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EPA-View of Stationary and Mobile No_x-Source Control

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ABSTRACT

Recent evolution of EPA's stand on the NO_x problem are developed. Some of the more significant aspects of this evolution in terms of established air quality bases and the adoption of standard analytical methodology and measurement techniques are presented. Changes in control strategies for stationary sources resulting from EPA's findings are also discussed.

Introduction

EPA's view of the NO_x problem has undergone considerable change since the passage of the Clean Air Act of 1970. A complete description of EPA's policy reflecting this change will be forthcoming within the near future. The most significant effect of this change in outlook was reflected in Administrator Ruckelshaus' testimony before the Senate Subcommittee on Air and Water Pollution during the week of April 16, 1973. The Administrator asked the Senate Committee to rescind the statutory requirement under Section 202(b) of the Clean Air Act that light duty vehicles and engines manufactured during and after the 1976 model year achieve a reduction of at least 90% from the average emissions of oxides of nitrogen actually measured from light duty vehicles manufactured during the 1971 model year. The 1971 emissions averaged 3.5 grams per mile and the 1976 standard is 0.4 grams per mile. The Administrator has also requested that Congress grant him the power under section 202(a) of the Act to set standards as he sees fit. If this were granted it is likely that a

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Table 1. Federal Light Duty Motor Vehicle Emission Standards (GM/MI)

Model year	*Hydrocarbons*	*Carbon Monoxide*	*Oxides of Nitrogen*
Prior to controls	(8.7)	(87)	(3.5)
1968-1969	50-100 cid—10.7	66	—
	101-140 cid— 8.5	57	
	over-140 cid— 6.8	43	
1970	4.1	28	—
1971	4.1	28	(3.5)
1972	3.0	28	
1973	3.0	28.0	3.1
1974	3.0	28.0	3.1
1975	California— 0.9	9.0	2.0
	National— 1.5	15.0	3.1
1976	0.41	3.4	0.4
1977	0.41	3.4	0.4

All standards for NC and CO are expressed in terms of the 1975 Federal CVS test procedure. The 1975 Federal NO_x standard has been prescribed pursuant to Section 202(a) of the Act.

standard would be set significantly higher than the 0.4 grams per mile currently in effect for 1976. Applicable standards expressed in terms of the 1975 Federal CVS procedure are given in Table 1.

EPA is particularly concerned about changing the 1976 emissions standards for oxides of nitrogen in motor vehicles because it no longer appears necessary for the achievement of national ambient air quality standards and because it represents a most difficult emissions control goal to achieve. In fact it has been determined that attempts to achieve the emission standard for oxides of nitrogen using a catalyst system could jeopardize achievement of the CO and hydrocarbon standards while imposing a sizable fuel penalty of about 15%. If given this authority, the Administrator would not change the standard immediately, but would wait until new health effects data were obtained and evaluated. The standard would then be set at a level that is adequate to protect against health effects and to provide for maintenance of the national ambient air quality standard by minimizing the impact of growth on existing ambient concentrations. In setting new emission limitations to maintain ambient air quality standards for nitrogen dioxide (NO_2) EPA would seek to obtain a balance in the requirements imposed on stationary sources and mobile sources.

This revision in EPA's evaluation of the NO_2 problem is primarily the result of the Agency re-examination of the air quality measurement method used in various presentations to establish the status of the NO_2 pollution problem. Some of these presentations were made before Congress prior to the passage of the Clean Air Act of 1970 and some constituted the air quality data used in the development of States' implementation plans. EPA is now convinced that important portions of the data base used in these two activities were unreliable.

It should be stated clearly at this point that a national ambient air quality standard has been established specifically for nitrogen dioxide (NO_2). No air quality standard has been established, nor is contemplated, for nitric oxide (NO) Emission standards and control strategy, on the other hand, have been expressed in terms of oxides of nitrogen in recognition of the fact that the major source of NO_2 associated with significant ambient concentrations is NO contained in the atmosphere as a result of emissions from combustion sources. Only a small and relatively insignificant amount of NO_2 is produced directly and emitted by these sources.

