

**POSITIVE MATRIX FACTORIZATION (PMF)
AND UNMIX APPLICATIONS FOR PM2.5
SOURCE APPORTIONMENT**

U.S. ENVIRONMENTAL PROTECTION
AGENCY'S OFFICE OF RESEARCH AND
DEVELOPMENT (ORD) AND OFFICE OF
AIR QUALITY PLANNING AND
STANDARDS (OAQPS)

**PHOENIX SOURCE
APPORTIONMENT STUDIES**

FEBRUARY 15, 2000 @ 8:00 A.M.

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OUTLINE

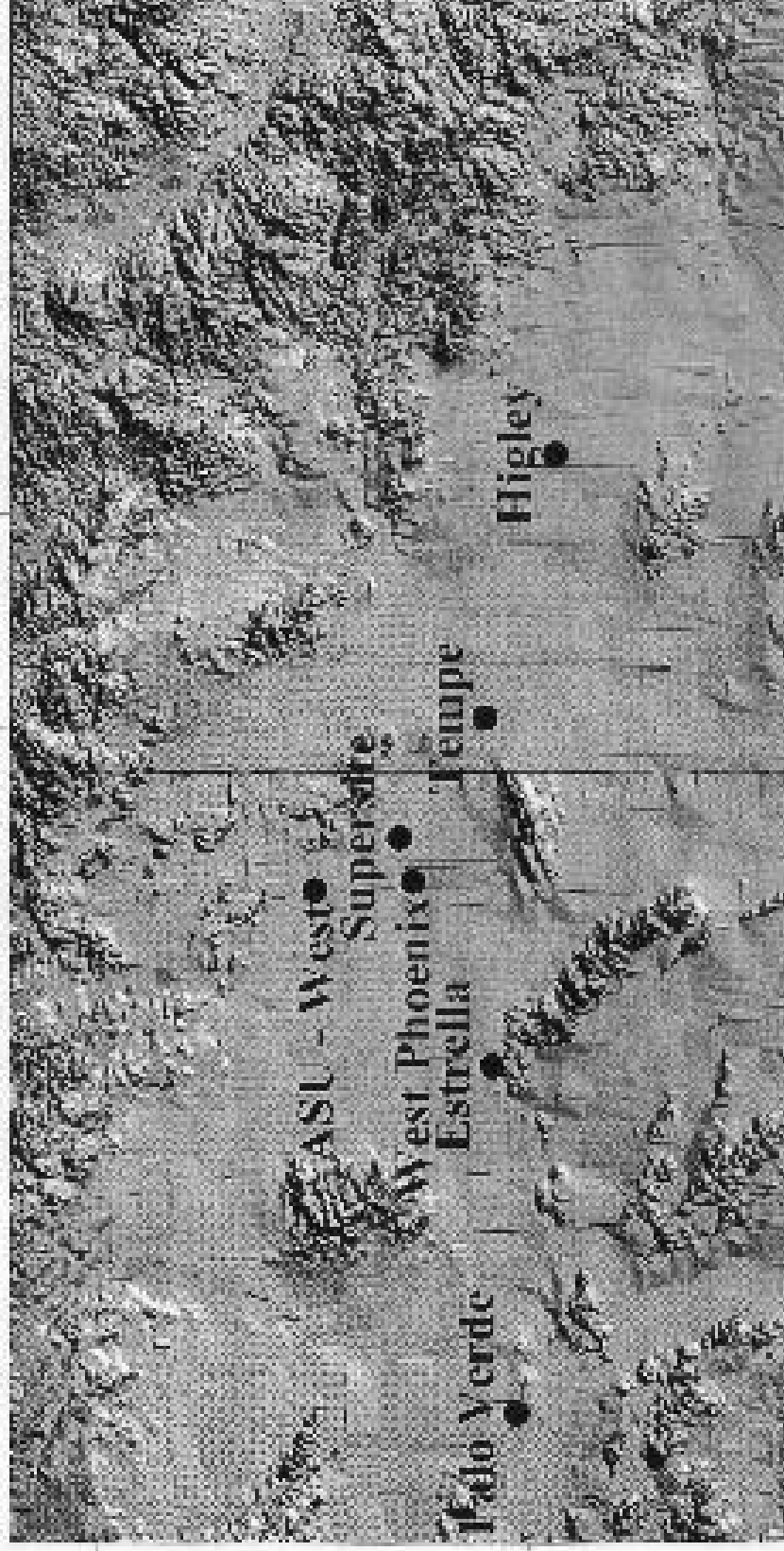
- I. INTRODUCTION
- II. 1989-90 URBAN HAZE STUDY
- III. 1994-95 MARICOPA ASSOCIATION
OF GOVERNMENTS/DRI BROWN
CLOUD ANALYSIS
- IV. 1994-96 ADEQ/ENSR ANALYSIS
- V. COMPARISON OF THE THREE
STUDIES
- VI. CONCLUSIONS

I. INTRODUCTION

PHOENIX, ARIZONA & ENVIRONS

- < POPULATION --- 2,800,000
- < ELEVATION -- 1100 FEET
- < GEOPHYSICAL PROVINCE --
SOUTHWEST DESERT (SONORAN)
- < ANNUAL RAINFALL --- 7 INCHES
- < SALT RIVER VALLEY -- GILA RIVER,
VERDE RIVER, AGUA FRIA RIVER
- < ECONOMY -- LIGHT
MANUFACTURING, TOURISM,
GOVERNMENT (STATE CAPITOL),
AGRICULTURE, SERVICE INDUSTRIES
(AIRLINES, CREDIT CARDS,
FINANCIAL, ETC.), EDUCATION
(ARIZONA STATE UNIVERSITY)

Greater Phoenix Area



EMISSIONS

VEHICULAR

1,900,000 REGISTERED VEHICLES

64,000,000 MILES DRIVEN PER DAY

34 MILES PER DAY DRIVEN BY THE
AVERAGE VEHICLE

[BUS SERVICE ONLY; NO OTHER MASS
TRANSIT]

FUELS CONSUMED

GASOLINE -- 4,800,000 GALLONS/DAY

DIESEL ----- 1,400,000 GALLONS/DAY

EMISSIONS FROM ALL SOURCES IN
METRIC TONS PER DAY

POLLUTANT	TONS
VOLATILE ORGANICS	238 ^A
NITROGEN OXIDES	283 ^A
CARBON MONOXIDE	652 ^B
FINE PARTICULATES	
NITRATE	3 ^A
SULFATE	21 ^A
CARBON	90 ^A
TOTAL FINE MASS	113 ^A

