

Final Report, CAL/ARB Project A7-068-30

HYDROCARBON CHARACTERIZATION OF  
AGRICULTURAL WASTE BURNING

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## ABSTRACT

This project was initiated primarily to determine hydrocarbon speciation and emission factors from burning residues of 8 selected field and orchard crops in an out-of-doors, instrumented burning tower; factors for particulate, carbon monoxide and total hydrocarbon were calculated, as is normal for such projects. In addition, for the first time from such burning, factors were determined for oxides of nitrogen, sulfur dioxide and some aldehydes. Considerable modification of the tower was required to meet project objectives. Field crops were burned as head and back fires, and orchard crops were burned in piles. Emissions of particulate, CO and total hydrocarbons were considerably less from orchard than from field crops. Methane constituted more than 50 percent of the hydrocarbons below C<sub>6</sub> from both residue types, with olefins making up about 33 and 25 percent, respectively; more than 70 percent of the olefin was ethylene. Some 17 hydrocarbons above C<sub>6</sub> were detected but yields were extremely small, exceeding 0.5 pounds in only a few instances and usually being less than 0.1 or even 0.01 pounds per ton of fuel burned. More than 70 percent of the oxides of nitrogen from both residue types appeared as NO, the yields of NO and NO<sub>2</sub> being about 2.4 and 0.8 pounds per ton, respectively. No direct measurement of SO<sub>2</sub> was possible but sulfur losses during the burning of the two crop types averaged 1.4 and 0.3 pounds per ton, respectively. Not all of this went to SO<sub>2</sub>, but if it had, maximum yields would be double these figures. Detection of aldehydes was very erratic and not altogether reliable. Three compounds were found with some regularity, varying from 12 pounds to less than a few tenths of a pound per ton of fuel burned.

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At the University of California, Riverside, Ervin Mateer supervised the operation of the burning tower, Mike Kienitz designed and built the electronic control for the modified hydrocarbon sampling system and repaired analytical instruments when these instruments failed, and Leonard Zielenski provided and redesigned essential parts for temperature records and heating controls as well as servicing analytical instruments. Their very valuable contributions were much appreciated. Technical assistance during burning operations and treatment of much of the data was provided by James Clark. Minn Poe supervised the handling of all data submitted to the Computer Center. Both are to be commended for their help and suggestions. Finally, special thanks and appreciation are due Donna Shaw for her typing of all drafts of the final report, a task performed under difficult conditions since the writer was some 1200 miles from Riverside during preparation of the report.

## CONCLUSIONS

Again, as in the previous ARB project on emissions from agricultural burning, we conclude that emissions for particulate, carbon monoxide and hydrocarbon from fine fuels as represented by field crops are at least two to three times greater than from the coarser woody fuels of orchard crops. The yields of hydrocarbons from rice were generally lower than in previous studies. Since some values were nearly the same, and yields from other crops were comparable to those of previous studies, it does not seem unreasonable to us to conclude that differences in yields from rice are very possibly variations one might expect due to differences in fuel burning conditions with time. The beneficial effect of using back fires for lowering particulate yield was less apparent in the present study but this does not alter the conclusion that back firing is the preferred technique to minimize what appears to be the more objectionable pollutant from agricultural burning.

Saturated hydrocarbons are the most prevalent materials of 21 hydrocarbons analysed for up through C<sub>6</sub>. Olefin yields were about half those of saturated compounds and ethylene alone constituted almost 70 percent of the olefins. Ranked in descending order, approximate percentages were, methane, 56; ethylene, 20; other olefins, 9; and other saturates, 8. Thus moderately to highly reactive compounds (Classes II and III<sup>a</sup>) constitute about one-third of the total light hydrocarbons. Ethylene, even though its reactive half life is something like 4.5 hours, is important because it is the only hydrocarbon which has a direct injurious effect on a few types of ornamental flowers at ambient concentrations.

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<sup>a</sup>California Air Resources Board (CARB) Reactivity Classification of Organic Compounds. Appendix A.

While the analyses of hydrocarbons above  $C_6$  revealed an array of some 17 compounds which may be of interest, the yields were very low. Benzene, a hydrocarbon with low reactivity, was the only material in yields exceeding 0.5 pound per ton of residue burned. Most of the others were well below 0.1 pound and many were not more than a few thousandths of a pound. In this writer's estimation,  $C_6$  and greater hydrocarbons do not add greatly to the total quantity of reactive hydrocarbon emissions. But even if all of the hydrocarbons from barley and wheat (the highest yields of all 8 crops) are added, the total yields are only about 0.5 and 0.7 pound, respectively, and most of this is benzene.

The results presented for oxides of nitrogen are the first attempt to calculate yields of  $NO$  and  $NO_2$ . Nitrogen dioxide yields were less than 1.0 pound per ton of fuel burned. Since this is the principal material in initiation of photochemical reactions, the total yield for areas of agricultural burning would have to be calculated to determine if such burning constitutes a significant source. Also the rate of conversion from  $NO$  to  $NO_2$  of the relatively low yields of about 2 pounds of  $NO$  would have to be taken into consideration.

Sulfur dioxide has never before been considered as a separate entity in pollution from agricultural burning. Our attempts to identify and quantify the compound in the smoke were unsuccessful. Losses of sulfur from the burning fuel, however, were calculated and found to be a little more than one pound for field crops and about one-third pound for orchard crops. But it is reasonable to expect that some of the sulfur is converted to  $SO_2$  and the effect this might have on aerosol formation would have to await very careful examination by competent chemists.

The results of aldehyde analyses may have only limited value since the yields were so erratic and only three materials, isobutyrl-, croton-,

and hexanaldehyde were found with any degree of consistency. Yields were generally less than 10 pounds per ton of residue burned and often less than 1 pound. But since these are aliphatic aldehydes (Class III)<sup>a</sup> and thus have a high degree of reactivity, it is reasonable to conclude that their presence may be of some importance and worthy of further examination.

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<sup>a</sup>California Air Resources Board (CARB) Reactivity Classification of Organic Compounds. Appendix A.

## RECOMMENDATIONS

In previous projects where the emissions from burning a large number of crop residues were related to fuel moisture and burning techniques, it was fairly straightforward to recommend those procedures which minimize the objectional effects of the resulting pollution.

The task of recommendations is not that straightforward with the present project, because the objectives were different. The main thrust here has been to determine the species composition and emission factors of the hydrocarbons as well as factors for  $\text{NO}_x$ , sulfur dioxide, and some aldehydes from burning a few selected crop residues. The ARB would then decide how this new information fits into existing concepts and practices for controlling pollution in areas where agricultural burning is permitted. What does appear appropriate here is to suggest areas of concern.

Highly reactive olefins make up about one-third of those compounds below  $\text{C}_6$ , and ethylene is the major constituent. Since this is the only hydrocarbon that has a direct effect on vegetation, its presence should be considered in relation to other sources to determine if agricultural burning adds significantly to ambient concentrations.

Hydrocarbons of molecular weights greater than  $\text{C}_6$  make up an even smaller proportion of the hydrocarbons, and it seems reasonable to suggest that their occurrence is of minor relative importance in considering oxidant control strategy.

Agricultural burning has generally been considered to be a negligible source of oxides of nitrogen, but since this is the first report of emission factors for  $\text{NO-NO}_2$ , and the latter material is a prime reactant in the photochemical process, burning as a source should be considered in emission inventories.

Sulfur losses which might be converted to  $\text{SO}_2$  seem unimportant so far as direct plant damage is concerned and its priority for concern would be low except as it might be involved in aerosol formation. If the opportunity is ever presented, more work should be done to measure  $\text{SO}_2$  directly in the fire effluent, and if possible, determine the unknown sulfur compound that was occasionally found in the few direct measurements that were attempted.

The information on aldehyde emissions should be treated with some caution because of the erratic nature of the analyses. But the data should not be overlooked since Class III reactive materials were occasionally found in relatively large amounts.

## BODY OF REPORT

### INTRODUCTION

In an earlier project for determining the emission factors from the burning of 31 agricultural crop wastes (1), individual hydrocarbons were not analyzed; only the total hydrocarbon yield was determined. Staff of the California Air Resources Board (ARB) felt that a more detailed analyses should be made, at least on a few of the more important crops burned earlier. Therefore, appropriate arrangements were made between the ARB and the Statewide Air Pollution Research Center (SAPRC) at the University of California, Riverside (UCR) to burn 26 fires with the wastes from five field and three orchard crops using the same burning tower that had been developed for determining the nature and amounts of emissions from such fires.

For this particular study, several modifications in physical features and/or procedures of tower operations were made which permitted more data to be collected than was normally done in most previous projects. Additional data included NO-NO<sub>2</sub> analyses, estimates of SO<sub>2</sub> emissions, hydrocarbons above C<sub>6</sub>, and some aldehyde determinations.

