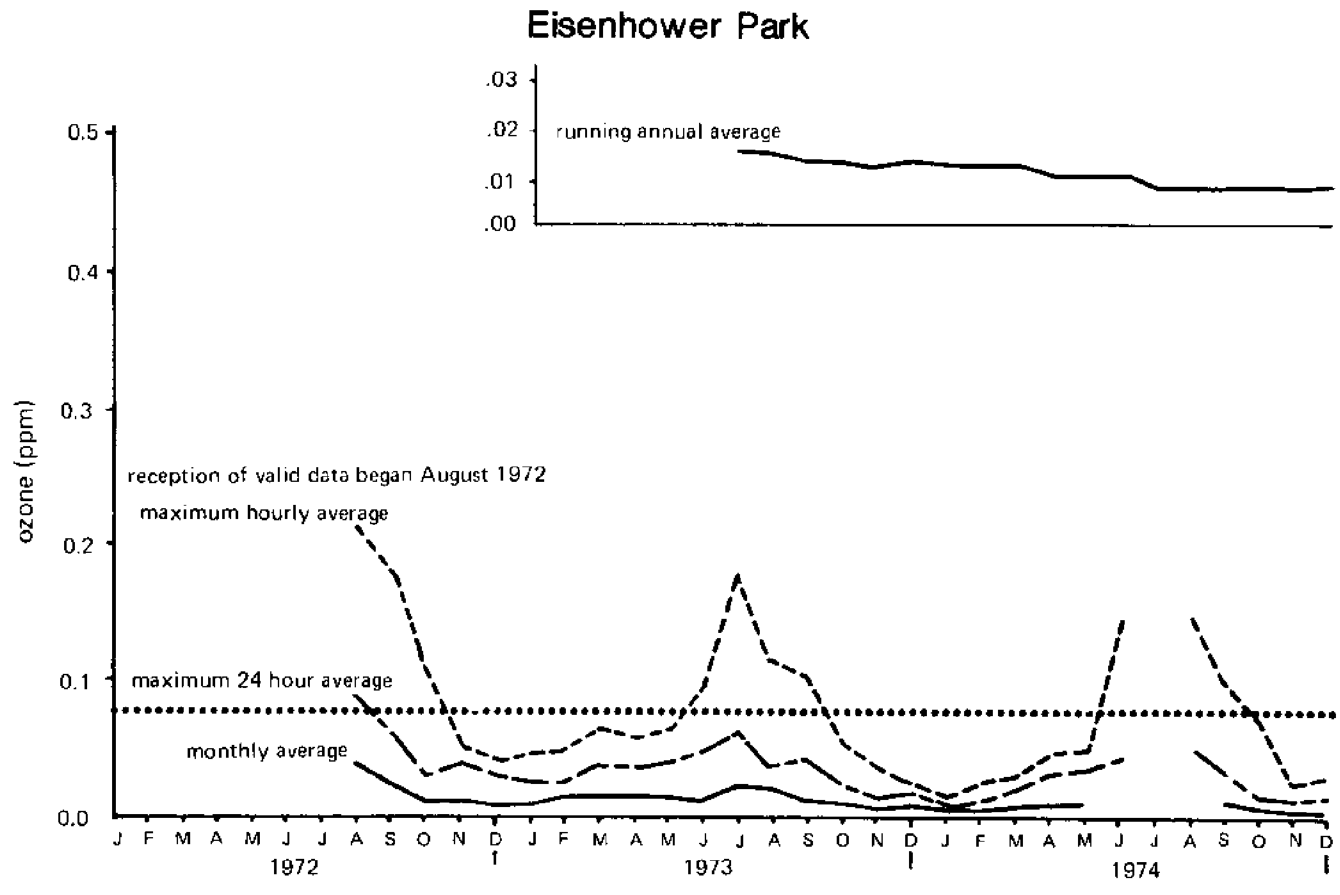
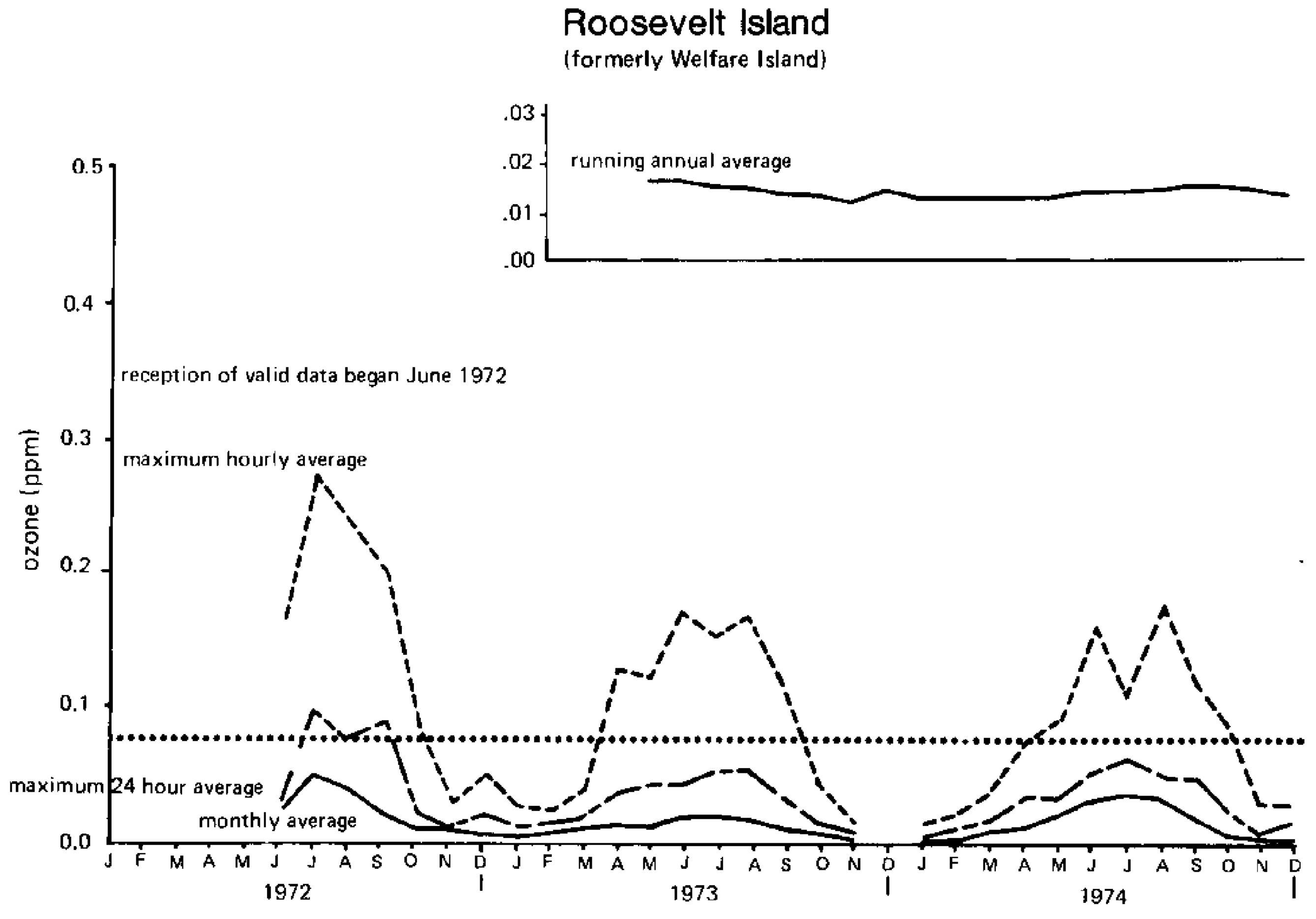