A. WINTER, 2004

B. WINTER, 2001

CARBON AND GEOLOGICAL FINE PARTICULATE EMISSIONS

**STANDARD INVENTORY BASED ON
TRADITIONAL EMISSION FACTORS**

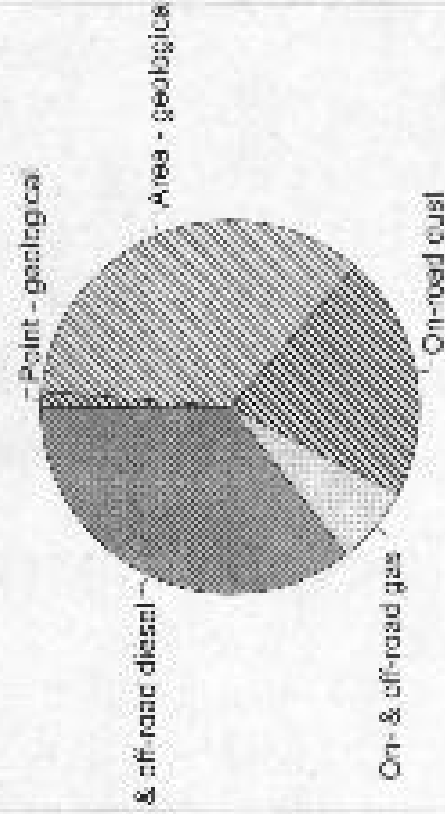
**RECEPTOR INVENTORY -- BY ADJUSTING
THE STANDARD INVENTORY TO BE
CONSISTENT WITH RECEPTOR
MODELING**

**CONSIDER ALL PRIMARY FINE PM TO
CONSIST OF ONLY GEOLOGICAL AND
COMBUSTION SOURCES**

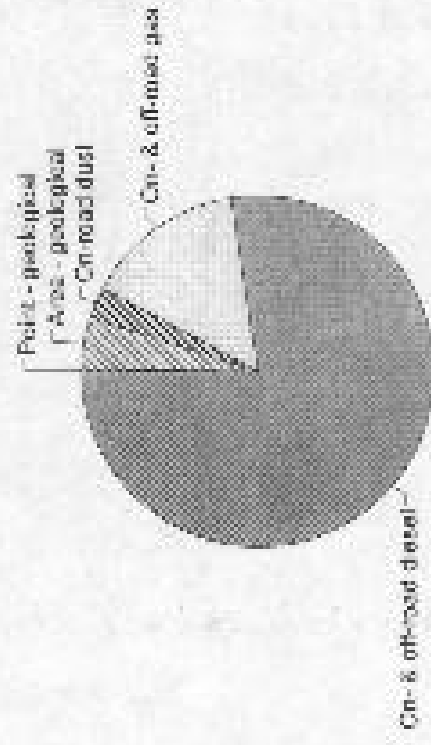
**COMBUSTION CONTRIBUTION TO
PRIMARY FINE PM IS 3.5 TO 4.0 TIMES AS
HIGH IN THE “RECEPTOR” INVENTORY AS IN
THE STANDARD INVENTORY**

**THE RECEPTOR INVENTORY IS MORE
BELIEVABLE**

Phx PM2.5 emissions inventory carbon & geological:standard inventory



Phx PM2.5 emissions inventory carbon & geological:receptor inventory



II. PHOENIX URBAN HAZE STUDY 1989-1990

< PRINCIPAL INVESTIGATORS

**JOHN G. WATSON & JUDITH C. CHOW
DESERT RESEARCH INSTITUTE**

< FALL/WINTER INTENSIVE

DAILY FROM 9/25/89 TO 1/22/90

< FOUR SITES -- ALL URBAN

**VALLEY BANK -- 175 METERS ABOVE
GROUND LEVEL (AGL)**

ICA -- 40 METERS AGL

WEST PHOENIX -- 3.5 METERS AGL

SOUTH SCOTTSDALE -- 5.0 M AGL

< SAMPLING TIMES

MORNING: 0600 - 1200

AFTERNOON: 1300 - 1900

< SAMPLE SIZE: 44 A.M. & 44 P.M.
SAMPLES AT EACH SITE

< MEASUREMENTS

FINE PM MASS -- DRI-MODIFIED
SEQUENTIAL FILTER SAMPLER

ELEMENTS -- X-RAY FLUORESCENCE
SPECTROSCOPY OF TEFLON FILTERS

IONS -- NITRATE & SULFATE BY
ION CHROMATOGRAPHY;

NITRATE FROM BOTH
TEFLON AND BACKUP
NYLON FILTER

CARBON BY
THERMAL/OPTICAL
ABSORBANCE OF QUARTZ
FILTERS

< SOURCE APPORTIONMENT METHOD

CHEMICAL MASS BALANCE MODEL
(VERSION 7)

