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POTENTIAL HEALTH HAZARDS ASSOCIATED WITH PARTICULATE MATTER RELEASED FROM RICE STRAW BURNING

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Abstract

The potential health effects associated with smoke released from the burning of rice straw was evaluated using two short term in vitro bioassays: the Ames mutagen assay and the pulmonary alveolar macrophage cytotoxicity assay. Chemical analyses included determination of pesticide residues on unburned rice straw from fields sampled for smoke, elemental analysis of the smoke and identification of polyaromatic hydrocarbons (PAHs) present in rice straw smoke extracts. Biological testing of fly ash released from a small scale incinerator (SSI) burning rice straw was also performed.

Biological analysis showed solvent extracts of rice straw smoke particulate matter were mutagenic with and without metabolic activation to Salmonella typhimurium strains TA98, TA100, TA1537 and TA1538. Solvent extracts of fly ash from the SSI were tested in TA98 and TA100 and found to be mutagenic in both tester strains. Rice straw smoke particulate matter and ethanol soluble organics were tested in the pulmonary alveolar macrophage assay and found to inhibit macrophage phagocytosis. Comparison of rice straw particulate matter with silica and coal fly ash shows the relative potency of phagocytosis inhibition to decrease in the descending order: silica > rice straw smoke > coal fly ash.

Chemical analyses revealed that pesticide residues in the unburned rice straw known to be treated with MCPA, molinate and ethyl parathion were below analytical detection limits for these compounds. Based on these results no further analysis for pesticide residues in smoke was made. Elemental analysis of smoke samples was in agreement with values cited in the literature for smoke from burning plant materials and characteristically had a high potassium to iron ratio. Initial identification of PAHs by computerized gas chromatography mass spectrometry revealed the presence of a number of mutagenic and nonmutagenic PAHs. Fluorescence spectrometry of the rice straw smoke extract also indicated the presence of PAHs. Funding for this project was provided by the California State Air Resources Board and the California State Energy Commission.

ACKNOWLEDGEMENTS

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Statewide Air Pollution Research Center (SAPRC), UC Riverside in the operation of a burning tower for controlled burn experiments.

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We also thank members of the rice industry for their cooperation in allowing rice straw smoke sampling to be performed on their properties.

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I. GENERAL INTRODUCTION

A. Rice Straw Burning

The half-million acres of rice fields in Northern California produce more than one million tons of rice annually with about the same quantity of rice straw and stubble. Burning is presently used to remove more than 90% of this rice residue. The volumes of rice and rice straw produced in recent years are shown in Table I-1.

In the Sacramento Valley, rice straw burning is of particular concern because it generates almost 10% of the Valley's total yearly output of carbon monoxide and hydrocarbons and 5% of its atmospheric particulate matter. This occurs largely in a two-month period in the fall and/or two-month period in the spring. The topography and the wind patterns of the Valley are such that these pollutants are capable of traveling for long distances and have relatively long residence times (Darley *et al.*, 1974). On days of burning, the concentrations of these pollutants can double in the Valley, and smoke in the sky and reduced visibility are clear indicators that populations are exposed to additional air pollutants. These additional emissions also contribute to the federal designation of areas in the Valley as non-attainment areas for the secondary standard for total suspended particulates (Air Resources Board, State of California) thus potentially creating regulatory restraints for industrial developmment in the affected areas.

Rice straw burning is likely to continue for some time due to its practical significance to the rice industry and the lack of feasible alternatives. Burning is at present, viewed as the most cost-effective

Table I-1 Annual Production of Rice and Rice Straw in California

Year	Rice (10^6 ton)	Rice Straw (10^6 ton)
1978	1.4	1.76
1977	0.9	1.12
1976	1.1	1.38
1975	1.5	1.89

(Source - personal communication with Mr. Milton Miller of the Rice Research Advisory Board).

Table I-2 Emissions from Rice Straw Burning in the Sacramento Valley in 1976[a].

Pollutant	Emission Factor (lb per ton of straw)
Particulate Matter	6.3 - 8.3
Carbon Monoxide	74.1 - 87.4
Hydrocarbons[b]	5.5 - 10.3

[a] Data from Darley, 1977

[b] Hydrocarbons Found in Rice Straw Smoke: Benzene, m-Xylene, 1,2,4-tetramethylbenzene, Toluene, o-Xylene, Benzofuran, Ethyl Benzene, Chlorobenzene, Indene, p-Xylene, Styrene, and Napthalene.