Eisenhower Park

Note •••••• hourly maximum standard



Roosevelt Island

(formerly Welfare Island)

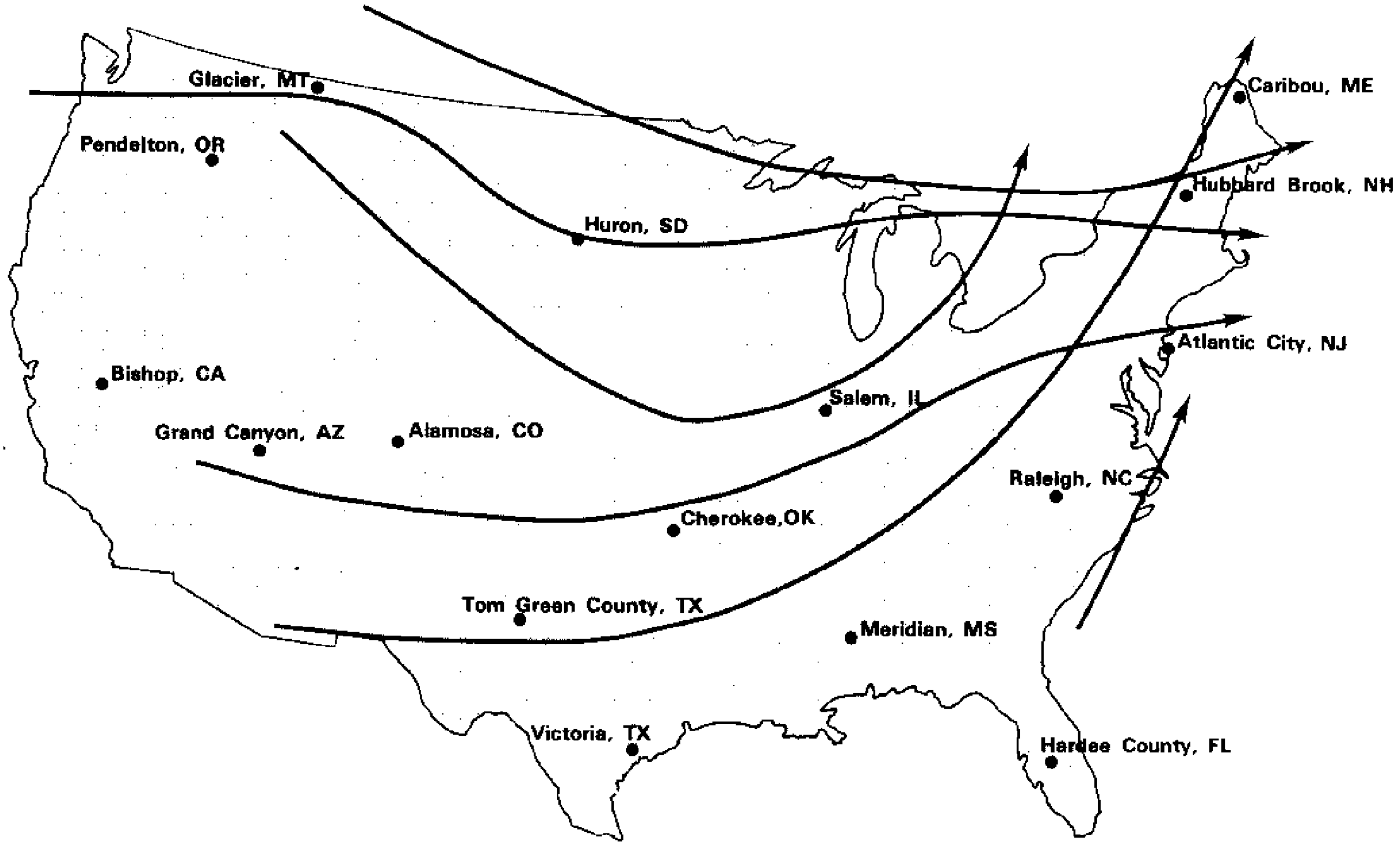
Note •••••• hourly maximum standard

Source: New York State Department of Environmental Conservation 1975

Figure 10. Ozone concentration at two New York stations, 1972-74

metropolitan area can be transported by prevailing winds on a 300 km (186 mi) northeast trajectory through Connecticut as far as northeastern Massachusetts. Thus, southwestern Connecticut has the highest ozone concentrations in the region, and Massachusetts has a substantial increase in ozone concentrations. The delay in the photochemical generation of ozone is like what happens in the Los Angeles Basin, where ozone concentrations increase with the movement of the air mass away from areas of strong emission sources; nitrogen dioxide and hydrocarbons are emitted primarily within the New York City metropolitan area. Ozone production from anthropogenic emissions and ozone transport down from the stratosphere peak in the spring and early summer, which explains the annual increase and decrease in ozone concentrations. Either production or transport is potentially capable of delivering enough ozone to the ground to exceed federal ambient air quality standards (Coffey and Stasiuk 1975).

Sulfates. Because the chemical transformation of sulfur dioxide into sulfates continues while air masses are moving away from emission sources, an increase in sulfates for some distance downwind of the sulfur dioxide source might be expected. Indeed, sulfates are considered a regional problem of even greater geographical extent than ozone. Scientists today believe that reactions leading eventually to sulfuric acid are mainly responsible for the gas-phase oxidation of sulfur dioxide (Wood, Castleman, and Tang 1975). Assuming an average concentration of 5×10^6 cm^{-3} for the hydroxyl radical concentration in "polluted" atmospheres, the average atmospheric lifetime for sulfur dioxide is three days. This corresponds to an average transport distance of at least 1,000 km (621 mi). The conversion of 3 parts per billion sulfur dioxide would yield 10 $\mu g/m^3$ of sulfates, demonstrating the large regional impact of any anthropogenic sulfur dioxide emission source. In "clean" air, the concentration of hydroxyl radicals is



Sources: Johnson, Reynolds, and Likens 1972; Missouri Botanical Gardens 1975

Figure 11. Weighted mean pH of precipitation, water year 1972-73, and common cyclonic storm trajectories across United States

thought to be on the order of 5 x 10^5 molecules/cm^3, resulting in an average lifetime of sulfur dioxide in the unperturbed atmosphere (provided all conversion mechanisms are at work) is two to three weeks. Hence, other chemical reactions will dominate as the air moves long distances downwind of major pollution sources, and the hydroxyl radical concentration decreases.

