# Particulate Emissions From a Mid-Latitude Prescribed Chaparral Fire

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Smoke aerosol was collected on filters from a helicopter during a 400-acre (1.62 km<sup>2</sup>) prescribed chaparral burn in the San Dimas Experimental Forest on December 12, 1986. Hi-Vol samplers were used to collect particles on both Teflon and glass fiber filters. Scanning electron microscopy of the filters revealed particles that ranged in size from about 0.1 to 100  $\mu$ m. Many of the large particles (>10  $\mu$ m) that appeared irregularly shaped at low magnifications were found at higher magnification to be highly agglomerated smaller spheres, often showing signs of partial coalescence. Energy dispersive analysis of X rays (EDAX) revealed carbon, oxygen, magnesium, aluminum, silicon, calcium, and iron as the primary elemental composition of the aerosols. Extractions of aerosol components in water/methanol mixtures, followed by ion chromatographic analysis, indicated that significant levels of nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sulfate (SO<sub>4</sub><sup>-</sup>), chloride (Cl<sup>-</sup>), phosphate (PO<sub>4</sub><sup>-</sup>), oxylate (C<sub>2</sub>O<sub>4</sub><sup>-</sup>), sodium (Na<sup>+</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), and potassium (K<sup>+</sup>) were associated with the particles. The proportions of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>-</sup>, Na<sup>+</sup>, and C<sub>2</sub>O<sub>4</sub><sup>-</sup> leached from the aerosol appeared to remain relatively constant in the smoke plume collections. Analysis of soluble NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, K<sup>+</sup>, and SO<sub>4</sub><sup>-</sup> ions, however, suggested that either possible changes in the nature of the emissions had occurred during different stages of combustion, or that ongoing smoke plume chemistry might have influenced the levels of these ions, or both. The soluble ionic portion of the aerosol extended to be about 2% by weight. The first known determinations of phosphate anion from particulates collected in a biomass burn plume are reported.

## INTRODUCTION

Emissions from forest fires and other biomass-burning processes (agricultural burning, clearing, etc.) are currently of much interest to environmental scientists. Copious amounts of both gases and aerosols are released into the atmosphere during biomass burning, the effects and consequences of which have not yet been adequately assessed at regional or global scales [Crutzen et al., 1979, 1985; National Academy of Sciences (NAS), 1984; Greenberg et al., 1984; Delmas, 1982; Seiler and Crutzen, 1980]. Estimates of the global land areas involved in burning each year are quite large  $(3-7 \times 10^6 \text{ km}^2)$ , involving about 2-5% of the land area of our planet [NAS, 1984]. About 3.6 Tg (10<sup>12</sup> g) of smoke particles have been estimated to be released into the atmosphere each year as a result of biomass burning in the United States alone [Ward et al., 1979]. Knowledge of the total mass, size distribution, and chemical composition of the particulates produced from biomass burning is important for studies of air quality, visibility, atmospheric chemistry, and global budgets and because of the potential for these emissions to impact climate [Radke et al., 1978; Stith et al., 1981; Patterson and McMahon, 1984; Ward, 1984; Patterson et al., 1986]. For example, the production of nitrogen-, carbon-, and sulfur-containing particulates during a biomass burn may be important components of the budgets of these trace species and must be included in the trace species balances for these elements. Furthermore, the production of water-soluble particulates and their wet- and dry-deposition processes (fertilization) at other locations could affect biogenic activity.

The amount, chemical composition, and rate of emissions

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Paper number 8D0124. 0148-0227/88/008D-0124\$05.00 released during biomass burning depend primarily upon the rate of energy release (intensity) and the fire spread. Both of these are strongly coupled to fuel moisture content, fuel type and size, fuel array, ignition pattern, terrain, and weather. While smoke released from forest fires is a complex chemical mixture of organic and inorganic material simultaneously involving the gaseous, liquid, and solid phases, the results discussed in this article will primarily focus on the morphology and inorganic chemistry of aerosols collected during a prescribed biomass burn in the San Dimas Experimental Forest, Angeles National Forest, Los Angeles County, California.