Air Quality Data Base

For several years various investigators have argued that discrepancies existed between air quality measurements of NO_2 made with the Jacobs-Hochheiser procedure used in the National Air Surveillance Network (NASN) and air quality data obtained through various other sampling techniques, particularly the Saltzman method. This argument climaxed on April 30, 1971, when EPA promulgated the National Ambient Air Quality Standards. The standard analytical methodology to be used to measure the ambient concentrations of each of the six pollutants for which national standards were being set was also stipulated. These were referred to as "reference methods." The reference method for NO_2 was the Jacobs-Hochheiser method. The regulation establishing this "reference method" would have to meet certain criteria in order to demonstrate their equivalence to the reference method. These criteria will be published in the near future.

When States attempted to develop implementation plans in 1971, they found that air quality data for carbon monoxide, nitrogen dioxide, and photochemical oxidants were generally sparse. In response to this need EPA in the summer of 1971 conducted a special study of air quality levels for these pollutants in those urban areas where data were sparse. This Summer Study using the Jacobs-Hochheiser method became the source of a considerable amount of the ambient NO_2 data used by the States to develop their implementation plans.

Based on the results of the Summer Study and various other data available from the NASN stations, state and local agency networks, it was determined by the end of 1971 that 47 Air Quality Control Regions (AQCR) in 29 states should be classified Priority I for NO_2.

Priority classifications of either I or III are assigned to AQCR's as a means of indicating the degree of control of emissions of oxides of nitrogen that may be necessary to provide for the achievement of the NO_2 standard. Priority I is assigned to those regions where air quality levels have equaled or exceeded 110 ug/m^3 or 0.06 ppm as an annual arithmetic mean. Those with lower concentrations are assigned a Priority III classification. The national ambient air quality standard was set at 100 ug/m^3 or 0.05 ppm as an annual arithmetic mean.

In order to determine the control strategy necessary to meet air quality standards for NO_2 in these regions, Federal regulations required the following procedures:

1. Assume certain emission reductions that will result from the Federal new motor vehicle emission standards.
2. Take credit for the impact of any transportation control measures taken to achieve carbon monoxide and photochemical oxidant standards.
3. Impose emission limitations attainable with reasonably available control technology on stationary sources.
4. If 1, 2, and 3 do not achieve sufficient NO_x emission reduction of hydrocarbons as may be possible by reasonably available control technology. (Hydrocarbons are associated with the conversion of NO to NO_2 in the atmosphere.)

EPA has determined that certain control technology for existing sources of oxides of nitrogen is reasonably available for combustion sources and nitric acid plants. The achievable emissions limitations are listed in Table 2 and compared with performance standards for new sources. In 1972 some states adopted regulations containing emissions limitations similar to these. Where States failed to adopt such emissions limitations EPA proposed them. In deference to the existing controversy over the accuracy of air quality data for NO_2 EPA refrained from making final promulgations.

Table 2. NO_x Emission Limitations Reflecting Available Technology

Source type	*Existing source—Appendix B*	*New sources—NSPS*
Fuel combustion		
Gaseous	0.2 (170)^A	0.20 (170)
Liquid	0.3 (230)^A	0.30 (230)
Solid	—	0.70 (525)
Nitric acid plants	5.5 lb per ton of 100% acid produced (400)	3.0 lb per ton (220)

( ) = PPM on a dry basis at 3% oxygen

A = About a 50% reduction in emissions from uncontrolled fuel burning equipment.

Measurement Techniques

Prior to 1970 there was one basic technique used for the measurement of ambient concentrations of NO and NO_2. This technique involved the Griess-Ilosvay reaction for NO_2 which was utilized in the Saltzman and the Jacobs-Hochheiser methods.

Other techniques not amenable to ambient sampling were gas chromatography, long-path infra-red spectroscopy and electrochemical oxidation or reduction. Over the past six years EPA has fostered the development of the gas phase chemiluminescence technique for application to air quality monitoring.