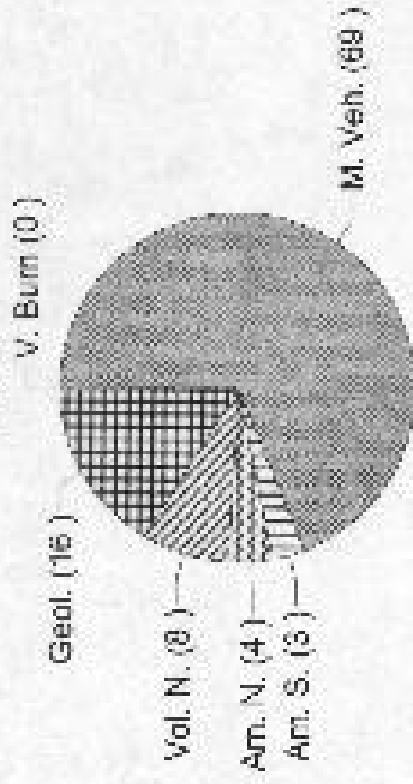
< BOTH FINE MASS AND LIGHT
EXTINCTION WERE APPORTIONED TO
SOURCE CATEGORIES

< LOCAL MOTOR VEHICLE AND
GEOLOGICAL SOURCE PROFILES
WERE DETERMINED

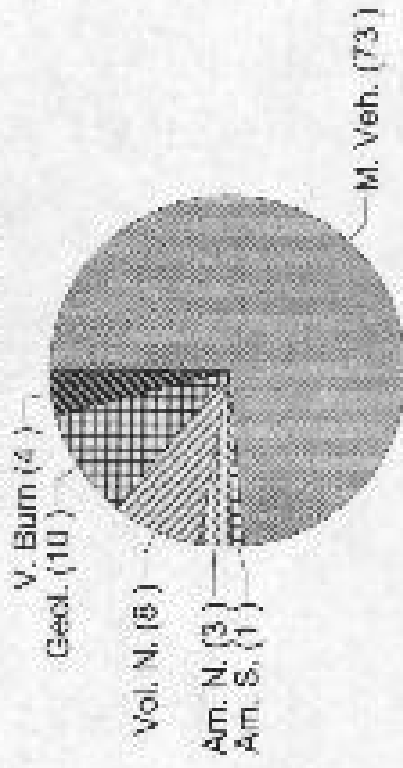
PM2.5: Phoenix Urban Haze Study 89/90

0600 - 1200

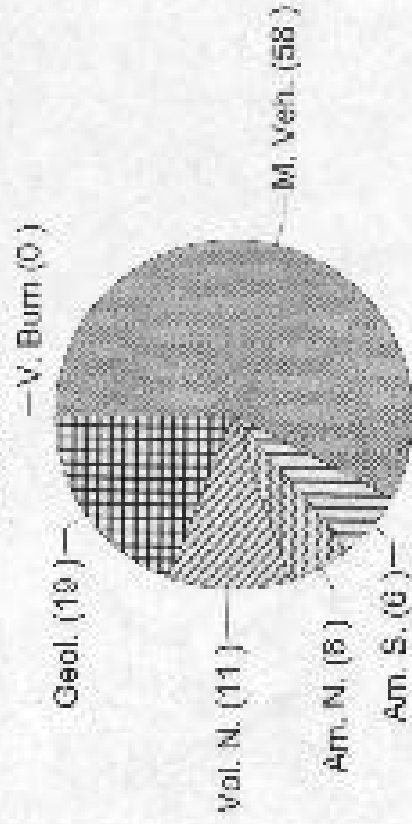
ICA



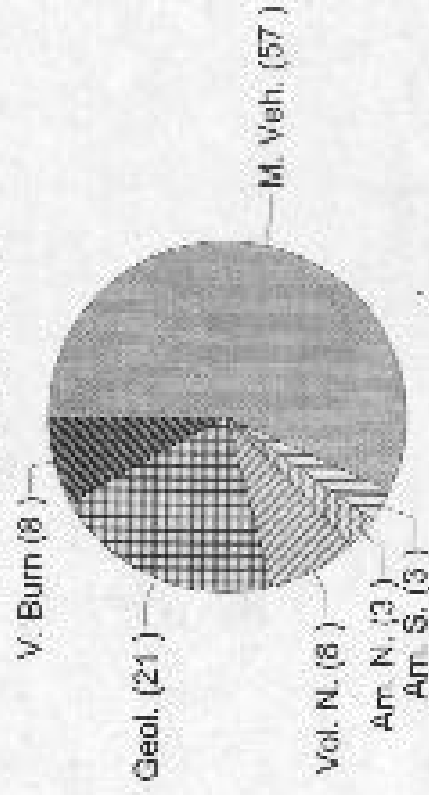
West Phoenix



Bank One



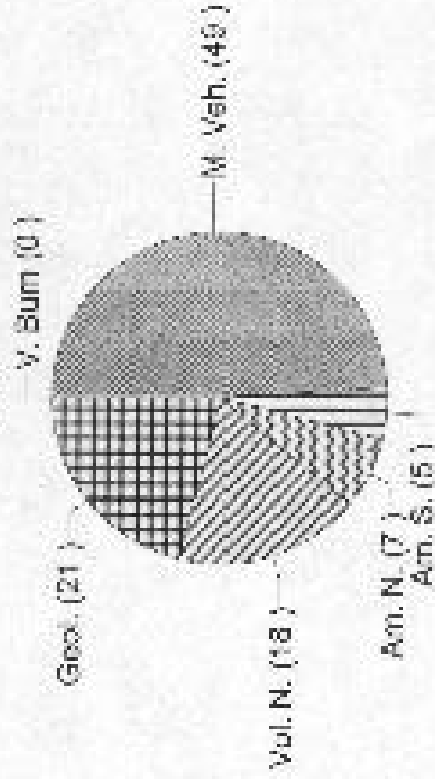
South Scottsdale



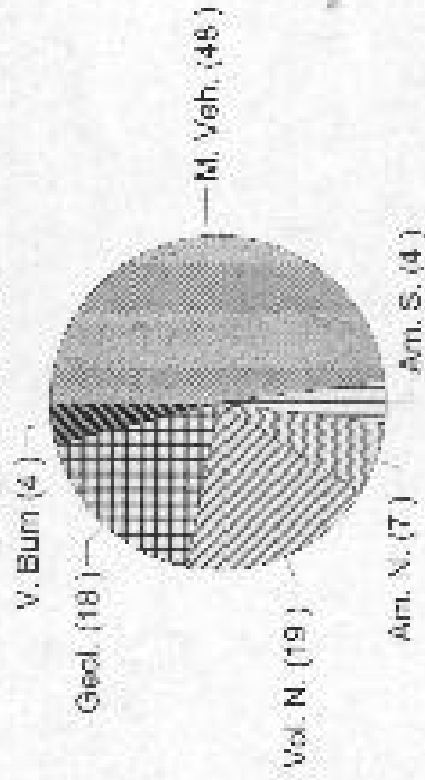
PM2.5: Phoenix Urban Haze Study 89/90

1300 - 1900

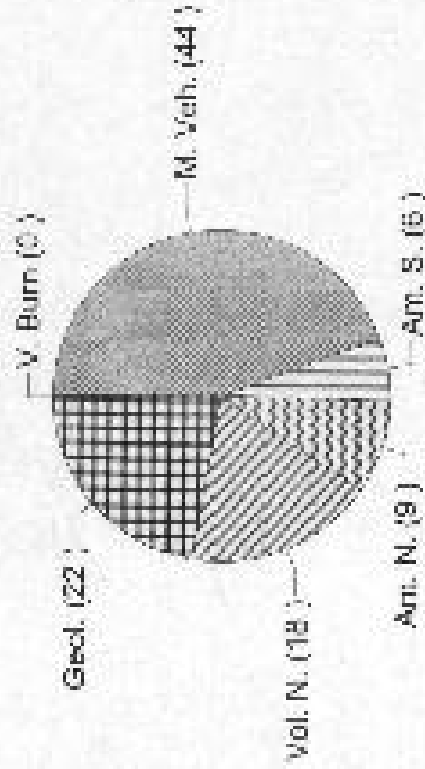
ICA



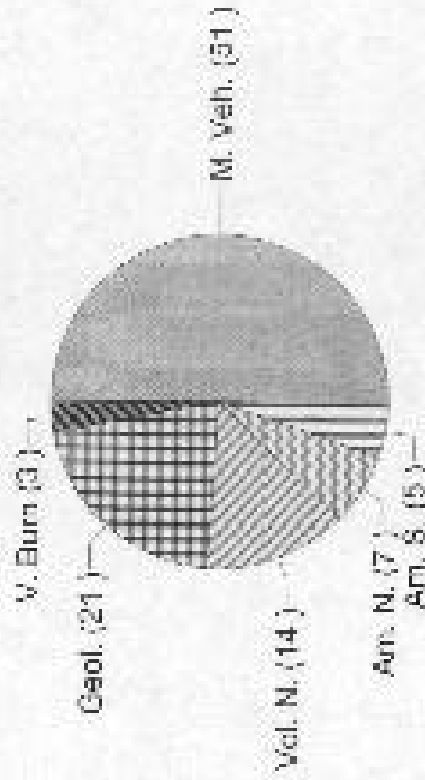
West Phoenix



Bank One



South Scottsdale



PM_{2.5} Source Contribution 1989-1990 Phoenix Urban Haze Study

Morning (0600 - 1200)

	ICA	West Phoenix	Bank One	South Scottsdale
Motor Vehicle	21±1	24±1	10±0.4	10±0.4
Ammonium Sulfate	0.84±0.07	0.43±0.08	0.97±0.05	0.58±0.07
Ammonium Nitrate	1.1±0.2	1.1±0.2	1.0±0.1	0.58±0.09
Volatilized Nitrate	2.4±0.1	2.6±0.1	1.9±0.1	1.4±0.1
Geological	5.0±0.2	3.4±0.2	3.3±0.1	3.7±0.1
Vegetation Burning	0	1.3±0.2	0	1.4±0.4
Calculated Mass	28±0.7	30±0.8	16±0.4	17±0.6
Measured Mass	28±0.3	30±0.3	15±0.2	17±0.2

Concentrations are in Fg m^{-3}

Source: Watson et al. (1991)

PM2.5 Source Contribution 1989-1990 Phoenix Urban Haze Study