### EXPERIMENTAL SITE

The Lodi Canyon encompasses about 1200 acres in the San Gabriel Mountains of Los Angeles County, California. It is a Mediterranean-type chaparral ecosystem, adapted to recurrent fire. It was last swept by fire in 1960. Chaparral is subject to intense and extensive fires, with fuel consumption rates of about 2-7 kg m<sup>-2</sup>. These fires propagate largely through live vegetation, mostly consuming foliage and small stems. The fire was ignited on December 12, 1986, with gelled gasoline dispersed by helicopter. The fire burned primarily on the south facing aspects of the canyon, in vegetation that was predominantly Ceanothus crassifolius and Adenostoma fasciculatum, with limited combustion of buckwheat, sage, and scrub oak. While the fire studied in this work had low rates of fire spread, the flames were intense, with flame lengths typically extending 6-12 m above the chaparral. About 400 acres (1.62 km<sup>2</sup>) were burned. Fuel moisture was 100% for live fuel and about 9% for dry sticks. Slightly more than 80% of the fuel was live. Surface winds were light and variable during the prescribed burn, and smoke plumes rose above the canyon and dispersed at 2000-2400 m above mean sea level.

## SAMPLING EQUIPMENT AND STRATEGY

Plume smoke samples were collected aboard a Los Angeles County Fire Department Bell 204B helicopter. Three Hi-Vol filtration systems were attached to a floor pallet mounted in the rear crew cabin of the helicopter. Aluminum sampling probes (1.75 cm ID) that protruded about 30 cm forward of the helicopter nose were extended through a modified nose

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access hatch. Flexible Tygon hoses (2 cm ID) were attached to the base of each probe and run a distance of about 4 m to the Hi-Vol samplers. Expansion cones were fabricated to interface between the Hi-Vol samplers and hoses. Hi-Vols were loaded with either 102-mm-diameter Teflon or glass fiber filters. The Teflon filters had nominal pore size diameters of 2  $\mu$ m and were efficient (>98% capture) for collection of particles down to 0.1  $\mu$ m in diameter. The glass fiber filters were fabricated of binderless glass and had a collection efficiency of 99.97% for 0.3-µm-diameter DOP (dioctyl phthalate) smoke particles. One Hi-Vol system was used exclusively for collection of smoke particles on Teflon filters; another was used for collections on glass fiber filters (this system was also used for filling Tedlar bags with filtered air samples for subsequent analysis of CO<sub>2</sub> and other trace gases). The third system served as a backup and was not used during the burn. The exhaust lines from the pumps converged into one large flexible hose that exhausted through a modified overhead cabin vent. Sampling flows (velocities) were chosen to match the planned forward aircraft speed of 40 knots ( $\sim$ 77 km h<sup>-1</sup>). Rotor downwash was well behind the sampling probes at forward speeds in excess of 30 knots ( $\sim 55.6$  km h<sup>-1</sup>). The sampling probes, however, did not extend far enough out from the helicopter nose to be in the free-stream airflow regime. Data acquired by Letko [1947] using 2.5-cm-diameter probes extended 30 cm from aircraft noses indicate that particle number density errors of as much as 40% could have resulted from our sampling configuration operated at a forward aircraft speed of 40 knots.

Typically, an extensive smoke plume was identified from the helicopter, and an appropriate sampling traverse was initiated. Usually, burning was initiated along a canyon ridge, and fire lines were typically 200–300 m long. At least two, sometimes three, sampling passes were made through the same region of smoke plume. Each numbered smoke plume sampling therefore consisted of at least two passes. Several samples were collected upwind of the canyon at various times during the burn and were used to determine incoming background particulate levels. A summary of sampling parameters appears in Table 1. Altitudes are reported as above ground level. Approximate flight paths for the Lodi samplings are shown in Figure 1 for traverses over vigorously flaming chapparal, mixed stages of combustion (flaming, transitional, and smol-

TABLE 1. Sampling Parameters for Lodi Canyon Prescribed Burn Experiment

Sample	Category	Time, PST	Altitude	Passes	
4	F	1105	60 m	2	
5	В	1110	60	1	
6	М	1145	35	2	
7	F	1150	90	3	
8	В	1155	90	1	
9	F	1230	90	3	
10	Μ	1235	670	2	
11	В	1240	670	1	
12	Μ	1256	310	2	
13	М	1303	90	2	
14	F	1326	90	3	
15	F	1335	60	3	
16	В	1340	90	1	
17a	М	1358	370	2	
17b	М	1402	90	2	
19	В	1415	90	ī	

Categories are as follows: B, background; F, vigorous flaming; M, mixed stages of combustion.

