CHAPTER 8

MATHEMATICAL MODELING OF THE FORMATION OF NITROGEN-CONTAINING POLLUTANTS—II. EVALUATION OF THE EFFECT OF EMISSION CONTROLS

MATHEMATICAL MODELING OF THE FORMATION OF NITROGEN-CONTAINING POLLUTANTS—II. EVALUATION OF THE EFFECT OF EMISSION CONTROLS

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ABSTRACT

A grid-based Eulerian airshed model is used to study the effect of specific emission control measures on ambient NO_2, total inorganic nitrate (TN), HNO_3, aerosol nitrate, PAN, NH_3 and ozone concentrations in the Los Angeles area. NO_x and reactive hydrocarbon (RHC) emission reductions of up to 61% and 37%, respectively, are examined. NO_2 and TN concentration reductions in excess of 50% averaged over 20 monitoring sites are achieved at the highest level of emission control studied. The distribution of TN air quality improvements between HNO_3 and aerosol nitrate is affected by the NH_3 emission rate of the NO_x control technologies employed. Peak 1-hr O_3 concentrations at many sites in the eastern portion of the air basin studied decline by more than 25% at the highest NO_x and RHC control levels studied, with the final increment of NO_x control alone capable of producing O_3 concentration improvements at locations with the highest O_3 concentrations.

1. Introduction

In Part I of this series, the performance of a grid-based photochemical airshed model for ozone, NO_2, total inorganic nitrate (TN), PAN, HNO_3, NH_3 and aerosol nitrate (AN) formation and transport was evaluated (1). Model predictions were compared against experimental observations made for this purpose in the Los Angeles area over the period August 30-31, 1982 (2). It was found that O_3 and PAN concentration predictions were in excellent agreement with observations, and that NO_2 predictions were in closer agreement with observed values than in many previous studies. On average, TN, NH_3 and HNO_3 concentration predictions differed from observations by very small absolute amounts: 2.7 μgm^{-3} (1.1 ppb), 0.7 ppb; and 4.2 μgm^{-3} (1.65 ppb), respectively. In the present paper, that model will be used to explore the predicted effect of specific emission control measures on ambient air quality.

2. Emission Control Opportunities

Emission control measures evaluated as part of this study are itemized in Table 1. That table has been divided into 5 groups. Group 1 controls reflect a subset of the reduction possibilities that have been documented as part of the 1982 Air Quality Management Plan (AQMP) for the South Coast Air Basin that surrounds Los Angeles (3). This group of controls approximates the effect of many of the emission reductions that can be expected to be implemented in the Los Angeles area in the years following the 1982 base year, but without extension of vehicular catalyst utilization or ammonia injection technology beyond that used in 1982. Group 2 and Group 3 controls simulate the effect of fleet-wide improvements in emissions from motor vehicles, at target levels that have been discussed by state and federal regulatory agencies (7,9). Group 4 and Group 5 controls would further reduce NO_x emissions from stationary sources through the use of non-catalytic ammonia injection or selective catalytic reduction (SCR) technology.

The 1982 emission inventory employed during the model verification effort of Part I of this study (1, 15) will be referred to as the Base Case. The 1982 Base Case emissions from each source class that will be considered for control are given in Table 1, along with the percentage reduction in those emissions that would result if the control measures had been in effect during 1982 (i.e. 84% reduction implies that (1-84/100) = 0.16 times the Base Case emissions from a stated source class would remain if the stated control measure had been implemented). Although several of the control measures cited are cross-referenced to the AQMP planning document, the base year emission inventory of the present study (1982) differs from the 1979, forecast 1987 and forecast year 2000 inventories used in the AQMP. The objective of the present study is to provide information on the air quality effects that would be observed if the controls listed in Table 1 had been applied during the 1982 Base Case model verification days in the amounts specified. No attempt will be made to simulate the effect of emission controls during some hypothetical future year.

The largest number of control measures in Group 1 of Table 1 (those designated B-1 through B-8) are aimed at reducing solvent vapor emissions from painting and surface coating operations, usually through reformulation of the coating material or through reduced overspray during application. Reduction in fugitive hydrocarbon emissions from landfill gas leaks and oil and gas field fixture leaks is anticipated. The remaining hydrocarbon controls would suppress solvent losses from cleaning operations and pesticide application, or capture certain industrial process emissions using incineration, activated carbon adsorption or other vapor recovery methods.

Stationary source oxides of nitrogen controls included in Group 1 involve relatively straightforward modification of combustion system design, but without the use of ammonia injection or selective catalytic reduction technology. The effect of a mandatory vehicle inspection and maintenance program involving a no-load idle

Table 1. Specific Emission Control Measures and Their Effect if Applied to 1982 Emissions in the South Coast Air Basin.

		1982 THC[a] Emissions (ton/day)	1982 NO_x Emissions (ton/day)	1982 NH_3 Emissions (ton/day)	Control Measure	Effect of Controls THC Change (%)[m]	NO_x Change (%)[m]	NH_3 Change (%)[m]	Notes and References
Group (1)									
1	Wood furniture finishing	16.6	—	—	Use of water-based coatings and reduced overspray. (B-5)	−54.1			3
2	Auto refinishing	6.7	—	—	Use of low solvent or water-based coatings. (B-8)	−21.0			3
3	Wood flatstock coating	1.5	—	—	Afterburners on drying and curing ovens: (B-1)	−75.0			3
4	Industrial maintenance coatings	6.3	—	—	Use of low solvent or water-based coatings. (B-2)	−39.3			3
5	Marine coatings	2.4	—	—	Use of low solvent or more durable coatings. (B-3)	−82.8			3
6	Motor vehicle mfg. (painting)	8.2	—	—	Electrostatic coating and high solids paint. (B-4)	−41.2			3
7	Metal parts mfg. (coatings)	25.8	—	—	Substitute coatings. (B-6)	−28.6			3
8	Aerospace coatings	4.6	—	—	Use of low solvent coatings. (B-7)	−40.5			3
9	Oil and gas well leak reduction	27.3	—	—	Semi-annual inspection and maintenance. (A-3)	−50.0			3
10	Pesticide application	12.9	—	—	Changes in formulation and application methods. (C-3)	−27.3			3
11	Metal and non-metal parts cleaning	40.6	—	—	Covers on circuit board degreasers; fewer exemptions. (C-1)	−12.8			3
12	Paper and fabric coating	10.6	—	—	Afterburners or activated carbon adsorption on curing ovens. (D-2)	−50.0			3
13	Dry cleaning	17.9	—	—	Reduced transfer emissions (wash & dry in a single unit). (G-3)	−35.8			3
14	Landfill gas recovery	778.0[a]	—	—	Methane recovery. (F-1)	−46.1[a]			3
15	Rubber products mfg.	3.6	—	—	Incineration or carbon adsorption on fugitive organics emissions. (D-3)	−10.3			3
16	Synthetic chemical mfg.	2.1	—	—	Chemical absorbers, carbon adsorption, and process changes. (G-1)	−90.9			3
17	Marine fuel transfer	0.4	—	—	Vapor recovery systems. (A-7)	−90.9			3
18	Graphic arts industry	11.9	—	—	High solids or waterborne ink; incineration or adsorption. (G-2)	−85.0			3
19	Refinery boilers and heaters	—	40.3	—	Combustion modification.		−8.0		4
20	Residential water heaters	—	10.3	—	Intermittent ignition devices and stack vent valves. (N-18)		(−25.0)		3
21	Non-refinery industrial boilers	—	35.0	—	Combustion modification. (G-11)		−25.0		3
22	Cement kilns	—	9.7	—	Combustion modification. (G-7)		−40.0		3
23	Glass furnaces	—	3.2	—	Process modification.		−45.3		5
24	Light-duty highway vehicle exhaust	439.0	427.0	—	Inspection and maintenance (no-load idle test & repair).	−11.3	−9.4		6
Group (2) Additional Mobile Source Control									
25	Light-duty highway vehicle exhaust	439.0	427.0	2.8	Entire fleet meets 0.7 g/mi NO_x and 0.41 g/mi THC objective; NH_3 emissions reach 0.035 g/km; inspection and maintenance program continued.	−84.8	−73.3	+222	(b) 7,8
26	Heavy-duty diesel highway vehicle exhaust	25.8	157.0	0.02	Entire fleet meets objective of 10.7 g NO_x/BHP-hr and 2.65 g/mi THC.	−30.0	−25.9	—	(c) 9
27	Heavy-duty gasoline highway vehicle exhaust	18.6	35.7	(0.1)	Entire fleet meets objective of 10.7 g NO_x/BHP-hr and 2.65 g/mi THC.	−49.2	−34.8	0	(d) 9
28	Medium-duty highway vehicle exhaust (gasoline and diesel)	32.6	38.7	(0.3)	Entire fleet meets 1.5 g/mi NO_x and 0.6 g/mi THC objective (NH_3 emissions reach 0.035 g/km).	−82.0	−62.1	(+83)	(e) 8,9

Table 1. Continued

	1982 THC[a] Emissions (ton/day)	1982 NO_x Emissions (ton/day)	1982 NH_3 Emissions (ton/day)	Control Measure	Effect of Controls: THC Change (%)[m]	Effect of Controls: NO_x Change (%)[m]	Effect of Controls: NH_3 Change (%)[m]	Notes and References
Group (3) Stringent Mobile Source Control								
29 Light-duty highway vehicle exhaust	439.0	427.0	2.8	Entire fleet meets objective of 0.40 g/mi NO_x and 0.41 g/mi THC (NH_3 emissions held at 0.035 g/km).	−84.8	−84.8	+222	(f) 7,8
30 Heavy-duty diesel highway vehicle exhaust	25.8	157.0	0.02	Entire fleet meets objective of 5.1 g NO_x/BHP-hr and 2.65 g/mi THC.	−30.0	−65	0	(f) 9
31 Heavy-duty gasoline highway vehicle exhaust	18.6	35.7	(0.1)	Entire fleet meets objective of 5.1 g NO_x/BHP-hr and 2.65 g/mi THC.	−49.2	−69	0	(f) 9
Group (4) Stationary Source NO_x Control-Non-Catalytic NH_3 Injection								
32 Refinery boilers and heaters	—	40.3	(0.5)	Direct NH_3 injection.		−50	+869	(g) 4
33 Utility boilers	—	57.6	(1.6)	Direct NH_3 injection.		−40	+344	(h),10
34 Non-refinery industrial boilers	—	35.0	(0.65)	Direct NH_3 injection + combustion modification.		−55	+392	(i) 10
35 Cement kilns	—	9.7	—	Direct NH_3 injection.		−50	+	11
36 Glass melting furnaces	—	3.2	—	Direct NH_3 injection.		−50	+	5
Group (5) Stationary Source NO_x Control-Selective Catalytic Reduction								
37 Refinery boilers and heaters	—	40.3	(0.5)	Selective catalytic reduction.		−44	+ small	(j),12
38 Utility boilers	—	57.6	(1.6)	Selective catalytic reduction.		−90	+ small	(k),13
39 Non-refinery industrial boilers	—	35.0	(0.65)	SCR plus combustion modification.		−92	+ small	(l),13
40 Cement kilns	—	9.7	—	Selective catalytic reduction.		−90	+ small	11
41 Stationary industrial IC engines	—	74.2	—	Use of cataytic converters.		−66.7	+ small	14
42 Glass melting furnaces	—	3.2	—	Selective catalytic reduction.		−90.0	+ small	5

Notes

(a) THC equals Total Hydrocarbon emissions; in all cases except landfill gas leak reduction and oil and gas well leak reduction, THC ≃ RHC (Reactive Hydrocarbon emissions). Landfill emissions are mostly methane, with only 1.4% non-methane hydrocarbons. Only the non-methane hydrocarbon (NMHC) data are used by the air quality model, and the % control shown applies to the NMHC content of the emissions only.

(b) Computed by multiplying vehicle miles traveled (VMT) per day times 0.7 g/mi NO_x and 0.41 g/mi THC. NH_3 emissions become 9.14 metric tons/day.

(c) Computed by taking emissions from a new (undeteriorated) 1984 heavy diesel truck as representing 6.5 g/BHP-hr NO_x and also as equaling 10.31 g/mi NO_x. Ratio gives scale factor of 1.59 g mi^{-1}/(g/BHP-hr) NO_x. If entire fleet achieves 10.7 g/BHP-hr NO_x (representing a fleet average of 1984 trucks *with* deterioration) then emissions factor for entire fleet would be 17.0 g/mi. Emissions computed by multiplying VMT for heavy diesel vehicles times 17.0 g/mi. Hydrocarbon emissions obtained by multiplying 2.65 g/mi times heavy diesel vehicle VMT.

(d) A new 1984 heavy gasoline truck emits 4.25 g/mile NO_x corresponding to 6.94 g/BHP-hr. Calculation proceeds as in note (c) above.

(e) Computed by multiplying medium truck VMT per day times 1.5 g/mi NO_x and 0.6 g/mi THC. NH_3 emissions become 0.55 metric tons/day.

(f) Emmission reductions computed by procedure analogous to that for Group (2) Mobile Source Controls (see notes (b), (c), or (d)).

(g) NH_3 breakthrough is assumed to be 50 ppm NH_3 for reduction of 75 ppm NO_x (50%). Final NH_3 emission is 5.04 metric tons/day.

(h) NH_3 breakthrough is 50 ppm NH_3 giving total NH_3 emissions of 7.1 metric tons/day.

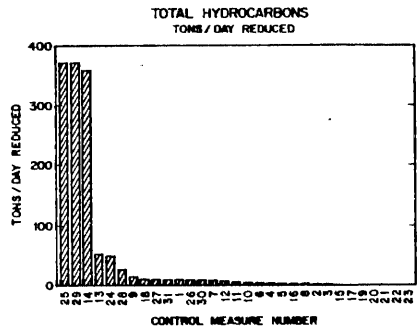
(i) Estimated based on utility boiler performance, see note (h) and reference 10.

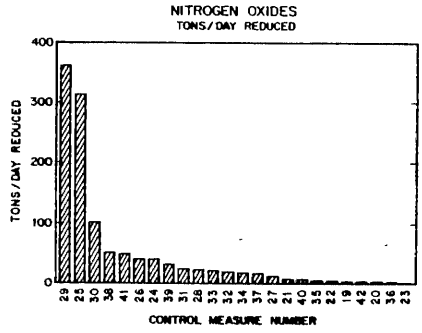
(j) SCR achieves 90% NO_x control but is applied only to the largest units, yielding 44% reduction relative to the entire source class.

(k) Ammonia bleed-through is 12 ppm.

(l) 25% control by combustion modification plus 90% control via SCR, see note (k) and also control measure 21 in Table 1 above. Rule-making process would probably choose to exclude smaller boilers, but no indication is yet given of where the line would be drawn. NH_3 break-through assumed to be 12 ppm.

(m) Percent change in emissions is defined as follows: −84% implies that (1 − 84/100) = 0.16 times original 1982 emission rate remains after control; +222% implies that (1 + 222/100) = 3.22 times original 1982 emission rate remains after control.





test, followed by repairs to the vehicle designed to correct defects observed also is included among the relatively simple control measures in Group 1.

Two further levels of mobile source NO_x control were considered. At the Group 2 level in Table 1, the entire light duty vehicle fleet was assumed to have achieved a NO_x emission rate of 0.7 g mi^{-1}, while the NO_x emissions from medium duty trucks were assumed to be reduced to 1.5 g mi^{-1}, and the NO_x emissions from heavy duty trucks were assumed to be reduced to 10.7 g/BHP-hr. There are two ways that one could view this case with 0.7 g mi^{-1} NO_x emitted from the light duty vehicle fleet. Since new cars sold in California must presently meet a 0.7 g mi^{-1} NO_x standard, this level of control could be used to approximate a successful completion of conversion of the entire vehicle fleet to meet current regulatory objectives for new cars, in combination with a high level of catalyst system durability and maintenance. In the absence of high durability and maintenance, catalyst system deterioration can be expected to increase actual on-road emissions to levels above legal objectives. The 0.7 g/mile NO_x fleet-wide emission rate employed here closely approximates the introduction of a fleet of cars initially set to achieve 0.4 g/mi NO_x when new, followed by a typical degree of control system deterioration in the hands of the final consumer. The 10.7 g/BHP-hr NO_x objective for heavy duty trucks reflects an intermediate level of control proposed by the U.S. Environmental Protection Agency (9).

Mobile source controls shown in Group 3 reflect the emissions pattern that would result if the 0.4 g/mi NO_x and 0.41 g/mi total hydrocarbon (THC) emission rate for light duty vehicles called for under the Clean Air Act in fact were achieved and maintained by the vehicle fleet. Increased control system durability or maintenance would be needed for this event to occur. Further NO_x reductions from heavy duty vehicles have been added to Group 3, at the most stringent level discussed by the federal government (9).

NO_x emission reductions from stationary combustion sources can be achieved by non-catalytic ammonia injection into the stack exhaust within a narrow exhaust temperature range. This direct NH_3 injection technology has been demonstrated on a utility boiler in the Los Angeles area (10). NO_x emission reductions in the vicinity of 50% are observed, accompanied by significant bleed-through of NH_3 into the atmosphere. Group 4 controls in Table 1 simulate the installation of such controls on all of the largest stationary combustion sources in the South Coast Air Basin. A major objective of our analysis of this group of controls is to determine if aerosol nitrate formation would be suppressed or enhanced by this NO_x emission reduction combined with NH_3 emission increase.

Selective catalytic reduction (SCR) technology involves NO_x abatement by injection of NH_3 into stationary source exhaust in the presence of a catalyst. Control efficiencies are generally higher than in the case of the direct non-catalytic NH_3 injection systems cited in control Group 4, and NH_3 bleed-through into the atmosphere is reduced. The effect of SCR technology applied to a variety of stationary sources in the Los Angeles area is indicated in Group 5 of Table 1.

By applying the controls in Table 1 in various combinations, a matrix of control opportunities can be constructed that represents the trade-off between increasingly stringent stationary source control vs. increasingly stringent mobile source control, as shown in Table 2. Ten cases will be defined. Beginning near the upper left corner of Table 2, the Base Case 1982 emission inventory first will be perturbed by applying the Group 1 controls from Table 1 to the emission sources. Moving from left to right across the top of the table, increasingly stringent mobile source controls are added to the Group 1 stationary source controls. Moving from top to bottom along the left edge of the table, increasingly demanding stationary source NO_x controls are added to a minimal motor vehicle control program. At the lower right corner of that table, the intersection of all of the most stringent mobile and station-

Table 2. Combinations of mobile and stationary source controls that will be examined for their effect on air quality in the South Coast Air Basin. Control measures refer to the control measures numbered in Table 1. Labels on columns and rows of this table are indicative of the maximum degree of NO_x control required.

BASE CASE

1982 Emissions (tons/day)
THC = 2416
RHC = 1224
NO_x = 1120
NH_3 = 164

MOBILE SOURCE CONTROLS

STATIONARY SOURCE CONTROLS	VEHICLE INSPECTION AND MAINTENANCE	LIGHT DUTY FLEET 0.41 g/mi THC; 0.7g/mi NO_x HEAVY DUTY FLEET 2.65g/mi THC 10.7g/bhp-hr NO_x	LIGHT DUTY FLEET 0.41g/mi THC; 0.4g/mi NO_x HEAVY DUTY FLEET 2.65g/mi THC 5.1 g/bhp-hr NO_x
AQMP EVAPORATIVE CONTROLS & COMBUSTION MODIFICATION	Control Measures: 1-24 Effect on Emissions: RHC -9.3% NO_x -5.4% NH_3 No change	Control Measures: 1-28 Effect on Emissions: RHC -37.2% NO_x -36.6% NH_3 +3.9%	Control Measures: 1-24, 28-31 Effect on Emissions: RHC -37.2% NO_x -47.6% NH_3 +3.9%
AQMP + NON-CATALYTIC AMMONIA INJECTION	Control Measures: 1-18, 20, 24, 32-36 Effect on Emissions: RHC -9.3% NO_x -10.0% NH_3 +8.7%	Control Measures: 1-18, 20, 24-28, 32-36 Effect on Emissions: RHC -37.2% NO_x -41.2% NH_3 +12.7%	Control Measures: 1-18, 20, 24, 28-36 Effect on Emissions: RHC -37.2% NO_x -52.2% NH_3 +12.7%
AQMP + SELECTIVE CATALYTIC REDUCTION	Control Measures: 1-18, 20, 24, 37-42 Effect on Emissions: RHC -9.3% NO_x -18.4% NH_3 +0.7%	Control Measures: 1-18, 20, 24-28, 37-42 Effect on Emissions: RHC -37.2% NO_x -49.6% NH_3 +4.7%	Control Measures: 1-18, 20, 24, 28-31, 37-42 Effect on Emissions: RHC -37.2% NO_x -60.6% NH_3 +4.7%

ary source controls is applied. The headings aligned with the columns and rows of Table 2 are suggestive of the maximum cumulative degree of NO_x control achieved in each case; the hydrocarbon controls shown in Table 1 also are included.

The tenth perturbed case examined here explores the effect of NH_3 emission reduction alone. The Base Case 1982 emission inventory for NO_x and hydrocarbons remains untouched, but all of the NH_3 emissions from livestock waste decomposition and farming activities in the air basin are removed. This perturbation completely eliminates the large spike in the NH_3 inventory centered over the Chino dairy area in western Riverside and San Bernardino Counties (see Figure 2 of reference 1). That emission reduction may occur in the near future without the action of governmental air pollution control agencies. Rapid urban development in that area of both counties could displace the dairy industry within a few years.

3. The Effect of Emission Controls

The grid-based air quality model evaluated in Part I of this study (1) was used to determine the effects on air quality that could be expected if each of the combinations of emission control measures defined in Table 2 were applied in the South Coast Air Basin (SoCAB). For each set of control measures considered, the Base Case 1982 emission inventory for the SoCAB discussed in references (1) and (15) was modified to reflect the addition of that particular group of control measures. Then the air quality modeling calculations were executed over two days of simulation using the modified emission inventory along with the meteorological conditions observed during the Base Case model verification days (August 30-31, 1982).

The initial conditions and boundary conditions supplied to the air quality model in each case were identical to those observed during August 30-31, 1982, as described in reference (1). The purpose of the first day of each two-day simulation was to establish initial conditions for the second day of calculations that reflect the altered emissions into the air basin. The effect of emission controls on air quality

then was determined by comparison between Base Case and post-control air quality predictions for the second day of each two-day simulation. As changes in emission controls might affect the boundary conditions supplied to the model, a perturbation analysis of the effect of altered boundary conditions was conducted. Reducing the inflow O_3 boundary conditions from those observed on August 30-31, 1982, to 0.04 ppm all around the border of the modeling region reduced Base Case peak O_3 concentrations by only 0.01 ppm. Inflow NO_x boundary conditions on August 30-31, 1982, were examined and found to be very low except along a small stretch of the southeast corner of the grid system. In summary, predicted changes in air quality on the second day of simulation are determined predominantly by changes in emissions into the model and not by altered initial or boundary conditions.

