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FINE PARTICULATE RECEPTOR MODELING IN LAS VEGAS USING COMBINED GASEOUS AND PARTICULATE SOURCE PROFILES

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Introduction

The chemical mass balance model (EPA) uses source fingerprints and chemical compositions of ambient aerosol samples at receptor sites to estimate source type contributions. The particulate fingerprints of some sources, in particular, diesel vehicle exhaust and wood smoke, are sufficiently similar that the CMB model cannot distinguish their contribution with a high level of certainty.

The purpose of this paper is to demonstrate development of fine particulate (PM2.5) and gaseous for three types of fuel combustion sources - Gasoline Vehicles, Diesel Vehicles and Woodburning - with the objective of estimating their individual source contributions with reasonable certainty when running the chemical mass balance model.[1]

The Las Vegas Valley is the most populated metropolitan area in Nevada with a 1987 estimated population of 600,000. The urban area is approximately 250 square miles and is lined by mountains on four sides. The valley floor slopes from west to east. The western urban fringe has an elevation of 2,500 feet; the low area at the eastern edge has an elevation of 1,700 feet. See Figure 1

The EPA has classified the Las Vegas Valley as a Group I (Non-Attainment) Area. Exceedances of the NAAQS have been measured for both the 24-hour and annual time periods. The 24-hour violations are associated with periods of high windspeed and appear to be fugitive dust related. The first and fourth quarters have the highest quarterly PM10 averages. High daily averages during the first and fourth quarters are usually associated with low wind episodes and evening/morning inversions. During inversion conditions, the air at ground level flows from higher to lower elevations.

Two dichotomous samplers were operated at our permanent urban site, called the East Charleston Site shown in Figure 1. The dichots were run on a 6-day cycle. Quartz filters were analyzed for carbon species by sequential thermal oxidation by ERT. Teflon filters were analyzed by NEA by x-ray fluorescence for elements. The data shows a wintertime fine to coarse particle ratio of approximately 1:1 and a summertime fine to coarse ratio of approximately 1:2.

From inspection of the chemical analyses for dichotomous and quartz teflon filter samples, it appears that combustion particles dominate the fine particle concentration and soil particles dominate the coarse particle concentration.

To help conduct the source apportionment exercise at the East Charleston Site, two dichotomous samplers were installed at the woodburning site and at the diesel truck stop site, (located in Figure 1), during the 1985/86 winter. The woodburning site was selected because it is upwind of the valley during inversion conditions. The samplers was

installed on the roof of a one-story elementary school (H. M. Smith). (Other locations which were believed to be good for woodburning were also evaluated, but the mobile source contribution was significant.) The samplers, one with quartz filters, the other with teflon filters, were operated on selected winter evenings from 7:00 p.m. to 12:00 midnight. The diesel truck stop site was selected because it is south of the urban area and should be dominated by diesel vehicles. Although it was only one half mile west of I-15, the traffic mix there favors diesel emissions. The truck stop samplers operated from 6:00 a.m. to 10:00 a.m. Samplers were powered by a portable propane generator at both sites.

Results

We encountered several difficulties with respect to collecting adequately loaded fine samples. First, there was only one night at the woodburning site that was well above background, or 20 ug/m^3. Second, there was only one day at the truck stop site that was adequately loaded. Third, we could not locate an automobile site (with little diesel or woodburning influence). Fourth, we did not activate the desert site until late 1987. At this writing, mass concentration data is available but chemical composition data is not for the desert site.

Selected species analyzed at our woodburning site are shown in Table 1. The ambient sample was considered a source sample. This profile compares favorably with limited woodburning results from the EPA Library in Table 2. Aluminum and silicon at the woodsmoke site are likely due to trace amounts of locally re-suspended dust. The lead may come from locally generated motor vehicle exhaust.

An automobile profile was derived by reviewing the literature [3,4] and by checking lead content reports from the California Air Resources Board. The following assumptions were made:

- PM2.5 emission factor for leaded gasoline operated cars/light trucks is 134 milligrams per mile. For unleaded gasoline operated cars/light trucks, it is 20 milligrams per mile.

- In 1987, approximately 65% of the Las Vegas fleet used unleaded gasoline and 35% was leaded. A third to half of leaded fleet are misfueled vehicles manufactured for unleaded fuel.

- Composite emission factor is 60 milligrams per mile.