Table I-3 Total Emissions of Three Major Air Pollutants from Rice Straw Burning in California.

Year	Rice Straw (10^6 ton	Total Emissions (1,000 ton)[a] PM	CO	HC
1978	1.76	5.5 - 7.3	65.2 - 76.9	4.8 - 9.1
1977	1.12	3.5 - 4.6	41.5 - 48.9	3.1 - 5.8
1976	1.38	4.3 - 5.7	51.1 - 60.3	3.8 - 7.1
1975	1.89	6.0 - 7.8	70.0 - 82.6	5.2 - 9.7

[a] Total emissions were calculated using data in Tables I-1 and I-2.

way to control stem-rot disease of rice, which may reduce crop yield up to 24%, and is also used to clean the field prior to the next planting. The possibilities for utilization of rice straw are, for the most part, still a long way from being economically feasible. Recently, the technical and economic potential of various alternatives for utilization of rice straw have been assessed by an ARB-supported study (Kubota et al., 1981). The alternatives assessed included soil incorporation, livestock feed, direct combustion, gasification, pyrolysis, anaerobic digestion, and cellulose conversion to alcohol for fuel or fiber for production of corrugatint medium and fireboard. Direct combustion to generate steam and in turn electricity, and cellulose conversion to alcohol showed the greatest promise for commercial and industrial application.

Opposed to the technological and economic reasons for rice straw burning is public concern over the potential health hazard associated with this practice. At present, very little is known about the specific health effects of rice straw smoke.

B. Extent of Exposure

A preliminary assessment of the significance of rice straw burning as a source of air pollution has been made by an ARB-supported study (Darley, 1977) and the emission factors for the three major air pollutants have been determined. As shown in Table I-2, burning of one ton of dry rice straw emits about 7 pounds of particulate matter, 80 pounds of carbon monoxide, and 10 pounds of hydrocarbons. Using the production data in Table I-1, the total emissions of these pollutants from rice straw burning were calculated as values shown in Table I-3. For example, in 1978, 1.76 million tons of rice straw was burned to generate about