The results of this comparison of alterative emission control strategies are presented in several formats. First, an account of the changes in basin-wide peak 1-hr average pollutant concentrations is given in Table 3. Base Case peak pollutant levels as they were calculated for August 31, 1982 in the absence of further emission controls are stated in the upper left hand corner of that table. Then for each combination of emission controls as defined in Table 2, the predicted basin-wide peak values are given, both in absolute concentration units and as a percent deviation from the pre-control Base Case. Since the effect of some control measures is to change the location or timing of the basin-wide peaks, the values shown in Table 3 may not be typical of the effects seen at most air monitoring sites. Therefore in Table 4, the average change in the peak 1-hr pollutant concentrations at the 20 sites shown in Figure 1 is given, along with the range of the changes observed between the least affected and most affected air monitoring stations.

As seen in the upper left corner of the matrix of control opportunities in Table 2, completion of the stationary source evaporative hydrocarbon controls that are a part of the 1982 AQMP for the Los Angeles area, plus stationary source combustion

Table 3. Effect of emission controls on basin-wide peak 1-hr average pollutant concentrations in the South Coast Air Basin, August 31, 1982. The combinations of emission control technologies considered in each cell of this matrix are defined in Tables 1 and 2. Values shown are the peak 1-hr average concentrations in the presence of the emission controls, followed by the % change relative to the Base Case (in parentheses).

BASE CASE

NO_2 0.156 ppm
TN^2 0.036 ppm
HNO_3 0.024 ppm
AN 91 $\mu g\ m^{-3}$
PAN 0.021 ppm
O_3 0.26 ppm

MOBILE SOURCE CONTROLS

STATIONARY SOURCE CONTROLS	VEHICLE INSPECTION AND MAINTENANCE	LIGHT DUTY FLEET 0.41 g/mi THC; 0.7g/mi NO_x HEAVY DUTY FLEET 2.65g/mi THC 10.7g/bhp-hr NO_x	LIGHT DUTY FLEET 0.41g/mi THC; 0.4g/mi NO_x HEAVY DUTY FLEET 2.65g/mi THC 5.1 g/bhp-hr NO_x
AQMP EVAPORATIVE CONTROLS & COMBUSTION MODIFICATION	NO_2 0.150 ppm (-4.0%) TN^2 0.033 ppm (-6.8%) HNO_3 0.022 ppm (-9.2%) AN 85 $\mu g\ m^{-3}$ (-5.5%) PAN 0.020 ppm (-2.2%) O_3 0.255 ppm (-1.6%)	NO_2 0.123 ppm (-21%) TN^2 0.021 ppm (-41%) HNO_3 0.013 ppm (-44%) AN 55 $\mu g\ m^{-3}$ (-39%) PAN 0.018 ppm (-14%) O_3 0.230 ppm (-11%)	NO_2 0.089 ppm (-43%) TN^2 0.018 ppm (-48%) HNO_3 0.011 ppm (-55%) AN 49 $\mu g\ m^{-3}$ (-47%) PAN 0.017 ppm (-19%) O_3 0.221 ppm (-15%)
AQMP + NON-CATALYTIC AMMONIA INJECTION	NO_2 0.152 ppm (-2.6%) TN^2 0.033 ppm (-6.1%) HNO_3 0.021 ppm (-13%) AN 81 $\mu g\ m^{-3}$ (-8.8%) PAN 0.020 ppm (-2.9%) O_3 0.254 ppm (-1.8%)	NO_2 0.118 ppm (-24%) TN^2 0.020 ppm (-42%) HNO_3 0.013 ppm (-45%) AN 52 $\mu g\ m^{-3}$ (-41%) PAN 0.018 ppm (-15%) O_3 0.230 ppm (-11%)	NO_2 0.090 ppm (-42%) TN^2 0.017 ppm (-52%) HNO_3 0.010 ppm (-57%) AN 46 $\mu g\ m^{-3}$ (-48%) PAN 0.016 ppm (-20%) O_3 0.219 ppm (-15%)
AQMP + SELECTIVE CATALYTIC REDUCTION	NO_2 0.155 ppm (-0.5%) TN^2 0.032 ppm (-9.2%) HNO_3 0.020 ppm (-13%) AN 78 $\mu g\ m^{-3}$ (-14%) PAN 0.020 ppm (-4.6%) O_3 0.251 ppm (-3.1%)	NO_2 0.117 ppm (-25%) TN^2 0.019 ppm (-47%) HNO_3 0.012 ppm (-50%) AN 48 $\mu g\ m^{-3}$ (-47%) PAN 0.017 ppm (-18%) O_3 0.224 ppm (-13%)	NO_2 0.073 ppm (-53%) TN^2 0.014 ppm (-59%) HNO_3 0.009 ppm (-59%) AN 39 $\mu g\ m^{-3}$ (-57%) PAN 0.016 ppm (-22%) O_3 0.215 ppm (-17%)

Table 4. Effect of emission controls on peak 1-hr average pollutant concentrations observed at the 20 sites shown in Figure 1. Values shown are averages over the 20 sites, followed by the range of the values observed among the 20 sites (in parentheses). Aerosol nitrate concentrations shown are computed as if the aerosol is pure NH_4NO_3.

BASE CASE		MOBILE SOURCE CONTROLS		
		VEHICLE INSPECTION AND MAINTENANCE	LIGHT DUTY FLEET 0.41 g/mi THC; 0.7g/mi NO_x HEAVY DUTY FLEET 2.65g/mi THC 10.7g/bhp-hr NO_x	LIGHT DUTY FLEET 0.41g/mi THC; 0.4g/mi NO_x HEAVY DUTY FLEET 2.65g/mi THC 5.1 g/bhp-hr NO_x
NO_2	0.087 ppm(0.135-0.029 ppm)			
TN^2	0.022 ppm(0.031-0.009 ppm)			
HNO_3	0.012 ppm(0.021-0.006 ppm)			
NH_3	0.070 ppm(0.668-0.010 ppm)			
AN	42 μg m^{-3} (85μg m^{-3}-16μg m^{-3})			
PAN	0.011 ppm(0.018-0.006 ppm)			
O_3	0.170 ppm(0.233-0.110 ppm)			
STATIONARY SOURCE CONTROLS	AQMP EVAPORATIVE CONTROLS & COMBUSTION MODIFICATION	NO_2 -5.1% (-8.3% to -1.4%) TN^2 -4.8% (-7.4% to -3.0%) HNO_3 -4.1% (-7.0% to -0.9%) NH_3 +1.0% (-3.5% to +10.1%) AN -3.4% (-6.7% to -1.1%) PAN -2.7% (-4.3% to -0.6%) O_3 -1.8% (-2.9% to -0.7%)	NO_2 -37.4% (-49.7% to -19.1%) TN^2 -35.7% (-41.2% to -22.1%) HNO_3 -31.8% (-46.5% to -14.8%) NH_3 +10.6% (-4.1% to +29.8%) AN -22.7% (-40.1% to -4.4%) PAN -15.6% (-25.7% to -1.3%) O_3 -11.7% (-18.9% to -4.1%)	NO_2 -45.6% (-59.5% to -26.1%) TN^2 -45.6% (-52.8% to -26.8%) HNO_3 -40.0% (-53.7% to -18.6%) NH_3 +9.0% (-5.9% to +27.4%) AN -34.0% (-52.8% to -17.1%) PAN -14.3% (-28.8% to +2.1%) O_3 -12.8% (-23.6% to -1.1%)
	AQMP + NON-CATALYTIC AMMONIA INJECTION	NO_2 -5.9% (-9.1% to -0.04%) TN^2 -5.5% (-8.4% to -3.2%) HNO_3 -9.3% (-25.0% to -3.6%) NH_3 +17.3% (-15.8% to +60.5%) AN +3.7% (-7.7% to +20.7%) PAN -2.0% (-4.2% to +2.2%) O_3 -1.7% (-3.1% to +0.6%)	NO_2 -38.4% (-50.9% to -19.0%) TN^2 -36.7% (-41.8% to -22.4%) HNO_3 -34.4% (-49.0% to -21.0%) NH_3 +27.9% (-7.3% to +68.0%) AN -19.0% (-39.0% to +3.3%) PAN -15.3% (-25.1% to -0.1%) O_3 -11.7% (-19.0% to -1.6%)	NO_2 -46.9% (-59.8% to -27.2%) TN^2 -46.8% (-54.5% to -28.2%) HNO_3 -42.5% (-55.7% to -24.9%) NH_3 +28.0% (-8.5% to +67.4%) AN -31.2% (-54.1% to -9.0%) PAN -14.3% (-30.0% to +3.1%) O_3 -13.4% (-24.4% to -1.2%)
	AQMP + SELECTIVE CATALYTIC REDUCTION	NO_2 -8.5% (-14.9% to -1.8%) TN^2 -8.9% (-14.3% to -5.0%) HNO_3 -9.9% (-13.3% to -6.0%) NH_3 +4.0% (-13.4% to +25.0%) AN -4.8% (-13.8% to +3.2%) PAN +0.4% (-7.1% to +7.7%) O_3 -1.4% (-4.9% to +3.0%)	NO_2 -42.4% (-55.3% to -21.4%) TN^2 -41.3% (-46.9% to -25.5%) HNO_3 -37.7% (-51.0% to -21.2%) NH_3 +12.6% (-8.2% to +36.0%) AN -27.6% (-46.8% to -8.6%) PAN -14.3% (-27.6% to +1.0%) O_3 -12.6% (-22.2% to -2.8%)	NO_2 -51.9% (-67.4% to -27.8%) TN^2 -52.3% (-60.0% to -33.1%) HNO_3 -47.3% (-60.7% to -27.1%) NH_3 +13.7% (-6.6% to +38.5%) AN -39.6% (-59.8% to -24.2%) PAN -14.8% (-36.0% to +7.2%) O_3 -15.0% (-28.2% to -0.7%)

modifications and a vehicle maintenance program would result in a 5.4% reduction in basin-wide NO_x emissions and a 9.3% reduction in reactive hydrocarbon (RHC) emissions. Comparison to Table 4 shows that the 1-hr peak levels of NO_2 and TN typically drop by an amount that is roughly proportional to the change in NO_x emissions. The greatest percentage decreases in total inorganic nitrate (TN) levels occur in the eastern portion of the air basin (from Pomona: TN = -5.5% to Rubidoux: TN = -7.4%), while TN levels decline by only 3% to 5% in the western part of the air basin. The effect on HNO_3 and AN levels likewise is highest in the eastern portion of the air basin. O_3 and PAN levels in this case decline by only 1.6% and 2.2% at the location of the basin-wide 1-hr peak, a reduction that is less than proportional to the degree of emission control achieved for either RHC or NO_x.

The effect of progressively more stringent NO_x controls on stationary sources alone is observed by moving down the left edge of Tables 2, 3 and 4. Addition of non-catalytic ammonia injection technology at major stationary NO_x sources combined with AQMP hydrocarbon controls produces a net 10% reduction in basin-wide NO_x emissions along with a +8.7% increase in basin-wide NH_3 emissions, as seen in Table 2. Most of these emissions changes occur in the heavily industrialized western portion of the air basin, which has very low ambient NH_3 levels at present (see Figures 2, 3 and 5 of reference 1). As a result of the NH_3 emissions from the ammonia injection systems, peak 1-hr average ambient NH_3 levels near industrial areas at the coast (Long Beach and Lennox) rise by nearly 60%, while ambient NH_3 levels at central Los Angeles, La Habra, Anaheim and Pico Rivera rise by 25% or more. HNO_3 levels drop by as much as 25% at Lennox, and by more than 13% at central Los Angeles, Anaheim, La Habra and Pico Rivera, but this is largely due to the formation of additional aerosol nitrates by reaction of HNO_3 with the increased NH_3. Peak 1-hr average aerosol nitrate levels rise by 14% to 21% at central Los Angeles, Long Beach and Lennox in the presence of this NH_3 emission increase.

Farther downwind, in the vicinity of the Chino dairy area where the air is already loaded with very high NH_3 levels even in the Base Case (e.g., 0.67 ppm 1-hr peak at Chino, see Table 4), the reduction in NO_x emissions achieved through this combination of controls that includes non-catalytic NH_3 injection at upwind sources does act to reduce TN and aerosol nitrate levels by 7% to 8%. In summary, use of non-catalytic ammonia injection technology for NO_x emission reduction has the potential to degrade NH_3 and aerosol nitrate air quality in the industrialized western portion of the South Coast Air Basin, accompanied by aerosol nitrate concentration reductions in already NH_3-enriched agricultural areas downwind.

Through addition of selective catalytic reduction (SCR) technology on stationary sources, combined with AQMP hydrocarbon controls, an 18% reduction in basin-wide NO_x emissions is achieved relative to Base Case 1982 emissions accompanied by only a 0.7% increase in NH_3 emissions (lower left corner, Tables 2, 3 and 4). These stationary source NO_x reductions are concentrated at a few major point source locations (e.g. power plants and petroleum refineries). As a result, the effect of these controls varies greatly between monitoring sites. When SCR is added to major point sources, NO_2 concentration reductions of 12% to 15% occur at Burbank, Long Beach, Azusa and Anaheim. Typically, NO_2 levels in that case decline by 8.5% averaged over the 20 locations cited in Figure 1 and Table 4. At the location of the basin-wide NO_2 concentration peak, and at Upland and Fontana, NO_2 concentration reductions are small (2.6% or less). Total inorganic nitrate concentration improvements show less variability between monitoring sites: TN levels decline by 11% to 14% in the eastern portion of the air basin (from Pomona to Rubidoux), and by 5% to 10% in the western area of the basin. Reductions in basin-wide 1-hr peak HNO_3 and AN levels of 13% and 14% respectively also are achieved. The basin-wide peak O_3 and PAN concentrations decline slightly as stationary source NO_xcontrols are applied. At 5 of the sites shown in Figure 1 in the area from central Los Angeles

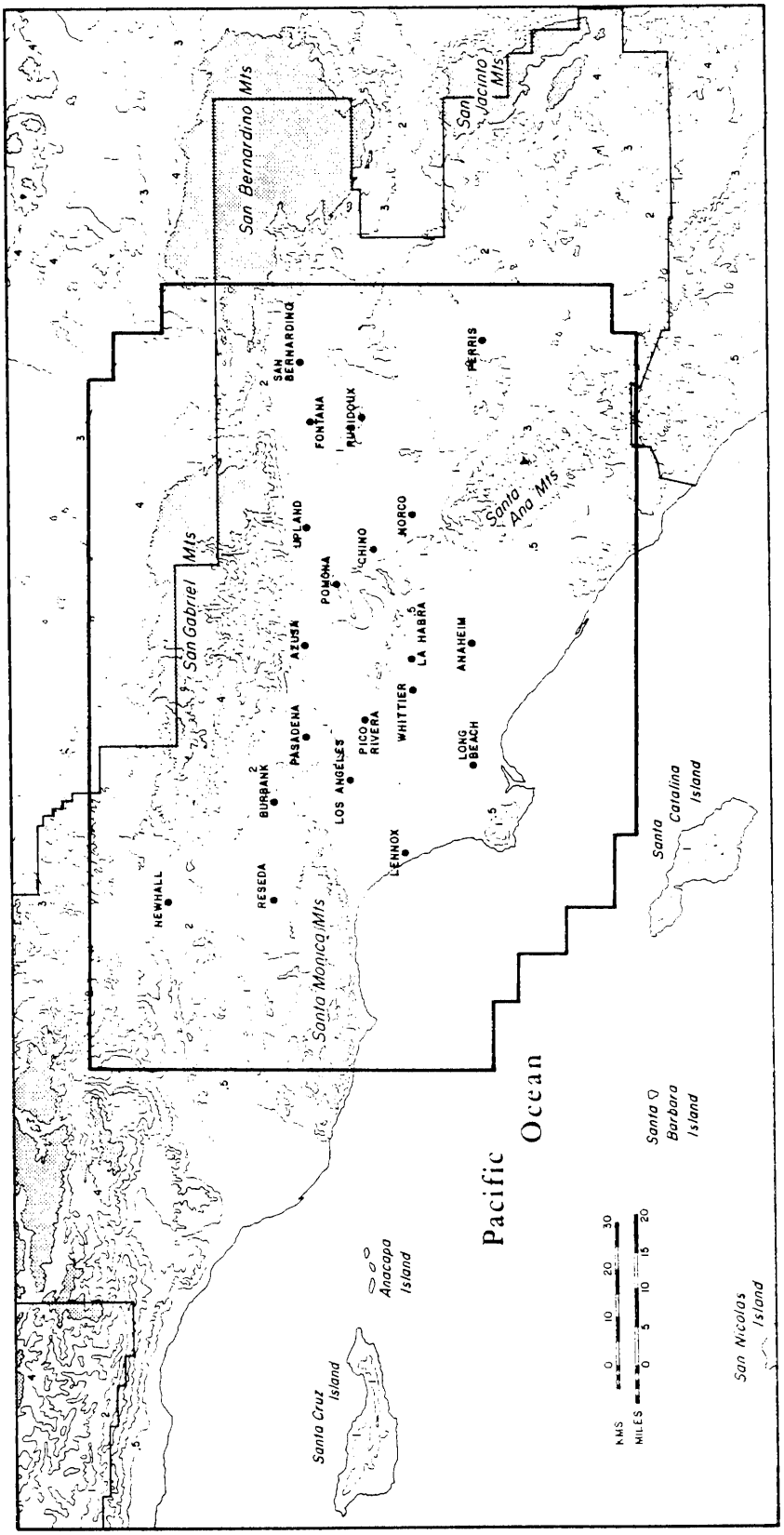


Figure 1. The South Coast Air Basin, showing 20 sites at which the effect of emission controls will be evaluated. Air quality modeling calculations are performed within the region bounded by the heavy solid line in the center of the map.

and Pasadena to La Habra, addition of SCR on stationary sources alone causes peak 1-hr O_3 levels to increase relative to the Base Case, but that increase is +3% or less. PAN air quality changes by amounts that are less than proportional to the NO_x reduction achieved, with 7 of the 20 sites studied experiencing a PAN increase. In short, with addition of SCR technology on stationary sources alone, improvements in many NO_x-related species concentrations are achieved. Those improvements are less than proportional to the NO_x emissions change, and are accompanied by slight increases in O_3 and PAN at a few locations.

The effect of progressively more stringent mobile source controls alone can be examined by moving from left to right across the upper row of Tables 2, 3 and 4. As seen in Table 2, complete conversion of the vehicle fleet to an intermediate level of mobile source control (light-duty fleet meets 0.41 g/mi THC; 0.7 g/mi NO_x along with additional heavy-duty vehicle controls plus AQMP stationary source controls) would result in a 37% reduction in basin-wide NO_x emissions and a 37% reduction in RHC emissions relative to the Base Case. Tables 3 and 4 show that major improvements in TN, HNO_3 and AN levels would result, with improvements almost directly proportional to the NO_x emission reduction achieved. Basin-wide peak O_3 and PAN concentrations both decline by 11% and 14% respectively.

Further reduction in NO_x emissions from motor vehicles alone is examined in the upper right hand corner of Tables 2, 3 and 4. If a 0.4 g/mi NO_x emission rate from the light-duty fleet had been achieved in 1982 along with strict heavy truck NO_x controls, NO_x emissions would have been reduced by 48% relative to the base case, with similar major improvements in ambient NO_2, TN, HNO_3 and AN concentrations. O_3 and PAN concentrations both decline as additional NO_x controls are added to the vehicle fleet without further hydrocarbon controls beyond the 0.41 g/mi THC light-duty vehicle standard examined in the preceding square on the top row of Table 2.

As seen in the lower right hand corner of Table 2, the simultaneous use of all mobile and stationary source control measures considered here would reduce NO_x emissions relative to the base case by 61% in the presence of a 37% decline in RHC emissions. This combination of controls is more effective than controls on either the mobile or stationary sources alone. Basin-wide peak total inorganic nitrate, HNO_3 and aerosol nitrate concentrations are reduced by nearly 60%. Basin-wide peak NO_2 concentrations are reduced by 53%. A 17% reduction in the basin-wide peak O_3 concentration is achieved. The 1-hr O_3 concentration peak is reduced relative to the Base Case at every site shown in Figure 1.

As is quickly seen from Tables 3 and 4, the simultaneous use of all of the mobile and stationary source control measures considered produces major improvements in many air quality parameters at the time of the daily pollutant concentration peaks. The performance of that combination of control measures is explored in detail in Figures 2-7. Figure 2 gives the spatial distribution of pollutant concentrations in the presence of the maximum degree of NO_x control studied. By subtracting these pollutant levels from the spatial distribution of concentrations predicted by the Base Case simulation (see Figure 3 of reference 1) it is possible to define the spatial distribution of pollutant concentration changes experienced due to the emission controls, as seen in Figure 3. Figures 4, 5 and 6 permit rapid visualization of changes in the diurnal pattern of pollutant levels at key monitoring sites characteristic of the western and eastern portions of the air basin. In Figure 7, the effect of this set of emissions controls on 24-hour average pollutant levels is explored.

One effect of the maximum degree of mobile and stationary source control considered in this study (case in lower right corner of Table 2) is to preferentially reduce the NO_2 concentrations during the early morning peak hours of the day at sites in the western portion of the air basin, like Los Angeles, and Anaheim, as seen

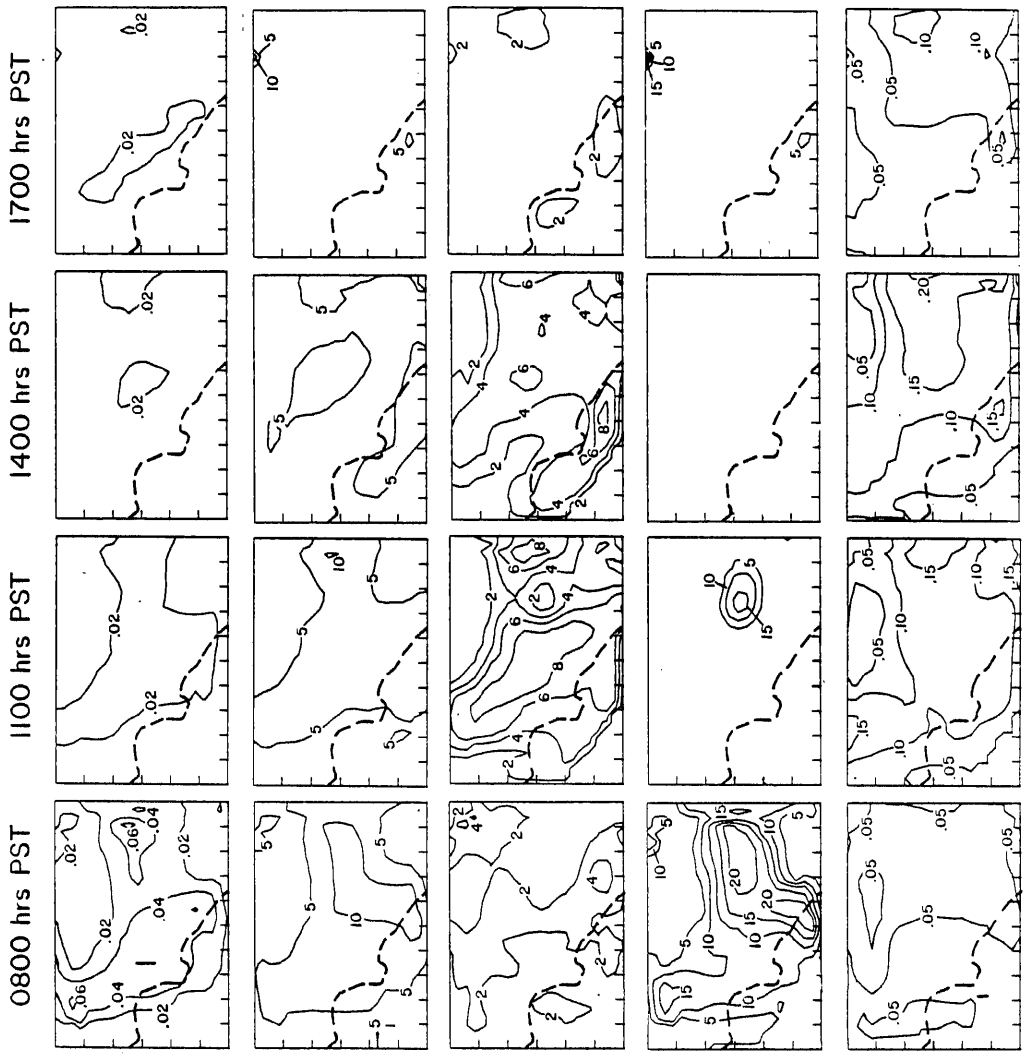


Figure 2. The spatial distribution of pollutant concentrations predicted in the presence of the maximum degree of NO_x and RHC control studied (case in lower right corner of Table 2).