The Griess-Saltzman method was deemed the most suitable manual method for measurement of NO_2 in the atmosphere by the Standardization Advisory Committee, National Air Pollution Control Administration, and the Intersociety Committee on Manual Methods for Ambient Air Sampling and Analysis. In this procedure NO_2 'containing air is bubbled through the Griess-Saltzman reagent for a period of up to 30 minutes. The Saltzman reagent consists of, among other things, sulfanilic acid and N-(1-napthly)-ethylenediamine dihydrochloride. NO_2 reacts with these compounds to form a diazo dye with a characteristic color whose intensity is proportional to the amount of NO_2 absorbed. This method is usable for NO_2 in air of 40 - 1500 ug/m^3 (0.02 to 0.75 ppm). Using sodium nitrite as a calibration standard, Saltzman found that 0.72 mole of nitrite produced about the same color as 1 mole of NO_2 gas. The method is fairly specific for NO_2 and no significant interferences commonly occur. SO_2 for example shows significant interference only at concentrations of about 30 times that of NO_2.

The problem with the field application of this method lies in the need to limit absorption time to about 30 minutes and the analysis time to one hour after color development. In order to develop a procedure to meet the need for sampling over periods as long as 24 hours, the Jacobs-Hochheiser method was developed.

In an EPA modification of this procedure sodium hydroxide (.1 N NaOH) is used as an absorbing reagent. Sulfanilamide replaces the sulfanilic acid of the Saltzman reagent and the acid is phosphoric acid rather than acetic. Since some of the NO_2 absorbed goes towards the formation of sodium nitrate, on the average only 0.63 mole of nitrite was required to produce the same color as 1 mole of NO_2 gas. This stoichiometric factor has been the source of considerable controversy in recent years with values reportedly ranging from 0.5 to 1.00 (for the equivalent quantity of nitrite ion).

All NASN measurements have used an NO_2-Nitrite stoichiometric factor of 1.0. That is to say, only nitrites and not nitrate ions were assumed to be formed during the absorption of the gas from the ambient air.

It was also determined that the absorption efficiency of NO_2 was highly variable with NO_2 concentration and was also dependent on the amount of NO present in the air. On the basis of detailed studies made under laboratory conditions the NASN system was assumed to have an efficiency of approximately 35%.

The Saltzman method was also adopted to continuous analyzers and was used in EPA CAMP stations as well as stations operated by various state and local agencies. Most of these analyzers were also used for measurement of NO by first oxidizing all NO to NO_2 and subjecting it to the process of diazotization. The