### METHODS AND MATERIALS

#### Facilities

Procedures for burning wastes and sampling emissions were carried out in an out-of-door tower and adjacent instrument building which has been described earlier by Darley et al. (2) and modified as described in some detail in a National Academy of Sciences publication (3). A brief description of the tower was given in the final report of the previous ARB project (1) and will be repeated below. Details of the modifications required for

the present project are also given as well as a discussion of problems encountered.

The facility (Figure 1) simulates open burning but channels the combustion products so that representative samples of gas and particles can be taken. The tower is in the form of an inverted funnel, 16 feet in diameter at the base, decreasing to 29-1/2 inches in a length of 20 feet, and topped with a stack 8 feet in length. The tower is erected above a table 8 feet in diameter which is positioned on a scale with a maximum capacity of 125 pounds.

The sample site for gases, particulate, and for recording temperatures and airflow is in the stack about two feet below the top. Stack gases for analyses of total hydrocarbon, CO, and CO<sub>2</sub>, were drawn through sample lines into the appropriate analyzers located in the instrument building to give a continuous millivolt equivalent recording of concentrations.

Airflow was monitored with a 4-cup anemometer mounted in the stack. A shaft encoder is positioned on the end of the anemometer shaft, just outside of the stack. The encoder generates a millivolt signal by making and breaking a light beam through an 800-slot disc. One revolution of the shaft creates 800 pulses, and 3000 pulses per second generates the full-scale 50 mv signals. The maximum airflow encountered during the peak of the hottest agricultural fires is between 40-45 mv, or approximately 10,000 cubic feet per minute. Of course, the rate of air flow and thus the rpm of the anemometer shaft varies with fire intensity. As will be described in more detail below, this mechanical feature was used to regulate sampling rates for the modified hydrocarbon and nitrogen oxide sampling system.

Particulates are collected isokinetically on standard Type A-E glass

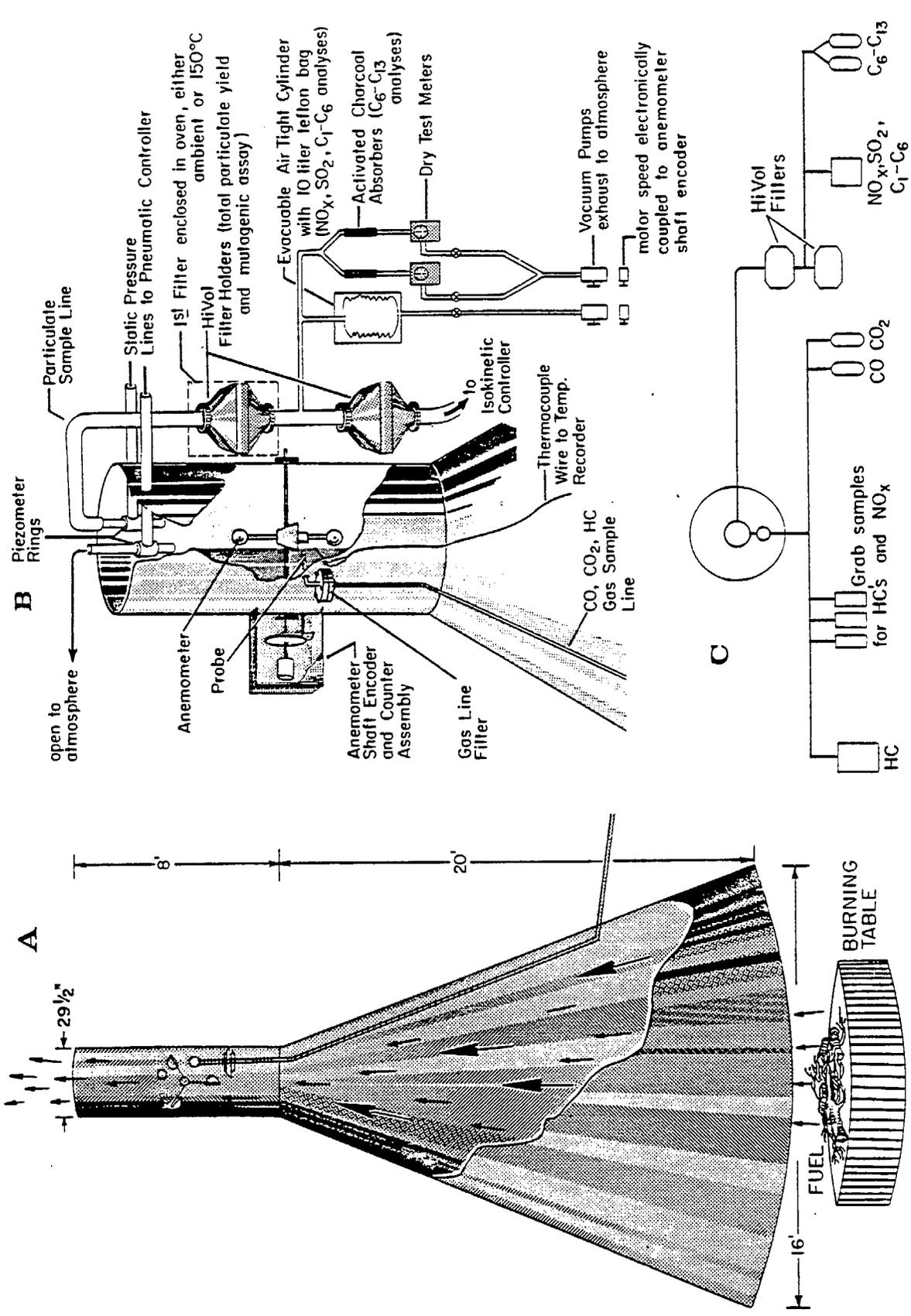


Figure 1. Drawing of UCR burning tower. (A) The unit showing relative position of the burning table, fuel bed, and stack. (B) Detail of instrumentation and sampling probes in the upper stack of the tower. (C) Schematic relationship of tower and instrumentation and/or sample sites. See text for detailed description.

fiber filters held in two modified HIVOL samplers positioned in series in the sample line and outside of the tower. A pneumatic controller senses differences in airflow in the stack and continuously adjusts a globe valve in the sample line so that isokinetic sampling is achieved. The sample volume is approximately 1/829th of the total flow through the stack. The principal use made of the isokinetic collection system has been to determine the total weight of particulate from given fuels to establish emission factors. For this project, the isokinetic sampling line was also used for the modified hydrocarbon and nitrogen oxide sampling system as described in more detail below.

In the past, data from all recording instruments were transferred to the Computer Center through a data acquisition system. The data from each fire was keypunched for subsequent processing by the Computer Center using a program from which the yield of pollutants in pounds per ton of fuel burned was calculated using information on temperature, gas concentrations, and airflow.

The first major modification was in the manner of sampling for individual hydrocarbons and this consisted of a bifurcated subsample system (see Figure 1,B). In all previous studies, if individual hydrocarbons were to be analyzed, grab samples were collected in 250 ml gas-sample bottles at specified intervals during the fire and run on a gas chromatograph. In the present study, ARB requested that an integrated sample be taken throughout the course of each fire. The isokinetic particulate line was tapped at a point between the two filters and a bifurcated line installed. One

leg was further split and led to two activated charcoal absorber tubes, and the second leg led to an inflatable Teflon bag. Sample air was drawn through the absorber and bag lines by individual vacuum pumps, the motors of which were electronically coupled to the anemometer shaft encoder. Thus, representative integrated samples were assured by two means. First, subsamples of air were taken from the isokinetic line whose flow was regulated by the Bristol pneumatic regulator. The subsample flow rate was also related to the total flow out of the stack because the speed of the pump motors was regulated by the speed of the anemometer. Dry test meters and needle valves were installed down stream from the charcoal absorbers so as to record and further regulate total volume. Specifications indicated that we should not exceed about 3 liters per minute at the peak of the fire, but that total volume collected should be at least 10 liters. The inflatable Teflon bag was enclosed in an air-tight cylinder so that as the cylinder was evacuated, the bag would fill. A valve down stream from the bag permitted regulation of total volume of about 10 liters during the fire.

Considerable time and effort involving numerous head and back test fires was required to successfully operate this system. First, the electronics to regulate the pump motor speed had to be designed and built for this specific use. The needle valves had to be preset, ideally, so that no adjustment need be made during a fire in order to obtain the desired flow rates through the absorbers and into the bag. Since no two burning days were exactly alike in temperature, wind and humidity, head fires burn

differently from back fires, and no two crop residues burn the same, it was impossible to exactly preset the valves; fine adjustments had to be made occasionally during fires.

While this system was designed principally for hydrocarbon analyses, we were also able to use the air in the bag sample for direct analysis of NO and NO<sub>2</sub>.