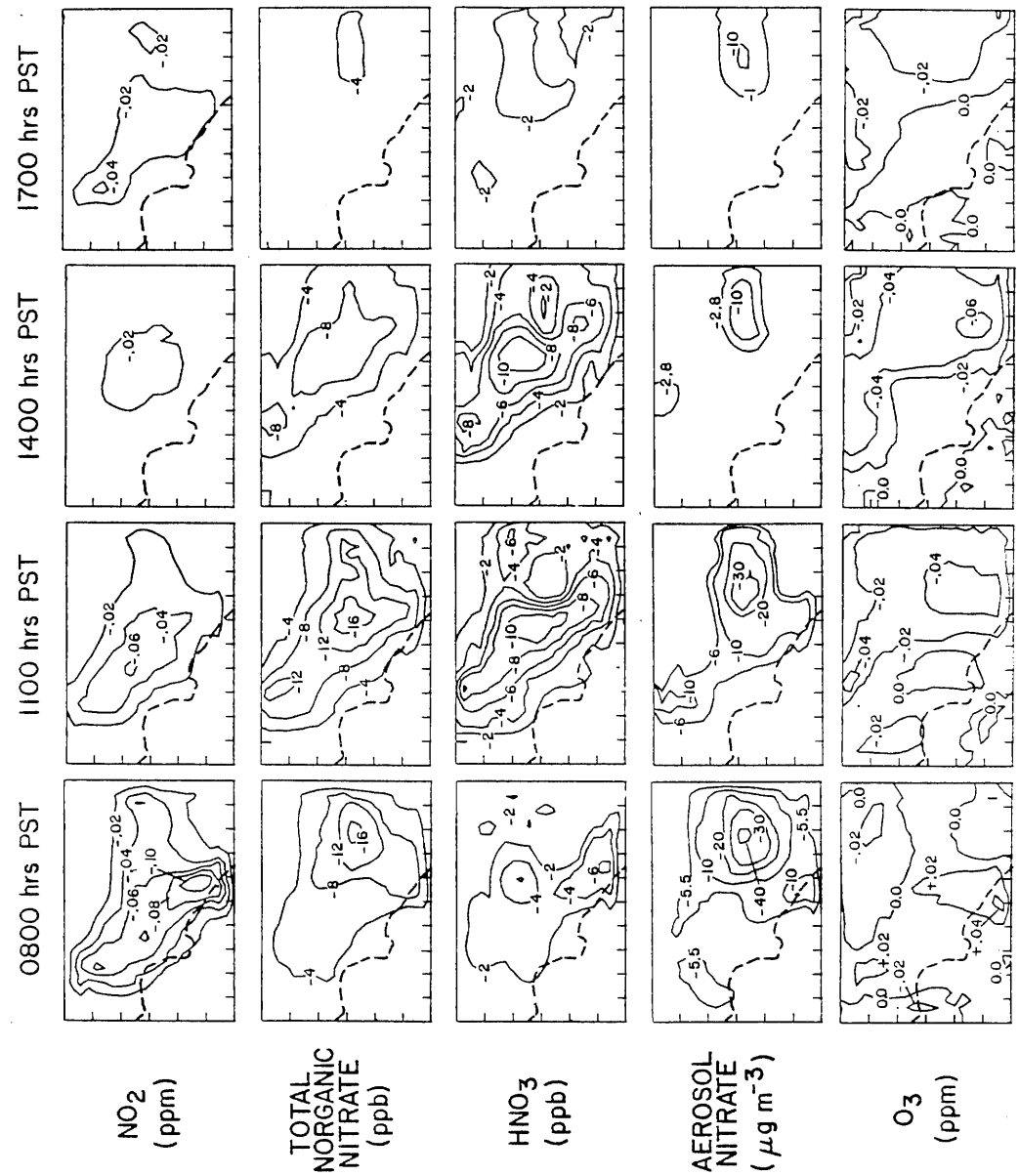


Figure 3. The spatial distribution of pollutant concentration changes predicted in the presence of the maximum degree of NO_x and RHC control studied (difference between the case in lower right corner of Table 2 vs. the Base Case).

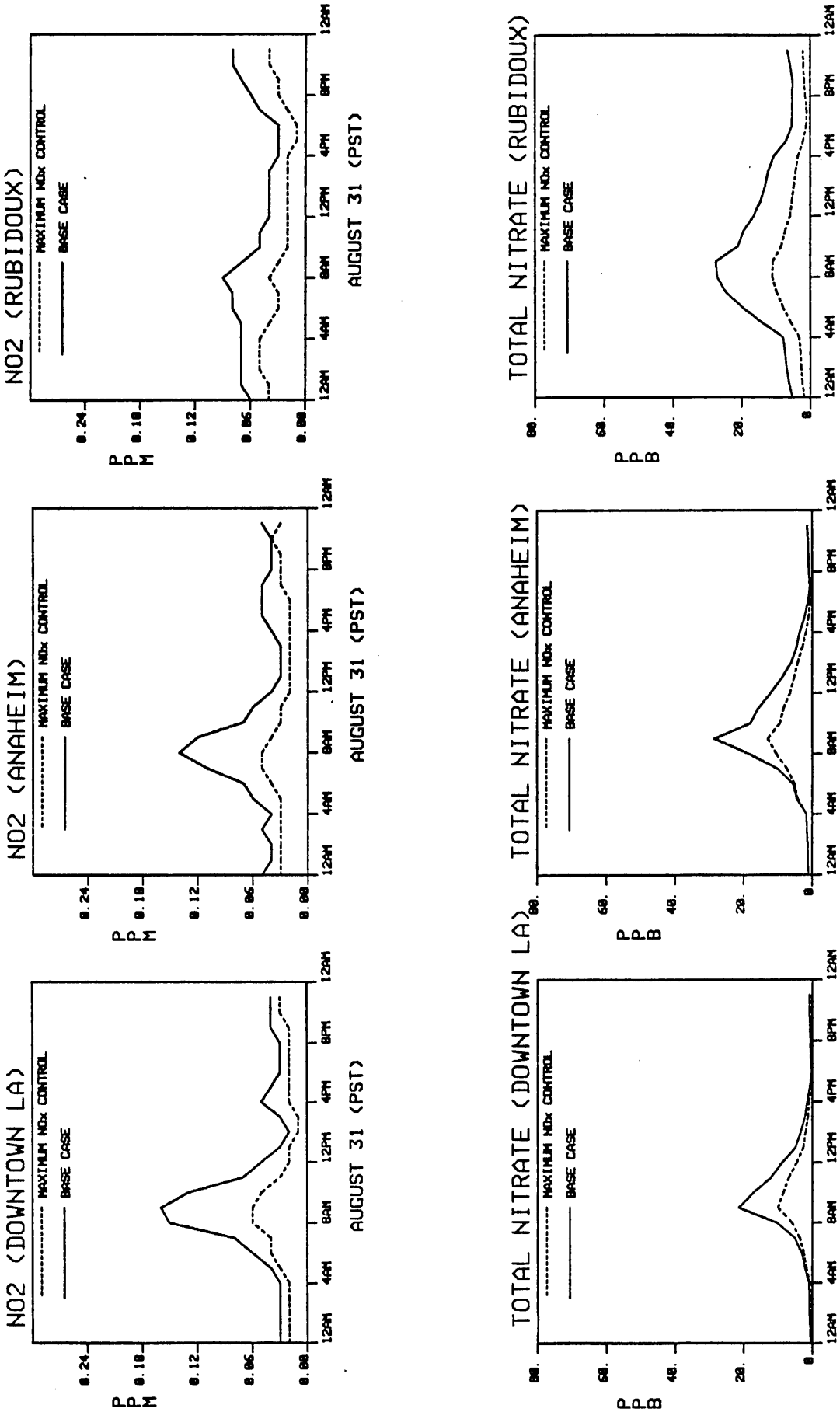


Figure 4. NO_2 and total inorganic nitrate (TN) concentrations at Los Angeles, Anaheim and Rubidoux under Base Case conditions and in the presence of the maximum degree of NO_x and RHC control studied.

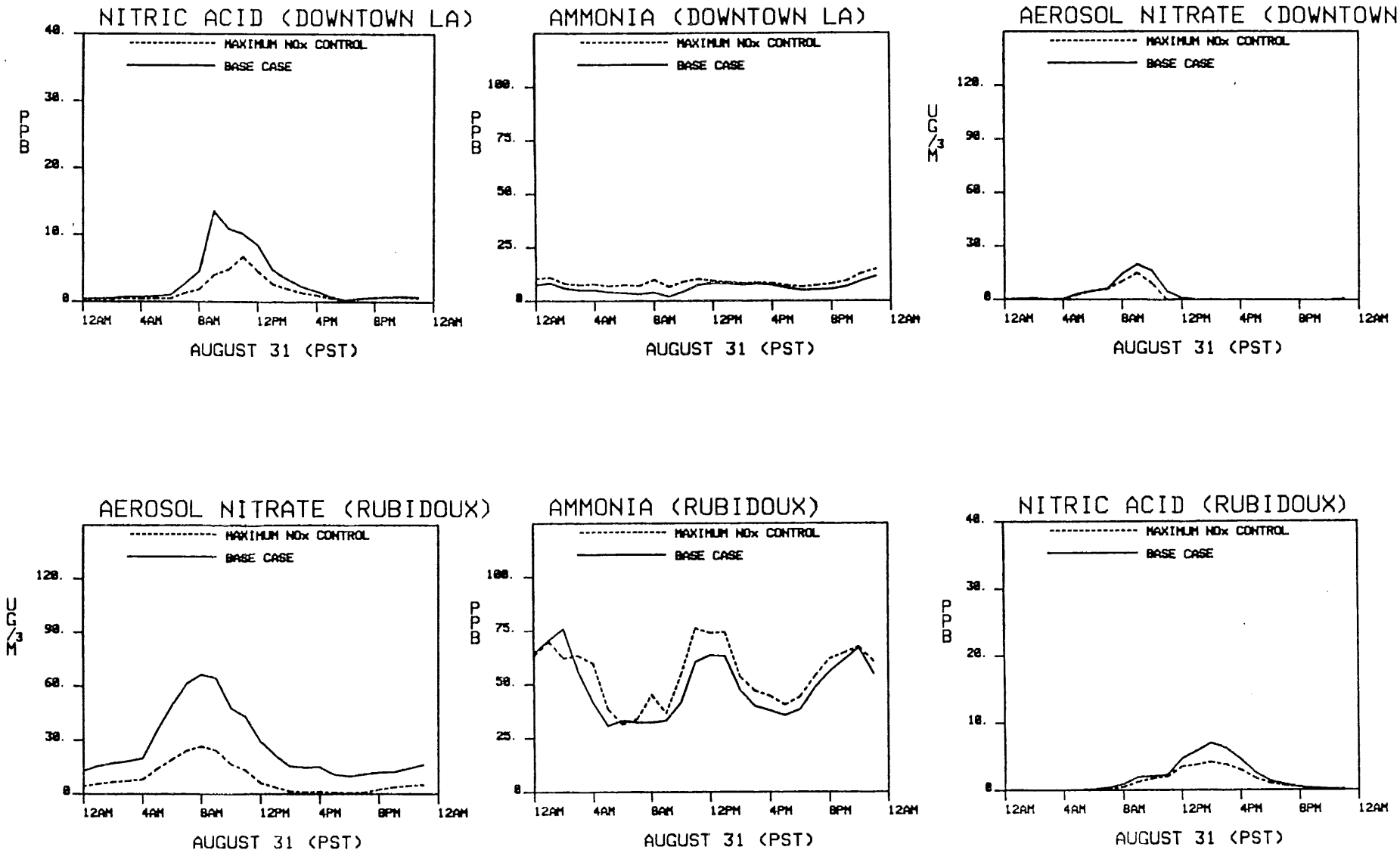


Figure 5. Nitric acid, ammonia and aerosol nitrate concentrations at Los Angeles and at Rubidoux under Base Case conditions and in the presence of the maximum degree of NO_x and RHC control studied.

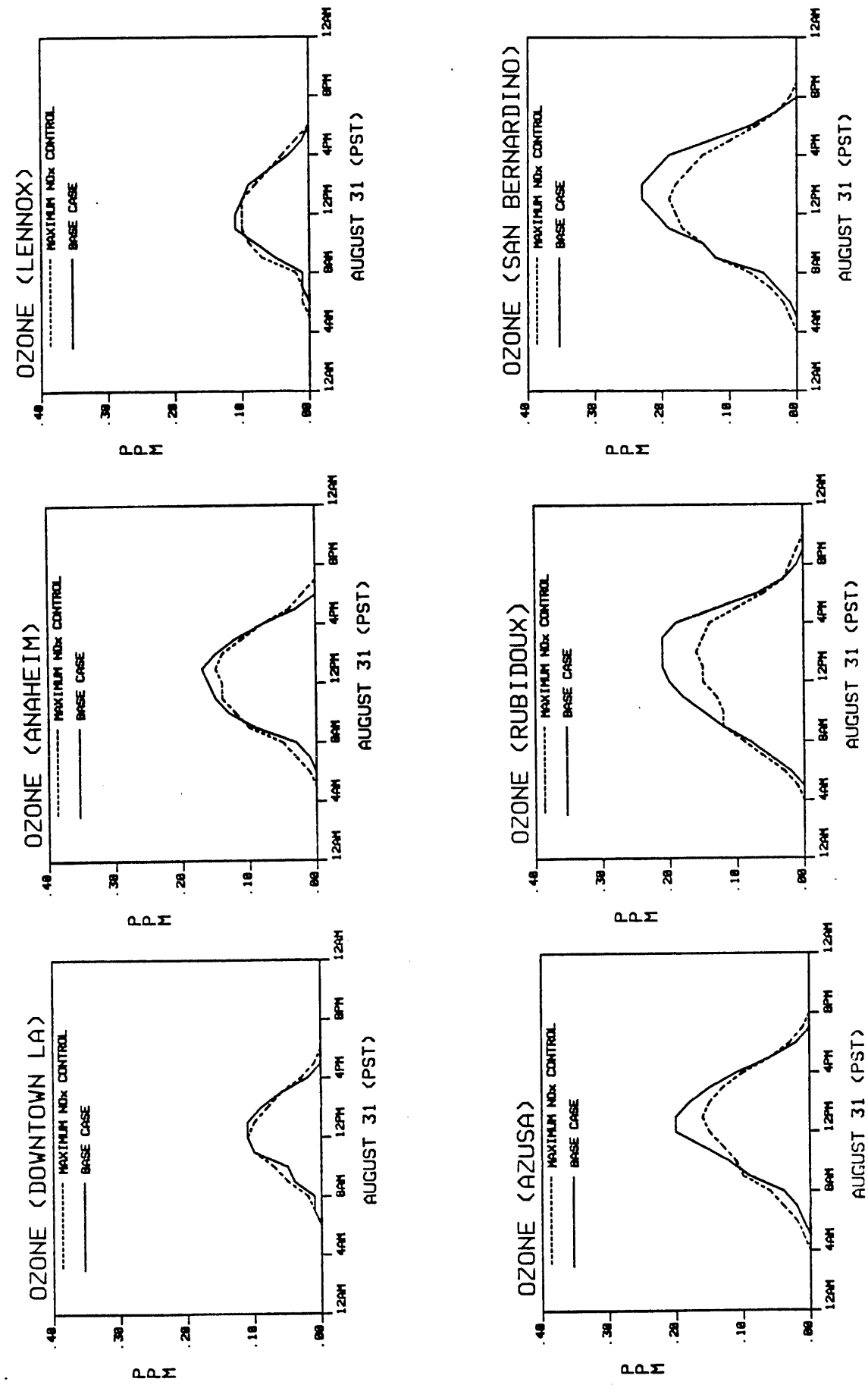


Figure 6. Ozone concentrations under Base Case conditions and in the presence of the maximum degree of NO_x and RHC control studied.

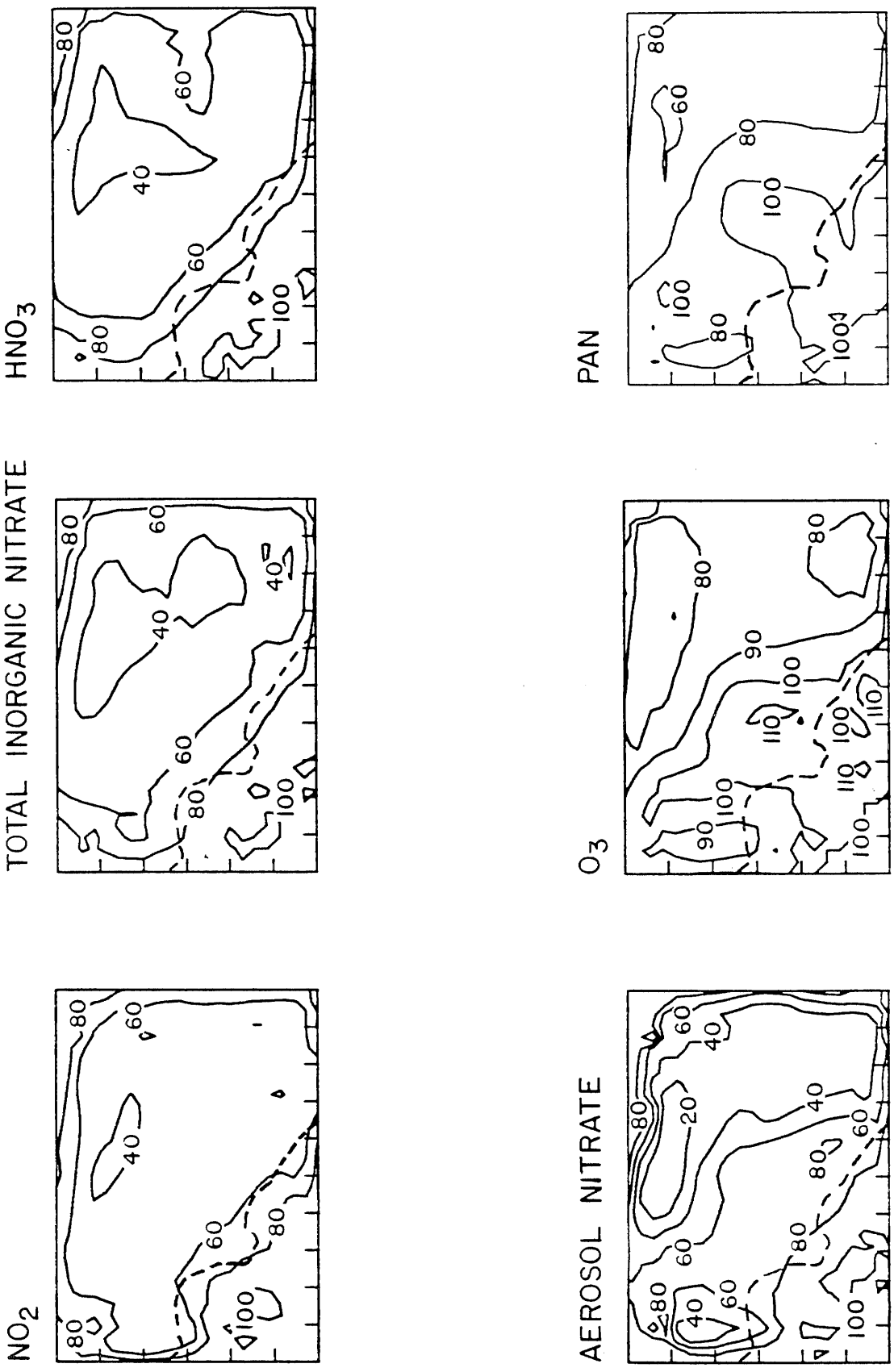


Figure 7. 24-hour average NO_2, inorganic nitrate, nitric acid, aerosol nitrate, O_3 and PAN concentrations in the presence of the maximum degree of NO_x and RHC control studied, expressed as a percentage of Base Case concentrations.

in Figures 3 and 4. NO_2 concentrations which exceeded 0.15 ppm during early morning hours under Base Case conditions have been reduced by more than 0.06 ppm at 0800 hours PST throughout much of the western area of the basin, and by as much as 0.10 ppm in portions of coastal Orange County, as seen in Figure 3. At sites in the eastern area of the basin, at Upland, Rubidoux and San Bernardino, NO_2 levels are reduced by large percentage amounts throughout the entire 24-hour period studied (Figure 4). As a result, 24-hour average NO_2 levels decline by between 40% and 60% throughout nearly the entire on-land portion of the air basin as seen in Figure 7.

The effect of NO_x emission controls on total inorganic nitrate levels is felt to the greatest extent in the central and eastern portions of the air basin. As seen in Figure 3, TN concentration reductions in excess of 16 ppb occur in the inland areas throughout the morning hours in response to the maximum degree of NO_x control studied here.

The partition of this inorganic nitrate air quality improvement between reductions in gas phase HNO_3 versus reductions in aerosol nitrate is determined by co-occurring NH_3 concentrations. In the western portion of the air basin, HNO_3 reductions, especially in the morning hours, are proportionally greater than aerosol nitrate reductions, as shown at Los Angeles in Figure 5. The use of selective catalytic reduction technology plus more effective reducing catalysts on mobile sources leads to a small increase in NH_3 emissions. While that NH_3 increase is very minor compared to basin-wide NH_3 emissions, the NH_3 emissions increase by a significant *percentage* in the NH_3-starved western urban area of the air basin (see the spatial distribution of Base Case NH_3 emissions in Figure 2 of reference (1)). NH_3 concentrations at sites like downtown Los Angeles that are located in the immediate vicinity of stationary combustion sources and heavy traffic density experience a rough doubling of base case NH_3 levels during the morning traffic peak hours. The pro-

duct of the NH_3 and HNO_3 concentrations is limited by the equilibrium dissociation constant for the NH_4NO_3–NH_3–HNO_3 system (16). The NH_3 concentration increase shifts the equilibrium HNO_3 concentration downward, while favoring aerosol nitrate formation. However, the same emission controls that produce the NH_3 emission increase also reduce NO_2 and TN concentrations by enough that a net increase in aerosol nitrate concentrations is not observed. Instead, both HNO_3 and AN decline in the western part of the air basin, but the HNO_3 reduction is more pronounced and begins in the morning as NH_3 levels rise, while the aerosol nitrate reduction relative to the base case occurs later in the day. In the central portion of the air basin, the combination of a major decrease in TN formation along with a small increase in NH_3 emissions is manifested by greater than a 10 ppb reduction in HNO_3 concentrations in the late morning and early afternoon (Figure 3).