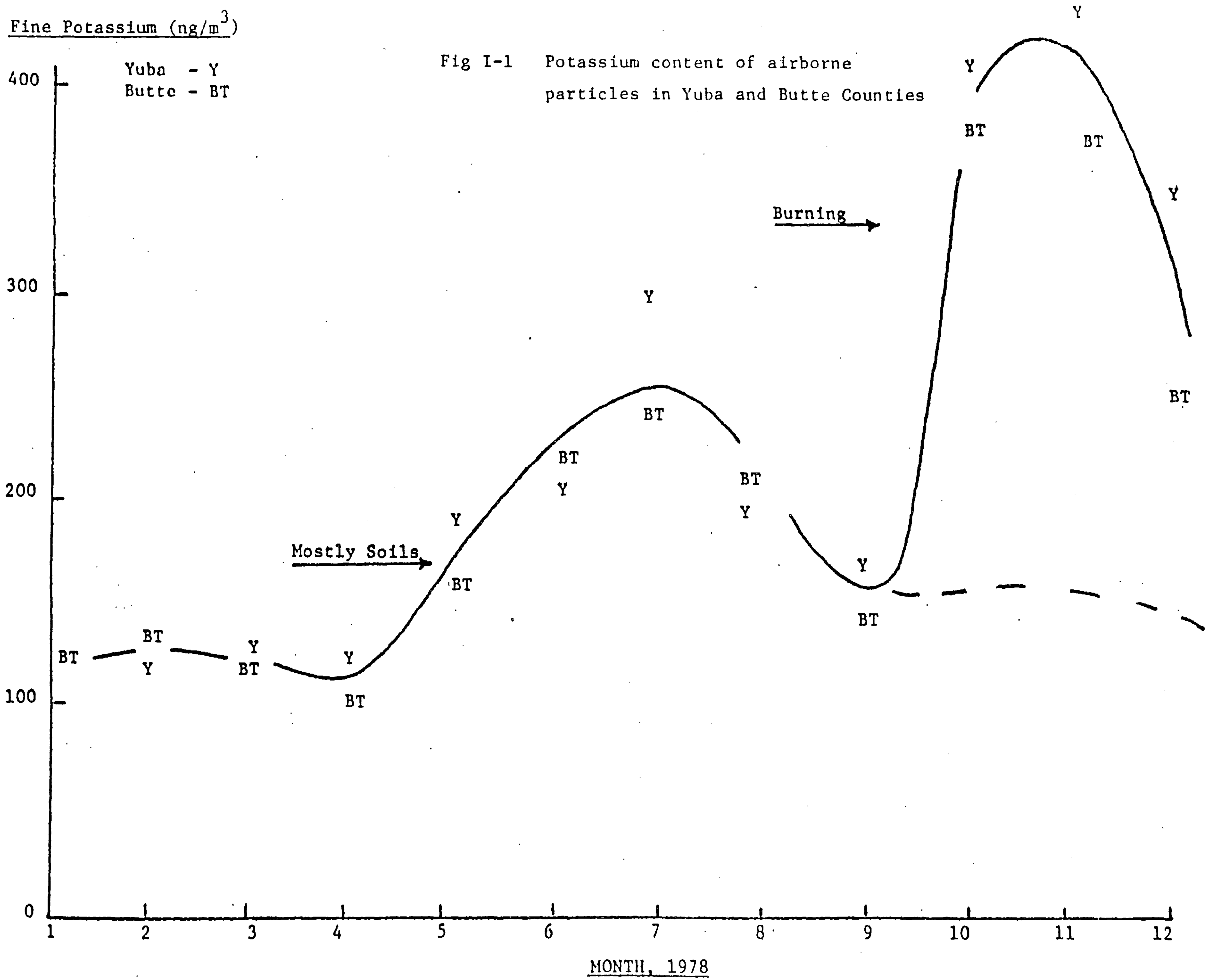
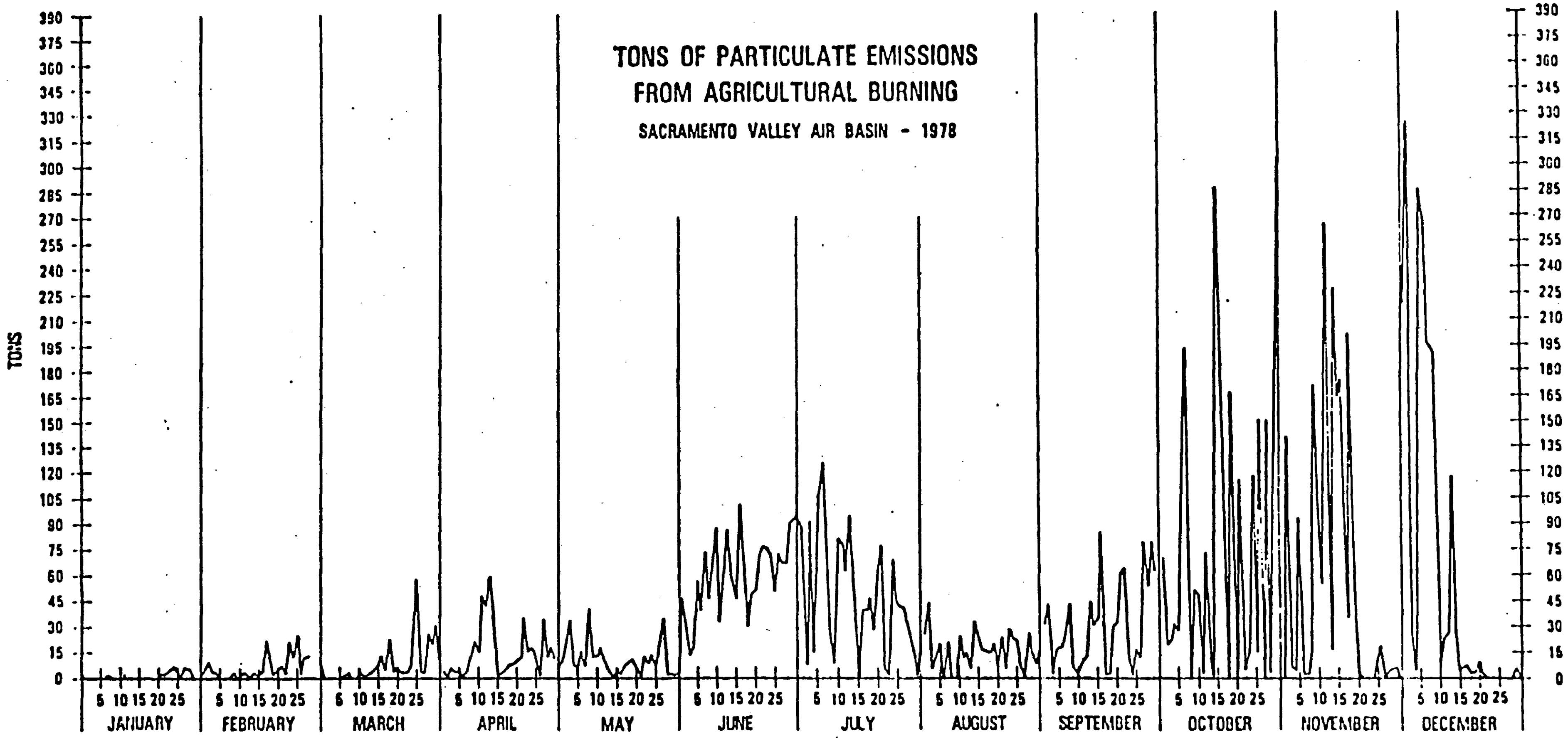