- In mid 1970'S lead content was 2 grams per gallon.

- Current Las Vegas/Southern California lead content estimate is 0.3 grams per gallon.

- In mid 1970's lead accounted for 21% of PM2.5 auto emission

- Current composite emission factor for lead is calculated as PB E.F. =

$$134 \text{ milligrams per mile } \frac{\text{X } 0.3 \text{ grams per gallon}}{2 \text{ grams per gallon}} \text{ X } 0.35$$

$$= 1.5 \text{ milligrams per mile}$$

$$\text{PB/PM2.5} = \frac{1.5 \text{ milligrams per mile}}{60 \text{ milligrams per mile}} = 2\text{-}1/2\ \%$$

Lead/Bromine/Chlorine/ are present in a Stoichiometric Ratio of 1:0.4:0.3

Our calculated automobile profile, presented in Table 1 for selected species, reflects a best estimate by considering Pierson's 1977 tunnel experiment,[5] the leaded profile in the 1985 draft CMB user manual,[6] and leaded and unleaded profiles in current CMB library.

These fuel combustion profiles along, with a local soil dust profile, were used by the CMB model for several sample days from October, 1986 through February, 1987 at our urban site. The sampling period included days outside our woodburning season and days during our woodburning season. The guidelines for validating CMB model [1,2] runs, specify acceptable ranges for the R square, Chi square, percent total mass and calculated to measured ratios of major elements (especially carbon) and describe the need to avoid collinearity of source profiles. One objective of the evaluation was to check for potential collinearity between the wood, automotive and diesel profiles. An additional objective of the evaluation was to see if the model predicts low woodburning contribution prior to the woodburning season.

The runs were successful in avoiding the collinearity problem and showing low warm weather woodburning contributions. However, one or more of the parameters - Chi square, percent mass, calculated carbon/measure carbon, was not acceptable on each of the runs. (The R square was satisfactory for all runs.)

Additional Species

The EPA guidelines for applying the CMB model suggest that the use of additional tracer species may improve model performance. Thus, we considered methods of enhancing the profiles using readily available data. Others[8] are considering methods of hydrocarbon speciation to help resolve differences among carbonaceous source profiles; however, a technique that could be more readily implemented was preferable. Since carbon monoxide and nitrogen oxides data are available at the urban monitoring site, we started to experiment with modified source profiles and modified receptor concentrations. The relative elemental composition of our three PM2.5 profiles are generally all of the same order of magnitude. But when these profiles are modified to include gaseous emissions, the relative proportion of several major

components will vary in order of magnitude as illustrated in Table 2.[3,7]

We quickly realized that the NOx percentage assigned to automobiles, which ranges from 3 to 8%, is an important variable. The emission rate of NOx is dependent on ambient temperature. The emission rate drops from 2.2 g/mi. to 1.3 g/mi. when the ambient temperature increases from 50° to 100°. The carbon monoxide emission rate is speed dependent. Carbon monoxide emissions drop from 36 g/mi. to 27 g/mi. when the speed increases from 16 mph to 22 mph. Over this speed range, the NOx emission rate is nearly constant and we assume that the PM2.5 emission rate is constant since no data for speed is available. But, the relative carbon monoxide component in the profile is fairly constant over these speed and ambient temperature changes, whereas the relative NOx component changes significantly. While we had ambient temperature available to us for each day of interest, records for daily variations in speed are not available. We find the CMB results are sensitive to the value assumed for the NOx percentage. For example, 4.8% versus 5.4% NOx made a substantial difference in the quality of the CMB run.

We surmised that we could solve the correct NOx percentage by checking over all CMB modeling statistics and the amount of NOx that could be contributed by diesel vehicles. For example, diesel vehicles according to our emissions inventory account for approximately 20 to 25% of our ambient NOx. But some CMB runs accounted for over 30% of ambient NOx to diesel vehicles. These CMB runs were considered invalid. Consequently, we ran a range of automobile NOx percentage for all sampling days and looked for those automobile NOx values that yielded good statistics and satisfied our emission inventory constraints. These runs are summarized in Table 7. Except for two days evaluated (one day prior to the woodburning season and one day during the woodburning season) one or more automobile NOx percentage yielded satisfactory CMB runs.

The complete profiles are presented in Table 8.