In the eastern area of the air basin, Base Case NH_3 concentrations due to dairy farming and other agricultural sources are so high that a small change in upwind NH_3 emissions does not affect ambient NH_3 levels by more than a few percent. Again, the amount of gas phase HNO_3 is limited by the co-occurring ammonia levels. In this case the post-control NH_3 levels are nearly unchanged as a percentage of the pre-control NH_3 levels and as a result, HNO_3 concentrations do not change greatly. The large drop in TN levels at Rubidoux and San Bernardino that occurs when all available RHC and NO_x emission controls are applied thus is reflected in a major reduction in aerosol nitrate levels, and to a lesser degree by reduced HNO_3 concentrations as seen in Figure 5. At eastern basin sites, aerosol nitrate levels are reduced throughout the day, not just during peak hours.

The effect of RHC and NO_x controls on O_3 air quality has been a matter of considerable debate (15-22). Most recent studies (15, 22) agree that large NO_x reductions (above 19%) in the Los Angeles area combined with moderate RHC controls will produce lower O_3 levels in the downwind and eastern areas of the SoCAB near

Rubidoux and San Bernardino where the highest O_3 levels often are observed. Concern has been voiced, however, that if NO_x emissions are controlled to the maximum extent possible, then O_3 levels will rise in the western portion of the air basin (22).

The results of the present study indicate that the maximum degree of NO_x and RHC control studied here produces significant O_3 reductions in the eastern area of the South Coast Air Basin. The peak measured and predicted O_3 levels on August 31, 1982 that occurred at Rubidoux and at San Bernardino would be reduced substantially as seen in Figure 6. Peak 1-hour average O_3 levels in this case decline relative to the Base Case by 25% or more at Pomona, Chino, Norco, Upland, Fontana and Rubidoux, and by 21% at Azusa. The additional NO_x emission reductions achieved when moving from the group of control measures specified in the center column of Table 2 to the right hand column of Table 2 leads to reduced O_3 levels in the high-O_3 concentration zone at the eastern end of the air basin without addition of further hydrocarbon emission controls.

At all western urban sites, O_3 concentrations respond to this package of emission controls in a manner like that shown for central Los Angeles and Anaheim in Figure 6. In the presence of stringent NO_x controls, O_3 levels begin to rise at a slightly earlier hour in the morning due to less effective scavenging of O_3 by fresh NO emissions during the early morning traffic peak. Peak O_3 levels are decreased at all sites at midday, as mentioned previously. Then O_3 levels at western basin sites exceed 1982 Base Case concentrations for a short period in the afternoon in the presence of stringent NO_x controls, again due to less effective O_3 scavenging processes in the presence of the NO_x controls. If viewed on a 24-hour average basis, O_3 concentrations do rise slightly in the western area of the air basin in response to this control program, as seen in Figure 7. But since O_3 concentration standards are written to control peak 1-hour averages and since peak O_3 values

decline at all stations, it is unclear that this change in 24-hour average O_3 concentrations is of any regulatory consequence. In summary, the change in total O_3 dose received by western basin residents due to the NO_x control program studied is very small: the areas under the pre-control and post-control O_3 concentration time series graphs are practically the same. The high O_3 dose received by residents in the Azusa, Pomona, Riverside and San Bernardino areas, however, is significantly reduced by the combination of emission controls given in the lower right corner of Table 2.

The final alteration in emissions studied involves removal of all agriculture-related NH_3 emissions from the Base Case 1982 emission inventory given in reference (15). NH_3 emissions from livestock waste decomposition in the Chino dairy area and elsewhere are suppressed, as are NH_3 emissions from chemical fertilizer application at farms. This type of change in emissions could occur as increasing urbanization displaces agricultural activities in the air basin. This alteration in NH_3 levels alone does not affect atmospheric NO_2, O_3 and PAN concentrations. Ammonia concentrations decline by 87% to 91% at Chino and Upland in the immediate vicinity of the dairy farms, and by about 70% at Rubidoux and San Bernardino downwind. Aerosol nitrate concentrations at San Bernardino, Fontana, Upland and Pomona decline by more than 50% as the agricultural NH_3 emissions are suppressed. In response, HNO_3 levels increase at eastern basin locations by 43% to 45% at San Bernardino and Upland, and by 89% to 100% at Fontana and Rubidoux. Suppression of aerosol nitrate formation without a corresponding decrease in NO_x emissions acts to shift inorganic nitrate from the aerosol phase to gas phase HNO_3. Total inorganic nitrate levels decline at Upland, Fontana and Rubidoux by 7% to 13% as this shift from AN to HNO_3 formation occurs, probably because the deposition velocity for HNO_3 is higher than for fine aerosols.

4. Summary and Conclusions

Emission control measures that would reduce reactive hydrocarbon and NO_x emissions in the Los Angeles area by up to 37% and 61%, respectively, have been examined for their effects on air quality. In most cases studied, NO_2 and total inorganic nitrate concentrations decline by amounts only slightly less than proportional to the degree of precursor NO_x emission reduction. Peak 1-hr average NO_2 and TN levels averaged over 20 monitoring sites would decline by more than 50% relative to 1982 Base Case conditions if the light-duty vehicle fleet in practice met the originally proposed federal exhaust emission standards (0.4 g/mi NO_x and 0.41 g/mi THC) in conjunction with heavy-duty vehicle control, evaporative hydrocarbon controls, plus installation of selective catalytic NO_x reduction systems on major stationary sources. This reduction in inorganic nitrate levels would be reflected in major improvements in HNO_3 and aerosol nitrate air quality.

The partition of inorganic nitrate air quality improvements between aerosol nitrate and HNO_3 can be affected by the choice of NO_x emission controls. In particular, widespread use of non-catalytic NH_3 injection technology for NO_x emission control at stationary sources alone has the potential to increase aerosol nitrate formation in near-source areas if significant co-ocurring bleed-through of NH_3 to the atmosphere occurs. Selective catalytic reduction technology at stationary sources and advanced catalyst systems on vehicles also have the potential to increase NH_3 emissions, but in those cases the NH_3 increase is so slight that the NO_x emission decrease achieved through use of these devices will drive aerosol nitrate levels downward in spite of the added NH_3 emissions.

Installation of the most stringent set of NO_x and RHC emission controls studied here causes peak 1-hr average O_3 concentrations to decline by 25% or more in the high O_3 concentration areas of eastern Los Angeles, Riverside and San Bernardino counties. The final increment of NO_x control alone produces O_3 concentration

improvements at the margin in the eastern portion of the air basin. In the western area of the air basin, near downtown Los Angeles, the most stringent package of NO_x and RHC controls studied leaves Base Case 1982 peak 1-hr average O_3 concentrations practically unchanged.

Acknowledgments

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APPENDIX A

AMMONIA EMISSIONS IN THE SOUTH COAST AIR BASIN 1982

(Environmental Quality Laboratory Open File Report 84-2)

AMMONIA EMISSIONS IN THE SOUTH COAST AIR BASIN 1982

by

S. Gharib and G. R. Cass

Open File Report 84-2

Environmental Quality Laboratory
California Institute of Technology
Pasadena, California 91125

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APPENDIX

Tabulation of Emission Factors, Activity Levels, and Ammonia Emission Rates

TABLE A.1

Emission Factors for Ammonia from Combustion Sources

	VALUE REPORTED	REFERENCE	EMISSION FACTOR (Kg $NH_3/10^9$ Btu)	VALUE ADOPTED FOR EMISSION INVENTORY USE (Kg $NH_3/10^9$ Btu)
STATIONARY SOURCES				
Fuel Combustion				
Natural Gas				
Average of Los Angeles Source Tests	0.4 mg/m^3 NH_3 in exhaust	(a)	0.119	
New York Emission Inventory Emission Factor	0.5 lb $NH_3/10^6$ ft^3 gas burned	(b)	0.214	
Literature Survey (1969)	0.3 to 0.56 lb $NH_3/10^6 ft^3$ gas	(c)	0.128-0.240	
Literature Review (1956)	0.010 tons $NH_3/10^6 ft^3$ gas	(d)	8.56	
Recent Source Test: 200,000 Btu/hr combustor				
(1) at 2% excess O_2; 17 test avg	14.44 ppm NH_3 in exhaust	(e)	3.25	3.25
(2) at 4% excess O_2; 23 test avg	6.00 ppm NH_3 in exhaust	(e)	1.351	1.35
(3) at 6% excess O_2; 15 test avg	1.00 ppm NH_3 in exhaust	(e)	0.225	0.22
Residual Fuel Oil				
Average of Los Angeles Source Tests	0.4 mg/m^3 NH_3 in exhaust	(a)	0.125	
New York Emission Inventory Emission Factor	1 lb/1000 gal oil	(f)	3.03	
Literature Survey (1956)	0.001 tons NH_3/ton oil	(g)	23.1	
Recent Source Test: 200,000 Btu/hr combustor at 2% excess air; avg of 2 tests	11.3 ppm in exhaust	(h)	2.8	2.8
Distillate Oil				
New York Emission Inventory Emission Factor	1 lb/1000 gal oil	(i)	3.29	3.3
Coal				
Literature Review (1956)	2 lb NH_3/ton coal	(j)	37.8	38
Mass Balance over N.W. Europe	1.21 g NH_3/920 g coal	(k)	50	
Recent Source Test: 200,000 Btu/hr combustor at 4% excess air, 1 test	85 ppm NH_3 in exhaust	(l)	~20	
Wood				
Literature Review (1956)	2.4 lb NH_3/ton wood	(m)		

Notes:

(a) Magill and Benoliel (1952)
(b) Hovey, Risman and Cunnan (1966), Range reported 0.3 to 20 lb $NH_3/10^6 ft^3$ natural gas
(c) Miner (1969); literature survey
(d) Wohlers and Bell (1956)
(e) Muzio and Arand (1976)
(f) Hovey, Risman and Cunnan (1966); Range reported 0.06 lb/1000 gal to 8 lb/1000 gal; converted at 0.011 scf prod/btu; 6.11×10^6 btu/bbl
(g) Wholers and Bell (1956); value appears high but note that data may be rounded up to 0.001 tons NH_3/ton oil
(h) Muzio and Arand (1976); 2 tests range 20 ppm - 2.54 ppm
(i) Hovey, Risman and Cunnan (1966); converted at 0.011 scf prod/btu; 5.8×10^6 btu/bbl
(j) Wohlers and Bell (1956)
(k) Soderlund (1977)
(l) Muzio and Arand (1976); combustion product data unavailable, converted from ppm to $Kg/10^9$ btu in proportion to oil and natural gas data
(m) Wohlers and Bell (1956)

TABLE A.2

Fuel Economy Calculation for 1982 Automobile Fleet

Age (years)	Model Year	Percentage of Total Vehicles in Use (a)	Percent Sold with Diesel Engines (b) (US)	Percentage of Vehicles in Use (gasoline engine)	Percentage of Vehicles in Use (diesel engine)	Annual Average Mileage Driven (c)	Fraction of Light Duty Fleet Miles Traveled by Gasoline Engines	Fraction of Light Duty Fleet Miles Traveled by Diesel Engines	Fuel Economy for Gasoline Cars MPG (d)	Weighted Average Fuel Economy for Gasoline Cars MPG	Weighted Average Fuel Economy for Diesel Cars MPG
1	1982	7.77	4.6	7.41	0.36	15,900	0.111	0.0054	26.2		
2	1981	7.77	5.9	7.31	0.46	15,000	0.104	0.0065	25.1		
3	1980	8.76	4.6	8.36	0.40	14,000	0.111	0.0053	23.5	21.10	24.69
4	1979	9.20	2.2	9.0	0.20	13,100	0.111	0.0025	20.3		
5	1978	8.50	0.4	8.47	0.03	12,200	0.098	0.0004	19.9	fleet avg. for	fleet avg. for
6	1977	6.73	0.1	6.72	0.01	11,300	0.072	0.00011	18.3	cat. autos	diesel autos
7	1976	5.51	0.1	5.5	0.01	10,300	0.054	0.00010	17.5		
8	1975	5.37	0.1	5.36	0.01	9,400	0.048	0.00009	15.8		
9	1974	6.45	0.1	6.44	0.01	8,500	0.052	0.00008	14.2		
10	1973	5.78	~	5.78		7,600	0.042		13.6		
11	1972	4.90	~	4.9		6,700	0.031		13.6	13.65	
12	1971	3.88	~	3.88		6,700	0.025		13.6	fleet avg. for	
≥13	1970(-)	19.38	~	19.38		6,700	0.123		13.6	non-cat. autos	
									13.6		

NOTES:

(a) Derived from California Department of Finance (1982), Table J-5, p. 170.

(b) Values for 1980 and previous years are from Diesel Impacts Study Committee (1982), pp. 1 and 90. Values for 1981 and 1982 are Automotive News, 7/5/82, as cited by Holman and Lauderdale (1983), p. 7. Data shown are based on nationwide sales statistics.

(c) U.S. Environmental Protection Agency, 1976.

(d) Motor Vehicle Manufacturers' Association (1983).

(e) A fuel economy value of 27 MPG is given by Cadle (1983) for General Motors light duty diesel vehicles. Since fuel economy for all automobiles has been improving in recent years, we estimate a fleet average fuel economy weighted over new and older diesel cars to be about 25 MPG.

TABLE A.3

Emission Factors for Ammonia from Highway Vehicles

	VALUE FOR VEHICLES IN PROPER OPERATING CONDITION (mg/km)	REFERENCE	VALUE ADOPTED FOR EMISSION INVENTORY (mg/km)	(kg $NH_3/10^9$ Btu)
HIGHWAY VEHICLES				
Autos and Lt. Trucks (gasoline engines)				
Catalyst Equipped Engines				
Oxidation Catalyst Only				
1. 1977 and 1978 production vehicles, 1975 FTP cycle	2.5	(a)		
2. California emission controls, 1975 FTP cycle	3.06	(b)		
3. 1978 Buick, Ford, Volvo, Oldsmobile, Chevrolet, Chrysler, 1979 FTP cycle, unleaded fuel	5.7	(c)	10 (x)	2.7
4. 1978 Chevrolet Malibu, 1978 Ford Granada, 1977 FTP cycle, unleaded fuel, with air pump	3.6	(d)		
5. 1978 Chevrolet Malibu, 1978 Ford Mustang II, 1977 FTP cycle, unleaded fuel, without air pump	3.1	(d)		
3-way Catalyst				
1. General Motors vehicles; 1975 FTP cycle	5.0	(e)		
2. 1978 Pontiac Sunbird; 1978 Saab 99; 1978 FTP cycle	3.6	(f)		
3. 1979 Mercury (2); 1978 Volvo; 1979 FTP cycle	10.7	(g)		
4. 1977 Volvo (California model); 1975 FTP cycle	4.7	(h)	35 (x)	
5. 1980 Lincoln Continental, 1975 FTP cycle	16.7	(i)		
6. 1978 Pontiac Sunbird; 1978 FTP cycle	11.1	(j)		
7. 1978 Saab; 1978 FTP cycle	60.8	(j)		
3-way Catalyst Plus Oxidation Catalyst				
1. 1978 Ford Pinto; 1979 Mercury Marquis; 1978 FTP cycle	2.6	(k)		
2. 1978 Ford Pinto; 1980 Chevrolet Caprice; 1975 FTP cycle	20.1	(l)	10 (x)	
3. 1978 Ford Pinto; 1979 Mercury Marquis; 1978 FTP cycle	5.6	(m)		
Non-Catalyst Pre-1975 Cars				
1. General Motors vehicles; 1975 FTP cycle; unleaded fuel	2.5	(n)		
2. 1977 AMC Pacer; 1977 FTP cycle; unleaded fuel	3.1	(o)	5 (x)	0.87
3. 1956 Oldsmobile engine on driving cycle	2.5	(p)		
4. 1972 HFW driving cycle	5	(q)		
Catalyst Medium Trucks				2.7 (y)
Non-Catalyst Medium and Heavy Gasoline Trucks				0.87 (z)
Diesel Vehicles				
Diesel Automobiles				
1. Diesel automobile	0.62	(r)	0.6	0.19
2. Experimental diesel auto, FTP cycle	0.6	(s)		
3. Peugot, driving cycle	10.92	(t)		
4. 1972 Mercedes Benz, 60 mph	0.35	(u)		
5. Lt. duty diesel vehicles	0-8	(v)		
Diesel Trucks				
1. Three 8-cylinder diesel engines	2.3	(w)	2	0.14
2. Heavy duty diesel	0-33	(v)		
LPG for Carburetion				0.87 (z)

NOTES:

(a) Cadle (1983); NH_3 emission rate from properly running oxidation catalyst car is about 4 mg/mi.
(b) Cadle and Mulawa (1980), Table V; Average of 5 tests (runs 9 through 13), range 0.6 to 14.8 mg/mi (avg. equals 4.9 mg NH_3/mi or 3.06 mg/km).
(c) Smith and Carey (1982), Tables C-1 to C-6; average values of oxidation-catalyst-equipped cars 1, 4, 6, 7, 8, 9, 10. All values are measured before tune-up in "as received" condition.
(d) Urban and Garbe (1979); Avg. values from Table 8.
(e) Cadle et al. (1979), Table 8; avg. value for dual and 3-way catalysts under normal operation. Note that NH_3 emissions from malfunctioning cars of this type can be very high, about 114 mg/km.
(f) Smith and Black (1980); value of 3.43 (mg/km) used for Sunbird as given in Table B-16; value of 3.83 mg/km used for Saab as discussed in text on page 2465. Value shown in table is average of these two results. Saab emissions are much higher (21.68 mg/km) if car is tested with initial malfunction.
(g) Smith and Carey (1982), Tables C-2 and C-4; avg. values for cars 2, 3, and 5 in "as received" condition.
(h) Bradow and Stump (1977), Table 5; average of two tests with sensor active.
(i) Braddock (1981); value from Figure 8 at 78°F. Value from test on Buick Century is not used because value is high (212.36 mg/mi) due to vehicle malfunction.
(j) Urban and Garbe (1980); Table 4.
(k) Smith and Black (1980), Table B-16; average of results for the two cars indicated.
(l) Braddock (1981), Figure 8; average of values for two cars indicated at 78°F.
(m) Urban and Garbe (1980), Table 4; average of values for two cars indicated.
(n) Cadle et al. (1979), Table 8; non-catalyst cars.
(o) Urban and Garbe (1979), Table C-1; unmodified condition.
(p) Harkins and Nicksic (1967); value reported is 2.2 ppm; converted to mg/km at fuel consumption rate of 13.6 mpg.
(q) Hunter (1971), Figure 2; standard carburetion.
(r) Cadle et al. (1979); text gives value of 1 mg/mile.
(s) Williams and Chock (1980), Table XIII.
(t) Hansin (1975), Table 3; original value equal to 11.1 ppm NH_3 in exhaust; converted to mg/km assuming stoichiometric combustion of the fuel and fuel economy of 24.69 mpg.
(u) Gentel et al. (1973), Table 38; original value equal to 0.36 ppm NH_3 in exhaust; converted to mg/km assuming stoichiometric combustion of the fuel and fuel economy of 24.69 mpg.
(v) Harvey et al. (1983), Table 1.
(w) Perez (1980); maximum value reported is 0.4 mg NH_3/m^3 exhaust; converted to mg/km assuming stoichiometric combustion of the fuel and fuel economy of 5.5 mpg.
(x) Based on recommended values given by Pierson and Brachaczek (1983), text page 759. Values adopted for use with emission inventory are higher than for average of properly operated cars. These higher figures are needed to reflect actual vehicle fleet that includes cars with malfunctions that lead to high NH_3 emission rates. See notes above.
(y) Assumed similar to catalyst automobiles.
(z) Assumed similar to non-catalyst automobiles.

TABLE A.4

Ammonia Emission Estimates for Stationary Combustion Sources

Six-County South Coast Air Basin--1982

	ESTIMATED 1982 FUEL USE (10^9 Btu/day)		EMISSION FACTOR (Kg $NH_3/10^9$ Btu)		AMMONIA EMISSIONS (metric tons/day)
STATIONARY SOURCES					
FUEL COMBUSTION					
Electric Utilities					
Natural Gas	802.	(a)	1.47	(k)	1.18
Residual Oil	134.	(a)	2.8	(l)	0.38
Digester Gas	0.6	(a)	1.47	(m)	0.0009
Refinery Fuel					
Natural Gas	101.	(b)	1.17	(n)	0.118
Residual Oil	5.3	(b)	2.8	(o)	0.015
Refinery Gas	334.	(b)	1.17	(p)	0.39
Industrial and Low Priority Commercial					
Natural Gas	324.	(c)	1.45	(q)	0.47
LPG	5.52	(d)	1.45	(r)	0.008
Residual Oil	8.	(e)	2.8	(s)	0.022
Distillate Oil	37.23	(e)	3.3	(t)	0.123
Digester Gas	18.04	(f)	1.45	(r)	0.026
Coke Oven Gas	37.53	(g)	0.40	(u)	0.015
Residental and High Priority Commercial					
Natural Gas	918.	(h)	0.225	(v)	0.207
LPG	16.85	(i)	0.225	(w)	0.004
Residual Oil	30.4	(i)	2.8	(x)	0.085
Distillate Oil	23.86	(i)	3.3	(x)	0.079
Coal	0.6	(j)	38.	(x)	0.023
TOTAL					3.15

NOTES:

(a) 1982 average daily use, from South Coast Air Quality Management District (1983a) and Ventura County (1983).
(b) 1982 average daily use, from South Coast Air Quality Management District (1983b).
(c) 1982 average daily use, by all industries from Southern California Gas Company (1983) and City of Long Beach (1983), less electric utility and refinery natural gas usage cited above.
(d) U.S. Department of Energy (1963) gives the ratio of industrial to chemical LPG sales in the U.S. as 0.22. This ratio was used for data from the state of California to break LPG sales into sales to chemical and industrial plants. This value includes sales for refinery fuel use which cannot be separated from the total.
(e) State of California total residual and distillate fuel oil use by industries other than oil companies and electric utilities was taken from U.S. Department of Energy (1983). Seventy-five percent of the non-refinery industrial heating demand in Southern California is within the six-county 1974 boundaries of the South Coast Air Basin (Cass, 1978), and 64% of state industrial fuel use is in Southern California (Stanford Research Institute, 1973). Therefore, air basin fuel oil use by industry is estimated as 0.48% of total state use by industry. Kerosene use has been added to the distillate fuel use number shown.
(f) From survey of eight large sewage treatment plants in the inventory area.
(g) Based on 1973 fuel use data at Kaiser Steel, from Cass (1978).
(h) 1982 average daily use by residential and commercial users taken from Southern California Gas Company (1983) and City of Long Beach (1983). Fuel use in south coastal strip of Santa Barbara County estimated as 78% of county total on the basis of fraction of 1970 population living in southern portion of that county (U.S. Bureau of the Census, 1972).
(i) State total LPG, residual fuel oil and distillate oil use by residential and commercial customers is given by U.S. Department of Energy (1983). Forty percent of residential/commercial oil use in the state is in Southern California (Stanford Research Institute, 1973) and 77% of Southern California population is within the six-county boundaries of the South Coast Air Basin (Southern California Association of Governments, 1982). SCAB LPG use thus is estimated as 31% of state total (i.e., 0.40x0.77=0.31).
(j) 1973 data from Cass (1978).
(k) Weighted average: 33% emission factor at 2% O_2 in stack, 22% factor at 4% O_2, 45% factor at 6% O_2 based on frequency of occurrence of O_2 levels given by Bartz et al. (1974; tests 279-289, 298-301).
(l) From Table A.1.
(m) Assumed similar to utility boiler burning natural gas.
(n) Weighted average: 19% emission factor at 2% O_2 in stack, 33% factor at 4% O_2, 48% factor at 6% O_2 based on frequency of occurrence of O_2 levels given by Bartz et al (1974; tests 12-73, 95-103).
(o) From Table A.1.
(p) Assumed similar to refinery equipment burning natural gas.
(q) Weighted average: 35% emission factor at 2% O_2 in stack, 15% factor at 4% O_2, 50% factor at 6% O_2 based on frequency of occurrence of O_2 levels for industrial fuel-burning equipment given by Bartz et al. (1974).
(r) Assumed similar to industrial equipment burning natural gas.
(s) From Table A.1.
(t) From Table A.1.
(u) Weighted average: 2% emission factor at 2% O_2 in stack, 10% factor at 4% O_2, 88% factor at 6% O_2 based on frequency of occurrence of O_2 levels for steel mill equipment given by Bartz et al. (1974; tests 104-157).
(v) Source tests by Bartz et al. (1974) show that home heaters have high levels of excess O_2 in their exhaust.
(w) Assumed similar to home heaters burning natural gas.
(x) From Table A.1.