Afternoon (1300 - 1900)

	ICA	West Phoenix	Bank One	South Scottsdale
Motor Vehicle	9.5±0.4	9.4±0.4	7.5±0.3	9.3±0.4
Ammonium Sulfate	1.0±0.1	0.88±0.05	1.1±0.04	0.83±0.05
Ammonium Nitrate	1.4±0.1	1.3±0.1	1.6±0.1	1.3±0.1
Volatilized Nitrate	3.5±0.1	3.7±0.1	3.1±0.1	2.6±0.1
Geological	4.0±0.1	3.6±0.1	3.7±0.1	3.8±0.1
Vegetation Burning	0	0.72±0.1	0	0.48±0.25
Calculated Mass	16±0.4	16±0.4	14±0.4	16±0.5
Measured Mass	15±0.2	16±0.3	15±0.2	15±0.2

Concentrations are in Fg m^{-3}

Source: Watson et al. (1991)

III. MARICOPA ASSOCIATION OF GOVERNMENTS BROWN CLOUD STUDY -- 1994 - 1995

< PRINCIPAL INVESTIGATORS

**ARIZONA DEPT OF ENVIRONMENT
(TOM MOORE ET AL)
DESERT RESEARCH INSTITUTE
(ERIC FUJITA)**

< SAMPLES TAKEN FROM PHOENIX URBAN HAZE NETWORK

< FALL/WINTER ROUTINE STUDY

**EVERY SIXTH DAY FROM NOVEMBER
1994 TO MARCH 1995**

< THREE SITES -- ALL URBAN

SUPERSITE -- 3.5 M AGL

ASU WEST -- 3.5 M AGL

TEMPE -- 5.0 M AGL

< SAMPLING TIMES

MORNING: 0500 - 1100

24-HOUR: MIDNIGHT TO MIDNIGHT

< MEASUREMENTS --

PM: SAME AS 1989-90 EXCEPT NO
BACKUP FILTER FOR VOLATILIZED
NITRATE

SEMIVOLATILE ORGANICS AND
POLYCYCLIC AROMATIC
HYDROCARBONS (ON A SUBSET OF 12

SAMPLES) -- USEFUL FOR
DISTINGUISHING GASOLINE FROM
DIESEL

< SOURCE APPORTIONMENT METHODS

CONVENTIONAL CHEMICAL MASS
BALANCE MODEL (CMB)