Fig I-1 Potassium content of airborne particles in Yuba and Butte Counties

Fig. I-1

Figure I-2


TONS OF PARTICULATE EMISSIONS
FROM AGRICULTURAL BURNING
SACRAMENTO VALLEY AIR BASIN - 1978
TONS
390
375
360
345
330
315
300
285
270
255
240
225
210
195
180
165
150
135
120
105
90
75
60
45
30
15
0
5 10 15 20 25
JANUARY
FEBRUARY
MARCH
APRIL
MAY
JUNE
JULY
AUGUST
SEPTEMBER
OCTOBER
NOVEMBER
DECEMBER

6,000 tons of particulate matter. As mentioned earlier, these amounts of pollutants were added to the air in a relatively short period of time (2-4 months), resulting in increases in the concentration of pollutants during field burning.

Even though the State regulatory agencies have mandated burning to be practiced only on days when weather projections favor vertical dilution of air pollutants, the increase in pollution burden of the air in the Sacramento Valley is still significant. This is demonstrated by the potassium content in the suspended particulate matter in the air (Air Quality Group, University of California, Davis, 1980) as shown in Fig. I-1. High potassium content is characteristic of particulate matter of plant origin. The summer peak in Fig. I-1 is probably associated with burning of agricultural wastes other than rice straw. The major autumn peak, however, coincides very well with the burning season of rice straw. This observation is consistent with the time-amount profile of particulate emissions from agricultural burning (Fig. I-2) calculated by using emission factors (Personal Communication with Dr. Westerdahl of ARB). Based on these data, there is little doubt that, during the burning season, the populations in the Sacramento Valley are exposed to additional amounts of pollutants produced by rice straw burning.

C. Potential Detrimental Effects

Since pollutants in the air come from a variety of sources, it is difficult to pinpoint the specific detrimental effects of pollutants from rice straw burning. However, rice straw burning is known to cause localized deterioration of air quality which is most often noticed as a reduction in visibility. It is also reasonable to assume that increases in particulate matter in the air could potentially cause eye irritation and irritations to the respiratory system. These irritations in turn could initiate or worsen acute respiratory diseases such as hay fever, asthma, and bronchitis. It has been postulated that long-term, low-level exposure could contribute to chronic lung diseases (Chrisp and Fisher, 1980). In addition to the aesthetic and health effects, the seasonal surge of these pollutants may contribute to certain areas in the Sacramento Valley being designated by The Environmental Protection Agency as non-attainment areas with respect to these pollutants (Air Resources Board State of California, 1984). Under the provisions of the current air pollution control law, industrial development in these areas may be affected.