Conclusions/Recommendations

The method of incorporating carbon monoxide and nitrogen oxides data into the source profiles and receptor concentrations used in PM2.5 source apportionment appears to be viable. This procedure could be implemented by those persons performing CMB source apportionment for PM10 if their particulate matter monitoring stations include continuous analyzers for carbon monoxide and oxide of nitrogen. Authors of the CMB software should consider modifications to allow display of carbon monoxide concentrations in the results showing measured versus calculated chemical species concentrations. Also, the uncertainties for relative contributions from each source to each specie in "SSCONT" should be calculated and displayed.

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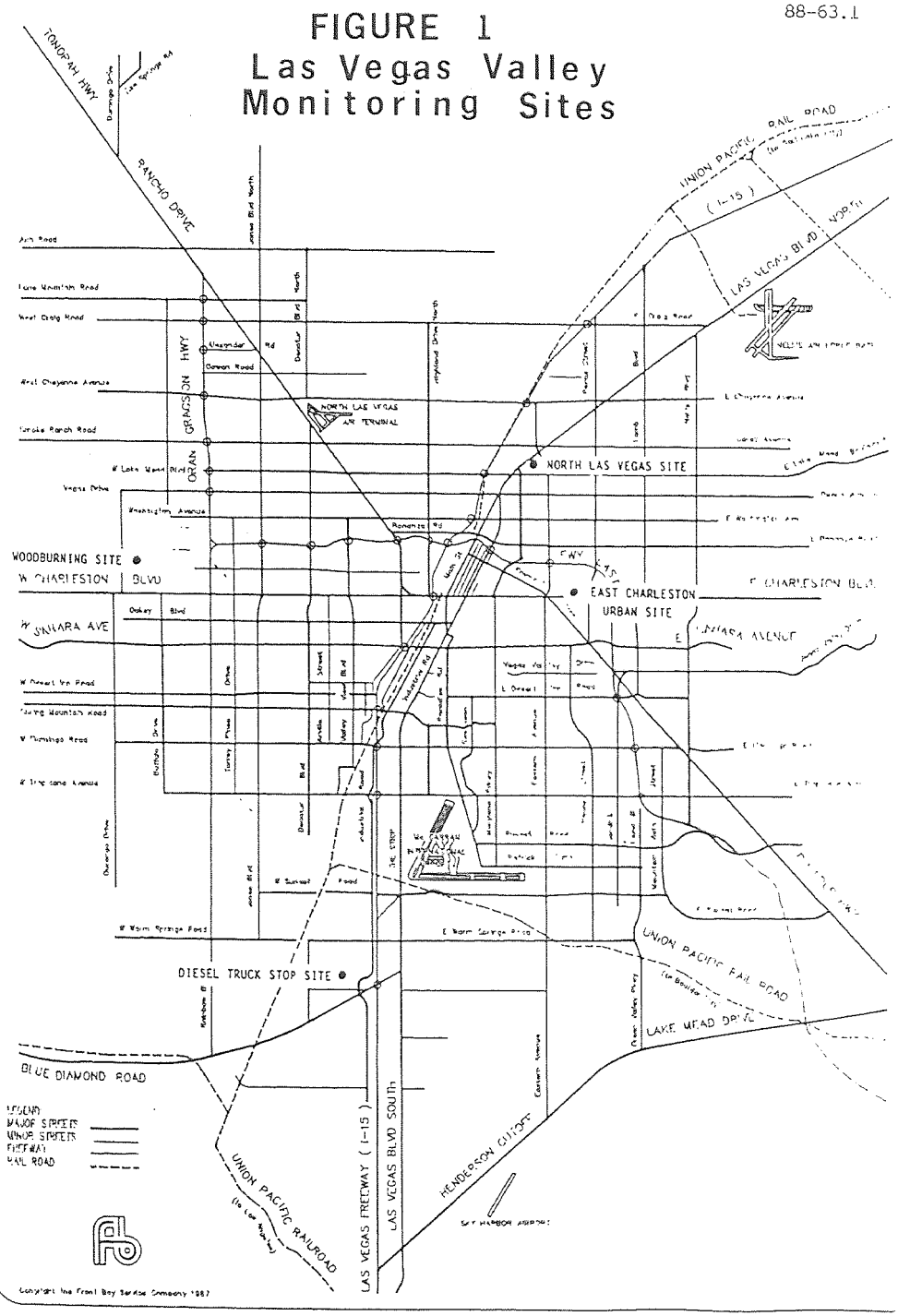
FIGURE 1
Las Vegas Valley Monitoring Sites