EXTENDED CMB FOR GAS/DIESEL
DISCRIMINATION

NO ATTEMPT AT APPORTIONING
WOOD BURNING

< ONLY FINE MASS WAS APPORTIONED

< SOURCE PROFILES

LOCAL (1989-90)
NORTHERN FRONT RANGE AIR
QUALITY STUDY
PHOENIX VEHICULAR PROFILES

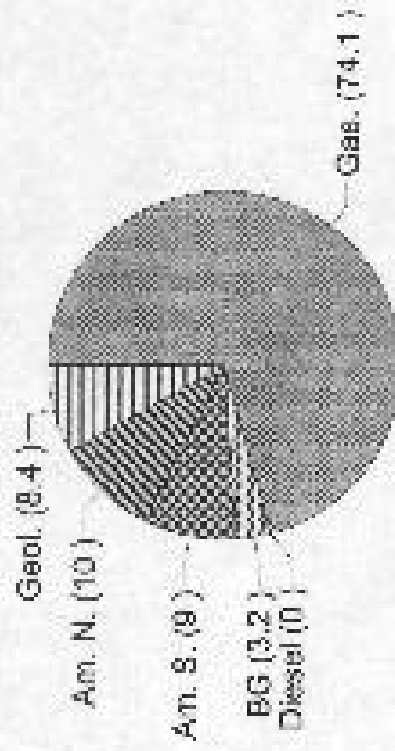
FROM THE INSPECTION &
MAINTENANCE TESTS

CHEMICAL MASS BALANCE MODEL

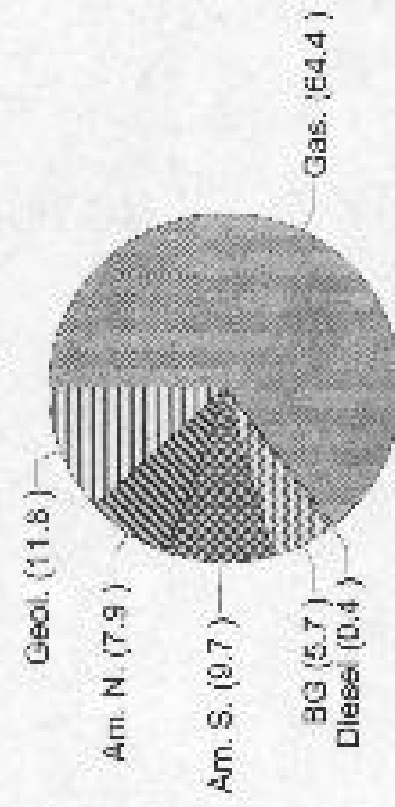
PM2.5 Conventional Species CMB

6-hour samples: 1994/1995

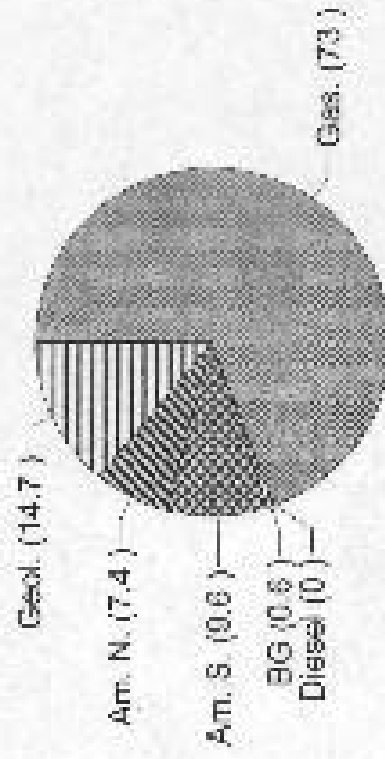
Supersite



Tempe

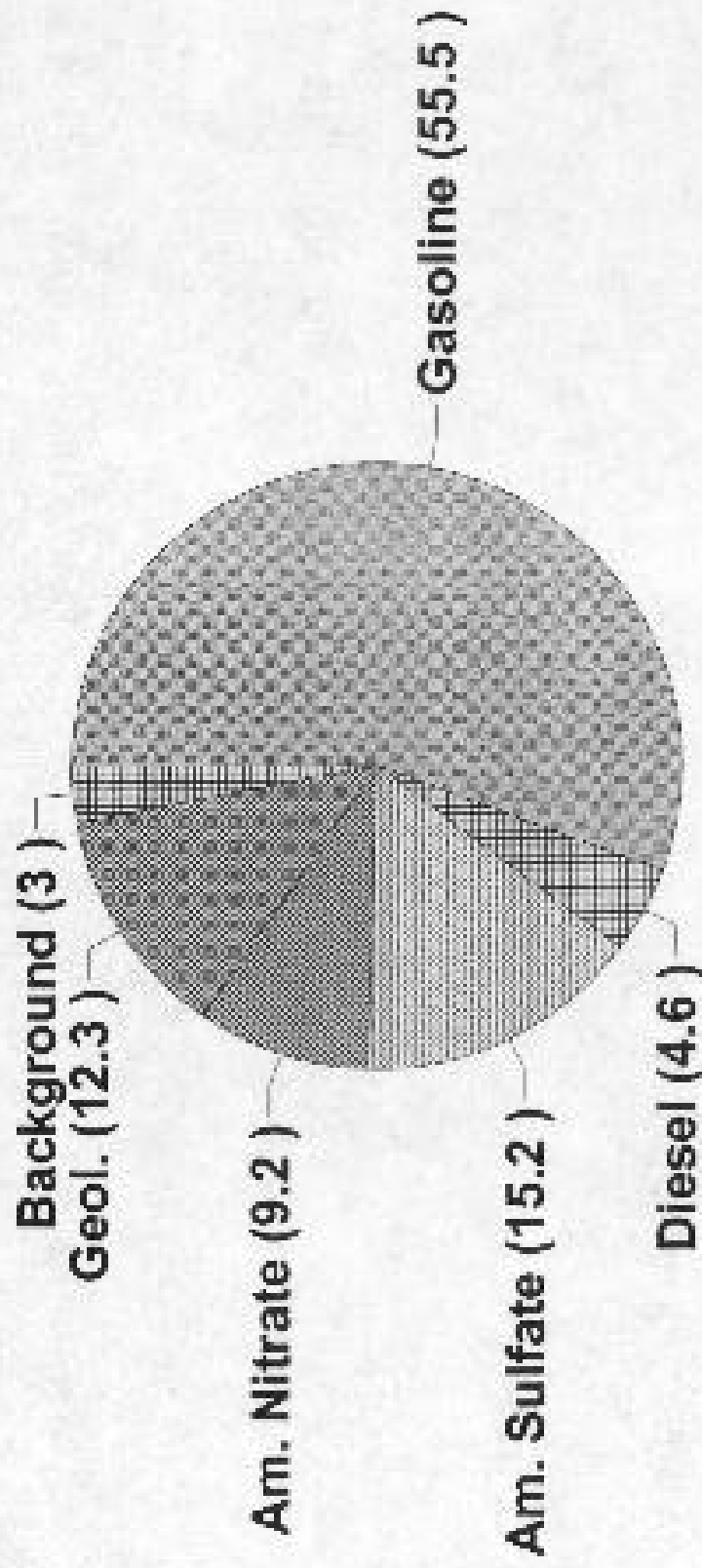


ASU - West



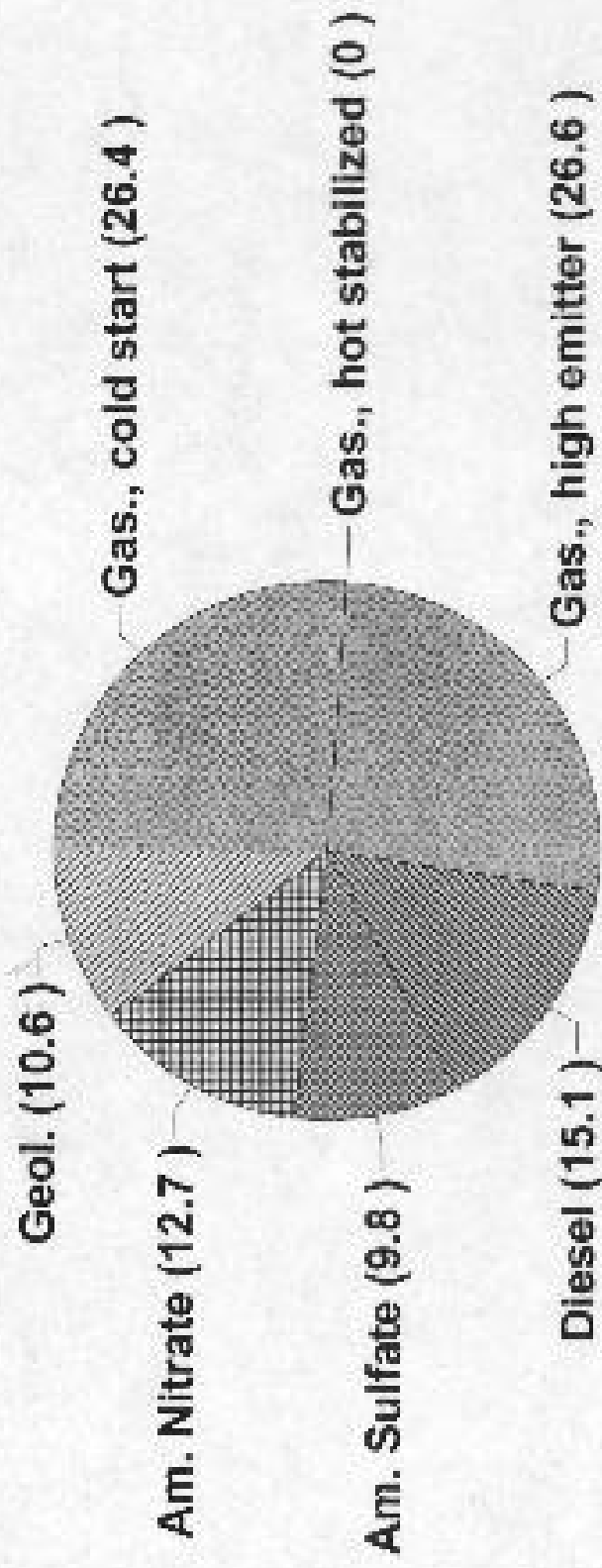
PM2.5 Conventional Species CMB

26 Samples: 1994/1995



PM2.5 Extended Species CMB

12 Samples: 11/94 to 3/95



PM2.5 Source Contribution 1999 Brown Cloud Project

Six Hour AM Samples (1994 / 1995)

	Supersite	Tempe	ASU-West
Observations	25	28	22
Gasoline Exhaust	13.7±2.2	8.9±1.8	9.7±1.5