The second principal modification of the tower facilities was to provide for heating the first particulate filter, and thus the hydrocarbon gas sample collected below it, to temperatures approaching 150°C. This was done mainly for the purpose of keeping hydrocarbon species, particularly those above C<sub>6</sub>, in the gas phase as they passed through the first filter and to minimize condensation as may have occurred in previous studies. The sample line above the filter holder had been wrapped with heating tape and the filter enclosed within a laboratory-type drying oven when the unit was assembled some years ago, but the apparatus had not been used extensively. Thermostats and controls provided with the oven were not sufficient to maintain the temperatures required for this project. Additional heaters and controls were added. Thermocouples were installed in the line above the oven, in order to monitor temperatures in the sample line, and within the filter holder itself just above the filter paper. After it was determined that the heating tape and thermostat in the sample line were quite reliable, the thermocouple from that site was moved into the second filter holder just above the filter paper.

Again, there was considerable time and effort required to learn how to adjust controls in order to maintain as near as possible the 150°C temperature in the first filter holder as requested. Since the heat from

the source from within the oven had to first heat the metal of the filter holder and then the moving air within the holder, there was considerable lag in response to any adjustments made in the heating control. This was partially overcome by preheating sample air in the line above the oven. But since the system was dynamic and we had no control over ambient temperatures or the variable temperatures of the fires due to differences in head or back firing and fuel composition, we empirically overshot the desired temperatures just before ignition and then manually operated the 3 switches (1 for the heating tape and 2 for the oven) during the fires.

For example, while all air systems were static just before ignition, the line above the oven was heated to about 210°C and the air within the holder to about 187°C. Since the first air moving into the system following ignition was relatively cool, temperature in the line dropped to about 100°C and the heating tape was turned on. If we were fortunate in our estimate, the temperature within the holder dropped to 150°C. Depending on the temperature trend as shown by the recorder, oven switches were turned on and off during the fire. Generally at a point about three quarters through the fire when air flow and fire temperatures were decreasing, the heating tape surrounding the sample line above the oven was switched off so as not to add excessive heat to the oven. To say the least, temperature regulation during each fire was most frustrating, because once ignition occurred, there was no opportunity for a "re-take" in case the "action" did not suit the needs of the "director".

The third modification, and one not shown in Figure 1, was the installation of an impinger sampling train for aldehydes. The sampling probe was inserted into the stack adjacent to that for the normal gas sample

line. The ice bath holding the impingers was placed on a temporary platform next to the stack so that sampling line connections were as short as possible. An air flow line from the outlet of the last impinger was connected to a rotometer and vacuum pump with needle valves placed near ground level.

### Analyses

When this project was first conceived, the principal change in analytical procedures was to be the analysis of hydrocarbons above  $C_6$ . As the program developed it was decided to use the Teflon bag sample for analysis of  $NO-NO_2$  and possibly  $SO_2$ . Additionally  $SO_2$  was to be estimated by differences in the sulfur content of the unburned fuel and resultant ashes and finally, a sampling train was to be installed for collection of and subsequent analysis of aldehydes. Pertinent details of the various procedures are given below.

Hydrocarbons -- The two charcoal absorbers from each fire mentioned above were used to provide samples to two laboratories. One absorber was given to the Analytical Research Laboratories, Inc. (ARLI) in Monrovia. The second absorber was given to the Chemistry Section of SAPRC at UCR. Each laboratory was to use their respective techniques for analyzing hydrocarbons above  $C_6$  by combined gas chromatography-mass spectroscopy. ARLI analysed each absorber individually, e.g., within barley, there were four absorbers, one for each of the two head fires and one for each of the two back fires. On the other hand, since SAPRC had agreed to do only one sample from each of the eight fuels, it was decided that only head fires would be run because experience had shown that these fires generally gave a higher hydrocarbon yield than back fires. Further, the absorbers from the two head fires were combined into one sample in order to maximize the yield. Similarly, the two absorbers from the duplicate pile fires within orchard fuels were

combined for the SAPRC analyses.

ARLI stated in their proposal that they would follow procedures employed in a hydrocarbon inventory program for KVB, Inc., the details of which were contained in their final report to ARB. For the present project the hydrocarbons were eluted from the charcoal tube with 2 ml of carbon disulfide. Four  $\mu$ l of the CS<sub>2</sub> solution were injected in a 6' Porapak Q column, the effluent of which went to a jet type molecular separator and on into a 21-104 mass spectrometer. Quoting from ARLI's report: "The mass spectra obtained were very weak because of the extremely small amounts of components present. Identification could be made for the C<sub>3</sub> and C<sub>4</sub> components which appear before the CS<sub>2</sub> elution, but the subsequent CS<sub>2</sub> elution interfered with identification of C<sub>5</sub> through C<sub>7</sub> materials." Although in this section of our report we are still dealing with methods, it is important to note here that no materials above C<sub>7</sub> were reported by ARLI. As will be noted below, SAPRC employed a capillary column which allowed for better resolution of small amounts of materials which ARLI's techniques did not reveal.

Dr. Schmid at SAPRC conducted the GC-MS analyses and his methods are summarized below. The two charcoal tubes were combined in a flask for extraction. The particles were covered with approximately 3-6 ml of CS<sub>2</sub> and the flask contents shaken for a time. The liquid was then removed with a pipette and transferred to a second flask. The latter procedure was repeated 3-4 times using 1-2 ml CS<sub>2</sub>. The extracts were concentrated under vacuum with a Rotovapor at room temperature but the final volume was not noted. One and one-half to 2.0  $\mu$ l of the resultant solution were injected into the Hewlett-Packard 5700 GC capillary column (32m x 0.44mm I.D.) coated

with Ucon LB using helium as the carrier gas. Temperature was programmed at 4°/min from 27°C to 140°C.

Oxides of Nitrogen -- As soon as the filled Teflon bag was removed from the tower, it was placed in a larger black plastic bag to prevent any photo reactions. After the second of a given pair of fires, the two bags were carried to the Chemistry building where a small portion of the bag contents was analysed for NO and NO<sub>2</sub> on a Beckman Model 952 analyser.

Sulfur Dioxide -- Sulfur lost to the atmosphere was determined by analyzing the sulfur content of the unburned fuel and of the resultant ashes. The analyses were performed by the laboratories of E. S. Babcock and Sons, Riverside, using perchloric acid digestion. Once the amount of sulfur lost was determined, the maximum possible yield of SO<sub>2</sub> was calculated assuming that all of the sulfur lost went to SO<sub>2</sub>.

A second method was attempted by analyzing the SO<sub>2</sub> content in the Teflon bag sample using the 1400 GC and FPD detector contained in the ARB Trailer located at UCR. The results were so erratic that, after considerable work involving many extra test fires, the method was abandoned.

Aldehydes -- Sampling and analysis for aldehydes followed the Stump method<sup>a</sup> from the Environmental Protection Agency. Two impingers are used in series for each sample. In the early part of the study, we were able to obtain only one of the correct sized impinger (approximately 100 ml) and had to use smaller impingers. We therefore used the large impinger upstream and two smaller ones down stream. Sampling air flow rate was approximately 1.5 l/min for the field crop fires and 1.0 l/min for orchard crop fires. The absorbing reagent was a saturated solution of

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<sup>a</sup>"Oxygenated Compounds in Automobile Exhaust--Gas Chromatographic Procedure," by Fred Stump. Mimeographed, 15 pp., Research Triangle Park, NC.

2,4-dinitrophenylhydrazine in 2N HCl. At the end of each fire, the impingers were rinsed into glass stoppered bottles and stored in the refrigerator until it was convenient to deliver them to ARLI for analysis.

The 2,4-dinitrophenylhydrazones of the aldehydes and ketones were extracted from the absorber solutions using n-hexane. The extracts were then evaporated to dryness under a stream of dry nitrogen at room temperature and taken up in 2 ml of a solution of anthracene (as internal standard) in benzene. Approximately 2  $\mu$ l of these solutions were injected into a GC column (9 ft x 1/8 inch O.D.) packed with 3 percent dexil on gas chrom Q 80/100 mesh to determine aldehyde and ketones in the combustion sample.

#### Plant Residue Samples

Samples of plant residues to be burned were collected in the field by ARB staff and air-freighted to Riverside. Five field crops and three orchard crops as noted below were collected.

#### Field Crops

Barley  
Corn  
Rice  
Sorghum  
Wheat

#### Orchard Crops

Almond  
Grape  
Peach

While not strictly classified as an orchard crop, grape is designated as such here to simplify preparation of tables and discussion of results.

#### Burning Procedure

Field Crops -- Two head fires and two back fires were conducted with each fuel. Head fires are defined as burning with the wind or up-slope. Back fires are defined as burning against the wind or down-slope. The two fire types were simulated in the tower by placing the fuel on a rack set

at a 25 percent slope.