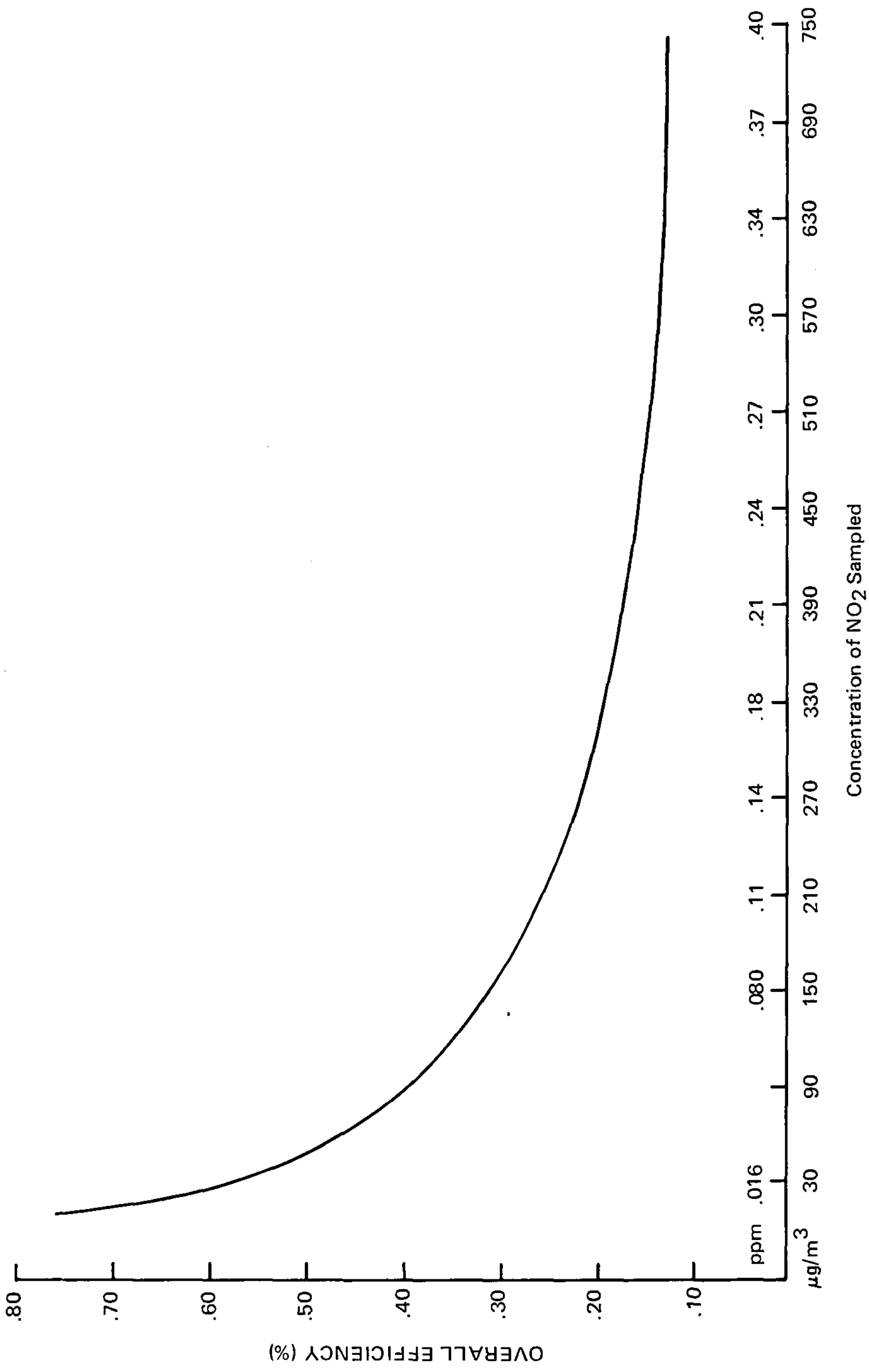
OVERALL EFFICIENCY (%)
.80
.70
.60
.50
.40
.30
.20
.10
ppm
.016
.080
.11
.14
.18
.21
.24
.27
.30
.34
.37
.40
µg/m3
30
90
150
210
270
330
390
450
510
570
630
690
750
Concentration of NO2 Sampled

Figure 1.

oxidation process reportedly has an efficiency ranging from 40% to 100% (using potassium permanganate or dichromate or chromium trioxide).

Differences in the air quality data obtained from the Saltzman and Jacobs-Hochheiser methods at the same sites led EPA to make a careful examination of the reliability of its reference method and the accuracy of the air quality data used for priority classification. A report on the first phase of the EPA investigations and the findings was made by Hauser and Shy in October 1972.

In this first phase, a test of the efficiency of the reference method was made using nitrogen dioxide, air mixtures of varying concentrations generated by the use of NO_2 permeation tubes. For each of the test atmospheres generated, at least five simultaneous samples were collected and analyzed. The results shown in Figure 1 indicate that the collection efficiency of the reference method varies nonlinearly with NO_2 concentration from about 15% at 740 ug/m^3 to about 70% at 20-30 ug/m^3. For an ambient level of about 120 ug/m^3 the previously assumed efficiency of 35% is valid. Above that level, the use of a 35% efficiency will underestimate the actual concentrations in ambient air. At lower ambient concentrations, the reference method will result in erroneously high estimates of concentration if a 35% efficiency is assumed.