Diesel Exhaust	-0.1±1.5	0.3±1.3	-0.4±1.0
Ammonium Sulfate	1.6±0.3	1.3±0.4	1.4±0.2
Ammonium Nitrate	2.6±0.4	1.3±0.3	1.3±0.3
Geological	1.6±0.6	1.7±0.6	1.9±0.4
Ambient Background	0.5±2.8	1.0±2.4	0.1±1.9
Unexplained	-0.2	-0.7	-0.5
Concentration	19.6±2.1	13.8±1.4	13.6±1.5
% Mass Attributed	101.7±4.6	104.7±4.6	103.6±4.0

Concentration are in Fg m^{-3}
Source: MAG (1999)

PM2.5 Source Contribution 1999 Brown Cloud Project

24-Hour Samples (Supersite)

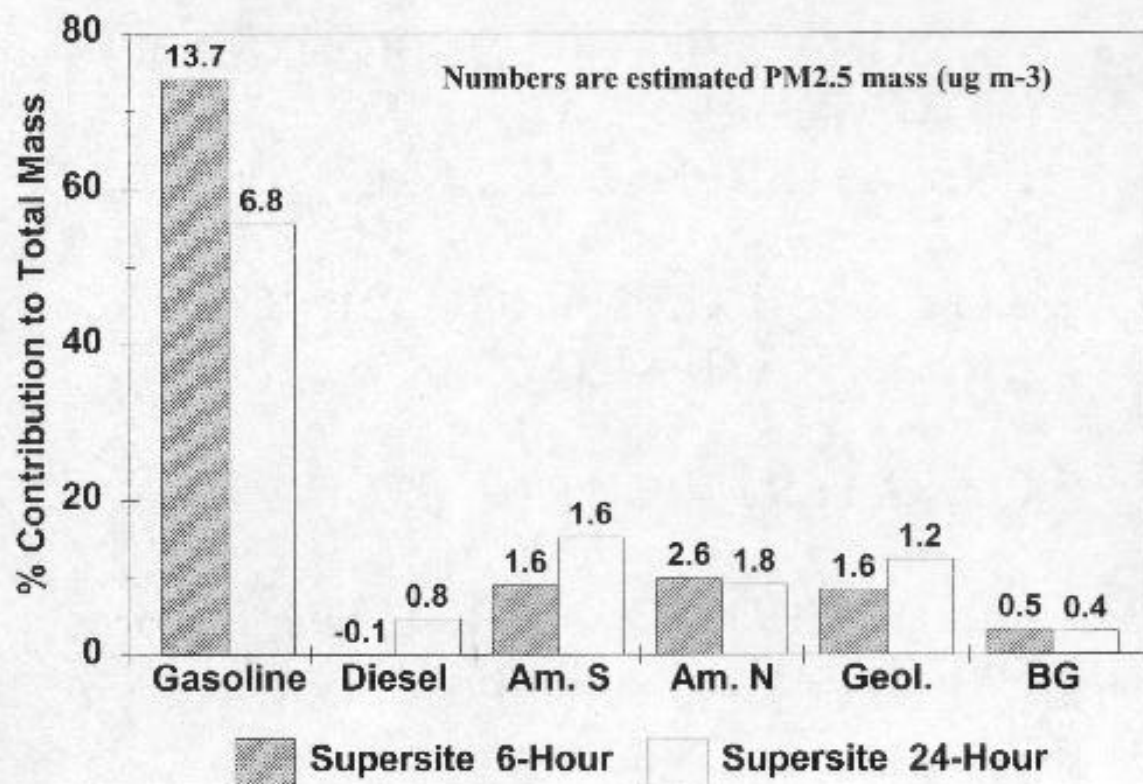
	Conventional Species	Extended Species
Observations	26	28
Gasoline Exhaust	6.8±1.2	---
cold start	---	3.8±4.2
hot stabilized	---	-0.2±1.2
high emitter	---	4.1±1.8
Diesel Exhaust	0.8±0.8	2.4±2.2
Ammonium Sulfate	1.6±0.2	1.3±0.2
Ammonium Nitrate	1.8±0.4	2.5±0.4
Geological	1.2±0.4	1.4±0.3
Ambient Background	0.4±1.2	---
Unexplained	-0.3	-0.1
Concentration	12.4±1.4	15.2±1.7
% Mass Attributed	103.5±2.7	100.8±1.7