Due to different collection times, variable heavy rains in the collection area, and various delays for modifications and test fires at the tower, the field crop residues arrived with vastly different fuel moisture contents. They were therefore all dried down to air-dry moisture content and remoistened a day or two before burning. At that time the air-moisture content was determined and sufficient water sprayed onto a given weight of fuel to bring the moisture up to about 13-15 percent based on the dry weight of the fuel. As soon as the fuel was moistened, it was placed into a large plastic bag and held for at least 24 hours. Just before the fuel was placed on the burning table, a small sample was taken and oven dried to determine moisture content.

Orchard Crops -- Orchard wastes were burned in piles, the fires being conducted in pairs. Since the fuels were received in a fresh condition, it was necessary to dry them down to the range of about 25-35 percent moisture on a dry weight basis. On the day the fuels arrived, two piles of 40 pounds each were weighed out and placed on a plastic sheet to permit easy handling. At the same time the moisture content of the fuel was determined. The piled fuel was then placed in a storage room and allowed to dry. Given the moisture content and the original weight of the pile, the weight that the pile should be when the desired moisture was reached was calculated. The rate of weight loss was monitored every two weeks by weighing each pile. Because bad weather and some instrumentation problems did not always permit us to burn when we wished, the grape and peach wastes dried down below the moisture content desired.

## RESULTS AND DISCUSSION

### Emissions of Particulates, Carbon Monoxide and Hydrocarbons

Emissions of particulates, CO and hydrocarbons in terms of pounds per ton of fuel burned for all 26 fires are given in Table 1. Crops are arranged alphabetically within the two categories and are not necessarily listed in the order burned. Type of fire and the moisture level are also shown.

Particulates -- Yields of particulate matter in this study were somewhat less for both field and orchard crops than in the previous ARB project (1). Averages in pounds per ton of fuel burned were, respectively, 18.3 and 6.3 pounds for field crops and 5.4 and 2.5 pounds for orchard crops. This was to be expected since the first filter was heated to 150°C and this in turn caused the second filter to be heated to approximately 93°C. Under conditions of the higher heat, materials would not condense as easily and would tend to pass on through the filters.

Particulate yields varied from a high of over 15 pounds per ton of fuel burned with barley and wheat head fires to a low of 1 pound or less with sorghum. It should be pointed out that yields from sorghum in the earlier study were very high (22 pounds from head fires), and this undoubtedly was due in a great part to differences in moisture of this fuel in the two studies, namely 55 versus 15 percent. Back fires usually yield less particulate than head fires, but this was true only for barley and wheat. Corn, rice and sorghum although quite low in particulate in both head and back fires, yielded slightly more with back fires.

Particulate yield from the three orchard crops was very low, ranging from 1.9 to 3.1 pounds; as a group, orchard fuels were again lower in particulates than field crops, the average being 2.5 and 6.3 pounds, respectively.

Table 1. Emissions of Particulate, Carbon Monoxide and Hydrocarbons from Burning Residues of Several Field and Orchard Crops.

Crop	Type of Fire	% Moisture dry wt. basis	Emissions, lbs. per ton fuel burned		
			Part. <sup>a</sup>	CO	HC
<u>Field Crops</u>					
Barley	Head	12.0	16.7	142.6	15.6
		<u>12.2</u>	<u>14.8</u>	<u>155.7</u>	<u>22.0</u>
	av.	12.1	15.8	149.2	18.8
	Back	13.4	8.0	152.2	14.4
		<u>12.7</u>	<u>11.7</u>	<u>154.4</u>	<u>10.8</u>
av.	13.0	9.9	153.3	12.5	
Corn	Head	15.7	4.3	72.3	6.3
		<u>16.4</u>	<u>4.4</u>	<u>71.2</u>	<u>5.1</u>
	av.	16.1	4.4	71.8	5.7
	Back	15.4	6.1	93.2	8.6
		<u>14.5</u>	<u>5.3</u>	<u>101.4</u>	<u>6.5</u>
av.	15.0	5.7	97.2	7.6	
Rice	Head	12.1	0.9	— <sup>b</sup>	2.1
		<u>13.4</u>	<u>1.8</u>	—	<u>3.5</u>
	av.	12.8	1.4		2.8
	Back	14.7	1.6	—	2.3
		<u>15.1</u>	<u>2.0</u>	—	<u>3.2</u>
av.	14.9	1.8		2.8	
Sorghum	Head	15.1	0.3	49.5	2.1
		<u>14.9</u>	<u>0.2</u>	<u>52.4</u>	<u>2.1</u>
	av.	15.0	0.3	51.0	2.1
	Back	20.8	1.0	55.8	2.9
		<u>18.2</u>	<u>1.0</u>	<u>72.7</u>	<u>4.1</u>
av.	19.5	1.0	64.3	3.5	
Wheat	Head	14.4	15.9	150.7	17.7
		<u>14.7</u>	<u>15.3</u>	<u>155.6</u>	<u>18.5</u>
	av.	14.6	15.6	153.2	18.1
	Back	14.9	7.9	127.7	7.0
		<u>14.3</u>	<u>5.6</u>	<u>132.1</u>	<u>11.7</u>
av.	14.6	6.8	129.9	9.4	

<sup>a</sup>Particulate samples collected at 150°C, which was different procedure than utilized in previous studies.

<sup>b</sup>CO instrument inoperative.

Table 1. (continued)

Crop	Type of Fire	% Moisture dry wt. basis	Emissions, lbs. per ton fuel burned		
			Part.	CO	HC
<u>Orchard Crops</u>					
Almond	Pile	26.2	2.1	31.3	4.7
		<u>26.2</u>	<u>1.7</u>	<u>27.1</u>	<u>4.2</u>
		av. 26.2	1.9	29.2	4.5
Grape	Pile	13.5	2.5	31.2	4.5
		<u>13.5</u>	<u>2.2</u>	<u>37.7</u>	<u>5.3</u>
		av. 13.5	2.4	34.5	4.9
Peach	Pile	15.7	3.1	32.5	2.9
		<u>15.7</u>	<u>3.0</u>	<u>31.5</u>	<u>3.5</u>
		av. 15.7	3.1	31.9	3.2
Average values for:					
	Field Crops	14.8	6.3	108.7	8.3
	Orchard Crops	15.1	2.5	31.9	4.2

Carbon Monoxide -- Emissions of carbon monoxide from field crops ranged from a low of 51 pounds with sorghum head fires to a high of 153 pounds with barley back fires and wheat head fires. Corn was intermediate in CO yields. As in previous studies, there was no consistent pattern showing an effect of head or back firing on CO yields. No data was obtained from rice fires. This was the last crop to be burned in the study and the CO instrument became inoperable just a few days before. Since special parts were required for its repair, we proceeded with the fires rather than delay the study any further.

The yield of CO from orchard fuels was quite consistent and varied little from the average of about 32 pounds per ton of fuel burned. Again the yields were considerably lower than from field crops, being 31.9 and 108.7 pounds, respectively. The yield from these three crops were similar to that of the previous study, although the average from all 13 orchard crops of that study was higher (54.3 pounds).

Hydrocarbons -- Emissions of hydrocarbon from field crops varied from a high of 18.8 pounds from barley head fires to a low of 2.1 pounds from sorghum head fires. The yields from barley and wheat are somewhat comparable to that from the previous study, but yields from corn, rice, and sorghum are quite a bit lower. In an earlier review of these data with staff of ARB, some concern was evident and questions of errors in calibration and calculations were raised. The hydrocarbon instrument was calibrated every burn day from a tank that had been on hand for over a year, but the contents of this tank were checked periodically on a GC. The calculations were also checked and verified. Thus the differences in results need to be discussed from other points of view. But first, it is pertinent to go on to

the results from burning the orchard crops and to note that the hydrocarbon yields from almond, grape and peach were not much different from those of the earlier study when the nearest comparable moisture and fire type are considered. The average value from the present study was 4.2 pounds while that from the earlier project was 3.0 pounds. Further, the yields of hydrocarbon from barley and wheat are also more nearly comparable to those of the earlier project. Thus, as fuels were burned randomly with time, some data agreed with variations in fuel and burning conditions rather than instrumentation. Also, if we go back to the Project Clean Air report (3, page 39, Fig. 11), we note that the hydrocarbon yield from some rice fires was not too different from those of the present study. In other words, it does not seem unreasonable to us to conclude that differences in yields from rice are very possibly variations one might expect due to differences in fuel burning conditions with time. One reason for the low yields from sorghum may be the much lower fuel moisture. No explanation for the low values in corn can be given except those of variation noted above.

Speciation and Yield of Individual Hydrocarbons -- As noted earlier, individual hydrocarbons were analysed from the integrated bag sample and from two sets of activated charcoal absorbers.