The effect of the presence of nitric oxides (NO) on the reverence method was also examined. The response of this method to various concentrations of NO_2 with and without NO is given in Table 3. A comparison of the expected and apparent NO_2 recovered shows positive interference from NO.

Since these problems with efficiency and interference were related to the

Table 3. Effect of NO on the Reference Method for NO_2

ug/m^3				
NO_2	NO	Ratio HO/NO_2	Expected HO_2 recovered %	Apparent NO_2 recovered %
100	0	0.0	39	38
102	63	0.6	39	38
105	127	1.2	38	52
122	627	5.1	36	57
189	0	0.0	29	29
244	1205	4.9	24	45
248	1279	5.2	23	55
215	1242	5.8	26	50
311	0	0.0	20	17
316	111	0.4	20	30
318	332	1.1	20	33
356	1060	3.0	18	44

absorbing solution, EPA examined several alternate solutions for possible adoption. Three different absorbing reagents were tested in the NASN network and two were rejected because of physical problems even though collection efficiencies were higher and more consistent than those of the Jacobs-Hochheiser Method [1]. The sodium arsenite-sodium hydroxide reagent has been found most satisfactory by EPA. This reagent (the method is called the Christie method) has been tested at all 200 stations of the NASN network since December, 1971, and has recently replaced the Jacobs-Hochheiser method in routine sampling.

In the second phase of this investigation beginning August, 1972, chemiluminescent equipment has been installed at selected urban sites in 41 of the AQCR's classified Priority I and at all CAMP stations where instruments using the continuous Saltzman methods were located.

The results of these measurements show that of the 47 AQCR's previously classified as Priority I only two, Los Angeles and Chicago, will definitely retain their former classification. Three other regions, Salt Lake City, Denver, and New York, are marginal. The remaining 42 AQCR's will all be reclassified Priority III.

Chemiluminescent analysers will also be maintained in 17 of the 47 AQCR's where annual average concentrations are expected to exceed 75 ug/m^3. Multiple sites will be located in New York, Los Angeles, and Chicago. The chemiluminescence method has been adapted to measure both NO and NO_2. In this technique NO undergoes a gas phase reaction with ozone to produce NO_2 in an excited State. The intensity of light emission from the reactor is proportional to the NO content of the sample. To measure concentrations of NO_2, a catalyst is first used to convert NO_2 to NO.

The NO thus produced is then reacted with Ozone.

Effects of Findings on Control Strategies for Stationary Sources in Implementation Plans

With the exception of Los Angeles and Chicago no control strategy for existing stationary sources over and above that which had been fully implemented by the end of 1972 is required to maintain the NO_2 standard in the absence of further growth. Where EPA has proposed emission limitations on sources of combustion for implementation plan purposes, these proposed regulations will be withdrawn.

Where states and localities have acted to promulgate regulations imposing emission limitations on these sources, EPA will work with the agencies in rolling back these actions as desired. There are some cases, however, in which states and localities have developed emissions standards prior to any EPA requirement for the purpose of meeting a local air quality standard or to reduce the potential for the production of photochemical oxidants. In these cases the matter remains one for local consideration. New York City is one of the latter. In the case of nitric acid plants or any other sources of NO_2 as a primary emission, existing control regulations will be required to stand.

In terms of control strategy to achieve the national air quality standard, it is estimated that Chicago will be able to show achievement by 1975 through the following measures:

1. Reductions attributable to the Federal new motor vehicle program through 1974.
2. Reductions obtained through the conversion in fuel from the use of coal to gas and oil.
3. Reduction in the formation of NO_2 in the atmosphere through the control of hydrocarbons.
4. Reductions obtained from the transportation control plan developed by Chicago to achieve CO and hydrocarbon standards.

Los Angeles was estimated to have an annual mean of 180 ug/m^3. The State of California already requires control of NO_x from motor vehicles. EPA believes that transportation control programs developed to meet the CO and photochemical oxidant standard existing stationary source controls and the vehicle emission control program will permit the achievement of the NO_2 standard in this AQCR.