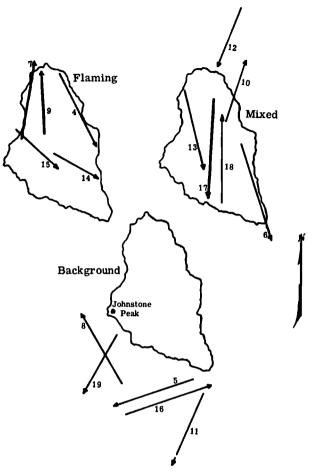


Fig. 1. Approximate flight sampling traverses over Lodi Canyon on December 12, 1986.

dering), and incoming background air. Filters were removed and packaged immediately after the completion of sampling maneuvers and were returned to our laboratory for analyses.

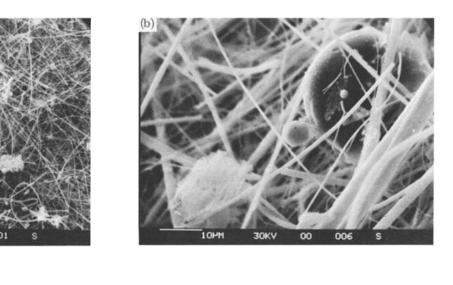
# ANALYSES

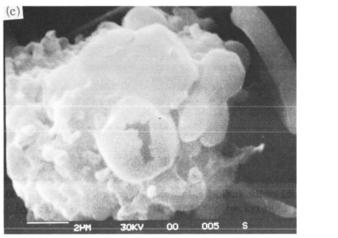
All filters were weighed before use and were reweighed after the experiment to determine accumulations. Chemical/ physical analysis of the particles consisted of scanning electron microscopy (SEM) for morphology, energy dispersive analysis of X ray (EDAX) for elemental composition, and particle extractions in a water/methanol mixture for subsequent ion chromatographic (IC) analysis of water soluble ion composition. The SEM-generated photomicrographs were not used to determine particle size distributions because the sampling was not conducted in the free-stream air, which precluded obtaining any quantitative number of mass densities (in microns per cubic meter) from our collections.

Extractions, followed by IC analyses, were performed on quartered portions of the Teflon filters. Mass densities (in microns per cubic meter) for soluble ions were calculated based on a premeasured  $0.4 \text{ m}^3 \text{min}^{-1}$  flow and a total collection time of 15 s. A Dionex model 14 ion chromatograph was used for the analyses. SEM analysis was performed on a Cambridge 150R coupled to an EDAX model 9100 with windowless detection.

# RESULTS

Representative SEM photomicrographs of the smoke particles collected on glass fiber filters are shown in Figures 2a-2d.





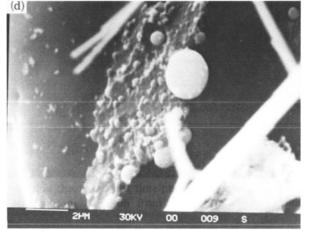


Fig. 2. Representative SEM photomicrographs of smoke collections.

Particles were found to extend over a broad range of sizes  $(0.1-100 \ \mu m)$ . Very often, particles would vaporize (either partially or totally) under electron bombardment in the microscope. These particles typically had high levels of carbon and oxygen associated with them, and the vaporized portions were probably composed of condensed nongraphitic carbon aerosols. Large particles with sides in excess of 50  $\mu$ m in length are visible in Figure 2a. Most of these particles, when examined at higher magnifications, were found to be composed of agglomerated spheres, with indications that coalescence had occurred (see Figure 2c). A hollow spherical particle can be seen in Figure 2c. These qualities are typical of combustion-generated particles. Individual submicron particles were also observed (see Figure 2d). A particle size distribution was not developed from these SEM photomicrographs because of the previously discussed potential collection bias. Although EDAX analysis was performed on many particles, quantitative analysis was impossible, since traces of many of the same elements were contained in or on the glass fibers that constituted the filters. However, notably enriched levels of elemental carbon, oxygen, magnesium, aluminum, silicon, calcium, and iron were almost always present in the aerosol.