TABLE A.5

Ammonia Emission Estimates for Stationary Combustion Sources

Six-County South Coast Air Basin--1982

	ESTIMATED 1982 FUEL USE (10^9 Btu/day)		EMISSION FACTOR (Kg $NH_3/10^9$ Btu)		NH_3 EMISSIONS (metric tons/day)
MOBILE SOURCES					
Highway Vehicles					
Catalyst Autos and Lt. Trucks	870.4	(a)	2.7	(1)	2.35
Non-Catalyst Autos and Lt. Trucks	557.3	(a)	0.87	(1)	0.485
Diesel Autos and Lt. Trucks	18.3	(b)	0.19	(1)	0.0035
Catalyst Medium Vehicles	85.1	(a)	2.7	(1)	0.23
Non-Catalyst Medium and Heavy Trucks	159.8	(a)	0.87	(1)	0.14
Diesel Trucks	162.4	(b)	0.14	(1)	0.023
LPG for Carburetion	8.2	(c)	0.87	(1)	0.0071
Civil Aviation					
Jet Aircraft	49.5	(d)	0.14	(m)	0.0069
Aviation Gasoline	2.4	(d)	0.87	(n)	0.0021
Commercial Shipping					
Residual Oil-Fired Ships' Boilers	24.3	(e)	2.8	(o)	0.068
Diesel Ships	11.2	(e)	0.14	(m)	0.0016
Railroad					
Diesel Oil	24.8	(f)	0.14	(m)	0.0035
Military					
Gasoline	5.65	(g)	0.87	(n)	0.0049
Diesel Oil	16.7	(h)	0.14	(m)	0.0023
Jet Fuel	16.71	(i)	0.14	(m)	0.0023
Residual Oil (Bunker Fuel)	0.28	(j)	2.8	(o)	0.0008
Miscellaneous					
Off-Highway Vehicles and Miscellaneous Sources	46.26	(k)	0.14	(m)	0.0065
TOTAL					3.34

NOTES:

(a) State of California total sales of leaded and unleaded gasoline taken from Ethyl Corporation (1982). Fuels apportioned to six-county air basin based on ratio of that region's population to entire state's population. Fuels apportioned among vehicle types based on fraction of VMT and fuel economy for each vehicle class.

(b) State of California total sales of distillate oil for on-highway use taken from U.S. Department of Energy (1983), apportioned to six-county air basin in proportion to percentage of state truck registrations in that region from County Supervisors Association of California (1981). Fuel apportioned among light trucks, autos, and heavy vehicles on basis of the fraction of VMT by each vehicle type.

(c) State of California total taken from U.S. Department of Energy (1983), value of LPG for internal combustion use. Apportioned to study region on basis of fraction of state population in that region.

(d) Aircraft operations taken from Carter and Trembley (1981). Fuel use computed from operations by the procedure outlined by U.S. Environmental Protection Agency (1980).

(e) Computed by procedure described by Cass (1978). Ship traffic in local harbors is given by U.S. Army Corps of Engineers (1980). Fraction of ships sailing northward and southward along the coast determined from data given by Alber (1984). Residual-to-distillate fuel use ratio taken from dockside fuel sales data of the U.S. Bureau of Census (1981a). Ship fuel economy given by U.S. Environmental Protection Agency (1981).

(f) Fuel sales to railroads in California taken from U.S. Department of Energy (1983). Fuel use apportioned to six-county study region in proportion to fraction of railroad track in the region versus in the entire state.

(g) Scaled from 1973 value given by Cass (1978). Scale factor is ratio of 1982 to 1973 diesel fuel sales to military in California from U.S. Department of Energy (1983) and the 1973 issue of that report series.

(h) 20% of statewide sales of distillate oil to the military as given by U.S. Department of Energy (1983). See Cass (1978) for justification of procedure.

(i) 1973 data from Cass (1978).

(j) 2% of total California sales of residual fuel oil to the military as given by U.S. Department of Energy (1983). See Cass (1978) for justification of procedure.

(k) California sales of distillate oil to off-highway vehicles plus "other" sources given by U.S. Department of Energy (1983). Fuel use apportioned to six-county study area on the basis of population. Kerosene use has been added to the distillate fuel use numbers shown.

(l) From Table A.3.

(m) Assumed to emit NH_3 at the same rate as a diesel truck from Table A.3.

(n) Assumed to emit NH_3 at the same rate as the non-catalyst gasoline engine automobile given in Table A.3.

(o) Assumed to emit NH_3 at the same rate as the industrial boiler given in Table A.1.

TABLE A.6

Emissions from Industrial Process Sources

	NH_3 Emissions (metric tons/day)	
Ammonia Storage	0.06	(a)
Refinery FCC Units	0.67	(a)
Refinery Waste Water Treatment	0.35	(a)
Steel Industry	0.23	(a)
Chemical Plants	0.76	(a)
Refrigerant Loss	0.38	(b)

NOTES:

(a) From survey of Cass et al. (1982).
(b) See Table A.28.

Table A.7 Estimated NH_3 Emissions from Municipal Waste Water Treatment - 1982 (excluding sludge processing)

Plant	Treatment Stage	Flow Rate (mgd)	Flow Rate (10^6 ℓ/day)	Influent NH_3-N (mg/ℓ)	Effluent NH_3-N (mg/ℓ)	Effluent NO_2^--N (mg/ℓ)	Effluent NO_3^--N (mg/ℓ)	NH_3-N Loss from water: To Bacterial Cells[a] (mg/ℓ)	NH_3-N Loss from water: To Atmosphere as NH_3 or as N_2[b] (mg/ℓ)	Nitrogen-Containing Gases to Atmosphere (metric tons -N/day)	NH_3 Emission to Atmosphere (metric tons/day as NH_3)
COUNTY SANITATION DISTRICTS OF L.A. COUNTY											
1. San Jose Creek	Secondary	36.84	139.4	19.9	15.6	0.603	2.0	0.8	0.9	0.125	0.15
2. Whittier Narrows	Secondary	13.41	50.8	20.4	16.4	0.967	1.5	0.82	0.71	0.036	0.044
3. Pomona	Secondary	9.26	35.0	18.8	11.8	0.845	2.0	0.75	3.4	0.119	0.144
4. Los Coyotes (Has 3 separate secondary units.)											
Unit 1	Secondary	11.36	43.0	23.3	10.5	1.326	2.6	0.93	7.94	0.342	0.414
Unit 2	Secondary	11.44	43.3	23.3	11.5	0.04	3.0	0.93	7.83	0.339	0.410
Unit 3	Secondary	11.37	43.0	23.3	7.6	0.719	4.8	0.93	9.25	0.398	0.482
5. Long Beach	Secondary	9.95	37.7	21.7	11.1	0.922	2.3	0.87	6.51	0.245	0.296
6. Joint Plant	Primary	360	1362.6	36	36					0	
CITY OF LOS ANGELES											
7. Hyperion Plant	Primary	379	1434.5	18.8	18.5	0	0	0	0.3	0.43	0.52
	Secondary	100	378.5	18.5	2.5	0.2	5.2	0.74	9.86	3.73	4.51
8. Terminal Island	Secondary	17.8	67.4	39.1	12.6	0.79	5.3	1.56	18.85	1.27	1.54
9. L.A. Glendale Reclaimation Plant	Secondary	10	37.9	19.5	6.5	(11.70)(c)		0.78	0.52	0.020	0.024

Table A.7 Estimated NH_3 Emissions from Municipal Waste Water Treatment - 1982 (excluding sludge processing) (Continued)

Plant	Treatment Stage	Flow Rate (mgd)	Flow Rate (10^6 ℓ/day)	Influent NH_3-N (mg/ℓ)	Effluent NH_3-N (mg/ℓ)	Effluent NO_2^--N (mg/ℓ)	Effluent NO_3^--N (mg/ℓ)	NH_3-N Loss from water To Bacterial Cells[a] (mg/ℓ)	NH_3-N Loss from water To Atmosphere as NH_3 or as N_2[b] (mg/ℓ)	Nitrogen-Containing Gases to Atmosphere (metric tons -N/day)	NH_3 Emission to Atmosphere (metric tons/day as NH_3)
ORANGE COUNTY SANITATION DISTRICT											
10. Fountain Valley	Secondary	60	227.1	23	12	(9.20)(d)		0.92	0.88	0.2	0.242
11. Huntington Beach	Secondary	160	605.6	23	12	(9.20)(d)		0.92	0.88	0.533	0.645
OTHER AGENCIES											
12. Water Factory 21	NH_3 Stripping Tower	8	30.3	24.22	19.59				4.63	0.14	0.17
13. Irvine Ranch Water District	Secondary	8.5	32.2	20	2	(17)(e)		0.8	0.2	0.0064	0.008
14. Los Alisos Water District	Secondary	2.5	9.5	50	12	(30)(f)		2.0	6	0.057	0.069
15. Aliso Water Management Agency	Secondary	3	11.4	35	20	(5.25)(g)		1.4	8.35	0.095	0.115
16. Laguna Hills Sanitation District	Secondary	4.5	17.0	(21)(h)	5	(3.15)(i)		0.84	12.01	0.204	0.247
17. South East Regional Reclaimation Authority	Secondary	8.5	32.2	(21)(h)	2	(3.15)(i)		0.84	15.01	0.483	0.584

Table A.7 Estimated NH_3 Emissions from Municipal Waste Water Treatment - 1982 (excluding sludge processing) (continued)

Plant	Treatment Stage	Flow Rate (mgd)	Flow Rate (10^6 ℓ/day)	Influent NH_3-N (mg/ℓ)	Effluent NH_3-N (mg/ℓ)	Effluent NO_2^--N (mg/ℓ)	Effluent NO_3^--N (mg/ℓ)	NH_3-N Loss from water To Bacterial Cells[a] (mg/ℓ)	NH_3-N Loss from water To Atmosphere as NH_3 or as N_2[b] (mg/ℓ)	Nitrogen-Containing Gases to Atmosphere (metric tons -N/day)	NH_3 Emission to Atmosphere (metric tons/day as NH_3)
OTHER AGENCIES (Cont)											
18. Moulton-Niguel Water District	Secondary	0.4	1.5	(21)(h)	(12)(j)	(3.15)(i)		0.84	5.01	0.0075	0.0069
19. South Coast County Water District	Primary	3.5	13.2	28	23	0		0	5	0.066	0.080
	Secondary	3.5	13.2	23	6	(3.45)(i)		0.92	12.63	0.167	0.202
20. City of San Clemente	Secondary	3.2	12.1	(21)(h)	0.5	(3.15)(i)		0.84	16.51	0.200	0.242
21. Capistrano Beach Sanitary District	Secondary	0.85×10^{-3}	3.2×10^{-3}	(21)(h)	(12)(j)	(3.15)(i)		0.84	5.01	0.016×10^{-3}	0.019×10^{-3}
22. City of Riverside	Secondary	23.5	88.9	24.5	12.5	(3.68)(i)		0.98	7.34	0.653	0.790
23. Hemet Treatment Plant	Secondary	5.1	19.3	22.5	15	(3.38)(i)		0.9	3.22	0.062	0.075
24. Sun City Treatment Plant	Secondary	0.7	2.6	(21)(h)	4.6	(3.15)(i)		0.84	12.41	0.032	0.039
25. Sunnymead Treatment Plant	Secondary	3	11.4	(21)(h)	(12)(j)	(3.15)(i)		0.84	5.01	0.057	0.069
26. City of San Bernardino	Secondary	21	79.5	19	16	(0)(k)		0.76	2.24	0.178	0.215

Table A.7 Estimated NH_3 Emissions from Municipal Waste Water Treatment - 1982 (excluding sludge processing) (Continued)

Plant	Treatment Stage	Flow Rate (mgd)	Flow Rate (10^6 ℓ/day)	Influent NH_3-N (mg/ℓ)	Effluent NH_3-N (mg/ℓ)	Effluent NO_2^--N (mg/ℓ)	Effluent NO_3^--N (mg/ℓ)	NH_3-N Loss from water: To Bacterial Cells[a] (mg/ℓ)	NH_3-N Loss from water: To Atmosphere as NH_3 or as N_2[b] (mg/ℓ)	Nitrogen-Containing Gases to Atmosphere (metric tons -N/day)	NH_3 Emission to Atmosphere (metric tons/day as NH_3)
OTHER AGENCIES (cont)											
27. Chino Basin Regional Plant #1	Secondary	19	71.9	20	6.4	(12)(1)		0.8	0.8	0.058	0.070
28. Chino Basin Regional Plant #2	Secondary	3.5	13.2	19.8	2.2	(11.88)(1)		.79	4.93	0.065	0.079
29. Chino Basin Regional Plant #3	Primary	3.2	12.1	25	25					0	
30. City of Colton	Secondary	3.4	12.9	(21)(h)	6	(3.15)(i)		0.84	11.01	0.142	0.172
31. City of Redlands	Secondary	4	15.1	(21)(h)	(12)(j)	(3.15)(i)		0.84	5.01	0.076	0.092
32. City of Rialto	Secondary	3.5	13.2	(21)(h)	(12)(j)	(3.15)(i)		0.84	5.01	0.066	0.080
33. City of Santa Barbara	Secondary	8.5	32.2	28	20	(4.20)(i)		1.12	2.68	0.086	0.104
34. Montecito Sanitation District	Secondary	1.0	3.8	21(h)	<1	(3.15)(i)		0.84	16.01	0.061	0.074
35. Goleta Sanitation District	Primary	6.2	23.5	(22.5)(m)	22.5					(0)	
36. Carpinteria Sanitation District	Secondary	1.3	4.9	(21)(h)	0.01	(3.15)(i)		0.84	17	0.083	0.1

Table A.7 Estimated NH_3 Emissions from Municipal Waste Water Treatment - 1982 (excluding sludge processing) (Continued)

Plant	Treatment Stage	Flow Rate (mgd)	Flow Rate (10^6 ℓ/day)	Influent NH_3-N (mg/ℓ)	Effluent NH_3-N (mg/ℓ)	Effluent NO_2^--N (mg/ℓ)	Effluent NO_3^--N (mg/ℓ)	NH_3-N Loss from water: To Bacterial Cells[a] (mg/ℓ)	NH_3-N Loss from water: To Atmosphere as NH_3 or as N_2[b] (mg/ℓ)	Nitrogen-Containing Gases to Atmosphere (metric tons -N/day)	NH_3 Emission to Atmosphere (metric tons/day as NH_3)
OTHER AGENCIES (cont)											
37. Summerland Sanitation District	SECONDARY	0.15	0.57	(21)(h)	(12)(j)	(3.15(i)		0.84	5.01	0.0028 10.77	0.0034 13.03

NOTES

(a) Estimated to be 4% of influent NH_3-N for secondary treatment processes (Hartling, 1984)

(b) By difference between influent, effluent and bacterial nitrogen fluxes, stated as mg/ℓ relative to influent flow.

(c) Most of the ammonia in the influent to this plant is oxidized during the secondary treatment process (Cecotti, 1984). A value equal to 60% of secondary influent NH_3-N is assumed to be nitrified.

(d) This agency tries to remove 40-50% of NH_3 during the secondary treatment stage (Pampson, 1984). A value equal to 40% of secondary influent NH_3-N is assumed to be nitrified.

(e) Nitrification removes almost all of the NH_3-N (Walters, 1984). A value equal to 85% of secondary influent NH_3-N concentration is assumed to be nitrified.

(f) Most of the NH_3-N at this plant is nitrified (Warner, 1984). A value equal to 60% of secondary influent NH_3-N concentration is assumed to be nitrified.

(g) Operators of this plant try not to nitrify the NH_3-N (Williams, 1984). The average percentage of nitrification during secondary treatment at L.A. County Sanitation District facilities is 15% and that degree of nitrification is assumed here.

Table A.7 Estimated NH_3 Emissions from Municipal Waste Water Treatment - 1982 (excluding sludge processing) (Continued)

Plant	Treatment Stage	Flow Rate (mgd)	Flow Rate (10^6 ℓ/day)	Influent NH_3-N (mg/ℓ)	Effluent NH_3-N (mg/ℓ)	Effluent NO_2^--N (mg/ℓ)	Effluent NO_3^--N (mg/ℓ)	NH_3-N Loss from water: To Bacterial Cells[a] (mg/ℓ)	NH_3-N Loss from water: To Atmosphere as NH_3 or as N_2[b] (mg/ℓ)	Nitrogen-Containing Gases to Atmosphere (metric tons -N/day)	NH_3 Emission to Atmosphere (metric tons/day as NH_3)

NOTES (Continued)

(h) Estimated based on average secondary influent NH_3-N concentration for Plants #1-5, 7, 9-11, 18, 20, 21, 24-26, 31.

(i) The average percentage nitrification of NH_3N at plants operated by the County Sanitation District of Los Angeles County is equal to 15% of secondary influent ammonia concentration. That degree of nitrification is assumed here.

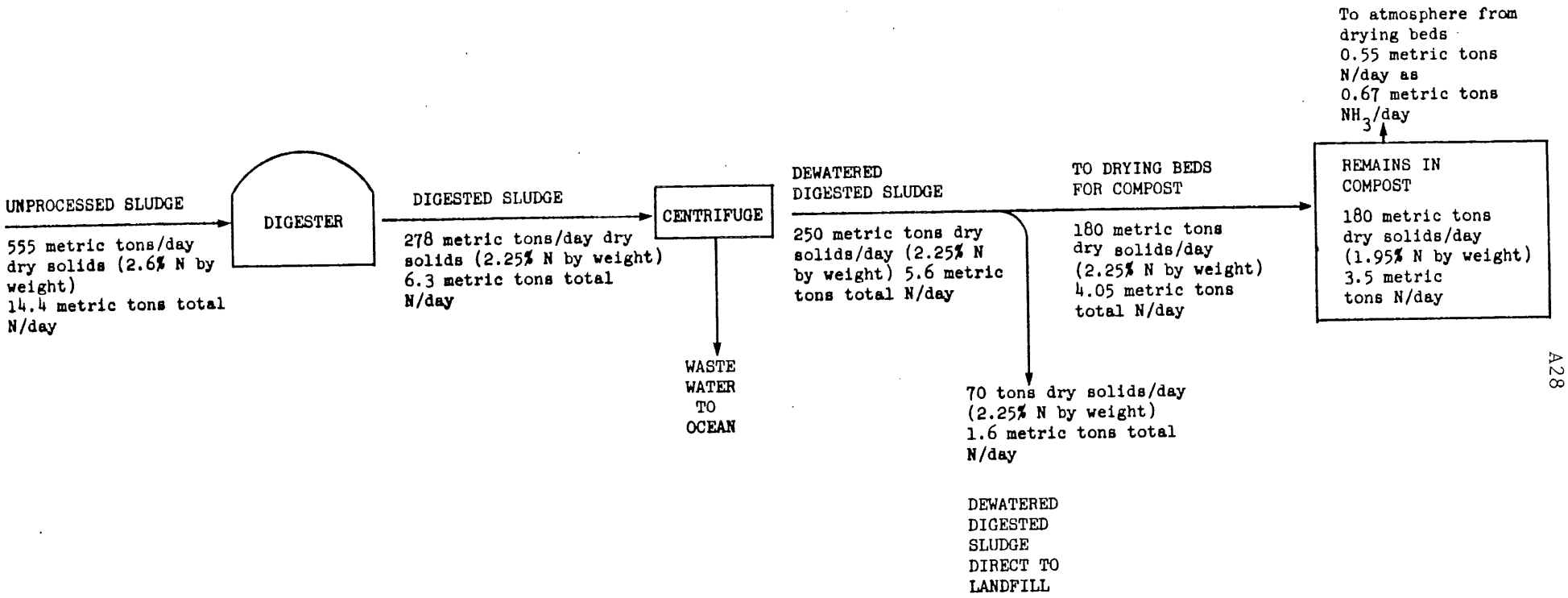
(j) Estimate based on average secondary effluent NH_3-N concentration for plants #1-5, 7, 9-11, 18, 20, 21, 24-26, 31.

(k) Since there is little difference between influent and effluent ammonia concentrations, it is assumed that very little nitrification occurred.

(l) Operators at this plant try to keep the NH_3-N concentrations low by encouraging nitrification (Coe, 1984). It is assumed that 60% of incoming NH_3-N is nitrified.

(m) For primary treatment only, influent NH_3-N will be very close to effluent NH_3-N.