Control Strategy to Provide for Maintenance and Growth

The requirement that implementation plans provide for the maintenance of standards into the far future imposes a need to develop control strategies which will adequately handle additional emissions associated with future growth. It is a very difficult problem to determine where the most cost effective reductions can be made whether in stationary or mobile sources, in high level or low level emissions.

An examination of the estimated emissions of NO_x in the U.S. in Tables 4

Table 4. NO_x U.S. 1968 (tons/yr)

Source	*Emissions*
Mobile fuel combustion motor vehicles	7,200,000
Other mobile sources	1,010,000
Stationary fuel combustion	9,980,000
Solid waste	556,000
Coal waste	190,000
Agricultural	1,533,000
Industrial processes	200,000
	20,669,000

Table 5. Emission Estimates, Millions T./Yr.

Source	*Part*	*SO_2*	*CO*	*HC*	*NO_x*
Transportation	1.0	1.0	77.5	14.7	11.2
Fuel combustion (Stationary)	6.5	26.3	1.0	0.3	10.2
Industrial processes	13.8	5.5	11.1	5.6	0.2
Solid waste disposal	0.7	0.1	3.8	1.0	0.2
Miscellaneous	5.2	0.1	6.5	5.0	0.2
1971 Total	**27.2**	**33.0**	**93.9**	**26.6**	**22.0**
1970 Total	**25.4**	**33.9**	**147.2**	**34.7**	**22.7**
1969 Total	**27.3**	**33.6**	**154.0**	**35.2**	**22.5**

The major changes from 1969-1971 are due to revised emission factors for transportation, HC and CO emissions and a considerable reduction in solid waste disposed by incineration.

and 5 shows that more than 99% of the total emissions are derived from combustion sources, more than 90% comes from the combustion of fossil fuels.

In the relatively high temperature conditions accompanying the combustion of fossil fuels and wastes, only a comparatively small amount of NO_2 is formed. In fact, the rate of oxidation of NO to NO_2 decreases with increasing temperature. It is estimated that at temperatures of 2000°F the NO_2 formed is only 0.5% of the NO_x. At the low concentrations of NO normally found in the atmosphere (1.0 ppm or 1200 ug/m^3) the subsequent oxidation of NO to NO_2 by direct reaction with oxygen in ambient air occurs very slowly. The rate of conversion is proportional to the square of the NO concentration leading to rapidly decreasing conversion with dilution. The primary mechanism for the formation of NO_2, therefore, is the photochemical process involving reactive hydrocarbons.

As a result of this, the diurnal variations in NO, NO_2 and ozone (or total oxidants) show the following pattern (Figure 2): An NO peak at approximately 7 a.m.; an NO_2 peak at approximately 10 a.m. and an ozone/oxidant peak around 12 noon to 3 p.m. The pattern is similar for both normal and stagnation conditions. Just as in the case of hydrocarbons and photochemical oxidants, it is the 6-9 a.m. emissions of NO which are most important in the production of the NO_2 maximum. There are also indications that the conversion from NO to NO_2 is a function of emission rate, meteorologically determined diffusion rate, and the reaction rate, which is determined by chemistry and meteorology. Because of the lag time in peak NO_2 production, total NO emissions are perhaps more important than individual point emissions from specific sources in determining peak NO_2 production. In built up areas like New York City, where daytime wind speeds near the surface are considerably lower than those at rooftop, the rate of dilution of emissions from motor vehicles is less rapid than the rate of