D. Objectives of Investigation

The objective of this investigation was to assess potential health hazards associated with particulate matter released from rice straw burning by quantitating two types of toxicity associated with organic substances contained in the particulate matter. Firstly, mutagenic activity was determined using the widely accepted Ames *Salmonella*/mammalian-microsome mutagenicity test (Ames *et al*., 1975). The results of this test provide a rough estimate of the quantity of mutagenic substances present in rice straw smoke particles. Mutagenic substances in the environment are important since they are known to be involved in the etiology of cancer (Doll, 1977) and genetic birth defects, and may possibly contribute to heart disease (Benditt, 1977), aging (Burnet, 1974), cataracts (Jose, 1979), and developmental birth defects. Secondly, the effect on the viability and functions of the pulmonary alveolar macrophage (PAM) a class of defensive cells in the lung, was determined using an *in vitro* PAM test developed on the Davis Campus

(Fisher et al., 1978). Positive results in this test indicate that particles at the doses tested are capable of impairment of lung defense mechanisms and predispose the lung to infections and other diseases. Comparison of the biological activities of rice straw smoke in these two *in vitro* assays is made with other types of combustion byproducts.

In addition to the biological tests, rice smoke samples were analyzed for elemental composition, polynuclear aromatic hydrocarbons, and other organic components in order to identify chemical agents which potentially might cause adverse biological effects. Pesticide residues in the samples of unburn rice straw were also analyzed to assess the potential exposure to pesticide residues released in rice straw smoke.

E. Scope and Magnitude of Work

This investigation called for activities in five areas: (1) sample collection, (2) physical and chemical analysis of rice straw smoke particles, (3) analysis of pesticide in unburn rice straw, (4) determination of mutagenic activity of organics exptracable from the particles, and (5) determination of the toxicity of the particles to PAM.

Rice straw smoke was collected by dry filtration using high volume air sampling techniques. Samples were collected from (1) burning rice fields, (2) small-scale incinerator combusting rice straw, (3) a rice straw smoke plume above and downwind of burning rice fields collected by an aircraft, and (4) a carefully controlled burning tower which stimulated field burns. Organic components of particulate matter in the rice straw smoke samples were extracted with solvent and the extracts fractionated using an acid-base partitioning procedure or by gel permeation chromatography. Sample fractions were analyzed for polynuclear aromatic hydrocarbons (PAHs), aliphatic hydrocarbons, and more polar constituents using gas-chromatography and mass spectrometry. Elemental analysis was performed directly on the smoke particles to confirm that these particles were, in fact, produced by burning plant material. Pesticide residue analyses were performed on unburned rice straw samples collected from the field for three chemicals applied to the rice early in the season, namely MCPA herbicide, molinate (Ordram) herbicide, and ethyl parathion.

Solvent extracts of rice straw smoke samples were tested in the Ames mutagen assay using a battery of tester strains of Salmonella typhimurium for two types of mutagenic activities, base-pair substitution and frameshift mutation. A rat liver enzyme preparation was employed for detection of those chemical species that require metabolic activation to become mutagenic. The tester strain, Salmonella typhimurium TA 98, was the most sensitive bacterial strain and was used to compare mutagenic potency of extracts from different samples.

A bovine PAM in vitro test was employed to simultaneously measure the effect of rice straw smoke particles (RSSP) on PAM phagocytic ability, attachment, adherence and viability.

F. Significance of Studies

Rice straw smoke is a complex environmental pollutant. The numerous physical, chemical, and biological factors affecting its environmental and biological fate make it extremely difficult to assess the health effects of the particulate matter from rice straw burning. It is unlikely that there will be useful epidemiological or animal toxicity data available in the near future because of experimental difficulty and cost. To our knowledge, the studies described in this report are the first ones ever directed towards determination of the biological effects of rice straw smoke. Even though the two tests used here are both short-term in vitro test systems, results are useful as a preliminary indication of potential acute and chronic toxicities of the smoke. Comparison of in vitro results between smoke samples collected under different conditions or between rice straw smoke and other types of combustion by-products should be used as a general guide. However, these comparisons are qualitative and not suitable for strict quantitative comparisons. Furthermore, these studies are to assess potential health effects, and can not be directly extrapolated to effects on human populations.

G. Outline of Final Report

The results of our work related to this project and their interpretation have been compiled in this final report, which consists of the following seven chapters:

1. General Introduction
2. Samples and Sampling Techniques
3. Physical and Chemical analysis
4. Pesticide Residue Analysis
5. Mutagenicity Tests
6. Pulmonary Aveolar Macrophage Toxicity Test
7. Overall Conclusion

A detailed table of contents preceding these chapters will serve as a subject index of this report.