Concentration are in Fg m^{-3}

Source: MAG (1999)

PM2.5 Conventional Species CMB

1994/1995



IV. ADEQ/ENSR ANALYSIS -- 1994-1996

< PRINCIPAL INVESTIGATORS

ARIZONA DEPT OF ENVIRONMENT
(TOM MOORE ET AL)
ENSR (STEVEN L. HEISLER)

< SAMPLES TAKEN FROM PHOENIX URBAN HAZE NETWORK

< LONG-TERM ROUTINE STUDY

EVERY SIXTH DAY FROM DECEMBER
1994 TO AUGUST 1996

< ONLY A SUBSET OF SAMPLES WERE FULLY ANALYZED: THESE WERE CHOSEN TO EQUALIZE THE LOW, MODERATE, AND HIGH PM DAYS

< FIVE SITES -- ALL 3-5 M AGL

SUPERSITE URBAN, CENTRAL

ASU WEST -- SUBURBAN --
NORTHWEST

TEMPE -- URBAN -- EAST CENTRAL

GILBERT -- SUBURBAN -- EAST

ESTRELLA -- URBAN FRINGE -- WEST

< SAMPLING TIMES & MEASUREMENTS
-- SAME AS STUDY #2, EXCEPT NO
GASEOUS SPECIES WERE EXAMINED

< SOURCE APPORTIONMENT METHOD

CONVENTIONAL CMB

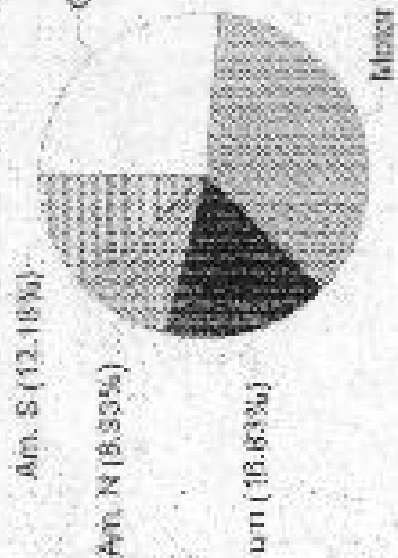
WOOD BURNING BY SOLUBLE K

- < FINE MASS AND LIGHT EXTINCTION
WERE APPORTIONED
- < SOURCE PROFILES -- SAME AS #2

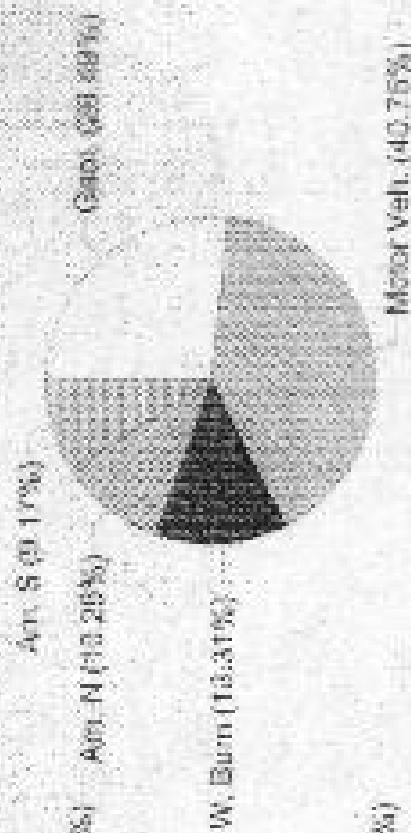
PM2.5 Source Contribution

1994-1996

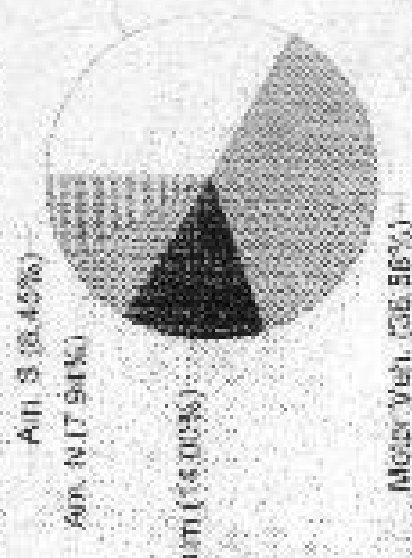
Supersite, 24-Hour



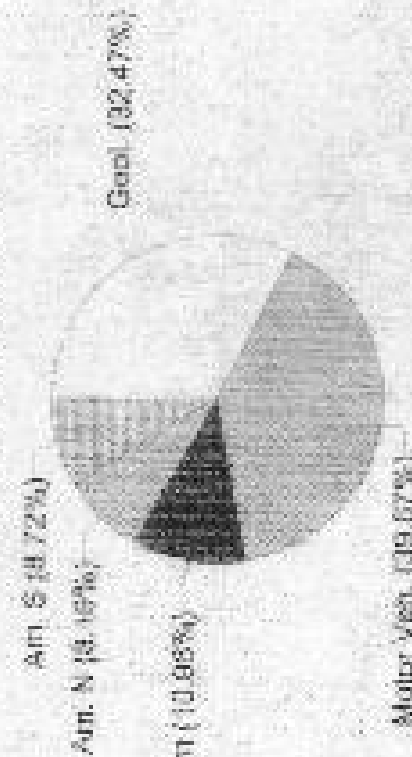
Supersite, 6-Hour



Tempe, 6-Hour



West Phoenix, 6-Hour