Figure A.1 Emission Factors for NH_3 Loss from Sludge Processing at the Joint Water Pollution Control Plant Operated by the County Sanitation Districts of Los Angeles County (Reference: Livingston, 1984)



Possible Emission Factors

NH_3 to atmosphere/ton of unprocessed sludge (corrected for sludge sent to landfill) = 1.36 kg NH_3-N/metric ton unprocessed sludge

NH_3 to atmosphere/ton of dry digested sludge sent to drying beds = 3.03 kg NH_3-N/metric ton digested sludge

NH_3-N loss as % of total N in unprocessed sludge (corrected for sludge sent to landfill) = 5.2%

NH_3-N loss as % of total N in digested sludge sent to drying beds = 13.5%

Table A.8 Ammonia Emissions from Sludge Processing at Wastewater Treatment Plants

Plant	Undigested Sludge metric tons/day (dry solids)[a]	Digested Sludge metric tons/day (dry solids)[a]	NH_3-N Content of digested sludge (a)	Emission Factor Used (c)	Ammonia lost to the atmosphere (metric tons/day)
1. Joint Water Pollution Control Plant	400[b]	180[b]	2.25% by weight	13.5% of NH_3-N in digested sludge	0.66
2. Terminal Island	27	11 $\sim$ (120×10^3 gal/day) 2.5% solids	700 mg/lit	13.5% of NH_3-N in digested sludge	0.052
3. Orange County Sanitation District	202.5	133	3200 mg NH_3-N/ kg of dry sludge	13.5% of NH_3-N in digested sludge	0.695
4. Irvine Ranch Water District		10	50 mg/lit	3.03 kg NH_3-N/metric tons of digested sludge	0.037
5. South East Regional Reclaimation Authority		65×10^3 gal/day (before drying) 12.12×10^3 gal/day (after drying)	(50 mg/lit)(d)	13.5% of NH_3-N in digested sludge	0.037×10^{-2}
6. Aliso Water Management Agency	9	4.8	1000 mg/lit	3.03 kg NH_3-N/metric tons of digested sludge	0.018
7. City of Riverside Plant		9.5		3.03 kg NH_3-N/metric tons of digested sludge	0.035
8. Hemet Treatment Plant	4.5	1.93	0.2% by weight(e)	13.5% of NH_3-N in digested sludge	0.0006

Table A.8 Ammonia Emissions from Sludge Processing at Wastewater Treatment Plants (Continued)

Plant	Undigested Sludge metric tons/day (dry solids)[a]	Digested Sludge metric tons/day (dry solids)[a]	NH_3-N Content of digested sludge (a)	Emission Factor Used (c)	Ammonia lost to the atmosphere (metric tons/day)
9. Sun City Treatment Plant	0.52			1.36 kg of NH_3-N/metric tons of unprocessed sludge	0.0009
10. Sunnymead Treatment Plant	0.32	0.013		3.03 kg NH_3-N/metric tons of digested sludge	0.0476×16^{-3}
11. City of San Bernardino	19			1.36 kg NH_3-N/metric tons of unprocessed sludge	0.0313
12. Chino Basin Regional Plant #1	14.5	9.1		3.03 kg NH_3-N/metric tons of digested sludge	0.0334
13. Chino Basin Regional Plant #2	3.6	2.3		3.03 kg NH_3-N/metric tons of digested sludge	0.0083
14. City of Colton		1.25		3.03 kg NH_3-N/metric tons of digested sludge	0.0046
15. City of Santa Barbara		5.5	0.8% by weight	13.5% of NH_3-N in digested sludge	0.0072
16. Summerland Sanitation District	0.34	0.11		3.03 kg NH_3-N/metric tons of digested sludge	0.0004
					1.584

(a) Sludge quantities and NH_3-N content are from mail survey form completed by each plant.

(b) Based on only that portion of sludge that will contribute to compacting operations (72% of total unprocessed sludge output of plant).

(c) Emission factor based on percentage of NH_3-N in sludge lost at Joint Water Pollution Control Plant. See Figure A.1 for nitrogen balance.

(d) Assume same value as Irvine Ranch Water District

(e) 1977 data are the latest available

TABLE A.9

Emission Factors for Ammonia Release from Soil Surface

LAND SURFACE TYPE	VALUE REPORTED	REFERENCE	EMISSION FACTOR ADOPTED ($kg\ NH_3/km^2$-day)
Cropland	11 kg N/ha-yr	(a)	3.65
Lawn Surface (campus sidewalk)	0.5 to 1.5 mg NH_3/m^2-day	(b)	1
Bare Soil	1 to 2 mg NH_3/m^2-day	(c)	1 (f)
Ungrazed Grass-Clover Pasture	2 g N/ha-hr	(d)	5.81
Forest Land (estimate)		(e)	(1)
Pasture (near animals - no manure)			
Pasture Grass (>30 m from manure source)	1 to 2 mg NH_3/m^2-day	(b)	1.5
Grassland Near Swine Barn with no manure	2 to 3 mg NH_3/m^2-day	(b)	2.5
Pasture (with manure)			
Pasture with dried manure	2 to 5 mg NH_3/m^2-day	(b)	(g)
Pasture with recent liquid dairy manure	5 to 20 mg NH_3/m^2-day	(b)	(g)
Grazed Pasture	15 kg N/ha-yr	(a)	(g)
	13 g N/ha-hr	(d)	(g)

NOTES

(a) Porter et al. (1975) and Elliot et al. (1971). Note that Denmead et al. (1978) give much higher values over short periods of time.
(b) Miner (1976)
(c) Miner (1976; bare soil located more than 30 m from university dairy farm
(d) Denmead et al. (1976)
(e) Release from decomposition of organic matter in forests estimated as being low
(f) Taken at low end of range given in order not to exceed estimate for lawns
(g) Not used; emissions of NH_3 due to presence of animal wastes will be estimated separately

TABLE A.10

Ammonia Estimates for Release from Soil Surfaces

	LAND AREA DEVOTED TO THIS USE (km^2) (a)	FRACTION OF LAND NOT MASKED BY BUILDINGS AND PAVEMENT	EMISSION FACTOR (Kg NH_3/Km^2-day)	NH_3 EMISSIONS METRIC TONS PER DAY
SOIL SURFACE RELEASE (Excluding Chemical Fertilizers & Manures)				
Urban or Built-up Land				
11 Residential (single and multiple)	2884.41	44% (b)	1 (e)	1.27
12 Commercial and Services	826.21	34% (b)	1 (e)	0.28
13 Industrial	429.16	47% (b)	1 (e)	0.2
14 Transportation, Communication & Utilities	218.91	55% (b)	1 (e)	0.12
15 Industrial and Commercial Complexes	20.83	40% (c)	1 (e)	0.01
16 Mixed Urban or Built-Up Land	43.95	43% (d)	1 (e)	0.02
17 Other Urban or Built-Up Land	348.23	43% (d)	1 (e)	0.15
Agricultural Land				
21 Cropland and Pasture	1770.72		3.4 (f)	6.02
22 Orchards, Groves, Vineyards, Nurseries, and Ornamental	857.65		(3.6) (g)	3.09
23 Confined Animal Feeding Operations	47.26		estimated separately (h)	
24 Other Agricultural Land	25.32		(3.4) (i)	0.09
Rangeland				
31 Herbaceous Rangeland	686.48		(1) (j)	0.69
32 Shrub and Brush Rangeland	8053.08		(1) (j)	8.05
33 Mixed Rangeland	1165.01		(1) (j)	1.17
Forest Land				
41 Deciduous Forest Land	12.53		(1) (k)	$\leq$0.01
42 Evergreen Forest Land	2291.58		(1) (k)	$\leq$2.29
43 Mixed Forest Land	40.08		(1) (k)	$\leq$0.04
Wetland				
61 Forested Wetland	33.10			neglected
62 Non-Forested Wetland	53.89			neglected
Barren Land				
72 Beaches	16.21		$\leq$ (1) (l)	$\leq$0.02
73 Sandy Areas (other than beaches)	107.35		$\leq$ (1) (l)	$\leq$0.11
76 Transitional Areas	149.76		1 (m)	0.15
77 Mixed Barren Land	10.62		1 (n)	0.01
				$\leq$23.79

NOTES:

(a) Obtained by counting areas in each category as shown on land use maps prepared by U.S. Geological Survey (1976a-e).
(b) Obtained by examination of aerial photographs (Fretz, 1980). Twenty-four zone photos distributed widely over Los Angeles County were overlayed with land use categories and examined to estimate the fraction of land in each category which had been paved or built upon. Values shown are averages of the 24 photographs examined.
(c) Estimated by average of commercial and industrial categories shown above.
(d) Estimated by weighted average of land use categories 11 through 14.
(e) Emission factor of lawn and bare soil from Table A.9.
(f) Average of cropland, ungrazed clover, and two types of grassland without animals present on land.
(g) Assumed same as cropland from Table A.9.
(h) Emissions from livestock operations estimated separately based on animal head count and wastes produced.
(i) Assumed similar to crop and pasture combination.
(j) Assumed similar to bare soil/grass combination.
(k) Estimate.
(l) Less than or equal to bare soil data from Table A.9.
(m) Bare soil data from Table A.9.

TABLE A.11

Nitrogen in Dry and Liquid Fertilizers for Farm Plus Non-Farm Use (3rd quarter 1982 from California Department of Food and Agriculture, 1982)

COUNTY	FERTILIZER TOTAL NITROGEN (metric tons/day)	PARTITION DRY[(a)]	PARTITION LIQUID[(a)]
Los Angeles	18	0.8	0.2
Orange	6.1	0.85	0.15
Riverside	49.6	0.21	0.79
San Bernardino	1.7	0.92	0.08
Santa Barbara	36.8	0.35	0.65
Ventura	17.3	0.47	0.53

(a) Fraction of total N applied in liquid and dry form estimated by summing N content of those liquid and dry fertilizers for which nitrogen content data were given.

TABLE A.12

Percentage of N Applied, Apportioned Between Farm and Non-Farm Use (California Department of Agriculture, 1982)

	FARM		NON-FARM	
COUNTY	DRY	LIQUID	DRY	LIQUID
Los Angeles	43	11	37	9
Orange	49	9	36	6
Riverside	20.7	77.7	0.3	1.3
San Bernardino	37	3	55	5
Santa Barbara	34.7	64.5	0.3	0.5
Ventura	45	50.5	2	2.5

(a) Example: Fraction (farm N/total N) x fraction dry from Table A.11.

TABLE A.13

Fertilizer Nitrogen Applied
(Tons N/day)

COUNTY	DRY		LIQUID	
	FARM	NON-FARM	FARM	NON-FARM
Los Angeles	7.7	6.7	2	1.6
Orange	3	2.2	0.5	0.4
Riverside	10.3	0.15	38.5	0.65
San Bernardino	0.63	0.94	0.05	0.09
Santa Barbara	12.8	0.11	23.7	0.18
Ventura	7.8	0.35	8.7	0.43

Estimated by combining data of Tables A.11 and A.12

TABLE A.14

Percentage of Farm Fertilizer Applied on Crops

(From U.S. Bureau of the Census, 1977)[a]

COUNTY	% of Farm Fertilizer Applied on Crops(a)	
	% DRY	% LIQUID
Los Angeles	63	80
Orange	57	34
Riverside	63	84
San Bernardino	31	42
Santa Barbara	79	95
Ventura	60	39

(a) Data taken from U.S. Bureau of the Census (1977) as shown in Table A.11 of Cass et al. (1982). 1982 Census of Agriculture does not contain this information.

TABLE A. 15

Nitrogen Applied on Crops, Orchards, and Non-Farm Areas
(County Totals in Metric Tons/day)

COUNTY	DRY			LIQUID		
	CROP[a]	ORCHARDS AND ORNAMENTALS	NON-FARM	CROP[a]	ORCHARDS AND ORNAMENTALS	NON-FARM
Los Angeles	4.85	2.85	6.7	1.6	0.4	1.6
Orange	1.7	1.3	2.2	0.17	0.33	0.4
Riverside	6.5	3.8	0.15	32.3	6.2	0.65
San Bernardino	0.2	0.43	0.94	0.02	0.03	0.09
Santa Barbara	10	2.7	0.11	22.5	1.2	0.18
Ventura	4.7	3.1	0.35	3.4	5.3	0.43

(a) Farm use split between crops vs. orchards and ornamentals using crop percentages of Table A.14 applied to total farm use given in Table A.13.

TABLE A.16

Percentage of Land Use in Each County Located within the Gridded Inventory Map Area and within the South Coast Air Basin

County	Cropland	Orchards	Non-Farm Fertilized Land (a)
Los Angeles	34	84	99
Orange	100	100	100
Riverside	53	43	77
San Bernardino	69	100	82
Santa Barbara	7	100	78
Ventura	95	100	100

(a) Estimated from percentage of county population living within the air basin in 1980.

TABLE A.17

Fertilizer Nitrogen Applied Inside the South Coast Air Basin
(metric tons/day)[a]

COUNTY	DRY			LIQUID		
	CROP	ORCHARDS AND ORNAMENTALS	NON FARM	CROP	ORCHARDS AND ORNAMENTALS	NON FARM
Los Angeles	1.65	2.4	6.6	0.54	0.34	1.58
Orange	1.7	1.3	2.2	0.17	0.33	0.4
Riverside	3.45	1.6	0.12	17.1	2.67	0.5
San Bernardino	0.14	0.43	0.77	0.01	0.03	0.07
Santa Barbara	0.7	2.7	0.09	1.58	1.2	0.14
Ventura	4.5	3	0.35	3.23	5.3	0.43
TOTAL	12.14	11.4	10.1	22.63	9.87	3.12

(a) Data of Tables A.15 and A.16 combined.

TABLE A.18

Ammonia Loss Due to Fertilizer Application by County—3rd Quarter-- 1982
(handling loss given separately)

COUNTY	DRY						LIQUID						TOTAL NH_3 LOSS KG/DAY
	CROPLAND		ORCHARDS AND ORNAMENTALS		NON-FARM		CROPLAND		ORCHARDS AND ORNAMENTALS		NON-FARM		
	FERTILIZER N APPLIED METRIC TONS/DAY	NH_3 LOSS KG/DAY(a)	FERTILIZER N APPLIED METRIC TONS/DAY	NH_3 LOSS KG/DAY(a)	FERTILIZER N APPLIED METRIC TONS/DAY	NH_3 LOSS KG/DAY(b)	FERTILIZER N APPLIED METRIC TONS/DAY	NH_3 LOSS KG/DAY(c)	FERTILIZER N APPLIED METRIC TONS/DAY	NH_3 LOSS KG/DAY(c)	FERTILIZER N APPLIED METRIC TONS/DAY	NH_3 LOSS KG/DAY(b)	
Los Angeles	1.65	200	2.4	290	6.6	2396	0.54	13	0.34	8	1.58	573.5	3480.5
Orange	1.7	206	1.3	157	2.2	799	0.17	4	0.33	8	0.4	145	1319
Riverside	3.45	417	1.6	194	0.12	44	17.1	414	2.67	65	0.50	182	1316
San Bernardino	0.14	17	0.43	52	0.77	280	0.01	0.24	0.03	0.73	0.074	27	377
Santa Barbara	0.7	85	2.7	327	0.09	33	1.58	38	1.2	29	0.14	51	563
Ventura	4.5	544	3	363	0.35	127	3.23	78	5.3	128	0.43	156	1396
TOTAL	12.14	1469	11.43	1383	10.15	3679	22.6	547	9.9	239	3.12	1135	8452

Total NH_3 Loss = 8452 kg/day (for the 3rd quarter)
= 8.45 metric tons/day

(a) Assuming 10% of N applied is lost to atmosphere as NH_3 (Meyer, 1981)

(b) Assuming 30% of N applied is lost to atmosphere as NH_3 (Meyer, 1981)

(c) Assuming 2% of N applied is lost to atmosphere as NH_3 (Meyer, 1981)

TABLE A.19
Loss of Anhydrous Ammonia Due to Handling and Field Application
(3rd Quarter, 1982)

COUNTY	ANHYDROUS AMMONIA (metric tons N/day) (County Total)[a]	% OF LIQUID FERTILIZER APPLIED ON CROPS	% OF CROPLAND IN BASIN	% OF ORCHARDS IN BASIN	ANHYDROUS AMMONIA IN BASIN[b] (metric tons N/day)	1% LOSS DUE TO HANDLING(c) (metric tons N/day)	3% LOSS DURING APPLICATION ON FIELD(c) (metric tons N/day)
Los Angeles	1.28	80	34	84	0.56	0.006	0.017
Orange	-	34	100	100	-	-	-
Riverside	15	84	53	43	7.71	0.08	0.23
San Bernardino	-	42	69	100	-	-	-
Santa Barbara	1.53	95	7	100	0.18	0.002	0.005
Ventura	-	39	95	100	-	-	-
TOTAL	17.8				8.45	0.088	0.25

Total loss = 0.34 metric tons N/day

= 0.41 metric tons NH_3/day

(a) From liquid fertilizer sales classed as 82-00-00 by the California Department of Food and Agriculture (1982)

(b) County total multiplied by [% of liquid fertilizer applied to crops (Table A.14) x % cropland in basin (Table A.16) + % of liquid fertilizer applied to orchards x % orchards in basin.]

(c) Walkup and Nevins (1966)

TABLE A.20

Summary of NH_3 Emissions from Fertilizer Application and Handling

COUNTY	LOSS FROM FARM APPLICATION OF FERTILIZER(metric tons/day) CROPS	ORCHARDS	LOSS FROM NON-FARM APPLICATION (metric tons/day)	LOSS DUE TO HANDLING (metric tons/day)	TOTAL NH_3 LOSS (metric tons/day)
Los Angeles	0.21	0.3	2.97	0.03	3.51
Orange	0.21	0.17	0.94	-	1.32
Riverside	0.83	0.26	0.23	0.38	1.7
San Bernardino	0.02	0.05	0.31	-	0.38
Santa Barbara	0.12	0.36	0.08	0.01	0.57
Ventura	0.62	0.49	0.28	-	1.39
				TOTAL	8.87

TABLE A.21

Summary of Animal Waste Data

ANIMAL	SOURCE	ANIMAL WEIGHT (kg)	MANURE (TOTAL WASTE) kg/head-day	TOTAL NITROGEN EXCRETED kg/head-day
Dairy Cattle	Dale (1971)	680	49	
	Fogg (1971)	600	45	0.17
	Luebs et al. (1973b)			0.18
	Adriano et al. (1974)			0.19
Value Used		640	47	0.18
Beef Cattle	Fogg (1971)	400	34	0.24
	Peters & Blackwood (1977)	500	27	
	Taiganides & Hazen (1966)	450	29	0.17
	Scholz (1971)	500	45	
Value Used		450	32	0.21
Horses	Fogg (1971)	450	25	0.22
Hogs	Fogg (1971)	70	3.9	0.03
	Muehling (1971)	70	5.5	0.038
	Scholz (1971)	70	3.6	
	Taiganides & Hazen (1966)	45	3.2	0.023
Value Used		70	3.9	0.03
Sheep	Fogg (1971)	45	1.8	0.018
Chickens	Fogg (1971)	2	0.11	0.0014
	Scholz (1971)		0.185	
	Taiganides & Hazen (1966)	2	0.11	0.0019
Value Used		2	0.14	0.0016
Turkey	taken in proportion to chickens on body weight basis	5.5	0.39	0.0044

TABLE A.22

DISTRIBUTION OF CATTLE BETWEEN DAIRY, FEEDLOT AND RANGE

COUNTY	CATTLE & CALVES (a)	BEEF COWS(a)	MILK COWS(a)	Heifers and Heifer Calves[a] BEEF HEIFERS(b)	MILK HEIFERS(b)	STEERS(a)	DAIRY CATTLE	FEEDLOT CATTLE[c]	RANGE CATTLE (c)
Los Angeles	33,604	4,907	6,019	5,116	4,536	13,026	10,555	12,677	10,372
Orange	12,889	4,000(d)	300(d)	2,226	592	4,226	892	48	11,949
Riverside	178,703	7,563	87,126	14,956	44,870	24,186	131,996	33,629	13,078
San Bernardino	283,742	6,707	167,120	80,167	10,932	18,816	178,052	42,276	63,414
Santa Barbara	94,605	30,425	4,628	18,210	3,997	37,345	8,625	43,850	42,130
Ventura	18,835	8,000(d)	2,500(d)	2,701	4,801	3,123	7,301	10,150	1,384

(a) U.S. Bureau of the Census (1984)

(b) Heifers and heifer calves apportioned between beef heifers and milk heifers in same ratio as given by U.S. Bureau of the Census (1977).

(c) Beef cattle apportioned between feedlot and range in same ratio as given by U.S. Bureau of the Census (1977).

(d) From California Crop and Livestock Reporting Service (1983).

TABLE A.23

Fraction of Animals Located Inside South Coast Air Basin Portion of Each County

ANIMAL TYPE	LOS ANGELES	ORANGE	RIVERSIDE	SAN BERNARDINO	SANTA BARBARA	VENTURA
Dairy Cattle	90[b]	100[a]	100[a]	97[b]	0[d]	100
Feedlot Cattle	(60)[c]	100	20	100	0[d]	100
Range Cattle	100	100	100	100	16[e]	100
Horses	98	100	98	98	16[e]	100
Sheep	10	100	(50)	100	16[e]	100
Hogs	10	100	90	90	16[e]	100
Chickens	100	100	100	100	16[e]	100
Turkeys	100	100	100	100	16[e]	100

Estimates are by Addis (1981) unless noted otherwise:

(a) Bishop (1981)
(b) 2000 dairy cows in desert area of Los Angeles County and 3835 dairy cows located in desert portion of San Bernardino County (Bishop, 1981).
(c) Most Los Angeles County feedlot cattle are located within the South Coast Air Basin; Addis (1981) estimates more than 10,000 within the air basin (i.e. 54% or greater are in the air basin). We will estimated that 60% of the total are in the air basin.
(d) U.S. Geological Survey (1976) maps show negligible land area devoted to confined animal feeding in the South Coast Air Basin portion of Santa Barbara Count.
(e) Estimated in rough proportion to the fraction of the county land area within the air basin boundary.

Table A.24a

Livestock Inventory

COUNTY	COUNTY TOTALS[a]			LOCATED IN SOUTH COAST AIR BASIN[b]		
	DAIRY	FEEDLOT	RANGE	DAIRY	FEEDLOT	RANGE
Los Angeles	10,555	12,677	10,372	9,500	7,606	10,372
Orange	892	48	11,949	892	48	11,949
Riverside	131,996	33,629	13,078	131,996	6,726	13,078
San Bernardino	178,052	42,276	63,414	172,710	42,276	63,414
Santa Barbara	8,625	43,850	42,130	-	-	6,741
Ventura	7,301	10,150	1,384	7,301	10,150	1,384
				322,399	66,806	106,938

(a) See Table A.22

(b) See Table A.23

TABLE 24b

Livestock Inventory (continued)

COUNTY	HORSES		SHEEP		HOGS	
	COUNTY TOTAL[a]	IN SOUTH COAST AIR BASIN[b]	COUNTY TOTAL[c]	IN SOUTH COAST AIR BASIN[b]	COUNTY TOTAL[c]	IN SOUTH COAST AIR BASIN[b]
Los Angeles	54,700	53,606	32,330	3,233	5,706	571
Orange	10,500	10,500	166	166	699	699
Riverside	30,300	29,694	58,228	29,114	5,289	4,760
San Bernardino	19,900	19,502	34,915	34,915	6,875	6,188
Santa Barbara	8,300	1,328	19,131	3,061	1,226	196
Ventura	7,200	7,200	8,290(d)	8,290	1,904	1,904
				78,779		14,318

(a) Anderson (1979)

(b) See Table A.23

(c) U.S. Bureau of the Census (1984)

(d) U.S. Bureau of the Census (1981b)

TABLE A.24c

Livestock Inventory - Continued

COUNTY	CHICKENS		TURKEYS	
	COUNTY TOTAL[a]	IN SOUTH COAST AIR BASIN[b]	COUNTY TOTAL[a]	IN SOUTH COAST AIR BASIN[b]
Los Angeles	711,793	711,793	133,196	133,196
Orange	260,089	260,089	20	20
Riverside	8,411,609	8,411,609	26,875	26,875
San Bernardino	6,039,468	6,039,468	24,709	24,709
Santa Barbara	797,009	127,521	16(e)	3
Ventura	(1,438,861)(c)	1,438,861	38	38
		16,989,341		184,841

(a) U.S. Bureau of the Census (1984)

(b) 1974 data from U.S. Bureau of the Census (1977); more recent yeara data all withheld by the government.