(1) Integrated bag samples

These samples were analysed at SAPRC by gas chromatography calibrated for 21 hydrocarbons up to C<sub>6</sub> which can appear in fire effluents. One chromatograph with a 5 foot Poropak N column, was used for methane, ethylene and ethane. A second instrument, with a 36 foot, 10 percent dimethylsulfolane column was used for the following compounds, listed in the order of emergence.

propane	3-methyl butene-1
propylene	1,3-butadiene
isobutane	methyl acetylene
n-butane	1-pentene
acetylene	2 methyl butene-1
1-butene	trans-2-pentene
isobutene	cis-2-pentene
trans-2-butene	2-methyl butene-2
cis-2-butene	

Most of the samples contained compounds up through cis-2-butene. Occasionally, compounds up through 1-pentene were found but very seldom did any hydrocarbon emerge beyond this point. The results of these analyses, expressed as percent yield of methane, other saturates, olefins, and acetylene are presented in Table 2.

By averaging the yields, it is seen that methane constituted more than half of the hydrocarbons found in both field and orchard crops, being 53.1% and 58.7%, respectively. Olefins were the next most plentiful, the yields being 32.7% and 24.9%, respectively, for field and orchard crops. Other saturates and acetylene were each less than 10 percent of the total. It is important to note here that ethylene was the largest component of the olefins; this hydrocarbon constituted 69.1% of the olefins from both field and orchard crop fires. Thus ethylene ranked second to methane in yield, being 22.6% and 17.2% of the total from field and orchard crops, respectively.

In general, the yield of a given hydrocarbon group from the various crops did not vary greatly from the above averages. Nor did the yield from head fires differ much from back fires. One exception might be the relatively higher yield of methane and lower yield of olefins from sorghum head fires which made these fires more nearly resemble those from orchard crops. Otherwise, orchard crop fires consistently produced more methane

Table 2. Percent Yield of Methane, Other Saturates, Olefins, and Acetylene from Integrated Bag Samples Taken During the Burning of Several Field and Orchard Crops.

Crop	Type of Fire	Percent of Hydrocarbons in Sample			
		Methane	Other Sat.	Olefins	Acetylene
<u>Field Crops</u>					
Barley	Head	47.5	17.2	31.7	3.6
		<u>51.0</u>	<u>10.9</u>	<u>34.4</u>	<u>3.8</u>
	av.	49.3	14.1	33.0	3.7
	Back	50.5	6.1	36.4	7.0
		<u>56.0</u>	<u>5.4</u>	<u>32.0</u>	<u>6.6</u>
	av.	53.3	5.7	34.2	6.8
Corn	Head	54.0	11.1	30.7	4.1
		<u>57.7</u>	<u>9.1</u>	<u>28.4</u>	<u>4.8</u>
	av.	55.9	10.1	29.6	4.5
	Back	52.9	9.4	31.4	6.3
		<u>---</u>	<u>---</u>	<u>---</u>	<u>---</u>
	av.	52.9	9.4	31.4	6.3
Rice	Head	59.4	5.6	28.3	6.8
		<u>49.0</u>	<u>7.5</u>	<u>37.7</u>	<u>5.9</u>
	av.	54.2	6.5	33.0	6.4
	Back	52.0	6.1	35.1	6.8
		<u>49.7</u>	<u>6.9</u>	<u>36.5</u>	<u>6.9</u>
	av.	50.1	6.5	35.8	6.9
Sorghum	Head	61.3	6.5	28.3	3.9
		<u>64.5</u>	<u>7.2</u>	<u>23.5</u>	<u>4.8</u>
	av.	62.9	6.9	25.9	4.3
	Back	57.0	6.8	30.2	6.0
		<u>53.3</u>	<u>7.7</u>	<u>33.1</u>	<u>5.9</u>
	av.	55.1	7.3	31.6	6.0
Wheat	Head	48.2	7.8	36.6	7.5
		<u>47.3</u>	<u>7.8</u>	<u>37.3</u>	<u>7.6</u>
	av.	47.7	7.8	37.0	7.6
	Back	50.9	5.1	33.6	10.6
		<u>48.1</u>	<u>5.3</u>	<u>37.6</u>	<u>9.0</u>
	av.	49.5	5.2	35.5	9.8

Table 2. (continued)

Crop	Type of Fire	Percent of Hydrocarbons in Sample			
		Methane	Other Sat.	Olefins	Acetylene
<u>Orchard Crops</u>					
Almond	Pile	61.0	8.3	24.8	5.9
		<u>60.0</u>	<u>9.3</u>	<u>25.0</u>	<u>5.6</u>
	av.	60.5	8.8	24.9	5.8
Grape	Pile	50.6	9.7	29.1	10.6
		<u>57.4</u>	<u>9.5</u>	<u>26.7</u>	<u>6.4</u>
	av.	54.0	9.6	27.9	8.5
Peach	Pile	58.4	6.2	23.5	11.9
		<u>65.1</u>	<u>7.1</u>	<u>20.5</u>	<u>7.4</u>
	av.	61.7	6.7	22.0	9.6
Average values for:					
Field Crops		53.1	8.0	32.7	6.2
Orchard Crops		58.7	8.4	24.9	7.0

and less olefins than did field crop fires.

(2) Activated charcoal absorbers

These samples were analysed by ARLI and by the chemistry section of SAPRC at UCR. As noted earlier, the ARLI techniques did not reveal any compounds above toluene, while the more sensitive methods used by SAPRC detected measurable quantities of some 17 compounds at C<sub>6</sub> or above. The hydrocarbons detected expressed in parts per billion and in pounds emitted per ton of fuel burned, are given in Table 3.

The analytical results for benzene and toluene, the only hydrocarbons reported by both laboratories, did not agree except for those of toluene from almond fires. Disagreement was usually less than a factor of 2 and the distribution of one laboratory reporting low values and the other reporting high values was about equal. One consistency, however, is the fact that the highest values for benzene and toluene reported by both laboratories were from barley and wheat fires.

Of all of the hydrocarbons detected, only benzene had yields in excess of 0.5 pound per ton of fuel burned, and this occurred only in barley head fires at 0.728 pounds and in wheat head and back fires at 0.734 and 0.618 pounds, respectively. Toluene was the next most plentiful with barley and wheat head fires again giving the highest yields at 0.297 and 0.185 pounds, respectively. In all but two instances, the yields of all other compounds from all fuels was well below 0.030 pounds per ton of fuel burned and in most cases yields did not exceed a few thousandths of a pound; the two exceptions were styrene from wheat head fires at 0.041 pounds and ethylbenzene from peach fires at 0.045 pounds. Even if all of the hydrocarbon values from the UCR analyses for barley and wheat (the

Table 3. Emissions of Hydrocarbons above C<sub>6</sub> from Burning Residues of Several Field and Orchard Crops.

Hydrocarbon	Head Fire				Back Fire	
	Conc. in charcoal tube sample, ppb.		Emissions, lbs/ton of fuel burned		Conc. in charcoal tube sample, ppb.	Emissions, lbs/ton of fuel burned
	ARLI <sup>a</sup>	UCR <sup>b</sup>	ARLI	UCR	ARLI <sup>a</sup>	ARLI
	<u>BARLEY</u>					
Benzene	795	270	0.728	0.247	150	0.183
Toluene	<u>275</u>	120	<u>0.297</u>	0.130	<u>25</u>	<u>0.036</u>
Ethylbenzene		15		0.019		
p-Xylene		5		0.006		
m-Xylene		16		0.020		
o-Xylene		8		0.010		
Tetrachloroethane		---		---		
Chlorobenzene		---		---		
Styrene		17		0.021		
Furfural		25		0.028		
1,2,4, Tetramethylbenzene		3		0.004		
p/m Ethylbenzene		---		---		
Phenylacetylene(?)		---		---		
Benzaldehyde		6		0.008		
Benzofuran		7		0.010		
Indene		5		0.007		
Napthalene		6		0.009		

<sup>a</sup>Values are average of two head fires and two back fires.

<sup>b</sup>Values are single analysis of the combined charcoal tubes of the two head fires. Back fires were not analysed at UCR.

Table 3. (continued)

Hydrocarbon	Head Fire				Back Fire	
	Conc. in charcoal tube sample, ppb.		Emissions, lbs/ton of fuel burned		Conc. in charcoal tube sample, ppb.	Emissions, lbs/ton of fuel burned
	ARLI <sup>a</sup>	UCR <sup>b,c</sup>	ARLI	UCR	ARLI <sup>a</sup>	ARLI
			<u>CORN</u>			
Benzene	101	140	0.093	0.129	172	0.214
Toluene	<u>56</u>	34	<u>0.061</u>	0.037	<u>67</u>	<u>0.098</u>
Ethylbenzene		4		0.005		
p-Xylene		2		0.003		
m-Xylene		4		0.005		
o-Xylene		6		0.008		
Tetrachloroethane		6		0.012		
Chlorobenzene		3		0.004		
Styrene		6		0.007		
Furfural		4		0.005		
1,2,4, Tetramethylbenzene		---		---		
p/m Ethylbenzene		---		---		
Phenylacetylene(?)		---		---		
Benzaldehyde		---		---		
Benzofuran		---		---		
Indene		---		---		
Napthalene		---		---		

<sup>a</sup>Values are average of two head fires and two back fires.