These days it is not surprising to find high sulfate levels in the atmospheric aerosol almost everywhere in the northeastern United States, even the most remote areas (Kellogg et al 1972). Typical nonurban sulfate levels are over 5 $\mu g/m^3$ throughout the Northeast. Evidently sufficient sulfur dioxide remains airborne long enough for the chemical transformation processes to produce significant concentrations of sulfate aerosol; its ultimate impact on air quality is experienced far downwind. The sulfate aerosol is present in the atmosphere in the submicrometer size range and can, therefore, remain in the atmosphere longer than the average aerosol; its terminal gravitational settling velocity is very small and the collection efficiency of rainout and washout for such particles is relatively low. In fact, the sulfate particle size falls near a minimum in the collection efficiency curve: smaller particles are removed more efficiently through Brownian diffusion to cloud droplets, and larger particles are removed more efficiently through collection by falling raindrops. The substantial interstate transfer of suspended sulfates, called long-range transport of pollutants, is now being considered a major air pollution problem on state, national, and international levels (Rodhe 1972). Preliminary estimates (Finlea 1973) indicate that health effects in surface air are thought to appear at concentrations of about 10 $\mu g/m^3$ of sulfates.

Another important problem directly connected to the atmospheric sulfate is precipitation quality (Likens 1976). The average pH of rain in the Northeast seems considerably lower than in the West and Southwest (Figure 11). Because the most common trajectories of cyclonic storms across the United States (Figure 11) touch the Bight area after passing over major emission sources hundreds or thousands of kilometers inland, it is strongly suspected that air and precipitation quality are influenced to some degree by those inland emission sources. A rain acidity of pH 4 cannot be caused by organic acids but rather by strong inorganic acids such as sulfuric acid. A considerable portion of the atmospheric sulfate is thought to exist in the form of sulfuric acid. Ammonia in the atmosphere is apparently not capable of neutralizing all the acid formed in the conversion from sulfur dioxide. Still, a major research problem is to identify the chemical form of the atmospheric sulfate and its propagation path into the water cycle.

In summary, the Bight coastal area represents a very large emission source, generating ambient air concentrations of particulates and gases far above the natural background. Through atmospheric chemical transformation processes, various secondary products are formed—sulfates, nitrates, and ozone, for example. These products are transported into the Bight area whenever the general wind direction is roughly west-southwest to north-northeast. Long-range transport (distances greater than 100 km or 62 mi) of pollutant material also has an impact on the Bight area. Atmospheric sulfate levels greater than 5 $\mu g/m^3$ and a rain pH of 4 to 4.5 (annual average) can be expected.

Air Quality Over the Bight

Air quality over New York Bight is determined by:

1. emission of particulate matter and gases from the ocean surface (natural process);
2. emissions of particulate matter and gases from land surfaces, stationary and mobile anthropogenic sources (Meteorological transport eventually distributes these primary materials into the Bight.) and;
3. particulate and gaseous products resulting from chemical transformation in the atmosphere. (Meteorological transport eventually distributes these secondary materials into the Bight, or chemical transformation continues in the air above the Bight.)

Although emission sources and the resulting air quality over land have been reasonably well assessed for a number of gases and for particulate matter, no such information exists for New York Bight (Environmental Protection Agency 1973). Air quality then must be discussed over the Bight with prediction models or experimental information obtained from other areas but which might be applicable to the Bight.

The Bight as Emission Source

Oceans are a source of particles. For example, sea salt particles are produced when myriads of bubbles break at the ocean surface. Whenever air masses above the Bight are of true oceanic origin, their main particulate content is sea salt.

The production of sea salt particles is a function of wind speed. Some experimental results from Hawaii (Blanchard and Syzdek 1972) show that concentration varies from about 2 to 20 $\mu g/m^3$ as wind speed increases from around 3 to 8 m/sec. The mass median radius is on the order of 3 μm and the number concentration of cloud condensation nuclei is around $250/cm^3$. Note that the total number of particles exceeds the number of cloud condensation nuclei. However, particles below 0.5 μm radius essentially do not contribute to the particulate mass-loading of the atmosphere as long as their number density is lower than or equal to the number density of particles above 0.5 μm radius.

The oceans are also an important source of atmospheric sulfate (salts). Their concentration in the oceans is 2.65 mg/kg; the estimated atmospheric concentration is 0.5 to 5 $\mu g/m^3$ (Junge 1963; Georgii 1970). Ocean sulfate transfers to atmospheric sulfate via breaking bubbles.

The important role that oceans play in the carbon dioxide cycle has already been elucidated. With an annual ocean temperature above 10°C (50°F) in the Bight, it might be expected that the carbon dioxide flux is either balanced or is from the ocean to the atmosphere (carbon dioxide source).

The oceans have been suggested as sources of hydrogen sulfide. Probably some hydrogen sulfide is liberated from tidal flats and estuaries, but little is emitted from the open ocean since its oxidation rate by dissolved oxygen is relatively rapid. Lovelock, Maggs, and Rasmussen (1972) found that the oceans are supersaturated with dimethyl sulfide. This organic compound, rather than hydrogen sulfide, is now assumed to be the gaseous sulfur emission into the atmosphere. However, dimethyl sulfide has yet to be identified in the ambient atmosphere. In the presence of ozone or free radicals, dimethyl sulfide is oxidized within hours to sulfur dioxide. The ambient concentration of sulfur dioxide in true maritime air varies from 1 to 5 $\mu g/m^3$ or 0.34 to 1.7 parts per billion. However, any background information about maritime air is not only very scarce but represents mostly single spot measurements taken over a short period of time.

True ocean air would exist only after an air mass has spent a minimum of three days over the open ocean prior to reaching the Bight. That restrictive prerequisite is rare and is the exception rather than the rule. Because weather commonly moves from west to east, air masses above the Bight have been over land surfaces exposed to natural continental and substantial anthropogenic emission sources just before reaching the Bight.

Atmospheric Dispersion

Consider an individual plume from a single point source transporting material downwind into the Bight. Assume that a 70 m (230 ft) high smokestack near the shore is emitting particulate or gaseous material at a constant rate of 200 g/sec. Whenever the wind direction is from northwest to west-northwest, the plume disperses over the Bight. The annual wind rose from La Guardia Airport assumed to be representative for New York City, indicates that those conditions occur 9.5% (NW) and 11.8% (WNW) of the time during the year. The annual wind speed for the New York area is about 7.3 m/sec (23.9 ft/sec). With this information the annual ground-level concentration downwind of the stack, under neutral atmospheric stability conditions, can be predicted (see Appendix 1). With a wind from the northwest, emission concentrations would be 19 $\mu g/m^3$ at 2.5 km (1.6 mi) and 8.5 $\mu g/m^3$ at 5 km (3 mi) downwind of the source. With a wind from west-northwest, emission concentrations would be 23 $\mu g/m^3$ at 2.5 km (1.6 mi) and 11 $\mu g/m^3$ at 5 km (3 mi) downwind of the source.