(c) Estimated as 1.19 times the sales data given for chickens based on ratio of inventory to sales in Los Angeles, Riverside, San Bernardino and Orange Counties. Inventory data in Ventura County withheld by the government.

(d) See Table A.23

(e) 1978 data from U.S. Bureau of the Census (1981b); 1982 data withheld by the government

TABLE A.25

Total NH_3 Emissions from Livestock in the Modeling Region of the South Coast Air Basin - 1982

ANIMAL	INVENTORY IN SOUTH COAST AIR BASIN (HEAD)	TOTAL ANIMAL WASTE kg/head-day	NITROGEN EXCRETED kg/head-day	NH_3 EMISSIONS AT 50% RATE OF NITROGEN EXCRETED IN TOTAL WASTE[a] metric tons/day
Dairy Cattle	322,399	47	0.18	29.84(b)
Feedlot Cattle	66,806	32	0.21	7.21(b)
Range Cattle	106,938		0.21	13.59
Horses	121,830	25	0.22	16.22
Sheep	78,779	1.8	0.018	0.86
Hogs	14,318	3.9	0.03	0.26
Chickens	16,989,341	0.14	0.0016	16.45
Turkeys	184,841	0.39	0.0044	0.49
				84.92

(a) Adriano et al. (1974); Adriano et al. (1971): Giddens and Rao (1975); Viets (1971); Leubs et al. (1973ab)

(b) Since only 85% of manure from these animals is spread on soil, totals have been multiplied by 0.85 (see Adriano et al. (1974).

TABLE A.26

Emission Factors for Ammonia Loss Due to Non-Farm Animals

NON-FARM ANIMALS	ANIMAL WEIGHT (kg)[a]	TOTAL N EXCRETED IN URINE[a] (mg/kg body wt-day)	NITROGEN EXCRETED IN URINE DAILY[b] (kg/head-day)	EMISSION FACTOR[c] (kg NH_3/head-day)
Cats	2.5	500 - 1100	$2x10^{-3}$	$2.2x10^{-3}$
Dogs	12	250 - 800	$6.3x10^{-3}$	$6.9x10^{-3}$
Goats	50	120 - 400	$1.3x10^{-2}$	$1.4x10^{-2}$
Monkey	12	140 - 400	$3.2x10^{-3}$	$3.5x10^{-3}$
Rabbits	2	120 - 300	$4.2x10^{-4}$	$4.6x10^{-4}$
Rats	0.33	200 - 1000	$2.0x10^{-4}$	$2.2x10^{-4}$

(a) From Altman and Dittmer (1968) p. 528.

(b) Based on body weight and mid-point of range of nitrogen excretion rates given in adjacent columns.

(c) Cattle data show that about half of the nitrogen excreted in manure is in urine and half is in feces, and that when manure is applied to dry alkaline soil half of the total nitrogen is lost to the atmosphere as NH_3 (i.e. total N lost as NH_3 is approximately equal to nitrogen content of urine). We will estimate that loss rate is similar for other animals and that in the absence of data on total animal waste a value equal to 90% of urine N will reasonably estimate loss of N from total animal wastes.

TABLE A.27

NH_3-Emissions from Human and Domestic Animal Populations

COUNTY	COUNTY POPULATION (1980)(a)	RATIO: PEOPLE TO DOGS	RATIO: PEOPLE TO CATS	SOUTH COAST AIR BASIN POPULATION(a)	SOUTH COAST AIR BASIN EMISSIONS ANIMAL WASTE(i) (metric tons NH_3/day) DOGS	CATS	HUMANS (metric tons NH_3/day) RESPIR.(j)	PERSPIR.(k)
Los Angeles	7,462,000	7.8(b)	7.0(g)	7,357,300	6.51	2.31	0.03	5.0
Orange	1,920,700	5.8(c)	(7.0)(h)	1,921,000	2.29	0.60	0.008	1.3
Riverside	655,900	(4.5)(d)	(7.0)(h)	505,900	0.78	0.16	0.002	0.34
San Bernardino	882,500	4.5(e)	(7.0)(h)	724,000	1.11	0.23	0.003	0.49
Santa Barbara	298,674	5.8(f)	(7.0)(h)	232,981	0.28	0.07	0.001	0.16
Ventura	524,800	5.8(f)	(7.0)(h)	523,700	0.62	0.16	0.002	0.36
					11.59	3.53	0.046	7.65

(a) County population figures from Southern California Association of Governments (1982) except for Santa Barbara County, which is 1980 data from U.S. Bureau of the Census (1982). The portion of Santa Barbara County located within the study area is estimated on the basis of 1974 data, at which time 0.78 of the total county population lived on the south coastal side of the county.
(b) Richards, B. (1981)
(c) Hudson, R. (1981)
(d) Estimated from San Bernardino data
(e) San Bernardino (1981)
(f) Estimated from Orange County data
(g) Richards, B. (1981)
(h) Estimated from Los Angeles County response
(i) Computed using emission factors from Table A.26; (dogs, 6.9×10^{-3} kg NH_3/head day; cats 2.2×10^{-3} kg/head-day)
(j) Respiration loss estimated at 4µl NH_3 per min per person (Kupprat et al., 1976) This implies 4.4×10^{-6} kg NH_3 respired/person-day
(k) 24.5 g urea produced in human body/day (Altman and Dittmer, 1968); 5% released in perspiration (Healy et al., 1970; all of that assumed lost as NH_3. This implies 0.68 g NH_3/person-day.

TABLE A.28

Ammonia Emission Estimates for Refrigerants and Household Cleaning Chemicals--1982

COUNTY	SOUTH COAST AIR BASIN POPULATION(a)	NH_3 EMISSIONS(d) metric tons/day	
		CLEANING AGENTS(b)	REFRIGERATION(c)
Los Angeles	7,357,300	0.37	0.25
Orange	1,921,000	0.098	0.065
Riverside	505,900	0.026	0.017
San Bernardino	724,000	0.037	0.025
Santa Barbara	232,981	0.012	0.008
Ventura	523,700	0.027	0.018
		0.57	0.38

(a) See Table A.27

(b) U.S. Ammonia Production for 1980: 30.99×10^9 lb = 15.5×10^6 short tons/yr (Chem. & Eng. News, 1983-May 2): 0.03% of total synthetic ammonia is used in the manufacture of household ammonia from Kirk-Othmer Encyclopedia (1963)

(c) 0.02% of total synthetic ammonia is used for refrigeration (Kirk-Othmer Encyclopedia, 1963)

(d) Emissions were calculated based on ratio of air basin population in 1980 to U.S. population. 100% NH_3 loss to the atmosphere was assumed. The population of the United States in July 1981 was 227.6×10^6 persons from U.S. Bureau of Census (1981c).

TABLE A.29

Summary of Ammonia Emissions by Source Category
in the South Coast Air Basin

1982

SOURCE CATEGORY	TOTAL EMISSIONS (kg/day)	
Stationary Fuel Combustion		
Electric Utility		
Natural Gas	1180.0	
Residual Oil	380.0	
Digester Gas	0.9	
Refinery Fuel Burning		
Natural Gas	118.0	
Residual Oil	15.0	
Refinery Gas	390.0	
Industrial Fuel Burning		
Natural Gas	470.0	
Liquified Petroleum gas (LPG)	8.0	
Residual Oil	22.0	
Distillate Oil	123.0	
Digester Gas	26.0	
Coke Oven Gas	15.0	
Residential/Commercial Fuel Burning		
Natural Gas	207.0	
Liquid Propane Gas (LPG)	4.0	
Residual Oil	85.0	
Distillate Oil	79.0	
Coal	23.0	
Subtotals	3145.9	(1.91%)
Mobile Source Fuel Combustion		
Automobiles		
Catalyst Autos and Light Trucks	2350.0	
Non-catalyst Autos and Light Trucks	485.0	
Diesel Autos and Light Trucks	3.5	
Catalyst Medium Vehicles	230.0	
Non-catalyst Medium and Heavy Trucks	140.0	
Diesel Trucks	23.0	
LPG for Carburetion	7.1	
Civilian Aircraft		
Jet	6.9	
Piston	2.1	
Shipping		
Residual Oil Boilers	68.0	
Diesel Ships	1.6	
Railroad—Diesel Oil	3.5	
Military		
Gasoline	4.9	
Diesel	2.3	
Jet Fuel	2.3	
Residual Oil	0.8	
Off-Highway Vehicles	6.5	
Subtotals	3337.5	(2.03%)
Industrial Point Sources	2450.0	(1.49%)
Sewage Treatment Plants	14,614.0	(8.88%)
Soil Surface	23,790.0	(14.5%)
Fertilizer		
Farm Crop	2010.0	
Orchards	1630.0	
Handling	420.0	
Non-farm	4810.0	
Subtotals	8870.0	(5.39%)
Livestock		
Cattle		
Dairy	29,840.0	
Feedlot	7210.0	
Range	13,590.0	
Horses	16,220.0	
Sheep	860.0	
Hogs	260.0	
Chickens	16,450.0	
Turkeys	490.0	
Subtotals	84,920.0	(51.6%)
Domestic		
Dogs	11,590.0	
Cats	3530.0	
Human Respiration	46.0	
Human Perspiration	7650.0	
Household Ammonia Use	570.0	
Subtotals	23,386.0	(14.2%)
*** Total ***	164.512.4	(100.0%)

APPENDIX B

ON SOME ASPECTS OF NIGHTTIME ATMOSPHERIC CHEMISTRY

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On Some Aspects of Nighttime Atmospheric Chemistry

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■ Nighttime atmospheric chemistry is simulated in two different situations: an offshore oceanic environment, the Santa Barbara Channel region of the south central coast of California, and a dry environment, the Mojave Desert of California. In the marine case, conversion of NO_x to peroxyacetyl nitrate (PAN) and HNO_3 is rapid; HNO_3 is formed by homogeneous hydrolysis of N_2O_5 and by nitrate radical reactions with organic gases, and the rate of HNO_3 production is limited by the abundance of O_3. Even in the desert case, predictions indicate that homogeneous hydrolysis of N_2O_5 dominates HNO_3 formation at night. The implications of recent studies concerning the unimolecular decomposition of NO_3 are discussed.

Introduction

The central species in nighttime atmospheric chemistry is the nitrate free radical NO_3. With utilization of its absorption spectrum, there have been a number of recent ambient measurements of NO_3 (*1–6*), as well as attempts to understand observed NO_3 behavior on a theoretical basis (*7–11*). Questions of continuing interest are (1) can the ambient nighttime measurements of NO_3 be explained on the basis of our current understanding of its chemistry and (2) how does nighttime chemistry vary in different environments? This paper addresses each of these questions by simulating nighttime chemistry in two distinctly different environments: an offshore regime, based on ambient hydrocarbon and NO_x data from the Santa Barbara Channel, in the Pacific Ocean off the coast of California, and a dry environment, the Mojave Desert of California. In the latter case, NO_3 measurements are available against which to evaluate the simulations.

Nighttime NO_x Chemistry

The nitrate radical, NO_3, is generated in the troposphere largely through the reaction of O_3 and NO_2:

$$NO_2 + O_3 \xrightarrow{1} NO_3 + O_2$$

This is the principal reaction driving the nighttime chemistry of the N_xO_y system. During the daytime hours, NO_3 concentrations are maintained at very low levels by photolysis (*12*). At night, however, NO_3 may accumulate due to reaction 1. NO_3 reacts with NO_2 to form N_2O_5, which itself may decompose to return NO_3 and NO_2:

$$NO_3 + NO_2 \xrightarrow[M]{2} N_2O_5$$

$$N_2O_5 \xrightarrow{3} NO_3 + NO_2$$

A second route exists for the NO_3–NO_2 reaction:

$$NO_3 + NO_2 \xrightarrow{4} NO + NO_2 + O_2$$

Also, NO_3 reacts with NO to form NO_2:

$$NO_3 + NO \xrightarrow{5} 2NO_2$$

The bimolecular reaction $2NO_3 \rightarrow 2NO_2 + O_2$ also occurs but can be neglected under atmospheric conditions. NO_3 reacts with a number of organic species. The aldehyde–NO_3 reaction proceeds according to

$$NO_3 + HCHO \xrightarrow[O_2]{6} HNO_3 + HO_2 + CO$$

$$NO_3 + RCHO \xrightarrow[O_2]{7} HNO_3 + RCO_3$$

where RCO_3 denotes an acylperoxy radical. The reaction of NO_3 with alkanes can be represented in general by the H-atom abstraction step:

$$NO_3 + ALK \xrightarrow[O_2]{8} HNO_3 + RO_2$$

The olefin–NO_3 reaction is generally thought to proceed by addition, where, for propylene, for example

$$NO_3 + C_3H_6 \rightarrow CH_3CHCH_2ONO_2$$
$$\rightarrow CH_3CH(ONO_2)CH_2$$

At low olefin concentrations, it is sufficient to represent the olefin–NO_3 reaction as

$$NO_3 + OLE \xrightarrow{9} RPN$$

where RPN denotes a nitrogen-containing product whose further participation in the chemistry can be neglected.

Finally, the N_2O_5 formed in reaction 2 may react with water vapor to form nitric acid:

$$N_2O_5 + H_2O \xrightarrow{10} 2HNO_3$$

And the acetylperoxy radical from reaction 7 can react with NO_2 to form peroxyacetyl nitrate (PAN):

$$RCO_3 + NO_2 \underset{12}{\overset{11}{\rightleftharpoons}} RCO_3NO_2 \text{ (PAN)}$$

Table I summarizes reactions 1–12 with their rate constants.

At night, due to the absence of NO_2 photolysis, the NO–O_3 reaction

$$NO + O_3 \rightarrow NO_2 + O_2$$

proceeds unimpeded to convert NO to NO_2 as long as both NO and O_3 are available. Generally, one expects, as a result, that nighttime NO levels will be very low if a reasonable quantity of O_3 is present from daytime photochemistry. Nighttime NO levels might be expected to increase once the O_3 has been consumed if there are continued fresh emissions of NO from sources.

At the concentration levels to be considered in this study, reactions 8 and 9 will not be important NO_3 consumption reactions. The NO_3–dimethyl sulfide reaction (*8*)

$$NO_3 + (CH_3)_2S \xrightarrow{13} \text{products}$$

might be an appreciable sink for NO_3 in the absence of other competing species.

Winer et al. (*8*) also studied the reaction of monoterpenes with NO_3:

$$NO_3 + \text{monoterpene} \xrightarrow{14} \text{products}$$

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Table I. Chemical Reactions of Nighttime Atmosphere[a]

reaction	rate constant, cm^3 molecule^{-1} s^{-1}	rate constant, 298 K, ppm^{-1} min^{-1}	ref
(1) $NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2 \times 10^{-13} e^{-2450/T}$	0.05	21
(2) $NO_3 + NO_2 \rightarrow N_2O_5$	1.7×10^{-12}	2.51×10^3	19
(3) $N_2O_5 \xrightarrow{M} NO_3 + NO_2$	$6.0 \times 10^{14} e^{-11080/T}$	2.9	21
(4) $NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$	$2.5 \times 10^{-14} e^{-1230/T}$	0.59	22
(5) $NO_3 + NO \rightarrow 2NO_2$	2×10^{-11}	2.956×10^4	21
(6) $NO_3 + HCHO \xrightarrow{O_2} HNO_3 + HO_2 + CO$	5.8×10^{-16}	0.86	10
(7) $NO_3 + RCHO \xrightarrow{O_2} HNO_3 + RCO_3$	2.4×10^{-15}	3.6 (R = CH_3)	10
(8) $NO_3 + ALK \xrightarrow{O_2} HNO_3 + RO_2$	3.6×10^{-17}	0.05 (R = C_4H_9)	24
(9) $NO_3 + OLE \xrightarrow{O_2} RPN$	7.6×10^{-15}	12.4	23
(10) $N_2O_5 + H_2O \rightarrow 2HNO_3$	$\leq 1.3 \times 10^{-21}$ [b]	$\leq 1.9 \times 10^{-6}$	11, 22
(11) $RCO_3 + NO_2 \rightarrow RCO_3NO_2$ (PAN)	4.7×10^{-12}	6.9×10^3 (R = CH_3)	22
(12) PAN $\rightarrow RCO_3 + NO_2$	$1.9 \times 10^{16} e^{-13543/T}$	0.022	22
(13) $NO_3 + (CH_3)_2S \rightarrow$ products	9.7×10^{-13}	1.4×10^3	8
(14) NO_3 + monoterpene $\rightarrow$ products	3.0×10^{-12}	4.4×10^3	8
(15) $NO_3 + M \rightarrow NO + O_2$[c]		$k_{15}[M] \simeq 0.13$ min^{-1}	16

[a] The reactions above are the major nighttime reactions of the N_xO_y species. Forty-four other reactions in McRae et al. (25) are included in the mechanism for completeness. [b] The rate constant given for this reaction is an upper bound. The text discusses the ramifications of decreasing this value. For a comprehensive evaluation of this reaction, see Atkinson et al. (11) and Russell et al. (9). [c] The NO_3 decomposition reaction was not included except as noted in the text.

And they indicated that this reaction could be of possible importance in clean environments.

At sufficiently high NO levels, like those found in urban areas, the RCO_3 may react with NO to generate NO_2. However, in the presence of greatly reduced nighttime NO concentrations, most of the RCO_3 produced instead will react with NO_2 to form PAN. For the same reason, the PAN produced by photochemical reactions the previous day will not decay substantially by the reverse reaction 12. Note, however, that for each PAN molecule formed by reaction 11 one HNO_3 molecule is formed from the preceding reaction 7 and two net NO_2 molecules are consumed, forming products PAN and HNO_3. Likewise, reaction 10 converts two reactive oxidized nitrogen species to two molecules of a stable product (HNO_3). However, the reaction between NO_3 and HCHO consumes only a single odd nitrogen molecule before reaching the final products (presumably the HO_2 produced will oxidize the NO or react to form H_2O_2).

While the rate equations for the system of nighttime reactions involving NO_x (Table I) plus those other reactions involving organic and inorganic species that might be important (see footnote to Table I) can be integrated numerically in order to compute atmospheric NO_3 and N_2O_5 levels, it is useful to investigate the formation of those species with steady-state analysis of the major nighttime reactions alone. On the basis of the first 12 reactions in Table I, the rate of change of the NO_3 concentration is given by

$$\frac{d[NO_3]}{dt} = k_1[NO_2][O_3] - k_5[NO_3][NO] - (k_2 + k_4)[NO_3][NO_2] + k_3[N_2O_5] - k_{org}[ORG][NO_3] \quad (1)$$

where $k_{org}[ORG] = k_6[HCHO] + k_7[RCHO] + k_8[ALK] + k_9[OLE]$. The characteristic reaction times for NO_3 and N_2O_5 are both sufficiently short that their concentrations can be assumed to be in a pseudo steady state:

$$[NO_3] = k_1[NO_2][O_3](k_3 + k_{10}[H_2O])/[(k_5[NO] + k_{org}[ORG] + k_4[NO_2])(k_3 + k_{10}[H_2O]) + k_2k_{10}[NO_2][H_2O]] \quad (2)$$

$$[N_2O_5] = \frac{k_2[NO_2][NO_3]}{k_3 + k_{10}[H_2O]} \quad (3)$$

Since it generally will be the case that $k_3 \gg k_{10}[H_2O]$, the NO_2–NO_3–N_2O_5 cycle of reactions 2 and 3 can be assumed to be near equilibrium at any instant of time:

$$[N_2O_5] = \frac{k_2[NO_2][NO_3]}{k_3} \quad (4)$$

And, as a result

$$[NO_3] = \frac{k_1k_3[NO_2][O_3]}{k_3(k_5[NO] + k_{org}[ORG] + k_4[NO_2]) + k_2k_{10}[NO_2][H_2O]} \quad (5)$$

The denominator comprises the four NO_3 sinks: NO_3 scavenging by NO, NO_3 reaction with organics, NO_3 reaction with NO_2 to form NO, and nitric acid formation by the N_2O_5–H_2O reaction. Equation 5 can be evaluated to give NO_3 concentration estimates with only the necessary rate constants plus the concentrations of basic precursors often available from ambient measurements.

Nitric acid is produced by N_2O_5 hydrolysis (reaction 10) and by the organic–NO_3 reactions 6–8. The rate of nitric acid production is

$$\frac{d[HNO_3]}{dt} = 2k_{10}[N_2O_5][H_2O] + (k_6[HCHO] + k_7[RCHO] + k_8[ALK])[NO_3] \quad (6)$$

The pseudo-steady-state expressions for NO_3 and N_2O_5 can be used in this equation to obtain the rate of HNO_3 production in terms of the concentrations of routinely measured pollutants. As will be seen in the next section, this steady-state analysis can be used to estimate the product distribution that arises from the numerical integration of the complete nighttime chemical mechanism.

Nighttime Chemistry in an Offshore Oceanic Environment

The first situation considered is an offshore oceanic environment, the Santa Barbara Channel off the south central coast of California. This region is of interest from the standpoint of atmospheric chemistry because of projected increases in emissions associated with offshore petroleum production (13). Although NO_3 data are not available in this area, other ambient concentration measurements have been carried out over the past 2 years (14). These measurements can serve to specify initial conditions for a simulation of the nighttime chemistry in the region

Table II. Initial Conditions for Simulation of Nighttime Chemistry in an Offshore Oceanic Environment[a]

species	less polluted, ppb	base case, ppb	more polluted, ppb
O_3	40	70	100
NO	0.1	1	1
NO_2	1.0	10	10
HCHO	0.5[b]	7[b]	7[b]
RCHO	0.5[b]	6[b]	6[b]
ALK	10 (40 ppbc)[c]	15[c]	37
ARO	2 (14 ppbc)[c]	3[c]	7
PAN	3	3	3

[a] Concentration ranges from South Central Coast Cooperative Aerometric Monitoring Program, the Santa Barbara Oxidant Study, and the 1983 Ozone Transport Study (*13, 14*). [b] Personal communication with Alan Lloyd. [c] Personal communication with Rei Rasmussen.

as predicted by the reactions in Table I. Of particular interest are the dynamics of NO_3 and the paths of conversion of NO_x into nitrate species. The photochemical trajectory model of Russell et al. (*9*) will be used to track the evolution of the NO_x species in an air column from sunset until 12 h thereafter.

Table II presents the range of initial concentrations that we will employ for simulating a nighttime air parcel in the Santa Barbara Channel. In the more polluted case, the air mass is expected to have originated from source-enriched areas such as the Los Angeles basin, while in the less polluted case the air is of "background" oceanic origin. The base case is in between. Four simulations were carried out, in the fourth of which the base case concentrations have been used and the rate constant for reaction 10 is decreased by a factor of 10. We include this case because of the uncertainty in the magnitude of k_{10}.

Each simulation begins at sunset and proceeds 12 h, with no fresh emissions. In the vertical diffusion calculation, surface roughness was taken as 10^{-4} m, corresponding to water. As will be seen, due to the presumably stable stratification at night and low surface roughness, turbulent transport of species to the surface is limited, and hence, removal by deposition at the ocean surface is relatively minor.

Results of the four simulations are given in Table III. Shown are the hourly NO_2 depletion rate, τ^{-1}, the HNO_3 formation rate (as % h^{-1} relative to the NO_2 present), net PAN formation rate (as % h^{-1} relative to the NO_2 present), maximum NO_3 and N_2O_5 concentrations, HNO_3 formation as percent of initial NO_x, total deposited HNO_3, and the maximum PAN produced.