<sup>b</sup>Values are single analysis of the combined charcoal tubes of the two head fires. Back fires were not analysed at UCR.

<sup>c</sup>An unknown (assume 8 carbons) was detected at 2 ppb.

Table 3. (continued)

Hydrocarbon	Head Fire				Back Fire	
	Conc. in charcoal tube sample, ppb.		Emissions, lbs/ton of fuel burned		Conc. in charcoal tube sample, ppb.	Emissions, lbs/ton of fuel burned
	ARLI <sup>a</sup>	UCR <sup>b</sup>	ARLI	UCR	ARLI <sup>a</sup>	ARLI
			<u>RICE</u>			
Benzene	172	100	0.099	0.057	109	0.082
Toluene	<u>40</u>	36	<u>0.027</u>	0.024	<u>4</u>	<u>0.004</u>
Ethylbenzene		8		0.006		
p-Xylene		3		0.002		
m-Xylene		7		0.006		
o-Xylene		5		0.004		
Tetrachloroethane		---		---		
Chlorobenzene		16		0.013		
Styrene		7		0.005		
Furfural		---		---		
1,2,4, Tetramethylbenzene		3		0.003		
p/m Ethylbenzene		---		---		
Phenylacetylene(?)		---		---		
Benzaldehyde		---		---		
Benzofuran		1		0.001		
Indene		3		0.003		
Napthalene		3		0.003		

<sup>a</sup>Values are average of two head fires and two back fires.

<sup>b</sup>Values are single analysis of the combined charcoal tubes of the two head fires. Back fires were not analysed at UCR.

Table 3. (continued)

Hydrocarbon	Head Fire				Back Fire	
	Conc. in charcoal tube sample, ppb.		Emissions, lbs/ton of fuel burned		Conc. in charcoal tube sample, ppb.	Emissions, lbs/ton of fuel burned
	ARLI <sup>a</sup>	UCR <sup>b</sup>	ARLI	UCR	ARLI <sup>a</sup>	ARLI
	<u>SORGHUM</u>					
Benzene	34	150	0.028	0.125	52	0.056
Toluene	<u>1</u>	20	<u>0.001</u>	0.020	<u>2</u>	<u>0.003</u>
Ethylbenzene		3		0.003		
p-Xylene		2		0.002		
m-Xylene		4		0.005		
o-Xylene		3		0.003		
Tetrachloroethane		---		---		
Chlorobenzene		5		0.006		
Styrene		---		---		
Furfural		---		---		
1,2,4, Tetramethylbenzene		---		---		
p/m Ethylbenzene		---		---		
Phenylacetylene(?)		---		---		
Benzaldehyde		---		---		
Benzofuran		---		---		
Indene		---		---		
Napthalene		2		0.003		

<sup>a</sup>Values are average of two head fires and two back fires.

<sup>b</sup>Values are single analysis of the combined charcoal tubes of the two head fires. Back fires were not analysed at UCR.

Table 3. (continued)

Hydrocarbon	Head Fire				Back Fire	
	Conc. in charcoal tube sample, ppb.		Emissions, lbs/ton of fuel burned		Conc. in charcoal tube sample, ppb.	Emissions, lbs/ton of fuel burned
	ARLI <sup>a</sup>	UCR <sup>b</sup>	ARLI	UCR	ARLI <sup>a</sup>	ARLI
			<u>WHEAT</u>			
Benzene	935	540	0.734	0.424	620	0.618
Toluene	<u>200</u>	130	<u>0.185</u>	0.120	<u>85</u>	<u>0.085</u>
Ethylbenzene		19		0.020		
p-Xylene		7		0.008		
m-Xylene		18		0.019		
o-Xylene		10		0.011		
Tetrachloroethane		---		---		
Chlorobenzene		---		---		
Styrene		32		0.041		
Furfural		14		0.014		
1,2,4, Tetramethylbenzene		4		0.005		
p/m Ethylbenzene		3		0.004		
Phenylacetylene(?)		4		0.004		
Benzaldehyde		---		---		
Benzofuran		7		0.008		
Indene		5		0.007		
Napthalene		10		0.013		

<sup>a</sup>Values are average of two head fires and two back fires.

<sup>b</sup>Values are single analysis of the combined charcoal tubes of the two head fires. Back fires were not analysed at UCR.

Table 3. (continued)

Hydrocarbon	Pile			
	Conc. in charcoal tube sample, ppb.		Emissions, lbs/ton of fuel burned	
	ARLI <sup>a</sup>	UCR <sup>b</sup>	ARLI	UCR
	<u>ALMOND</u>			
Benzene	141	120	0.116	0.099
Toluene	<u>23</u>	23	<u>0.022</u>	0.022
Ethylbenzene		2		0.002
p-Xylene		1		0.001
m-Xylene		3		0.003
o-Xylene		1		0.001
Tetrachloroethane		7		0.012
Chlorobenzene		1		0.001
Styrene		2		0.002
Furfural		4		0.004
1,2,4, Tetramethylbenzene		2		0.003
p/m Ethylbenzene		---		---
Phenylacetylene(?)		---		---
Benzaldehyde		---		---
Benzofuran		1		0.001
Indene		---		---
Napthalene		2		0.003

<sup>a</sup>Values are average of two pile fires.

<sup>b</sup>Values are single analysis of the combined charcoal tubes of the two pile fires.

Table 3. (continued)

Hydrocarbon	Pile			
	Conc. in charcoal tube sample, ppb.		Emissions, lbs/ton of fuel burned	
	ARLI <sup>a</sup>	UCR <sup>b</sup>	ARLI	UCR
			<u>GRAPE</u>	
Benzene	139	210	0.084	0.127
Toluene	<u>46</u>	52	<u>0.033</u>	0.037
Ethylbenzene		7		0.006
p-Xylene		4		0.003
m-Xylene		8		0.007
o-Xylene		4		0.003
Tetrachloroethane		8		0.010
Chlorobenzene		3		0.003
Styrene		6		0.005
Furfural		---		---
1,2,4, Tetramethylbenzene		---		---
p/m Ethylbenzene		---		---
Phenylacetylene(?)		---		---
Benzaldehyde		---		---
Benzofuran		2		---
Indene		---		0.002
Napthalene		3		0.002

<sup>a</sup>Values are average of two pile fires.

<sup>b</sup>Values are single analysis of the combined charcoal tubes of the two pile fires.

Table 3. (continued)

Hydrocarbon	Pile			
	Conc. in charcoal tube sample, ppb.		Emissions, lbs/ton of fuel burned	
	ARLI <sup>a</sup>	UCR <sup>b,c</sup>	ARLI	UCR
			<u>PEACH</u>	
Benzene	152	170	0.104	0.116
Toluene	<u>35</u>	45	<u>0.028</u>	0.036
Ethylbenzene		48		0.045
p-Xylene		3		0.003
m-Xylene		8		0.007
o-Xylene		3		0.003
Tetrachloroethane		---		---
Chlorobenzene		3		0.003
Styrene		4		0.004
Furfural		9		0.008
1,2,4, Tetramethylbenzene		---		---
p/m Ethylbenzene		---		---
Phenylacetylene(?)		---		---
Benzaldehyde		---		---
Benzofuran		---		---
Indene		---		---
Napthalene		5		0.006

<sup>a</sup>Values are average of two pile fires.

<sup>b</sup>Values are single analysis of the combined charcoal tubes of the two pile fires.

<sup>c</sup>Other minor components identified include trimethylbenzenes or methyl-ethylbenze, benzaldehyde, benzofuran, 1,2,2-tetrachloroethane, limonene (?), alkanes C-10 to C-15 and benzonitrite.

highest yields of all 8 crops) are added together, the total yields are only 0.519 and 0.698 pounds, respectively. Similarly, if the yield from almond (one of the lower yields) is totaled, the value is only 0.154 pounds. Since benzene constitutes a relatively large portion of the total yield (e.g., 47% in barley and 60% in wheat), and this hydrocarbon is of reactivity (Class I), it would appear that the other hydrocarbons are of relative minor importance if only because of their small yields.

There were not enough data to determine if any consistent differences existed in yield of hydrocarbons between head and back fires. Emissions from head fires exceeded those from back fires in barley, rice and wheat, but the reverse in corn and sorghum.

Differences in crops for particular hydrocarbons, other than those noted earlier, appear to be very minor and are not discussed further.

#### Emissions of Oxides of Nitrogen

Analyses of NO and NO<sub>2</sub> were made from the integrated bag sample. The results of these analyses in parts per million, and calculations of emissions in pounds per ton of fuel burned are presented in Table 4.