References

1. "CMB User's Manual" (Version 6.0)
EPA-450/4-83-014R May, 1987

2. "Protocol for Applying and Validating the CMB Model"
EPA-450/4-87-010 May, 1987

3. "Compilation of Air Pollutant Emission Factors,
Highway Mobile Sources" EPA March, 1981

4. "Heavy Duty Diesel Particulate Emission Factors"
K. Bains et al, EPA Journal The Air Pollution Control Association Vol. 29 Page 616 (1979)

5. "Particulate Matter Associated with Vehicles on the Road II", W. R. Pierson and W. Brachaczek, Aerosol Science and Technology Volume II, Page 1, (January 1983)

6. "Draft -- Users Manual for Chemical Mass Balance Model"
EPA, OAQPS, EPA-450/4-83-014 (July 1983)

7. Mobile III Emission Factors Printout for Clark County Nevada (Local Vehicle Miles Traveled Mix) August, 1984 (Run September 1985)

8. Program Work Plan for "Pacific Northwest PM-10 Source Profile Library Development", Oregon DEQ, Washington DOE, Puget Sound APCA, Idaho AQB, Lane RAPCA, EPA Region 10 by John Core, Oregon DEQ, April 1, 1987

TABLE 1 Estimated Auto PM2.5 Profile

	PERCENT OF PM2.5	ESTIMATED UNCERTAINTY
ALUMINUM	0.046	0.0046
SILICON	0.092	0.0092
SULFUR	0.092	0.0092
POTASSIUM	0.32	0.032
CARBON	57.6	10.0
CHLORINE	0.83	0.083
LEAD	2.5	0.25

TABLE 2 Percent Composition

	AUTO	DIESEL	WOOD
PM2.5	0.22	5.9	13.9
NOx	3.0-8.0	61.4	1.7
CO	91.2	32.7	84.4
(NOx/CO Ratio	.06	1.9	.02)
TOTAL	100	100	100

TABLE 3 Woodburning Site Ambient Profile (#515)

	PERCENT OF PM2.5	ESTIMATED UNCERTAINTY
Aluminum (Al)	0.3	0.03
Silicon (Si)	0.8	0.08
Sulfur (S)	1.01	0.1
Potassium (K)	0.87	0.1
Carbon (C) (Total)	61.0	10.0
Chlorine (Cl)	0.25	0.025
Lead (Pb)	0.25	0.025

Total measured concentration 53 ug/m^3

TABLE 4 Comparison of Wood Profiles

	WOODSMOKE SITE	EPA LIBRARY "FPLSOFT"	EPA LIBRARY "RESWDCM"
	PERCENT OF PM2.5		
Aluminum	0.3	Not Reported	0.021
Silicon	0.8	Not Reported	Not Detected
Sulfur	1.01	Not Reported	0.182
Potassium	0.87	.606	0.86
Carbon	61.0	71.0	70.3
Chlorine	0.25	Not Reported	0.509
Lead	0.25	Not Reported	Not Detected

TABLE 5 Diesel Truck Site Ambient Profile (#507)

	PERCENT OF PM2.5	ESTIMATED UNCERTAINTY
Aluminum	0.37	0.04
Silicon	1.03	0.10
Sulfur	0.62	0.06
Potassium	0.16	0.03
Carbon	44.	4.4
Chlorine	<Det. Limit	
Lead	0.21	0.02

Total measured 32.2 ug/m^3

TABLE 6 Trial Diesel Profile

	DIESEL AMBIENT % PM2.5	EPA & PIERSON % PM2.5	TRIAL PROFILE % PM2.5	REMARKS TO JUSTIFY TRIAL
Al	0.37	1.00	0.35	Some ambient Al from soil
Si	1.0	1.6	0.90	Some Si from soil
S	0.63	2.7	0.60	Some S from soil
K	0.16	0.17	0.17	We agree with EPA
C	44.0	75.0	45.0	We do not agree with EPA
Cl	<D.L.	<D.L.	<D.L.	We agree with EPA
Pb	0.21	1.3	0.10	Most lead from autos