It is evident that one major emission source near the shore can have a substantial impact on the annual ambient air quality over the Bight. Normally the vertical plume dispersion is limited by the effective mixing height (limit of vertical mixing). The plume then homogeneously fills the space between the surface and the upper limit for vertical mixing. For the New York metropolitan area, this mixing height is 750 m (2,460 ft) during the night and 1,214 m (3,982 ft) during the afternoon (annual averages). Under neutral atmospheric stability any plume will be homogeneously mixed in the vertical direction 6.3 km (3.9 mi) during the night and 12.7 km (7.9 mi) during the afternoon downwind of the emission source. Under those conditions, the predicted annual ambient ground-level concentrations are:

Wind from	Concentrations	Mixing Height 15 km (9 mi) Downwind of Source
Northwest	0.6 $\mu g/m^3$	750 m (2,460 ft)
	0.4 $\mu g/m^3$	1,214 m (3,982 ft)
West-northwest	0.7 $\mu g/m^3$	750 m (2,460 ft)
	0.5 $\mu g/m^3$	1,214 m (3,982 ft)

From this example, two conclusions about air quality in the Bight area are possible. First, a major, single emission source near the shore would have a measurable impact on the annual ambient air quality over the Bight for some 10 to 15 km (6 to 9 mi) downwind of that source. Under very stable atmospheric conditions (stability E and F, Table A1), the plume might maintain its identity tens of kilometers downwind of its origin, as has been shown in satellite pictures of plumes over the Bight area (Lyons 1975). However, it is customary to apply neutral stability (stability D, Table A1) as an annual average.

Second, any plume homogeneously fills the vertical space between the surface and the limit of vertical mixing 6 to 12 km (4 to 8 mi) downwind of its origin. The plume continues to disperse horizontally, however. This means that the pollutant material entering the Bight region is uniformly mixed vertically or will be within a short distance of the shore. Since the anthropogenic emission sources are distributed over a large area inland and along the shore, and since the emitted material disperses both vertically and horizontally, individual small and large plumes merge together and cause some uniform horizontal mixing (for example, the 50 $\mu g/m^3$ isoline in Map 2). To obtain some estimate of the maximum impact of an urban plume on the annual ambient air quality 200 km (124 mi) downwind of New York City, assume that an urban plume acts from a great distance like a pseudo-point source. Approximately 67% (236,985 metric tons/yr) of the total annual particle emissions enter the atmosphere within 64 km (40 mi) zone around New York City (1970). The resulting annual ambient suspended particle concentration 200 km (124 mi) out over the ocean would be 1.7 $\mu g/m^3$ for an average mixing height of 800 m (2,624 ft) and an average wind speed of 7.3 m/sec (23.9 ft/sec), with winds from northwest to west-northwest at an annual frequency of 10% for either direction. At an assumed wind speed of 7.3 m/sec (23.9 ft/sec), it would take the urban plume only 7.5 hr to travel 200 km (124 mi). This anthropogenic contribution of particulate matter might be just barely detectable in the total mass since the natural oceanic background level seems to be about 15 $\mu g/m^3$. Experimental evidence of urban plumes extending hundreds of kilometers into the ocean does exist (Hogan 1976). However, more sensitive measuring must be applied. Since there is considerably less particle production over the ocean, the total number of particles rather than the total particulate mass can be measured.

During the transition from urban-continental air to mixed continental-maritime air, a change in the mass of the aerosol size distribution can be expected as an annual average. Here, plume modeling has been used as a diagnostic tool. The lack of ambient air quality data for the Bight prevents validation of this model prediction. This is a serious restriction because the air flow in the Bight might be quite different from what was expected (Appendix 1).

Even greater caution is necessary when attempts are made to model long-range transport. Appendix 2 presents an example of transport of material along the Washington, DC-New York City-Boston axis, with lateral diffusion over the Bight. At this time, the model only demonstrates that material of various atmospheric residence time can be transported over long distances; the model is not a prediction tool.

Atmospheric Cleansing

Next, it is necessary to consider the removal of particulate and gaseous matter. For this, an area extending 80 km (50 mi) into the Bight and 320 km (199 mi) along the Bight shores is defined. Based on previous discussions, it can be postulated that within this region the pollutant material originating from the continent over one year is well-mixed between the ocean surface and the effective mixing height. It can be further postulated that annual air quality in this region is still governed by continental emissions. Finally, it can be assumed that the ambient air quality has the following concentration levels: for sulfur dioxide (1973-75 level), 16 $\mu g/m^3$ from the shoreline to 40 km (25 mi) into the Bight, 8 $\mu g/m^3$ from 40 km (25 mi) to 80 km (50 mi) into the Bight; for suspended particulate matter (roughly the 1973-75 level), 45 $\mu g/m^3$ from the shoreline to 40 km (25 mi) into the Bight, 22 $\mu g/m^3$ from 40 km (25 mi) to 80 km (50 mi) into the Bight. Atmospheric dilution essentially will reduce the concentration by one-half if the distance is increased by a factor of two, under conditions of vertically limited transport.

There exists at this time no experimental verification of the confidence level for these assumptions, but it is believed they describe the actual annual conditions within ± 50%.

Nearly all air pollution is eventually cleansed from the atmosphere by the natural processes of *precipitation-scavenging* (removal of pollutants by clouds and raindrops) and dry deposition.

Gases. The dry deposition flux of gases is usually dictated by the chemistry of dissolution rather than by the physical processes in the atmosphere. It is convenient to consider the dry flux to the water surface proportional to the ground-level (2 m or 7 ft above the water surface) ambient air concentration (Chamberlain 1966). The proportionality constant, known as deposition velocity, has a maximum possible value over ocean waters of about 5 cm/sec for a completely absorbed gas. The "theoretical" deposition velocity of 5 cm/sec is rarely attained except for very reactive gases like iodine and sulfuric acid vapor. In gas deposition to oceans, for reasonably reactive gases, the atmosphere may be rate-limiting since mixing in the water body promotes transfer in the sink. According to Liss and Slater (1975), the movement of sulfur dioxide, ammonia, nitrogen dioxide, sulfur trioxide, and hydrogen chloride to the ocean is limited by atmospheric transport, whereas the movement of gases such as nitrogen dioxide, carbon monoxide, methane, and carbon tetrachloride is rate-limited by transport in the ocean.

For sulfur dioxide a deposition velocity of 2 cm/sec is typical for oceans. The maximum amount of sulfur dioxide delivered to the Bight via dry deposition is on the order of 190,000 metric tons/yr (1973-75 level). The amount of sulfur dioxide delivered by *wet deposition* (when a gas is dissolved into falling rain and transported to the ground) is about 13 metric tons/yr, negligible compared with the dry deposition amount.