Actual weighings of the nominally 1.0-g Teflon filters resulted in mean weight gains and standard deviations of  $0.0069 \pm 0.0028$  g for the four unexposed blank filters (denoted by U),  $0.0098 \pm 0.0037$  g for the five background filter

collections (denoted by B),  $0.0170 \pm 0.0133$  g for the five mixed stage combustion collections (denoted by M), and  $0.0278 \pm 0.0194$  g for the five vigorously flaming collections (denoted by F).

Results from the gaseous carbon dioxide (CO<sub>2</sub>) determinations using thermal conductivity chromatography and from the IC analyses are presented in units of microns per cubic meter in Table 2. Smoke plume samples show significant increases above ambient background levels for CO<sub>2</sub> and all measured water/methanol leached cations and anions. Smoke plume concentrations of soluble potassium (K<sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) are conspicuously elevated. Potassium has been previously identified and used as a tracer for biomass-burnproduced aerosol [Andreae, 1983; Ward, 1986; Andreae et al., 1988]; thus elevated levels were anticipated. Large amounts of soluble NO<sub>3</sub><sup>-</sup> were also determined. Hegg et al. [1987], in data collected during the same burn at higher altitudes from their C-131 aircraft, have also noted very high levels of  $NO_3^{-1}$ . Both sodium (Na<sup>+</sup>) and chloride (Cl<sup>-</sup>) ions are prominent in our smoke samples. Chloride is enriched above the  $Na^+/Cl^$ sea-salt ratio in the flaming collections but, surprisingly, not in the mixed collections. Phosphate  $(PO_4^{\equiv})$  anion can also be seen to have been leached from our smoke aerosol and is identified as a major soluble ionic product of this burn. We believe that this is the first time phosphate has been identified as a significant emission from a burning biomass plume.

Sample	CO <sub>2</sub> (×10 <sup>6</sup> )	Cl−	NO <sub>2</sub> <sup>-</sup>	PO <sub>4</sub> =	NO <sub>3</sub> -	SO4=	$C_2 O_4^{=}$	Na <sup>+</sup>	NH4 <sup>+</sup>	K+
18U	NA	0.3		0.8	1.3	6.2		4.9	6.2	3.4
20U	NA	0.3		0.7	1.0	6.2		6.7	7.7	2.9
21U	NA	0.1		0.6	1.0	4.8		6.7	7.2	3.3
22U	NA	0.2		0.9	1.0	5.3		4.7	6.2	3.1
5B	0.73	0.9		1.6	5.2	6.7	1.2	6.9	6.7	8.5
8B	0.74	0.7		1.8	7.8	7.2	2.1	6.4	6.5	6.1
11B	0.72	1.5		1.2	2.4	6.2	1.0	8.6	6.4	4.7
16B	0.73	1.0		1.4	5.0	6.6	1.0	6.0	7.0	6.3
19B	0.74	1.7		1.6	4.8	7.7	1.1	5.1	9.3	7.8
6M	0.83	6.9	1.9	9.0	56.6	33.7	3.4	14.9	12.9	47.0
10M	0.78	10.4	2.4	10.1	35.5	35.3	3.8	22.6	11.5	61.4
12M	0.80	6.9	4.3	6.5	48.9	33.8	3.6	16.8	9.1	85.5
13M	0.90	9.6	3.4	9.6	34.1	27.3	2.7	13.9	12.4	36.8
17 <b>M</b> *	0.83	14.4	1.9	15.0	79.2	47.9	4.5	14.9	17.2	105.8
4F	1.12	67.2	9.1	24.9	176.6	173.0	8.2	33.6	14.4	360.0
7F	1.36	64.4	9.6	27.8	144.5	170.9	8.0	50.4	13.9	320.0
9F	1.07	55.7	7.7	27.0	119.5	126.0	6.7	36.0	10.6	270.0
14F	1.18	49.5	7.6	21.6	115.7	120.7	6.2	21.6	11.5	260.0
15F	1.12	65.8	8.2	24.9	152.2	144.4	8.2	36.5	14.4	330.0