TABLE 7 PM2.5/CO/NOx Profiles for Auto, Diesel and Wood

		AUTO		DIESEL		WOOD	
		FRACTION	UNCER-TAINTY	FRACTION	UNCER-TAINTY	FRACTION	UNCER-TAINTY
1.	NOx	.042000*	.002100	.65	.032	.016880	.001688
2.	CO	.912000	.046000	.32	.032	.844090	.084400
3.	C	.001251	.000152	.0264	.00264	.084800	.014000
4.	Al	.000001	.0000003	.000205	.00002	.000413	.000038
5.	Si	.000002	.000001	.000527	.000053	.001118	.000061
6.	S	.000002	.0000005	.00035	.000035	.00141	.000106
7.	Cl	.000014	.000003	.000006	.000006	.000348	.000033
8.	K	.000007	.000004	.000099	.000018	.001217	.000067
9.	Ca	.000000	.000000	.00041	.000041	.000970	.000053
10.	Mn	.000000	.000000	.000018	.000002	.00006	.000004
11.	Fe	.000007	.000002	.000047	.000005	.000175	.000013
12.	Cu	.0000001	.00000003	.000000	.000000	.000015	.000004
13.	Zn	.000001	.0000001	.000094	.000009	.000071	.000006
14.	Br	.000021	.000005	.000023	.000002	.000111	.000011
15.	Pb	.000054	.000014	.000057	.000006	.000352	.000022
16.	PM 2.5	.002170	.000220	.05865	.00586	.139030	.014000

* The Auto NOx fraction is a variable, values ranging from 0.042 to 0.066 were checked for adequate CMB statistics in Table 9.

TABLE 8 Partial Displays from Example Run with CO/NOx/PM2.5 Profile East Charleston 11/28/86

"SOURCE CONTRIBUTION ESTIMATES"

R SQUARE 1.00 MASS 103% CHI SQUARE 0.02

SOURCE	CONTRIB UG/M^3	STD ERROR	TSTAT
AUTOMOBILE EXHAUST	8665.0	633.0	13.7
SOIL DUST	0.6	2.3	0.3
WOOD SMOKE	124.5	38.2	3.3
SULFATES	0.6	1.4	0.5
DIESEL VEHICLE EXHAUST	201.0	88.1	2.3

"UNCERTAINTY/SIMILARITY/CLUSTERS"
BLANK

(SOURCE SPECIFIC CONTRIBUTIONS) "SSCONT"

	PERCENT AUTO	SOIL	WOOD	SULFUR	DIESEL
PM2.5	28	2	27	1	18
CO	98	0	1	0	1
NOx	80	0	NEGL	0	20
C	40	NEGL	40	0	20
Pb	97	NEGL	9	0	2
K	19	6	58	0	8
S	3	2	33	49	13
Si	5	42	41	0	31

"SPECIES CONCENTRATION"

	Measured	Calculated	Ratio C/M
TOTAL	***	***	1.02
CO	***	***	1.00
NOx	653.	653.	1.00
C	27.	27.	1.00
Pb	0.48	0.52	1.09
K	0.38	0.24	0.57
S	0.53	0.53	1.00
Si	0.34	0.40	1.20

TABLE 9 Status of CMB Runs According to Auto NOx

AUTO NOx %	PERCENTAGE PRIOR TO/DURING WOOD SEASON 4.2	4.8	5.4	6	6.6
			PRIOR		
10/23/86	NOx D >30%	OK	W T >1	W T >1	W T >1
10/29/86	W T <-1	W T <-1	OK	OK	W T >1
11/04/86	D T <2	D T <2	D T <2	D T <2	D T <2
02/08/87	W T <-1	W T <-1	W T <-1	W T <-1	OK
			DURING		
11/28/86	W T <2	NOx D >30%	OK 78% PM2.5	OK 76% PM2.5	D T <2
12/04/86	W T <2	NOx D >30%	NOx D >30%	OK 87% PM2.5	D T <2
12/16/86	NOx D >30%	OK	OK	D T <2	D T <2
01/03/87	W T <2	NOx D >30%	OK	OK	D T <2
01/21/87	W T <2	W T <2	OK	D T <2	D T <2
01/27/87	W T <2	67% PM2.5	60% PM2.5	64% PM2.5	D T <2
02/02/87	OK	D T <2	D T <2	D <2	D T <2

NOTE: PM2.5, Total not run as fitting elements in CMB

W - WOOD D - DIESEL T - TSTAT

NOx D = NOx Contribution from diesel

67% PM2.5 = Means only 67% of measured PM2.5 Mass was calculated