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II. SAMPLES AND SAMPLING TECHNIQUES

A. Introduction

No study involving environmental sampling is better than the samples taken. Therefore, sampling protocol, the reliability of the sampling equipment, and the environmental conditions under which the samples are obtained are of paramount importance. In this study, a major part of which was obtaining samples of airborne particulate matter resulting from the burning of rice straw, the sampling protocol had to accommodate three different sources of rice straw smoke: (1) Burning rice fields; (2) a small-scale incinerator burning rice straw; and (3) a carefully controlled large-scale laboratory combustion apparatus. Moreover, the samples had to be suitable for use in the Ames mutagen assay, for the pulmonary alveolar macrophage assay, and for chemical and elemental analysis. To meet these constraints, we designed and constructed much of the sampling equipment. Sampler design involved dry filtration of rice straw smoke. Particles could be easily recovered for the alveolar macrophage assay or the smoke residue could be extracted with common solvents for the Ames assay and chemical analysis. Elemental analysis could be performed directly on the filtered smoke. The sampling equipment was simple, yet reliable; it could be easily transported to any source of rice straw smoke; and the equipment operated with high efficiency so that useful samples could be obtained during brief sampling periods.

B. Smoke Samplers

Smoke from rice straw burning was collected using high volume (Hivol) air sampling techniques employing filtration through glass fiber (GFF),

Table II-1 Particle Size Cut-offs (microns)
for Particles at 1.12 m^3/min.[a]

Stage no.	Sp. Gr[b]-1	Sp. Gr[b]-2.5
1	10	6.4
2	4.9	3.1
3	2.7	1.7
4	1.3	0.80
5	0.61	0.39
6 (20 x 25 cm GFF)	0.01	0.01

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[a] Data provided by Sierra-MISCO, Berkeley, CA.

[b] Specific gravity

Table II-2 Summary of Field Sampling

Source	Sample Code	Method of Collection	Size Range	Milligrams Collected	Volume of Sample	$^{mg}/_{m^3}$	Tests Completed
<u>Butte County</u> (12/5/78)							
0 mile		Low volume sampler, XAD-4 resin	All sizes	47	2.4 m^3	19.58	Ames test
1/4 mile		Glass fiber filter-Hivol	All sizes	179	91.6 m^3	1.95	Ames test
1/4 mile		XAD-4 resin only	All sizes	--	--	--	Ames test
1/4 mile		XAD-4 resin behind filter	Collected vapor phase material	--	91.6 m^3	--	Ames test
1 mile		Glass fiber filter (2)	All sizes	15 for 2 filters	120 m^3	0.125	Ames test
<u>Aircraft Plume Sample</u>		Glass fiber filter versapor filter	All sizes	77	--	--	GC-MS; Macrophage
<u>Energy Commission Samples</u>							
Incinerator (2/28/80)		Two stage sampler					
		a) glass fiber filter	< 3.8 µm	75	195 m^3	0.385	Ames test
		b) versapor filter	< 3.8 µm	--	102 m^3	--	Macrophage
Upwind Control (Incinerator)		Two stage sampler					
		a) glass fiber filter	< 3.8 µm	1.1	148 m^3	0.007	
		b) versapore filter	< 3.8 µm	Note: H_2O on filter may alter weight	102 m	--	