 TABLE 2.
 Mass Concentrations of Gaseous CO2 and of Water-Soluble Aerosol Ions Collected on Teflon Filters Over Lodi Canyon Prescribed Burn

U indicates unexposed filter; B, background sample; M, mixed stages of combustion; F, vigorous flaming combustion; NA, not applicable. Concentrations are given in micrograms per cubic meter. \*Two samplings on one filter.

Lesser, but still significant, amounts of oxylate  $(C_2O_4^{=})$ , ammonium  $(NH_4^{+})$ , and nitrite  $(NO_2^{-})$  ions were measured. Our analysis indicates a large excess of anions based on electroneutrality considerations. Although ionic calcium, aluminum, magnesium, etc., were not determined, it seems reasonable to expect from the ion charge imbalance that the aerosols were acidic.

The geometric means for the soluble ions are presented by category in Table 3. The  $CO_2$  normalized emission ratios of some of these means will be used later in this text during discussions about potential physical/chemical processes that might be occurring in the fire or in the aging smoke plumes, as they interact in the atmosphere.

# DISCUSSION

SEM examinations of the aerosols collected during the Lodi Canyon biomass burn have yielded several interesting results. Aerosol particles in general appeared larger than anticipated. While this result may be compromised somewhat, since our samplings were not made in an aerodynamical free-stream condition, some very large particles were clearly produced during the biomass burn. Results from Ward [1986] have indicated that a higher percentage of large particles are emitted from intensely flaming fires. Of additional interest is our observation that many of these large particles that appeared irregularly shaped actually consisted of smaller agglomerated spherical particles, which frequently showed signs of coalescence. All of these characteristics are typical of combustiongenerated particles. Small spherical submicron particles were also captured, but questions about our potential collection bias negate determination of a particle size distribution from these collections.

Many particles vaporized in the electron beam of the SEM/EDAX and were largely composed of carbon and oxygen. These aerosol particles were composed of nongraphitic carbon. Most of the nondestructible (in the electron beam) particles examined with EDAX had spectra that included significant amounts of carbon, magnesium, calcium, aluminum, silicon, and iron.

Geometric mean weight gain for filter-collected total aerosol had a large standard deviation in each category. Nevertheless, these mean weight gains were used to derive an estimate of the weight ratio of water-soluble inorganic aerosol to the total weight of accumulated smoke aerosol. Weight gain for the background filters was subtracted from the weight gain of the flaming samples to arrive at a total mean weight gain for the smoke aerosol. The same was done for the IC data; that is, background was subtracted from weight gain for flaming sample solubles. For these data the percentage of watersoluble inorganic material was estimated at about 2%. Although our analysis utilizes imprecise weight gain data, does not account for ongoing chemical reactions in the plume potentially generating further soluble aerosol, and does not account for all possible water-soluble inorganic ions, we feel that our estimate of 2% by weight of water-soluble inorganics in this smoke aerosol is a good first-order approximation.

TABLE 3. Geometric Mean Concentrations of Water-Soluble Aerosol Ions and Ratios of CO<sub>2</sub> Normalized Emissions From Flaming and Mixed Combustion

Category	Cl-	NO <sub>2</sub> <sup>-</sup>	PO₄ <sup>≡</sup>	NO <sub>3</sub>	SO4=	$C_{2}O_{4}^{=}$	Na <sup>+</sup>	NH4 <sup>+</sup>	K+
Background	1.0		0.6	3.3	1.3	1.3	0.8	0.4	3.5
Mixed	7.2	2.2	7.0	38.9	23.9	1.8	7.4	3.3	49.4
Flaming	59.5	8.4	23.9	137.5	139.7	6.2	29.0	5.8	301.3
$\Delta X / \Delta CO_2(F)$	1.9	0.9	0.8	0.8	1.3	0.8	0.9	0.4	1.4
$[\Delta X/\Delta CO_2(M)]$	-1						512		