A rough comparison between the total sulfur dioxide emissions within the Bight region land area and the total sulfur dioxide deposition to the Bight itself reveals:

1. reported sulfur dioxide emissions for 1970—1,214,019 metric tons;
2. estimated emissions for 1973-75—about 600,000 metric tons/yr (control measures brought about a 50% reduction);
3. estimated deposition for 1973-75—about 190,000 metric tons/yr.

Therefore, at most, 32% of the total sulfur dioxide emissions are deposited in the Bight as sulfur dioxide.

Approximately 65% of the time the prevailing winds in the Bight area are between north-northeast, west, and south-southwest. This means that potentially 65% of the total annual sulfur dioxide emissions could be carried to the Bight (more than 390,000 metric tons/yr for 1973-75). This would leave over half the sulfur dioxide unaccounted for. This discrepancy can be explained, however: sulfur dioxide is very efficiently deposited on land surfaces; it is transported above the mixing layer; it is chemically transformed into sulfates; it is transported beyond 80 km (50 mi) offshore; and, most important, this budget calculation represents only a crude estimate.

Particles. With dry deposition of particles, the deposition velocity depends on particle size. Deposition velocity is rather low over smooth surfaces such as oceans. An average deposition velocity of 0.1 cm/sec seems representative. Over the entire Bight region, dry deposition of particles amounts to 52,900 metric tons/yr and wet deposition, 93,470 metric tons/yr, for a total of 146,370 metric tons/yr of deposited particulate matter. This figure should not be compared with the total anthropogenic particulate emission figure from the Bight region land area. It must be remembered that substantial natural sources of particulate matter exist on both land and sea surfaces, contributing to the ambient level of suspended particulate matter forming the natural background. The derived deposition-to-anthropogenic emission ratio might therefore overemphasize a short-range deposition pattern for particles.

Reported total particulate matter emission for 1970 was 351,887 metric tons. Estimated emissions for 1973-75 were about 315,000 metric tons/yr (10% lower). Estimated deposition for 1973-75 was about 146,370 metric tons/yr. At most, 46% of the total suspended anthropogenic emissions are deposited in the Bight. Potentially 65% of the total annual anthropogenic particulates (more than 206,000 metric tons/yr for 1973-75) could be carried into the Bight on the basis of annual wind frequency. This would leave at least 30% of the particulate matter unaccounted for. Again, deposition over land surfaces, transport above the mixing layer, transport beyond the Bight, and the inherent uncertainty in these estimates can easily account for the imbalanced budget. Again it should be noted that small particles (less than 0.5 micron radius) are least efficiently removed from the atmosphere and can travel with air masses for hundreds of kilometers.

Finally, water deposition or precipitation should be considered. The annual precipitation rate over the Bight is on the order of 109 cm/yr (43 in/yr). The acidity of this rain over the entire Bight will most likely not differ from the rain acidity over the adjacent land. It was documented earlier that the annual pH was between 4 and 4.5. From this it can be calculated that a hydrogen ion concentration of 6.8×10^{-2} moles/m^2/yr (calculated for pH = 4.3) is deposited throughout the Bight.

Conclusion

Air quality over New York Bight is strongly influenced by anthropogenic emission sources. A detailed impact analysis cannot be performed at this time due to the lack of even the most fundamental air quality data. The basic processes and essential background for air pollution have been presented to the reader, enabling appreciation of the necessary crude estimates made to try to assess air pollution over the Bight.

Appendixes

Appendix 1. Fundamentals of plume modeling

To introduce some fundamental aspects of dispersion modeling, we consider a "puff" of trace gases released at time $t = 0$ from a point source. After time t, the width σ increased to:

$$\sigma = 2 \cdot K \cdot t \qquad (1)$$

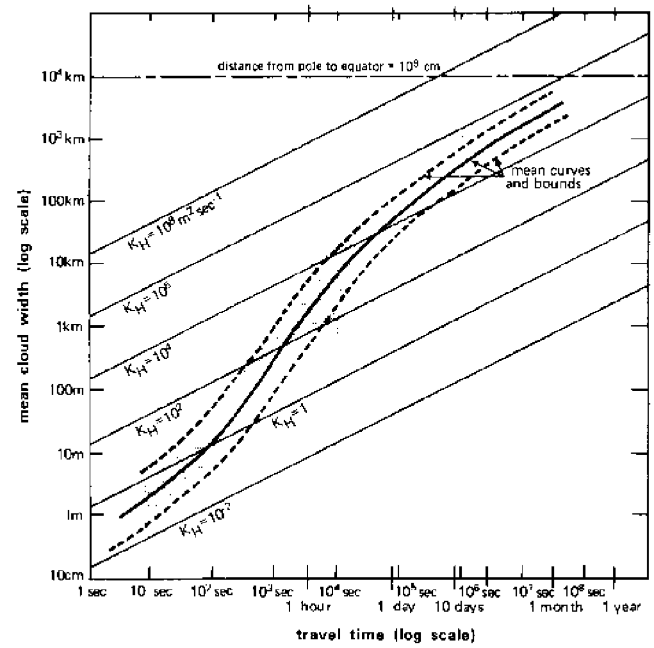
Here, K represents the eddy diffusion coefficient (diffusivity) in m^2/sec. This coefficient is not constant with time and is different for the horizontal and vertical directions. It is necessary therefore to consider the cloud width separately, resulting in

$$\sigma_H = 2K_H \cdot t \qquad (2)$$

and

$$\sigma_V = 2K_V \cdot t \qquad (3)$$

Figure A1 shows horizontal dispersion (mean width) as a function of time (travel time in the atmosphere due to transport by wind) as a function of K_H for the lower part of the atmosphere (called the Ekman layer). The area between the dashed lines indicates approximate values for the lower atmosphere. After a travel time of one day, the width of the "puff" expanded horizontally to 60 km (37 mi). The more sophisticated dispersion models for point sources assume that the density gradient of the constituent within the released "puff" can be described by a Gaussian distribution function both horizontally and vertically. The mean width is then given by the standard deviation of the Gaussian distribution function, again differentiating between the horizontal σ_y (y = direction) and vertical σ_z (z = direction) component. Figure A2 shows the geometry of this type of plume dispersion. Turbulent motions in the atmosphere superimposed on organized motion (wind)—the basis of dispersion—vary considerably. The overall parameter for this variation is called atmospheric stability. Lack of convenient measurement techniques has led