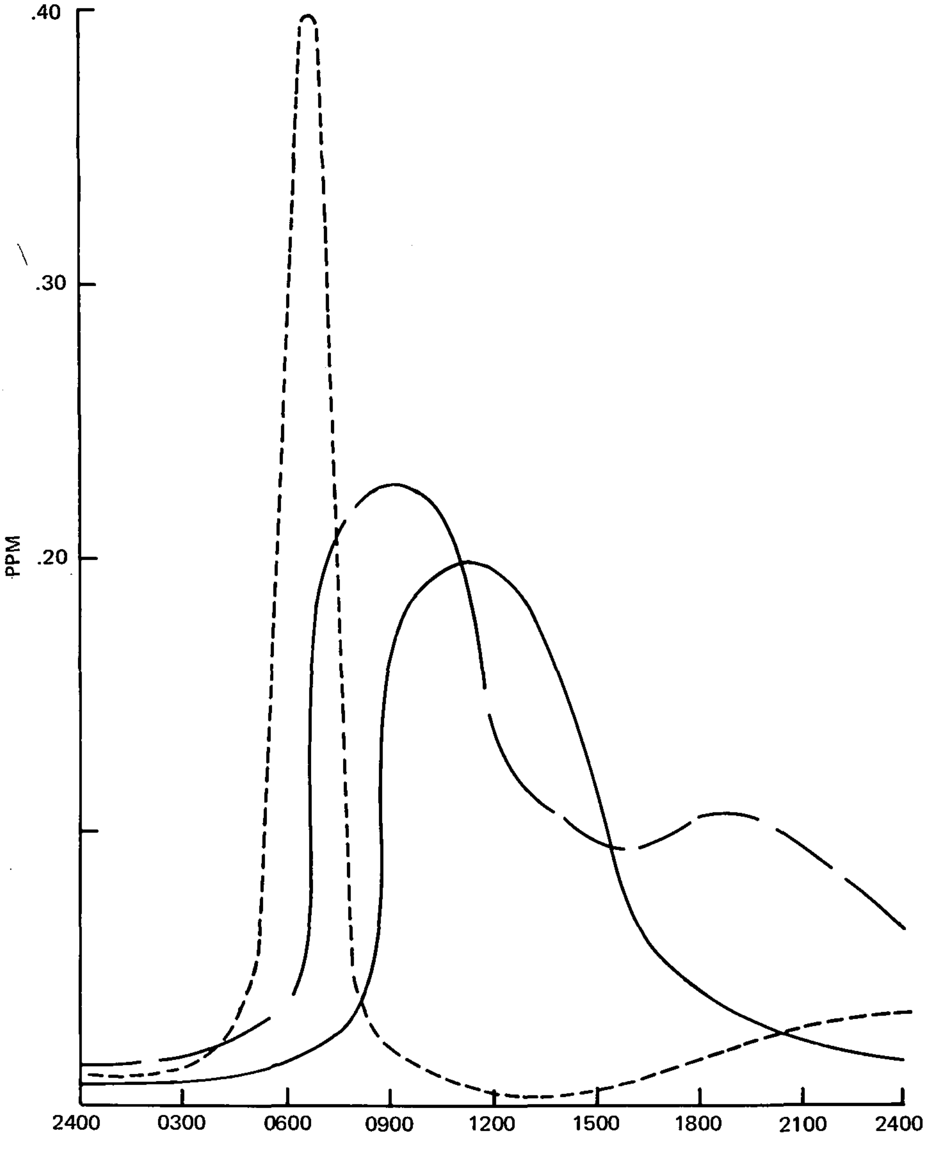

Figure 2. Average daily 1-hour concentrations of selected pollutants in Los Angeles, July 19, 1965.

dilution of emissions from rooftop and elevated sources. Since 40% of NO_x emissions are estimated to be derived from mobile sources, these sources must remain a primary source for emission reduction in future control strategy. This would hold true even in New York City where it has been estimated that 93,000 out of 332,000 tons of NO_x (or 28%) are produced by mobile sources. However, based on air quality measurements of SO_2 (for which a reliable inventory is available) it appears likely that emission of NO_x from stationary sources in New York City are considerably overestimated and that mobile sources play a greater role in NO/NO_x emissions in New York City than currently estimated.