Nitric acid formation rates, expressed relative to the NO_2 concentration, vary between 16% and 36% h^{-1}. Formation of PAN is responsible for the bulk of the remaining NO_2 consumed. Again, on the basis of the chemistry involved, the HNO_3 formation rate must be at least as great as that for PAN. The absolute increase in PAN concentration due to nighttime reactions varies between about 1 and 3 ppb, or between 2% and 23% of the initial NO_2. As can be seen from the last column in Table III, reducing the value used for k_{10} has little effect on the NO_2 loss rate, but it does affect the split between the predicted HNO_3 and PAN formation. Significant quantities of HNO_3 still are formed. Note that in the absence of fresh emissions initially NO_2 is transformed to HNO_3 very rapidly, faster, in fact, than would be predicted during the day by reaction with OH. Likewise, PAN formation is rapid. The rate of NO_3 (and, hence, PAN and HNO_3) formation is limited by the O_3 and NO_2 concentrations and the extent of formation by the initial NO_2 concentration. In all cases studied, there is an

Table III. Results of Simulations of Nighttime Chemistry in an Offshore Oceanic Environment

	case[a] 1	2	3	4
NO_2 depletion rate (τ^{-1}), % h^{-1} [b]	17	27	37	25
HNO_3 formation rate, % h^{-1} of NO_2[b]	16	26	36	17
PAN formation rate, % h^{-1} of NO_2[b]	1	1	1	5
max NO_3, ppt	25	45	70	260
max N_2O_5, ppt	30	540	700	1700
max PAN increase, ppb (% of $[NO_x]_0$)	0.02 (2)	0.6 (5)	0.6 (5)	2.6 (23)
HNO_3 produced, % of $[NO_x]_0$[c]	84	92	92	71
HNO_3 produced, % of $[NO_x]_0$,[c] by				
NO_2 + OH	~0	~0	~0	~0
N_2O_5 + H_2O	80	86	84	43
NO_3 + HCHO	0.5	1	1	5
NO_3 + RCHO	3	5	6	23
HNO_3 deposited, % of $[NO_x]_0$[c]	1.4	1.7	1.9	1.1

[a] These four cases correspond to the initial conditions in Table II as follows: (1) less polluted; (2) base case; (3) more polluted; (4) base case, k_{10} reduced by a factor of 10. [b] Average over first 6 h. After 6 h, very little NO_2 remains. [c] Percent at the end of a 12-h simulation.

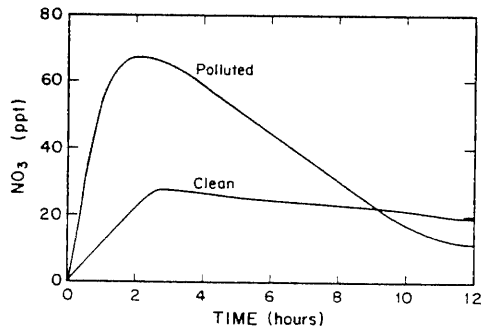

Figure 1. Time evolution profiles of NO_3 for a relatively clean and a more polluted oceanic environment.

abundance of aldehydes to form PAN.

For the more polluted marine situation, about 49% of the NO_2 is oxidized to form NO_3; 5% reacts with the RCO_3 radical to form PAN, and 43% reacts with NO_3 to form N_2O_5 (and then HNO_3). Less than 2% of the initial NO_2 deposits out in any form.

Figure 1 shows a comparison of the predicted NO_3 concentration for the more and the less polluted cases. Note that the peak in the NO_3 concentration for the polluted case is much sharper, rising much higher and then dropping below the less polluted profile. Because of the lower ozone concentrations in the less polluted case, the NO_x is not converted to HNO_3 and PAN as quickly, allowing noticeable NO_3 concentrations to be sustained. The more polluted case more closely reproduces the spiked profile found just after sunset in urban environments (*9*).

Mechanistic explanation of the rate of NO_2 conversion and the product split between HNO_3 and PAN can be obtained by inserting the pollutant concentration data of Table II into the equations derived on the basis of the previous steady-state analysis. From the base-case concentrations in Table II, it is seen that the HCHO and ALK reactions together are about 3 times less important than

the RCHO–NO_3 reaction as a sink for NO_3. The only sinks from the NO_2–NO_3–N_2O_5 cycle back to NO and NO_2 are reactions 4 and 5, with reaction 4 being the only route to produce NO in the absence of fresh emissions. Note that at both the polluted and the unpolluted concentration levels reaction 4 is dominated by reaction 7. Thus, once an NO_3 molecule has been formed, it is highly probable that that molecule will end up as HNO_3 and that an associated NO_2 molecule will react to form either HNO_3 or PAN, in accordance with the results of the full-model simulation. Thus, the rate of NO_2 depletion at night should be about twice the rate of NO_3 formation by reaction 1:

$$\frac{d[NO_2]}{dt} \simeq -2k_1[NO_2][O_3] \quad (7)$$

which can be expressed as

$$\frac{d[NO_2]}{dt} = -\tau^{-1}[NO_2] \quad (8)$$

where $\tau = (2k_1[O_3])^{-1}$ is the characteristic decay time for NO_2 by reaction 1, followed by reaction 10 or 11.

Next, the formation rates of PAN and HNO_3 can be considered. An expression for the rate of nitric acid formation was given in eq 6. Using the pseudo-steady-state expressions for $[NO_3]$ and $[N_2O_5]$ gives

$$\frac{d[HNO_3]}{dt} = [2k_2k_{10}[H_2O][NO_2]/k_3 + k_6[HCHO] + k_7[RCHO] + k_8[ALK]][k_3k_1[O_3][NO_2]/(k_3(k_5[NO] + k_{org}[ORG] + k_4[NO_2]) + k_2k_{10}[NO_2][H_2O])] \quad (9)$$

Since NO_2 is converted almost quantitatively to HNO_3 and PAN, both nitric acid and PAN formation rates can be expressed with the NO_2 decay rate as

$$\frac{d[HNO_3]}{dt} = \frac{1}{2}\tau^{-1}[NO_2](2 - f) \quad (10)$$

Similarly for PAN

$$\frac{d[PAN]}{dt} = \frac{1}{2}\tau^{-1}[NO_2]f \quad (11)$$

where f is the fraction of NO_3 formed by reaction 1 that reacts with RCHO. Comparing (9) and (10), it is seen that f will be a function of the pollutant concentrations. Once f has been computed by equating (9) and (10), the formation rate of PAN is apparent from (11). Given the conditions for the base case in Table II, the rates of nitric acid and PAN formation are approximately 4 and 0.2 ppb h^{-1}, respectively. The dominant route for nitric acid production is reaction 10.

Analysis of the reaction rate equations for the mechanism in Table I shows that the depletion rate of NO_2 should be approximately equal to twice the rate of reaction 1. Comparison of the decay rate obtained by the full computer simulation to that based on twice the initial rate of reaction 1, which should represent an upper limit to the NO_2 loss rate, gives close agreement in all simulations. The small deviations between the approximate calculation and the full model are due to reactions of NO_3 with HCHO and with NO_2 to form NO and NO_2 and to the continued decrease of the O_3 level.

Simulation of Nighttime Atmospheric Chemistry in a Desert Environment

We now turn our attention to a desert environment, typically very dry (relative humidities of about 20%) with low pollutant loadings. In this case, one could expect that the important chemical reactions dominating the nighttime chemistry of N_xO_y might differ from those over the ocean, particularly because of the lower water vapor concentrations. In this section, the trajectory model is used to investigate the fate of nitrogen oxides in the desert at night.

Table IV. Initial Conditions for Desert Simulations

	Edwards AFB[a]	Death Valley[b]
O_3, ppb	35	35
NO_2, ppb	0.95	0.15–0.075
NO, ppb	0.1	0.01
NO_3, ppb	0	0
RCHO, ppb	0.5	0.5
monoterpene, ppb	0.005[c]	0.005[c]
CO, ppm	0.1	0.1
RH, %	29	31
temp, °C	31	29

[a] Data for 23 May 1982 at Edwards Air Force Base. [b] Data for 3 May 1982 at Death Valley. [c] From Winer et al. (*8*).

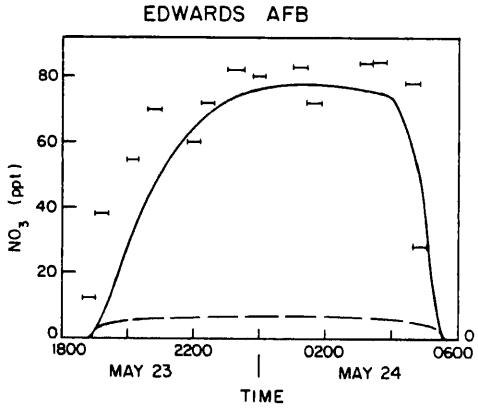

Figure 2. Predicted (solid line) and measured (data bars) NO_3 concentrations (*3*) at Edwards Air Force Base, CA, 23–24 May 1982. The dashed line near the bottom is the predicted concentration if the unimolecular decomposition of NO_3 is included in the simulation.

The chemical mechanism used is identical with that described for the ocean cases, except that the reaction of NO_3 with monoterpenes (MNT, see Table I) is included. A very small NO emission rate was included in the calculations, corresponding to arid, bare soil conditions (*15*). The initial conditions used for the simulations are from measurements taken by Platt et al. (*3*) in the Mojave Desert of California and are shown in Table IV. In this case, the predictions are compared against NO_3 measurements at Edwards Air Force Base and at Death Valley, CA (*3*). Results of this evaluation are shown in Figures 2, 3, and 4 for the Edwards and Death Valley locations. As seen, model predictions at Edwards closely track observations for both NO_3 (Figure 2) and NO_2 (Figure 3).

At Death Valley, the measured NO_2 concentrations were below the detection limit (0.3 ppb) of Platt et al. (*3*). For the simulations, the initial concentration of NO_2 was set equal to one-half and one-fourth of that value. At this site, two calculations were performed with the 0.15 ppb initial condition: with and without emissions of NO. As seen (Figure 4), the predicted NO_3 concentrations over time with and without NO emissions are different, though the peak NO_3 concentrations are about equal (~35 ppt). Emissions of NO slightly retard the rise in NO_3 concentrations due to scavenging by NO. The peak measured concentration of 19 ppt is about 40% less than that predicted and is attributable, in part, to the uncertainty in the initial NO_2 concentration. NO_3 scales approximately with the NO_2 concentration, so a lower initial NO_2 concentration would provide closer agreement and still be

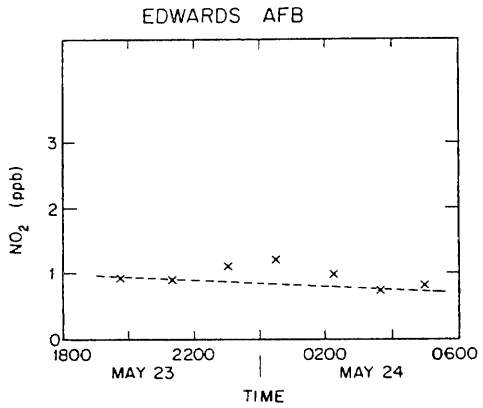

Figure 3. Predicted (dashed line) and measured (data points) NO_2 concentrations (*3*) at Edwards Air Force Base, CA, 23–24 May 1982.

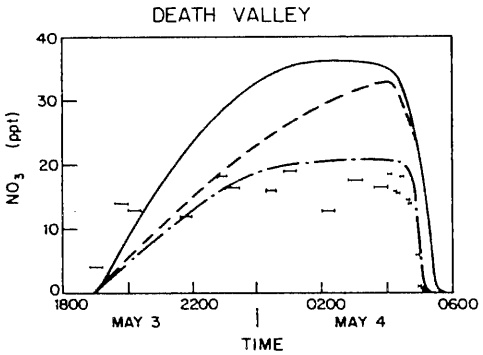

Figure 4. Predicted and measured (data bars) NO_3 concentrations (*3*) at Death Valley, CA, 3–4 May 1982. The solid line shows the predicted concentration given an initial NO_2 concentration of 0.15 ppb if no emissions of NO are included in the calculations, and the dashed line includes a very small emission rate (*15*). The alternating dashed line shows the predicted concentration of NO_3 given an NO_2 initial concentration of 0.075 ppb (one-fourth the detection limit of NO_2).

consistent with measurements. Using $[NO_2]_0 = 0.075$ ppb proves this to be the case.

Integrating the reaction fluxes indicates that the homogeneous hydrolysis of N_2O_5 is the dominant reaction producing nitric acid, even in a dry environment. In the Edwards case, approximately 77% of the nitric acid is produced by reaction 10, constituting 22% of the oxidized nitrogen originally in the air column plus that emitted during the night. Seven percent of the oxidized nitrogen is converted to PAN by the following morning. Due to the atmospheric stability and low nitric acid concentrations, less than 1% of the total NO_x deposits out during the night. The peak N_2O_5 concentration is predicted to be about 25 ppt.

Unimolecular Decomposition of NO_3

Recently Johnston et al. (*16*) reported that a number of experiments (*17–20*) contain evidence for the unimolecular decomposition of the NO_3 radical. Though the experiments varied widely in nature and reaction volume, reinterpretation of the results from the three room temperature experiments led to approximately the same first-order rate constant of about $(3 \pm 2) \times 10^{-3}$ s^{-1}. Using results from the high-temperature experiment, they derived the temperature-dependent expression of

$$k_{15}[M] = 2.5 \times 10^6 \exp(-6.1 \times 10^3/T) \text{ s}^{-1}$$

at 1 atm and T in K, (reaction 15, Table I). They cited further evidence for this reaction rate from field experiments in which NO_3 and NO_2 were measured in relatively clean atmospheres at an altitude of 3 km (*4, 5*). These measurements indicated the loss rate of NO_3 by scavenging is about 1×10^{-3} s^{-1}, that the scavenger is not depleted, and that the products of the NO_3 scavenging are neither NO nor NO_2. Reaction 15 satisfies the first two conditions, and Johnston et al. (*16*) give reasoning that the final criterion can be explained by other phenomena.

In this section, the unimolecular decomposition of NO_3 is discussed in light of the recent review (*16*) and the field measurements of Platt et al. (*2, 3*). In very clean atmospheres, such as the desert cases considered in this study, the proposed NO_3 unimolecular decomposition would be the major loss reaction from the NO_3–N_2O_5 system. An upper bound on the NO_3 concentration then can be found by steady-state analysis, as done previously, and by assuming that reaction 15 is the only loss mechanism. Inclusion of any other reactions of NO_3 or N_2O_5 would only lower the calculated NO_3 concentration. In this case

$$[NO_3]_{MAX} = \frac{k_1[NO_2][O_3]}{k_{15}[M]} \qquad (12)$$

By rearranging this equation, the measured concentrations can be used to estimate an upper bound for $k_{15}[M]$. For the two desert cases previously discussed, use of the proposed rate constant for NO_3 decomposition and the observed NO_2 and O_3 concentrations gives $[NO_3]_{MAX}$ of about 9 and <1.5 ppt for Edwards and for Death Valley, respectively. This is in substantial disagreement with the measured NO_3 concentrations of 81 and 19 ppt. In fact, using the data for other sites and times (*2, 3*) in the same calculation gives the same results: the measured NO_3 concentration is much greater than the maximum calculated with steady-state analysis and the proposed decomposition rate (*16*), except at higher relative humidities. [This indicates that the loss of NO_3 (or N_2O_5) is due to hydrolysis, either homogeneous or on deliquesced aerosols.] Likewise, many of the data from the field studies in Germany (*2*) are at variance with $k_{15}[M] \approx 3 \times 10^{-3}$ s^{-1}. The magnitude of the effect of including this reaction in the mechanism is seen in Figure 2. As shown, the peak predicted concentration drops substantially, from 78 to 7 ppt. Inclusion of the decomposition reaction in the simulations of the offshore environment would decrease the formation of HNO_3 and PAN. This reaction would have little effect on simulations of urban environments because of the much heavier loadings of hydrocarbon pollutants, plus the effect of continued fresh emissions.

It is difficult to explain the reason for the discrepancy between the experiments of Platt et al. (*2, 3*) and the study of Johnston et al. (*16*), though a number of hypotheses can be proposed: (1) the proposed rate of NO_3 decomposition is too high, (2) the rate of formation of NO_3 (or N_2O_5) is much greater than is implied by our general knowledge of N_xO_y chemistry, or (3) there is a systematic bias in the measurements. The actual rate of reaction 15 could lie between that implied by the field measurements (*2, 3*) and those derived from laboratory measurements (*16*). A small uncertainty in the comparison is introduced by the possibility that the air parcels were not uniform over the path of the measurement beam. However, the consistency of the O_3 measurements would indicate that the error introduced from the nonuniformities would be small compared to the apparent discrepancy. Inhomogeneities induced by nocturnal emissions would tend to increase the apparent discrepancy, whereas air parcels enriched in both NO_2 and O_3 would tend to decrease the discrepancy.

Conclusions

A series of calculations were performed to elucidate the important chemical reactions of N_xO_y species at night in two quite different environments and under different pollutant loadings. Calculations performed for conditions found over the ocean near the California coast showed a rapid conversion of NO_x to nitric acid and PAN, predominantly by hydrolysis of N_2O_5 and by production of peroxyacetyl radicals from the NO_3–aldehyde reaction. The same reactions dominated the desert calculations, even though the ambient conditions and pollutant levels were quite different. However, the time evolutions of pollutant species in the two cases were quite different, and a much lower conversion rate of NO_x to HNO_3 and PAN was found for the desert case. In the desert case, predicted NO_3 concentrations compare well with experimental measurements.

The predicted NO_3 concentration–time profile for the polluted, ocean environment case shows a sharp peak just after sunset, much like that found in earlier calculations for urban environments, though for different reasons. In the urban environment, the sharp peak is due to ozone loss by scavenging by NO emissions and deposition, whereas over the ocean the NO emissions are small and the sharp drop in NO_3 concentration is due to NO_2 depletion. In the desert solution, low ambient ozone levels and small NO emissions lead to a very small change in NO_x concentration and a smooth, sustained NO_3 profile that plateaus instead of peaks. Calculations for marine, urban, and desert environments indicate that nighttime reactions of N_xO_y can be important in forming nitric acid and PAN in all three situations.

Steady-state analysis and simulation indicate that there is a discrepancy between field measurements and a recently proposed rate for the unimolecular decomposition of NO_3. Given our current knowledge of atmospheric chemistry, the proposed value for the rate of decomposition of NO_3 is too high, some other aspect of the NO_3–N_2O_5 system is not well understood, or a systematic bias in the measurements exists.

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Registry No. PAN, 2278-22-0; NO_x, 11104-93-1; HNO_3, 7697-37-2; N_2O_5, 10102-03-1; NO_3, 12033-49-7; O_3, 10028-15-6.

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greater than or equal to zero. In constructing (11) it was assumed that the chloride ion present is found as sodium chloride. The HCl produced by reaction (9) might, in some cases, react with NH_3 to form NH_4Cl, and thus alternative forms of (11) could be hypothesized.

The choice between the two types of external mixtures just described has no effect on the calculated equilibrium dissociation constant of ammonium nitrate, as K is solely a function of T and r.h., but it does affect the calculated gas and aerosol phase pollutant concentrations. If pure ammonium nitrate is present and is at equilibrium with the gas phase, then the equilibrium dissociation constant should be equal to the observed partial pressure product of NH_3 times HNO_3 to within experimental and calculation uncertainties. If the FREE NITRATE concentration is zero, then ammonium nitrate may not be present, and the calculated dissociation constant has no bearing on the partial pressure of ammonia and nitric acid gas, except that it should act as an upper bound on the measured concentration product, CP.

Given the external mixture hypotheses, the theoretically predicted partition of measured total nitrate and total ammonia between the aerosol and gas phases was computed at each monitoring site shown in Fig. 1 over each sampling interval during the period 30–31 August 1982. Results at three locations in the basin will be discussed in detail: a near coastal site, Long Beach, a mid-basin site, Anaheim, and a far inland site, Rubidoux. Data on aerosol speciation at these sites are presented elsewhere (Russell and Cass, 1984). The Long Beach sampling station, which is located about 6 km from the Pacific Ocean, experienced lower temperatures (down to 18°C) and higher relative humidities (1-h average above 90%) than the inland sites. This led to a minimum 2-h average calculated NH_4NO_3 dissociation constant of less than 0.75 $(ppbv)^2$. Rubidoux, located about 60 km inland, was typically hotter and dryer, with peak temperatures above 38°C, and a correspondingly high calculated dissociation constant that exceeded 650 $(ppbv)^2$ over one 2-h sampling interval. Comparison between theory and experiment thus will be discussed for dissociation constants varying over about three orders of magnitude.

The calculated NH_4NO_3 dissociation constant, K, and the product of the measured $HNO_3(g)$ and $NH_3(g)$ concentrations at Anaheim are shown in Fig. 3. One standard error about each calculated value of K is given by the vertical bars, while the standard error of the measured concentration product is indicated by the dashed horizontal lines. Agreement between the theoretical calculations and measurements generally is good, especially for the second day when shorter sampling intervals were used. Recall that the calculated dissociation constant should serve as an upper bound on the concentration product, CP.

In the first of the two external mixture cases considered, all of the aerosol nitrate is assumed to be present as ammonium nitrate. Given the time history of the computed dissociation constant, the measured

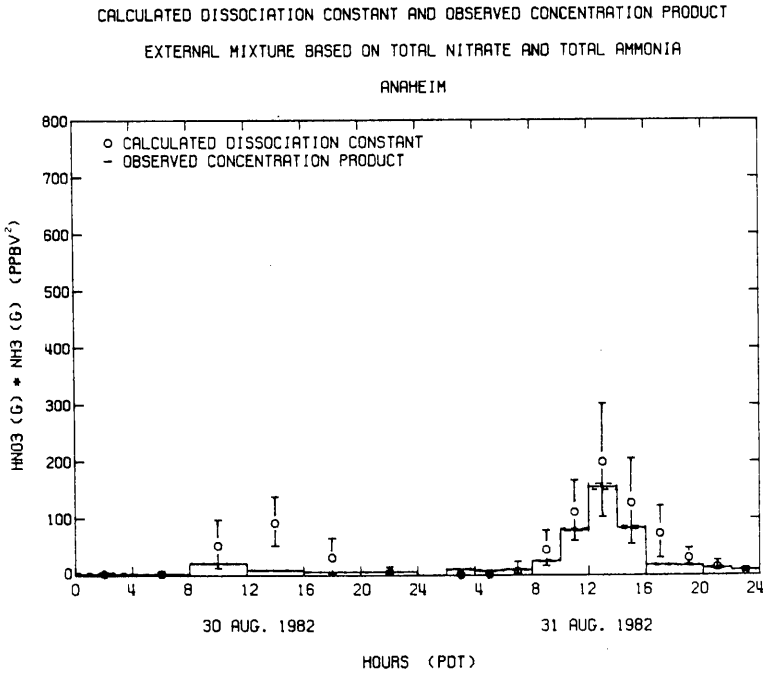

Fig. 3. Observed $[HNO_3][NH_3]$ concentration product and calculated dissociation constant of pure NH_4NO_3 at Anaheim, CA. No data between 0000 and 0200 on 31 August.

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