The major portion of the NO<sub>x</sub> appeared as NO; about 76% in field crops and 71% in orchard crops. Yields, however were relatively low, none exceeding the 3.2 pounds from rice head and back fires. Except for rice, the yield of NO from back fires was slightly higher than from head fires.

The emissions of NO from field crops was slightly higher than from orchard crops, the average being 2.6 and 2.2 pounds, respectively. There was essentially no difference in the yield of NO<sub>2</sub> from the two types of crops; the averages were 0.8 and 0.9 pounds, respectively.

Table 4. Emissions of Nitric Oxide and Nitrogen Dioxide from Burning Residues of Several Field and Orchard Crops.

Crop	Type of Fire	Concentration in integrated bag sample, ppm		Emissions, lbs. per ton of fuel burned	
		NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
<u>Field Crops</u>					
Barley	Head	5.6	2.3		
		<u>5.2</u>	<u>3.1</u>		
	av.	5.4	2.7	1.9	1.5
	Back	6.1	1.0		
<u>6.2</u>		<u>1.7</u>			
	av.	6.2	1.4	2.9	1.0
Corn	Head	6.6	0.3		
		<u>6.8</u>	<u>0.6</u>		
	av.	6.7	0.5	2.4	0.3
	Back	5.1	0		
<u>6.2</u>		<u>0.7</u>			
	av.	5.7	0.4	2.7	0.3
Rice	Head	10.0	0.5		
		<u>19.0</u>	<u>4.8</u>		
	av.	14.5	2.7	3.2	0.9
	Back	9.9	2.2		
<u>12.3</u>		<u>2.7</u>			
	av.	11.1	2.5	3.2	1.1
Sorghum	Head	9.1	0.7		
		<u>7.7</u>	<u>1.3</u>		
	av.	8.4	1.0	2.7	0.5
	Back	7.2	0.8		
<u>7.5</u>		<u>0.6</u>			
	av.	7.4	0.7	3.0	0.4
Wheat	Head	5.2	2.4		
		<u>6.0</u>	<u>3.0</u>		
	av.	5.6	2.7	1.7	1.2
	Back	5.6	1.5		
<u>5.4</u>		<u>1.3</u>			
	av.	5.5	1.4	2.1	0.8

Table 4. (continued)

Crop	Type of Fire	Concentration in integrated bag sample, ppm		Emissions, lbs. per ton of fuel burned	
		NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
<u>Orchard Crop</u>					
Almond	Pile	5.2	0.9		
		<u>5.8</u>	<u>1.5</u>		
	av.	5.5	1.2	1.7	0.6
Grape	Pile	11.0	3.9		
		<u>10.3</u>	<u>3.7</u>		
	av.	10.7	3.8	2.5	1.3
Peach	Pile	11.1	2.9		
		<u>8.2</u>	<u>1.4</u>		
	av.	9.7	2.2	2.5	0.9
Average values for:					
	Field Crops	7.7	1.6	2.6	0.8
	Orchard Crops	8.6	2.4	2.2	0.9

The compilation of emission factors published by EPA (5) lists the factor (perhaps an estimate) for  $\text{NO}_x$  at 2 pounds per ton of fuel burned. So far as we are aware, the data in the present project are the first on fire effluents collected throughout the course of the fire. Our earlier work (2) indicated that the concentration of total  $\text{NO}_x$  in grab samples taken at the temperature peak varied from 21 to 42 ppm; no effort was made to estimate emission factors. Thus, it appears  $\text{NO}_x$  emissions are relatively low and that our data are in close agreement with the values given by EPA.

#### Emissions of Sulfur/Sulfur Dioxide

As noted above, direct analysis of  $\text{SO}_2$  emissions contained in the fire smoke was tried but was unsuccessful. Therefore emissions were calculated based on the sulfur lost from the fuel. Sulfur loss was calculated from differences in sulfur content of the unburned fuel and of the ashes. The pounds of sulfur lost and pounds of  $\text{SO}_2$  per ton of fuel burned are presented in Table 5. It is important to stress that calculations of the  $\text{SO}_2$  assume that all of the sulfur lost was converted to  $\text{SO}_2$ . We know that this is not so because the direct chromatographic analytical work that we did do, though erratic and quantitatively unreliable, did demonstrate that small amounts of  $\text{H}_2\text{S}$  were present as well as variable, but at times comparatively large amounts of an unknown sulfur material were present. The chromatographic conditions were such that  $\text{H}_2\text{S}$  and  $\text{SO}_2$  emerged at 41 and 80 seconds, respectively. The unknown emerged at about 52 seconds, at times driving the recorder off scale, which was in excess of 1 ppm. Several suggestions were made as to what the compound might be but no attempts were made to identify it.

Table 5. Emissions of Sulfur Dioxide Calculated from Difference in Sulfur Content of Unburned Fuel and Resultant Ashes from Burning Residues of Several Field and Orchard Crops.

Crop	Type of Fire	Sulfur			Emissions, lbs. per ton fuel burned	
		%	lbs. in sample	lbs. lost	S	SO <sub>2</sub> <sup>a</sup>
<u>Field Crops</u>						
Barley	Head					
	Straw	0.19	.01033			
	Ash <sup>b</sup>	1.22	.00549	.00484	1.78	3.6
	Back					
	Straw	0.19	.01026			
	Ash <sup>b</sup>	1.21	.00303	.00723	2.67	5.4
Corn	Head					
	Straw	0.03	.00163			
	Ash	0.26	.00104	.00059	0.22	0.4
	Straw	0.03	.00165			
	Ash	0.29	.00116	.00049	<u>0.18</u>	<u>0.4</u>
	av.				0.20	0.4
	Back					
	Straw	0.03	.00166			
	Ash	0.09	.00072	.00094	0.34	0.7
	Straw	0.03	.00168			
	Ash	0.35	.00140	.00028	<u>0.10</u>	<u>0.2</u>
	av.				0.22	0.5
Rice	Head					
	Straw	0.05	.00308			
	Ash	0.08	.00064	.00244	0.79	1.6
	Straw	0.05	.00317			
	Ash	0.09	.00072	.00245	<u>0.77</u>	<u>1.5</u>
	av.				0.78	1.6
	Back					
	Straw	0.05	.00314			
	Ash	0.09	.00054	.00260	0.83	1.7
	Straw	0.05	.00313			
	Ash	0.06	.00042	.00271	<u>0.87</u>	<u>1.7</u>
	av.				0.85	1.7

<sup>a</sup>The SO<sub>2</sub> values given are calculated from the S lost assuming that all of the S lost went to SO<sub>2</sub>.

<sup>b</sup>For barley, one sample each was made by combining the ashes of the two head fires and the ashes of the two back fires.

Table 5. (Continued)

Crop	Type of Fire	Sulfur			Emissions, lbs. per ton fuel burned	
		%	lbs. in sample	lbs. lost	S	SO <sub>2</sub> <sup>a</sup>
<u>Field Crops (continued)</u>						
Sorghum	Head					
	Straw	0.03	.00175			
	Ash	0.07	.00035	.00140	0.48	1.0
	Straw	0.03	.00170			
	Ash	0.09	.00045	.00125	<u>0.44</u>	<u>0.9</u>
	av.				0.46	1.0
	Back					
	Straw	0.03	.00171			
	Ash	0.09	.00045	.00126	0.44	0.9
	Straw	0.03	.00178			
	Ash	0.06	.00048	.00130	<u>0.44</u>	<u>0.9</u>
	av.				0.44	0.9
Wheat	Head					
	Straw	0.19	.01146			
	Ash	0.42	.00210	.00936	3.10	6.2
	Straw	0.19	.01143			
	Ash	0.40	.00240	.00903	<u>3.00</u>	<u>6.0</u>
	av.				3.05	6.1
	Back					
	Straw	0.19	.01124			
	Ash	0.34	.00170	.00954	3.20	6.4
	Straw	0.19	.01064			
	Ash	0.47	.00188	.00876	<u>3.10</u>	<u>6.2</u>
	av.				3.15	6.3
<u>Orchard Crops</u>						
Almond	Pile					
	Wood	0.007	.00181			
	Ash	0.007	.00029	.00153	0.12	0.2
	Wood	0.007	.00190			
	Ash	0.003	.00013	.00177	<u>0.13</u>	<u>0.3</u>
	av.				0.13	0.3

Table 5. (Continued)

Crop	Type of Fire	Sulfur			Emissions, lbs. per ton fuel burned	
		%	lbs. in sample	lbs. lost	S	SO <sub>2</sub> <sup>a</sup>
<u>Orchard Crops (continued)</u>						
Grape	Pile					
	Wood	0.04	.00809			
	Ash	0.09	.00243	.00566	0.56	1.1
	Wood	0.04	.00809			
	Ash	0.05	.00120	.00689	<u>0.68</u>	<u>1.4</u>
	av.				0.62	1.3
Peach	Pile					
	Wood	0.005	.00117			
	Ash	0.01	.00031	.00086	0.07	0.1
	Wood	0.005	.00117			
	Ash	0.01	.00037	.00079	<u>0.07</u>	<u>0.1</u>
	av.				0.07	0.1
Average values for						
	Field Crops				1.4	2.8
	Orchard Crops				0.3	0.6

Since the factor for conversions of S to SO<sub>2</sub> is 2, only the values for pounds of sulfur lost will be cited for discussion purposes.