170

150

130

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90

The mean for each  $CO_2$ -normalized ( $\Delta X/\Delta CO_2$ , with X equal to each ion, measured in micrograms per cubic meter) water-soluble ion in the flaming category was ratioed with its counterpart from the mixed category (F/M, see Table 3). If the extent of ambient air dilution of the smoke plumes primarily accounted for the differences in mass accumulations per cubic meter or sample volume for the ions measured or if the species were released in the same proportions during all stages of combustion, the calculated ratios (F/M) for each  $CO_2$ -normalized ion pair (e.g.,  $Cl_F^{-}/Cl_M^{-}$  versus  $NO_3^{-}F/$  $NO_3 M$  should be essentially the same and close to unity for the entire group of ion pairs. Table 3 reveals that most  $CO_2$ -normalized ion pair ratios (F/M) are essentially the same, generally falling between 0.8-0.9. That these ratios are somewhat lower than the ideal of unity may have been an artifact of our conversion of CO<sub>2</sub> mixing ratios from the units of their measurement (parts per million by volume (ppmv)) to concentration (microns per cubic meter). Our conversions may have slightly overpredicted CO<sub>2</sub> concentrations in the hotter less-dense "flaming" parcels relative to their "mixed" counterparts. This density effect would be expected to be less significant with the heavier and less mobile particles. If our conversions from ppmv to microns per cubic meter did overpredict in the manner suggested, a net lowering of the  $\Delta X / \Delta CO_2$ ratios for the flaming collections, relative to the mixed, would result. In turn, the overall ratios (F/M) would also be depressed somewhat from unity. We hypothesize that such an effect is reasonable and that the consistency of the  $CO_2$ -normalized emission ratios determined for  $NO_2^{-1}$ ,  $NO_3^-$ ,  $PO_4^=$ ,  $C_2O_2^-$ , and  $Na^+$  from these samplings, coupled with their closeness to unity, should be interpreted as evidence for a process predominantly reflecting additional dilution in the mixed stage smoke plume and/or constant proportion emissions during different stages of combustion.

Conspicuously, the corresponding ion pairs for  $NH_4^+$ ,  $Cl^-$ ,  $K^+$ , and  $SO_4^-$  do not fall within the established 0.8–0.9 emission ratio and thus do not appear to be as strongly governed by dilution or constant proportion emissions. Since the  $NH_4$ <sup>+</sup> ratio is very low (0.4), we suggest that conversion of ammonia gas (NH<sub>3</sub>) in the aging smoke plumes to  $NH_4^+$  ion on the particles is a reasonable explanation of this result. This conversion would be expected to occur quickly in an acidic environment, which might be implied by our excess of soluble anions. Hegg et al. [1987] have noted elevated NH<sub>3</sub> levels in smoke plume samplings from this burn. Our flaming samples were obtained earlier in the smoke cloud history and thus would be expected to have accumulated smaller levels of secondary (gas-to-particle conversion, condensation, etc.) aerosol. However, changes in the source emission rates of NH<sub>3</sub> from the burning biomass or the hot soils cannot be ruled out as an equally plausible explanation.

Chloride ion, based on its high CO<sub>2</sub>-normalized F/M ratio, appears to have decreased in concentration in the mixed smoke plumes. Whether this observation is the result of emission changes, smoke plume chemistry, or both, is uncertain. Ward [1986] has noted that potassium, chlorine, and sulfur emissions are strongly coupled to combustion temperature and are higher during intense flaming phases. Our elevated ion pair ratios for F/M chloride would seem easier to reconcile with Ward's observations than with mechanisms that necessitate the postulation of a loss of particulate chloride as the aerosol ages.