Source: Reiter 1973

Figure A1. Horizontal dispersion as function of travel time in Ekman layer

Table A1. Dispersion coefficients as function of downwind distance

Stability A:	$\ln\sigma_z = 5.81122 + 1.85573 \ln x + 0.21286 \ln^2 x$	$0.1\ km < x < 0.5$
	$\ln\sigma_z = 6.11949 + 2.11172 \ln x - 0.01403 \ln^2 x$	$0.5\ km < x < 3.0$
Stability B:	$\ln\sigma_z = 4.67051 + 1.10332 \ln x + 0.04673 \ln^2 x$	$0.1\ km < x < 0.5$
	$\ln\sigma_z = 4.69056 + 1.09809 \ln x - 0.00141 \ln^2 x$	$0.5\ km < x < 30$
Stability C:	$\ln\sigma_z = 4.11299 + 0.91978 \ln x - 0.00230 \ln^2 x$	
Stability D:	$\ln\sigma_z = 3.41719 + 0.72416 \ln x - 0.03011 \ln^2 x$	
Stability E:	$\ln\sigma_z = 3.05358 + 0.68065 \ln x - 0.04518 \ln^2 x$	
Stability F:	$\ln\sigma_z = 2.61422 + 0.65736 \ln x - 0.05307 \ln^2 x$	
Stability A:	$\ln\sigma_y = 5.35811 + 0.87909 \ln x - 0.00640 \ln^2 x$	
Stability B:	$\ln\sigma_y = 5.05796 + 0.90491 \ln x - 0.01009 \ln^2 x$	
Stability C:	$\ln\sigma_y = 4.65255 + 0.91822 \ln x - 0.00784 \ln^2 x$	
Stability D:	$\ln\sigma_y = 4.22930 + 0.92311 \ln x - 0.00844 \ln^2 x$	
Stability E:	$\ln\sigma_y = 3.92676 + 0.92255 \ln x - 0.00725 \ln^2 x$	
Stability F:	$\ln\sigma_y = 3.52621 + 0.92286 \ln x - 0.00755 \ln^2 x$	

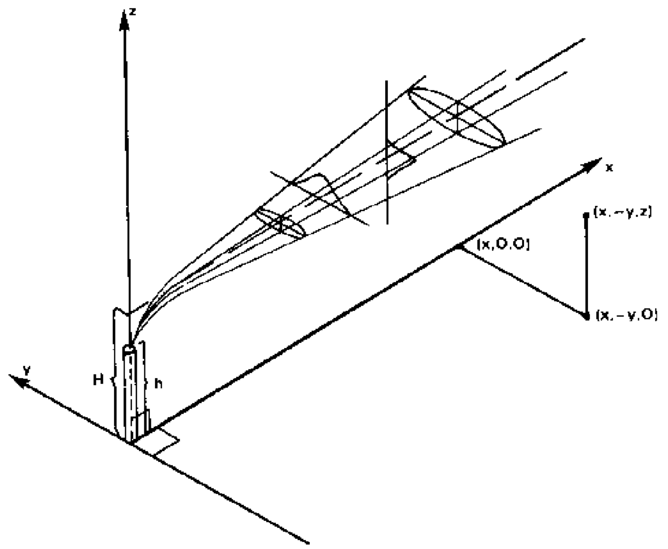
x in km

OR:

Stability D: $\sigma_z = 0.2048\ x^{0.7242}$ [x in m]

Stability C: $\sigma_z = 0.11\ x^{0.915}$

ln— logarithm natural



Source: Turner 1969

Figure A2. Gaussian distribution in horizontal and vertical

Table A2. Dispersion model for point sources

$$\chi \cdot \left(\frac{Q \cdot f_j}{u_j}\right)^{-1} = \left\{ \frac{9.923}{X^{1.724}} \cdot \exp\left(- \frac{H_j^2}{0.0839 \cdot X^{1.45}}\right)\right\} \longrightarrow \text{"D" stability}$$

$$\chi \cdot \left(\frac{Q \cdot f_j}{u_j}\right)^{-1} = \left\{ \frac{18.45}{X^{1.915}} \cdot \exp\left(- \frac{H_j}{0.0242 \cdot X^{1.83}}\right)\right\} \longrightarrow \text{"C" stability}$$

Q—emission rate in grams/sec
u_j—wind speed in direction j
X—downwind air force in meters
f_j—frequency with which wind is blowing in direction j (N, NNE, NE, ENE, E, . . . and others)

X[m] =	250	500	750	1000	1250	1500	2000	2500	3000	4000	5000
	3.53×10^{-8}	5.81×10^{-6}	1.45×10^{-5}	1.76×10^{-5}	1.74×10^{-5}	1.30×10^{-5}	1.24×10^{-5}	9.67×10^{-6}	7.67×10^{-6}	5.12×10^{-6}	3.66×10^{-6}
H_j = 50m											
C	6.90×10^{-6}	3.81×10^{-5}	3.27×10^{-5}	2.38×10^{-5}	1.73×10^{-5}	1.58×10^{-5}	8.01×10^{-6}	5.40×10^{-6}	3.87×10^{-6}	2.27×10^{-6}	1.50×10^{-6}
D	–	2.65×10^{-7}	2.61×10^{-6}	5.69×10^{-6}	7.66×10^{-6}	8.46×10^{-6}	8.21×10^{-6}	7.17×10^{-6}	6.09×10^{-6}	4.40×10^{-6}	3.28×10^{-6}
H_j = 70m											
C	1.90×10^{-7}	2.02×10^{-5}	2.02×10^{-5}	1.79×10^{-5}	1.44×10^{-5}	1.14×10^{-5}	7.40×10^{-6}	5.11×10^{-6}	3.73×10^{-6}	2.22×10^{-6}	1.47×10^{-6}
D	2.30×10^{-14}	3.16×10^{-8}	8.04×10^{-7}	2.62×10^{-6}	4.36×10^{-6}	5.49×10^{-6}	6.18×10^{-6}	5.83×10^{-6}	5.20×10^{-6}	3.96×10^{-6}	3.04×10^{-6}
H_j = 80m											
C	1.61×10^{-8}	5.94×10^{-6}	1.45×10^{-5}	1.47×10^{-5}	1.26×10^{-5}	1.03×10^{-5}	7.10×10^{-6}	4.93×10^{-6}	3.63×10^{-6}	2.33×10^{-6}	1.46×10^{-6}
D	2.50×10^{-17}	6.00×10^{-9}	3.20×10^{-7}	1.43×10^{-6}	2.81×10^{-6}	3.92×10^{-6}	4.94×10^{-6}	4.97×10^{-6}	4.57×10^{-6}	3.65×10^{-6}	2.86×10^{-6}
H_j = 85m											
C	2.35×10^{-9}	4.03×10^{-6}	1.12×10^{-5}	1.26×10^{-5}	1.14×10^{-5}	9.64×10^{-6}	6.71×10^{-6}	4.79×10^{-6}	3.56×10^{-6}	2.16×10^{-6}	1.45×10^{-6}
D	–	9.90×10^{-10}	1.17×10^{-7}	7.37×10^{-7}	1.74×10^{-6}	2.72×10^{-6}	3.88×10^{-6}	4.17×10^{-6}	4.02×10^{-6}	3.35×10^{-6}	2.69×10^{-6}
H_j = 90m											
C	2.90×10^{-10}	2.24×10^{-6}	8.48×10^{-6}	1.07×10^{-5}	1.02×10^{-5}	8.91×10^{-6}	6.40×10^{-6}	4.65×10^{-6}	3.48×10^{-6}	2.13×10^{-6}	1.43×10^{-6}
D	–	1.06×10^{-10}	3.40×10^{-8}	3.25×10^{-7}	9.65×10^{-7}	1.72×10^{-6}	2.88×10^{-6}	3.36×10^{-6}	3.40×10^{-6}	3.00×10^{-6}	2.49×10^{-6}
H_j = 100m											
C	2.15×10^{-11}	1.08×10^{-6}	5.99×10^{-6}	8.72×10^{-6}	8.90×10^{-6}	8.08×10^{-6}	6.04×10^{-4}	4.47×10^{-6}	3.38×10^{-6}	2.10×10^{-6}	1.42×10^{-6}
D	–	–	4.35×10^{-9}	8.40×10^{-8}	3.62×10^{-7}	8.13×10^{-7}	1.74×10^{-6}	2.35×10^{-6}	2.58×10^{-6}	2.50×10^{-6}	2.18×10^{-6}
H_j = 110m											
C	–	3.22×10^{-7}	3.37×10^{-6}	6.20×10^{-6}	7.10×10^{-6}	6.67×10^{-6}	5.49×10^{-6}	4.20×10^{-6}	3.23×10^{-6}	2.04×10^{-6}	1.39×10^{-6}