PM2.5 Source Contribution 1994 - 1996

	Supersite	Supersite	Tempe	ASU-West
# of Hours	24	6	6	6
Observations	55	54	57	51
Motor Vehicle	5.31	7.07	6.06	6.10
Ammonium Sulfate	1.81	1.59	1.40	1.34
Ammonium Nitrate	1.33	1.78	1.31	1.25
Geological	3.92	4.60	5.47	4.99
Wood Burning	2.50	2.31	2.32	1.69
Measured Mass	13.05	15.23	11.67	11.91
Calculated Mass	14.86	17.35	16.57	15.37

Concentrations are in Fg m^{-3}

Source: ENSR (2000)

V. COMPARISON OF THE THREE STUDIES

< CAVEATS

DIFFERENT SITES

DIFFERENT STUDY DURATIONS

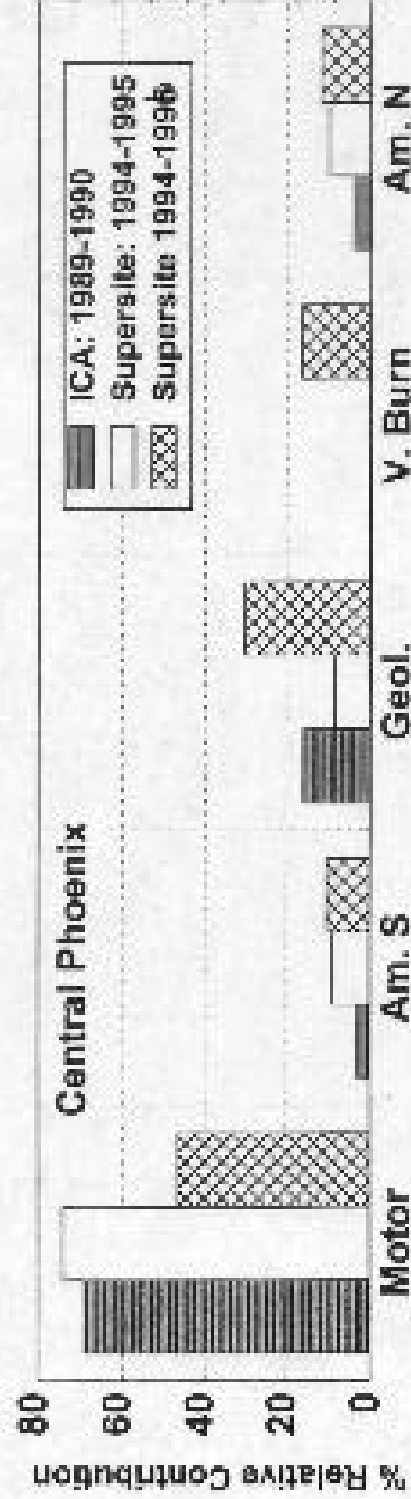
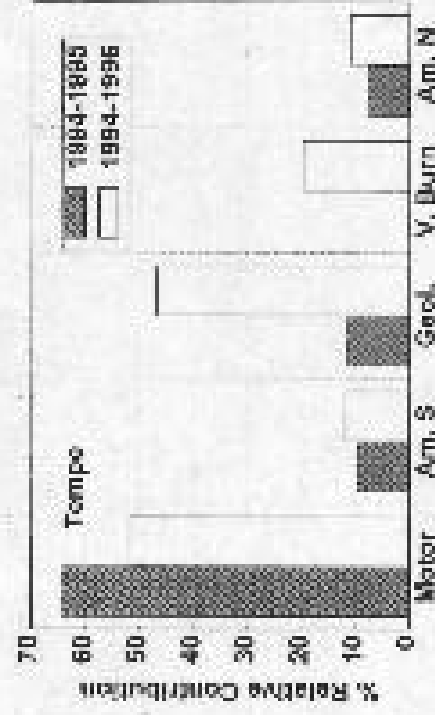
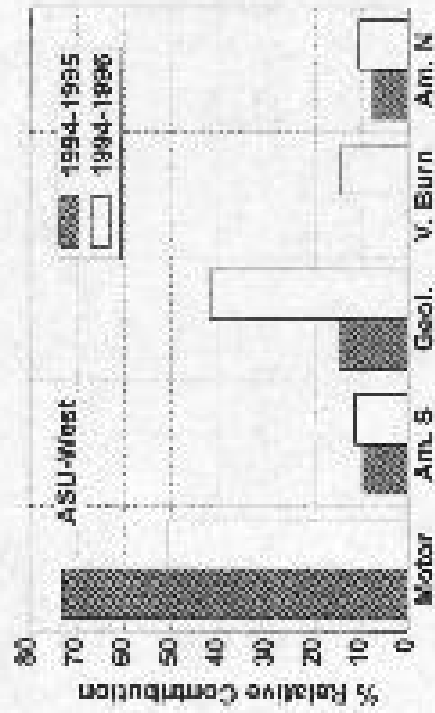
DIFFERENT SAMPLING TIMES

DIFFERENT SAMPLING METHODS

< STUDY #1 IS THE ONLY DAILY INTENSIVE STUDY

< STUDIES #2 AND #3 HAVE LIMITED NUMBERS OF SAMPLES

< STUDY #2 IGNORES WOOD BURNING, AND STUDY #3 OVER ESTIMATES IT



Comparison of CMB Studies. Samples are 6-Hour Morning

VI. CONCLUSIONS

- < ALL STUDIES SHOW THAT MOST FINE MASS COMES FROM COMBUSTION**
- < ALL SHOW SIMILAR PROPORTIONS BETWEEN GEOLOGICAL AND COMBUSTION SOURCE CATEGORIES**
- < ALL SHOW RATHER LOW CONTRIBUTIONS FROM SECONDARY NITRATE AND SULFATE**

Comparison of Two CMB Studies

24-Hour Samples: Supersite