Hegg et al. [1987] also report high levels of SO<sub>2</sub> in the Lodi Canyon smoke plume samplings at higher altitudes. Given this alone, sulfate ratios might be expected to increase on the samples that were collected at higher average altitudes and at

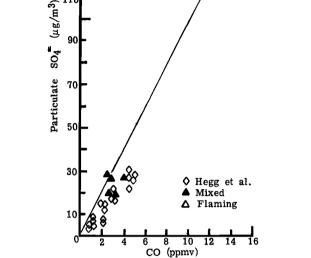


Fig. 3. Comparison of nitrate results from the December 12 Lodi Canyon prescribed fire.

times later in the smoke cloud history, as a result of chemical transformation of  $SO_2$  to  $SO_4^{=}$ . Sulfate concentrations determined from our analyses, however, indicate that sulfate was more heavily concentrated in the flaming samples. Again, our data would seem to support the conclusion of Ward, that sulfur emissions are higher during the flaming stages of combustion. However, collections categorized as flaming had an average collection altitude of 80 m above ground level, while mixed collections averaged 205 m. This might have complicated the interpretation, since intense fires generate large particles and the collection of large particles would be favored at lower altitudes.

Hegg et al. [1987] also made measurements of aerosol sulfate and nitrate in the Lodi Canyon smoke plume. Hegg's data thus allow us to compare our aerosol sulfate and nitrate measurements with a second independent data set. We have plotted our sulfate and nitrate results as a function of CO concentration in the same manner as the work by Heag et al. [1987] in Figures 3 and 4. Our CO mixing ratios were determined from collections made simultaneously with our Lodi Canyon particle collections [Cofer et al., 1988]. We have incorporated the results of Hegg et al. [1987] into these figures. Our data can be seen to be in general agreement with theirs. Our aerosol nitrate determinations appear to be in better agreement with theirs than our sulfate determinations do. It is both interesting and suggestive to note that NO<sub>3</sub><sup>-</sup>, unlike  $SO_4^{=}$ , was one of the soluble aerosols found to have a relatively constant F/M CO2-normalized emission ratio.

Similarly, we calculated  $\Delta K^+/\Delta CO_2$  emission ratios for flaming and mixed conditions for comparison with results obtained by Andreae et al. [1988] in smoke plumes over Amazonia. Our calculations yielded  $\Delta K^+/\Delta CO_2$  emission ratios of  $6.8 \times 10^{-4}$  and  $4.9 \times 10^{-4}$  for flaming and mixed, respectively Results from the Amazonian smoke plumes revealed a

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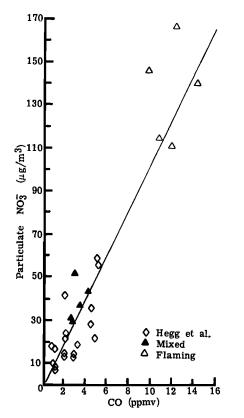


Fig. 4. Comparison of sulfate results from the December 12 Lodi Canyon prescribed fire.

mean  $CO_2$ -normalized emission ratio for potassium of 2.4  $\times 10^{-4}$ . Our  $\Delta K^+/\Delta CO_2$  emission ratios might be expected to be somewhat higher, since our samplings were made over intensely burning chaparral and represent relatively unaged collections.

#### **CONCLUSIONS**

Substantial quantities of particulate NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>=</sup>, and K<sup>+</sup> were released into the atmosphere during a prescribed chaparral burn in southern California. Significant amounts of soluble PO<sub>4</sub><sup> $\equiv$ </sup>, Cl<sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, and oxylate (C<sub>2</sub>O<sub>4</sub><sup>=</sup>) were also associated with the smoke aerosol. We believe this work represents the first quantitative measurement of phosphate from a biomass smoke plume. While concentrations of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup> $\equiv$ </sup>, Na<sup>+</sup>, and C<sub>2</sub>O<sub>4</sub><sup> $\equiv$ </sup> appeared to remain in relatively constant proportions in the smoke plumes, concentrations of NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, K<sup>+</sup>, and SO<sub>4</sub><sup> $\equiv$ </sup> appeared variable, suggesting possible changes in the source emissions during different stages of combustion or ongoing chemical reactions in the aging smoke plumes. The soluble ionic portion of the aerosol was estimated to be about 2% by weight.

Smoke particles were examined by SEM. Many large particles (>10  $\mu$ m) were observed. These particles appeared irregularly shaped at low magnifications, but examination at higher magnifications revealed that the large particles were agglomerated smaller spherical particles, some showing signs of coalescence. Many small discrete particles ( $\leq 1 \mu$ m) were present on the filters. A size distribution was not determined.

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