to the acceptance of six stability classes for air pollution modeling (A, B, C, D, E, F), each characterized by a set of dispersion coefficients $\sigma_z\ \sigma_y$ (Table A1). It is well known that vertical dispersion is limited to an effective mixing height L above ground, which is determined by atmospheric stability. For vertical distances larger than L, the dispersion coefficient σ_z decreases markedly. The most drastic limitation for vertical mixing is represented by an inversion, which acts like a boundary. The plume homogeneously fills the space from the ground to the effective mixing height with negligible penetration while still dispersing in the cross wind distance (y direction). The following method has been adopted to take care of this situation: the vertical dispersion coefficient σ_z is allowed to increase with distance to a value of L/2.15. At this downwind distance X_L, the plume is assumed to have a Gaussian distribution in the vertical. By the time the plume has traveled twice this far, $2X_L$, the plume has become uniformly mixed, that is, the concentration does not vary with height further downwind. The plume concentration is then given by:

$$\chi\,(X, y, z, H) = \frac{Q}{2\pi\ \sigma_y \cdot L \cdot u}\ \exp\left[-\tfrac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \qquad (4)$$

The Gaussian-type transmission model described above depends crucially on the knowledge of σ_y and σ_z at any place between source and sink. The longer that distance, the greater the chance of changes in atmospheric stability encountered by the plume in between, particularly above rough terrain (cities, mountains), and in the transition between land and ocean. Furthermore, changes in wind speed and direction (wind meandering around an average direction) can impose great uncertainties upon the transmission model.

For predicting ground-level concentrations over one hour, a further modification is introduced that allows the prediction of seasonal or annual ground-level concentrations. This requires knowledge of the stability wind rose (u_j and σ_{zs} for every wind direction θ: N, NNE, NE, ENE, E, and others). The average concentration can then be expressed by

$$\chi\,(X, \theta) = \sum_{(\text{stability})} \sum_j \left\{ \frac{2Q\ f_j\ (\theta, \text{stability}, j)}{2\pi\ \sigma_z\ (\text{stability}) \cdot u_j\left(\frac{2\pi X}{16}\right)}\ \exp\left[-\tfrac{1}{2}\left(\frac{H_j}{\sigma_{z,s}}\right)^2\right]\right\} \qquad (5)$$

Using stability classes C and D (most representative for seasonal or annual averages) and σ_z from Table A1, we find numerical values for

$$\chi \cdot \left(\frac{Q \cdot f_j}{u_j}\right)^{-1}$$

as functions of H_j and downwind distance X. For example, a point source emitting gases or particles at a rate of 10g/sec from 50 m (164 ft) above ground under annual meteorological conditions of $u = 5\ \text{m}\cdot\text{s}^{-1}$ and $f_j = 0.25$ (wind was blowing 25% of the time from one of the 16 compass directions) would cause a ground-level exposure 3,000 m (9,843 ft) downwind from the source of

$$\chi = \frac{7.67 \cdot 10^{-6} \cdot 5}{10 \cdot 0.25} = 15\ \mu\text{g/m}^3 \quad \text{(D stability)}$$

$$\chi = \frac{3.87 \cdot 10^{-6} \cdot 5}{10 \cdot 0.25} = 7.7\ \mu\text{g/m}^3 \quad \text{(C stability)}$$

Several point sources (regardless of height of release) within a limited area make individual plumes indistinguishable at some distance downwind, depending on the separating

Table A3. Wind speed and mixing heights, New York City

New York upper air observation point is located at Kennedy International Airport, elevation 13 ft, lat 40°39′, long 73°47′

A. Mean seasonal and annual morning (M) and afternoon (A) mixing heights and wind speeds when there was no precipitation.

	Height (m)	Wind Speed (m/sec)		Height (m)	Wind Speed (m/sec)
WINTER			SPRING		
M	875	8.3	M	788	6.9
A	901	8.2	A	1,360	8.7
SUMMER			AUTUMN		
M	662	5.5	M	675	6.6
A	1,512	6.8	A	1,086	7.4
ANNUAL					
M	750	6.8			
A	1,214	7.8			

B. Total number of episode days in five years for various mixing heights and wind speeds with no significant precipitation for episodes lasting at least two days

Example: For a mixing height of 500 m or less and wind speeds less than or equal to 6.0 m/sec, 1-3 W means one episode with a total of three episode days, winter being the season of greatest episode days.

W = Winter, S = Spring, SU = Summer, and A = Autumn

Mixing Height (m)	Wind Speeds (m/sec)		
	2.0	4.0	6.0
500	0-0	1-2 A	3-7 A
1,000	0-0	3-6 A	11-31 W
1,500	0-0	4-9 A	28-80 A
2,000	0-0	5-12A	39-111A

C. Total number of episode days in five years for various mixing heights and wind speeds with no significant precipitation for episodes lasting at least five days.

Mixing Height (m)	Wind Speeds (m/sec)	
	4.0	6.0
500	0-0	0-0
1,000	0-0	1-5 W
1,500	0-0	4-22A
2,000	0-0	4-22A

Note: Between 1 August 1960 and 3 April 1970 the southern half of New York State had about 10 forecast days of high meteorological potential for air pollution in a five year period.