The loss of sulfur from all crop residues was relatively low but even so, that from field crops was about 5 times that from orchard crops; averages were 1.4 and 0.3 pounds, respectively. By far, the greatest contribution within field crops was from barley and wheat. The average value from these two crops compared with the remaining three crops was 2.7 versus 0.5 pounds. This difference appears to be related directly to the sulfur content of the fuels. Both barley and wheat straws had about 5 times the sulfur than that of the other 3 fuels. There appeared to be no real difference in emissions between head and back fires.

Although still less than one pound, the emissions from grape residues were almost 5 times greater than that from almond and about 10 times greater than from peach. Again, this was related directly to the sulfur content of the fuels.

Again referring to EPA published emission factors (5), they did not include sulfur oxides because emissions from agricultural burning were considered to be negligible. In view of the small sulfur losses reported here, and the fact that some of the sulfur goes to other compounds, it seems that, in the absence of better data, EPA's approach is reasonable. That there may be exceptions is indicated by the results from barley and wheat wherein over 3 pounds of sulfur were lost. But until we have better analytical methods for smoke from open field burning, it is hazardous to speculate on how much of the sulfur lost actually was converted to SO<sub>2</sub>.

### Emissions of Aldehydes

ARLI reported that gas chromatographic analyses were made for the following seven compounds, using the Stump method as noted earlier.

Formaldehyde  
Acetaldehyde  
Acetone (included propionaldehyde and/or acrolein, the hydrozones  
of which have the same retention time as that of acetone)  
Isobutyraldehyde  
Crotonaldehyde  
Hexanaldehyde  
Benzaldehyde

The results of the acetone analyses were extremely erratic, varying from less than 1 to more than 1800 ppm. Since ARLI suggested that contamination may have been a factor, the data are not reported here.

Formaldehyde and benzaldehyde were not detected. This was an unexpected result and was probably due to poor collection efficiency. Acetaldehyde was detected only in sorghum, wheat and almond fires, and then in amounts that gave yields of a maximum of 0.5 pounds per ton of fuel burned from sorghum head fires down to 0.05 pounds or less from sorghum back fires and all wheat and almond fires.

Isobutyral-, croton-, and hexanaldehyde were found somewhat more consistently but the results were still very erratic. While the Stump method was designed for automobile exhausts, ARLI suggests that the sampling method may not have been suitable for our task, at least without more tests to determine efficiency of the impingers. While great care was taken to number the impingers in sequence, second and/or third impingers at times contained more of a given material than the first. The data thus may have limited value, but the results for the three aldehydes are presented in Table 6 in terms of concentration in ppm and emissions in pounds per ton of fuel

Table 6. Emissions of Three Aldehydes from Burning Residues of Several Field and Orchard Crops.

Crop	Type of Fire	Parts per Million			Lbs./ton of Fuel Burned <sup>a</sup>		
		Iso-butyl-	Croton-	Hexan-	Iso-butyl-	Croton-	Hexan-
<u>Field Crops</u>							
Barley	Head	12.26	8.36	---	11.3	4.8	---
		<u>14.50</u>	<u>3.30</u>	---			
	av	13.38	5.83				
	Back	--- <sup>b</sup>	---	---			
	av.		<u>.20</u>				
			.10				
Corn	Head	---	1.60	1.30	---	0.7	0.8
		---	---	<u>.10</u>			
	av.		.80	.70			
	Back	---	---	---			
	av.		---	---			
Rice	Head	---	3.20	2.30	---	0.8	1.8
		---	---	<u>2.50</u>			
	av.		1.60	2.40			
	Back	---	8.30	25.00			
	av.		<u>---</u>	<u>---</u>			
			4.15	12.50		2.8	12.1
Sorghum	Head	3.90	3.00	2.60	5.0	2.7	3.9
		<u>3.80</u>	<u>1.20</u>	<u>1.64</u>			
	av.	3.85	2.10	2.12			
	Back	2.50	.13	.85			
	av.	<u>4.50</u>	<u>.20</u>	<u>1.70</u>			
		3.40	.17	1.28	3.4	0.2	1.8
Wheat	Head	1.40	23.50	---	6.3	8.3	---
		<u>15.90</u>	---	---			
	av	8.65	11.75				
	Back	2.00	---	.02			
	av	<u>15.80</u>	<u>.40</u>	<u>---</u>			
		8.90	.20	.01	8.2	0.2	0.01

<sup>a</sup>Calculations for pounds emission made from average concentration values only.

<sup>b</sup>Compound not detected.

Table 6. (Continued)

Crop	Type of Fire	Parts per Million			Lbs./ton of Fuel Burned <sup>a</sup>		
		Iso-butyr1-	Croton-	Hexan-	Iso-butyr1-	Croton-	Hexan-
<u>Orchard Crops</u>							
Almond	Pile	6.00	1.20	.14			
		<u>5.20</u>	<u>1.10</u>	<u>.06</u>			
	av.	5.60	1.15	.10	4.3	0.9	0.1
Grape	Pile	8.20	1.70	---			
		<u>8.40</u>	<u>1.30</u>	---			
	av.	8.30	1.50		4.6	0.8	---
Peach	Pile	---	---	.70			
		---	---	<u>.60</u>			
	av.			.65	---	---	0.6

<sup>a</sup>Calculations for pounds emission made from average concentration values only.

burned. Analytical results are combined from the three impingers from all other crop fires.

Crotonaldehyde was found in some fires of all crops except peach, while hexanaldehyde was not found in barley or grape and isobutyraldehyde was not detected in corn, rice or peach.

Except in two instances, yields were less than 10 pounds per ton of fuel burned and often less than 1 pound; the two exceptions were in barley head fires which yielded 11.3 pounds of isobutyraldehyde and rice back fires at 12.1 pounds of hexanaldehyde. Data were too meager to compare yields from head and back fires or those from field and orchard crops.

Since these materials are classed as aliphatic aldehydes and thus are highly reactive (Class III)<sup>a</sup>, yields of up to 12 pounds per ton of fuel burned may assume importance and should be considered in relationship to other sources in burning areas.

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<sup>a</sup>California Air Resources Board (CARB) Reactivity Classification of Organic Compounds. Appendix A.

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APPENDIX A

California Air Resources Board (CARB) Reactivity  
Classification of Organic Compounds

Class I (Low Reactivity)	Class II (Moderate Reactivity)	Class III (High Reactivity)
C <sub>1</sub> -C <sub>2</sub> paraffins	Mono-tert-alkyl- benzenes	All other aromatic hydrocarbons
Acetylene	Cyclic ketones	All olefinic hydro- carbons (including partially halogenated)
Benzene	Alkyl acetates	Aliphatic aldehydes
Benzaldehyde	2-Nitropropane	Branch alkyl ketones
Acetone	C <sub>3</sub> + paraffins	Cellosolve acetate
Methanol	Cycloparaffins	Unsaturated ketones
Tert-alkyl alcohols	N-alkyl ketones	Primary & secondary C <sub>2</sub> + alcohol
Phenyl acetate	N-methyl pyrrolidone	Diacetone alcohol
Methyl benzoate	N,N-dimethyl acetamide	Ethers
Ethyl amines	Alkyl phenols <sup>a</sup>	Cellosolves
Dimethyl formamide	Methyl phthalates <sup>b</sup>	Glycols <sup>a</sup>
Perhalogenated hydrocarbons		C <sub>2</sub> + alkyl phthalates <sup>b</sup>
Partially halogenated paraffins		Other esters <sup>b</sup>
Phthalic anhydride <sup>b</sup>		Alcohol amines <sup>b</sup>
Phthalic acids <sup>b</sup>		C <sub>3</sub> + organic acids + di acid <sup>b</sup>
Acetonitrile <sup>a</sup>		C <sub>3</sub> + di acid anhydrides <sup>b</sup>
Acetic acid		Formin <sup>b</sup> (Hexa methylene- tetramine)
Aromatic amines		Terpenic hydrocarbons
Hydroxyl amines		Olefin oxides <sup>b</sup>
Naphthalene <sup>a</sup>		
Chlorobenzenes <sup>a</sup>		
Nitrobenzenes <sup>a</sup>		
Phenol <sup>a</sup>		

<sup>a</sup>Reactivity data are either nonexistent or inconclusive, but conclusive data from similar compounds are available; therefore, rating is uncertain but reasonable.

<sup>b</sup>Reactivity data are uncertain.