EPA considers the existing schedule up through 1974 for control of NO_x emissions from mobile sources through the Federal new motor vehicle program essential for the maintenance of standards. Additional limitations are also needed for 1976 and later model year cars, but not as stringent limitations as the 90% reduction required by the Clean Air Act. The actual needs have not yet been determined.

To assist in maintaining air quality standards, EPA will retain standards of performance for NO_x emissions from new and modified stationary sources. In addition to this, future performance standards for sources of significant NO_x emissions will include NO_x emissions limitations that reflect best available control technology.

Effect of New Data on the National Standard

These findings concerning the reliability of the Jacob-Hochheiser method are important in respect to the determination of the national primary standard for NO_2 in which the Chattanooga School Children Study played an important role. The results obtained in that study with a modification of the reference method were compared with measurements made by the U.S. Army using continuous monitors based on the Saltzman method. These monitors, running simultaneously within 0.4 miles of the air monitoring sites established in the EPA study area, showed values of 0.099 ppm and 0.087 ppm in the period November, 1968, through April, 1969, as compared with a value of 0.109 ppm at the EPA study site. In addition, the individual measurements were adjusted on the basis of the true collection efficiency curve. The new estimates for the critical Chattanooga site showed an increase of 11.3% in exposure. Moreover, the U.S. Army collected NO data in the area which demonstrated that the NO/NO_2 ratio observed at Chattanooga would have had little effect on the apparent collection efficiency of NO_2.

These independent measurements of NO_2 exposures at Chattanooga, the findings on the efficiency of the Jacobs-Hochheiser method and the low level of possible NO interference, clearly indicate that the application of the Jacobs-Hochheiser method in the circumstances of the Chattanooga study did not significantly effect the choice of the national air quality standards. Further health effects studies are being conducted at CHESS sites using the Saltzman method and are expected to further substantiate the current standard. EPA is seeking, within the next 18 to 24 months, to establish the basis for a short term standard for NO_2.

Enforcement Standards

The major emphasis by EPA over the next few years will be in the area of standards and implementation plan enforcement. Federal Standards for NO_x have been promulgated for new motor vehicles only. Achievement of these emission standards will be determined through extensive Federally observed certification procedures of vehicle engines. There is still some question whether all vehicles will, in the future, be required to achieve the standards individually or whether averaging will be allowed. Certification requirements include durability tests for engines to maintain performance over 50,000 miles. Compliance by in-use vehicles will be monitored through inspection/maintenance programs.

Only in Chicago and Los Angeles will credit have to be taken for transportation control measures to demonstrate achievement of air quality standards. Enforcement of state developed transportation control plans will be the primary responsibility of the state. Where EPA is bringing direct actions to enforce an approved State plan or Federally promulgated section of a State plan, the Agency will proceed under Section 113(a)(1) of the Act. Under such circumstances EPA is bound to give a violator 30 days notice before issuing an order or bringing civil or criminal action.

EPA could also seek criminal penalties against an individual violator under Section 113(c)(a) of the Act. For cases in which there is widespread violations or cases in which a state has failed to enforce its strategies, it is EPA's current policy to seek compliance by the state under Section 113(a)(2) of the Act. Under this section EPA can issue orders and bring civil actions against the Director of state or city agencies charged with implementation of specific strategies.

For cases on which EPA might have to promulgate a plan the Agency will operate on the theory that the state is an emission source in that a highway or other publicly owned property on which motor vehicles operate is an emission source. On this principle, EPA would enforce a transportation control regulation through the issuance of an order to the responsible state or city agency rather than directly against a motorist. In these cases no 30-day notice is required.

Enforcement of stationary source control requirements for existing sources required to apply reasonably available control technology will be the primary responsibility of the states. Sources covered by new source performance standards will be regulated by EPA until the states obtain delegation of this responsibility and in cases where states have emission limitation regulations will occur at start-up of new sources and on an ad hoc basis in conjunction with states thereafter.

REFERENCE

1. T. Hauser and C. Shy, Position Paper: NO_x Measurement, *Environmental Science and Technology*, October 1972.