Source: Holzworth 1972

distance of the individual sources and the effective mixing height. Area sources such as automobile traffic further aid in the buildup of urban domes with rather uniform distribution of emitted gases and particles. With proper ventilation, such an urban dome can be considered a pseudopoint source if the areal dimensions are small compared with the downwind distance from that point source. Equation (5) can be simplified, assuming that further vertical mixing is limited to below the effective mixing height L

$$\chi = \frac{Q \cdot f_j}{L \cdot u \frac{2\pi X}{16}} \qquad \frac{2.55 \cdot Q}{L \cdot u \cdot X} \cdot f_j \tag{6}$$

This equation expresses the principal parameters affecting air quality: low effective mixing height and low ventilation increase the concentration of gaseous or particulate material emitted into the atmosphere at a rate Q.

Seasonal average mixing heights and wind speeds are found in Lettau (1976). The air pollution potential for New York City, which in part applies to the air pollution situation in the Bight, is shown in Table A2.

Appendix 2. Example for long-range transport

The Bight coastal area not only represents a large emission source by itself, but it is surrounded by districts with similar emission characteristics. Probably some of these emissions are transported into the Bight area. With the appropriate transmission function (transport model), simplified source configurations were used to demonstrate the types of pollutant patterns that might be encountered in the Washington, DC-to-Boston corridor. The trace gas used for demonstration is carbon dioxide ($T_{1/2} = \infty$), estimated from total values of fuel usage in each state in the study area:

$$\chi = \frac{Q}{2\pi\left(\sigma_{y_0}{}^2 + \sigma_y{}^2\right)^{1/2} \cdot L \cdot u} \cdot \exp\left[-\tfrac{1}{2}\frac{y^2}{\left(\sigma_{y_2}{}^2 + \sigma_y{}^2\right)} + \frac{0.693 \cdot t}{T_{1/2}}\right] \tag{7}$$

σ_{y_0}: one-fourth of the diameter of a circle with an area equal to a particular county's area (m);

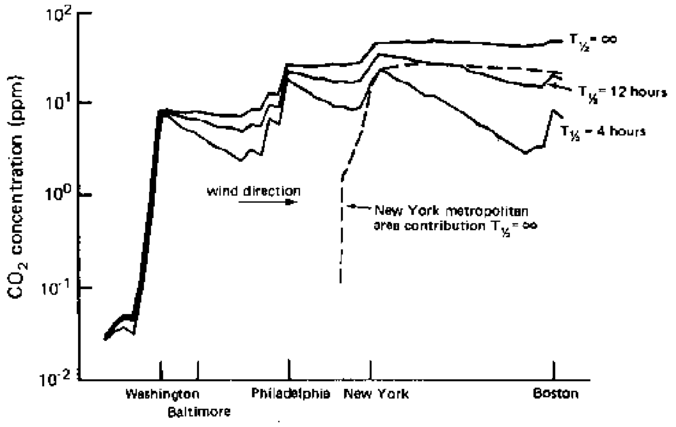
χ: average concentration g/m^3, later converted to ppm;

t: travel time from a county center to a computation point (sec);

$T_{1/2}$: half-lifetime of constituent (sec).

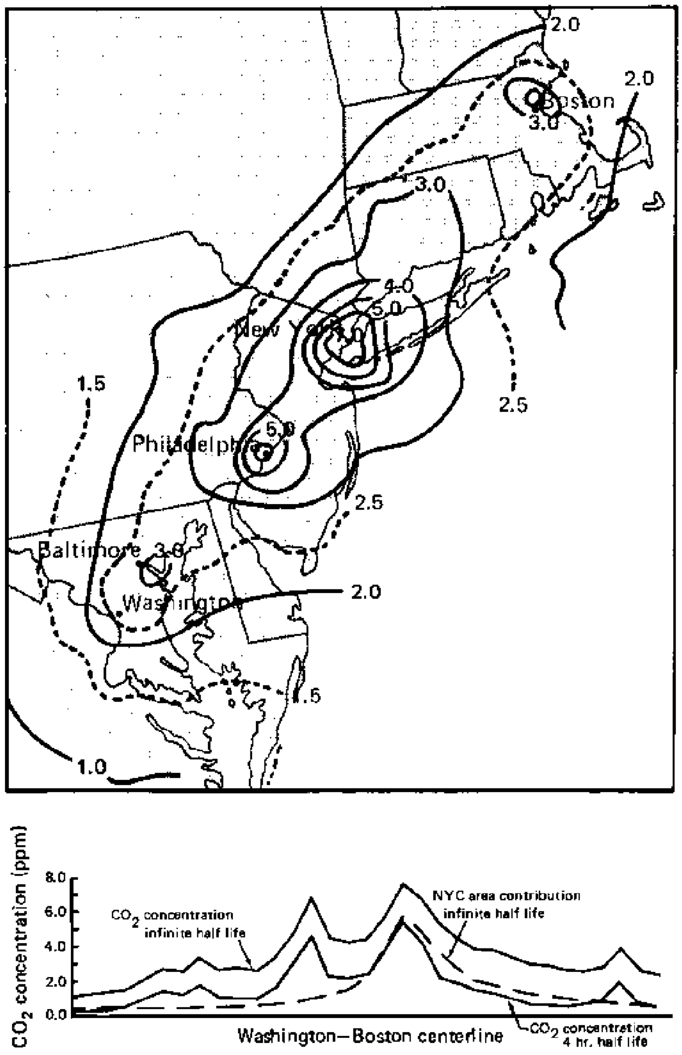
The decay exponential was included so that the model could be evaluated by some other pollutant that might be released in proportion to carbon dioxide but that would be affected by scavenging during its travel.

The downwind concentration in the pollutant plume described by equation (6) in Appendix 1 was computed for each of 110 counties within approximately ± 150 km (± 93 mi) of the Washington, DC-Boston axis. The contribution of each county's plume to each of 50 possible grid points (15 km or 9 mi apart) in the center line was obtained, and all contributions were totaled at each grid point.



Source: Slade 1967

Figure A3. Carbon dioxide concentration along Washington, DC-Boston axis, with wind blowing toward Boston



Source: Slade 1967

Figure A4. Average annual carbon dioxide concentration isopleths, Washington, DC-Boston axis

When the three lines of Figure A4 are considered as representing three different hypothetical pollutants released in identical quantity, it can be seen that for the same maximum permissible concentration (10 ppm, for example), pollution would be a problem in the entire region from Philadelphia to Boston for the infinite or 12-hr half-life material but would constitute an essentially metropolitan problem for the 4-hr half-life material. The effect of the New York metropolitan area on maintaining high trace gas concentrations between New York and Boston is also shown in Figure A3. The New York metropolitan area, defined as comprising 15 counties, extends about 150 km (93 mi) along the computation axis and 40 km (25 mi) to either side.

Figure A4 shows the isopleths of average annual concentration for an atmospheric constituent with $T_{1/2} = \infty$ (in reality, longer than two weeks), such as carbon monoxide and carbon dioxide. The possibility of pollutant influx into the New York Bight area can definitely not be dismissed.

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