Table II-2 Continued

Source	Sample Code	Method of Collection	Size Range	Milligrams Collected	Volume of Sample	$^{mg}/_{m^3}$	Tests Completed
Yolo County (11-8-79)							
Upwind	F1UA	Two stage sampler glass fiber filter	50% < 3.8μm	14.5	163.53 m^3	0.088	Ames
Upwind	F1UM	Two stage sampler-versapor filter	50% < 3.8μm	8.2	99.39 m^3	0.082	Macrophage; elemental
Downwind	F1DA	Two stage sampler-glass fiber filter	50% < 3.8μm	70.6	124.87 m^3	0.565	Ames
Downwind	F1DM	Two stage sampler-versapor filter	50% < 3.8μm	77.6	93.33 m^3	0.831	Macrophage; elemental
Sacramento County (11-9-79)							
Upwind	F2UA	Two stage sampler-glass fiber filter	50% < 3.8μm	28.4	91.99 m^3	0.308	Ames
Upwind	F2Um	Two stage sampler-versapor filter	50% < 3.8μm	31.0	79.38 m^3	0.390	Macrophage; elemental
Downwind	F2DA	Two stage samples-glass fiber filter	50% < 3.8μm	30.6	71.58 m^3	0.427	Ames
Downwind	F2DM	Two stage sampler-versapor filter	50% < 3.8μm	37.7	77.92 m^3	0.484	Macrophage; elemental
Sacramento County (11-21-79)							
Upwind	F3UA	Two stage sampler-glass fiber filter	50% < 3.8μm	20.4	97.52 m^3	0.209	Ames
Upwind	F3UM	Two stage sampler-versapor filter	50% < 3.8μm	21.6	74.30 m^3	0.291	Macrophage; elemental
Downwind	F3DA	Two stage sampler-glass fiber filter	50% < 3.8μm	52.2	137.05 m^3	0.381	Ames
Downwind	F3DM	Two stage sampler-versapor filter	50% < 3.8μm	62.9	118.36 m^3	0.531	Macrophage; elemental

Versapor (VF) acrylic plastic, quartz fiber (QFF), and PTFE membrane (MF) filters. A fifth filtering medium, 20-50 mesh XAD-4 resin, a divinyl copolymer of polystyrene, was used to trap primarily vaporized compounds. In many instances, XAD-4 was also used downstream of GFF, VF and QFF to trap volatiles released by the filters during sampling.

Figure II-1 shows a schematic of a Hivol sampler fitted with a 20 x 25 cm filter and charged with 100 ml XAD-4 resin. Such a device is capable of processing air at a rate of 0.5-1.0 m^3/min. Figure II-2 shows the same sampler connected to a cyclone separator. This particular configuration was designed by us to allow preseparation of non-respirable particles (greater than 2um diameter) by the cyclone. The cyclone was designed to have a collection efficiency of 50% for 2.5 um particles when operating at the optimum flow of 1.4m^3/min. In many cases, a fraction of the airstream was sampled isokinetically after the cyclone and filtered through a 47 mm diameter Fluoropore® membrane filter at a rate of 12 L/min. To maintain isokinetic conditions, the primary sampler was held to a flow rate of 0.6 m^3/min. According to the expression $C_{p2}=C_{p1}(Q_1/Q_2)^{1/2}$, where Q_1=initial flow, Q_2=new flow, C_{p1}=initial cut point, and C_{p2}=new cut point, the sampling efficiency of the cyclone at 0.6 m^3/min would be 50% for 3.8um diameter particles. Similar samplers with smaller cyclones, but without the membrane filter and XAD-4 resin, were borrowed from the State Department of Health Service, Berkeley, California. They operated at 1.12 m^3/min flow rate; the cyclones were 50% efficient for 3.5 um particles.

Figure II-3 shows a Hivol sampler fitted with a six-stage cascade impactor, without XAD-4 resin. Table II-1 shows the cut-off characteristics for a nominal flow of 1.12 m^3/min (range: 0.6-1.7 m^3/min) using special test particles. This type of sampler allows the determination of the size distribution of airborne particulate matter.

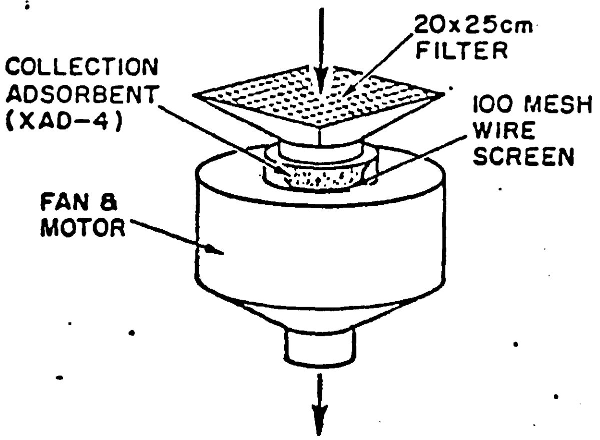

Fig. II-1. Hivol sampler with filter and XAD-4 resin.

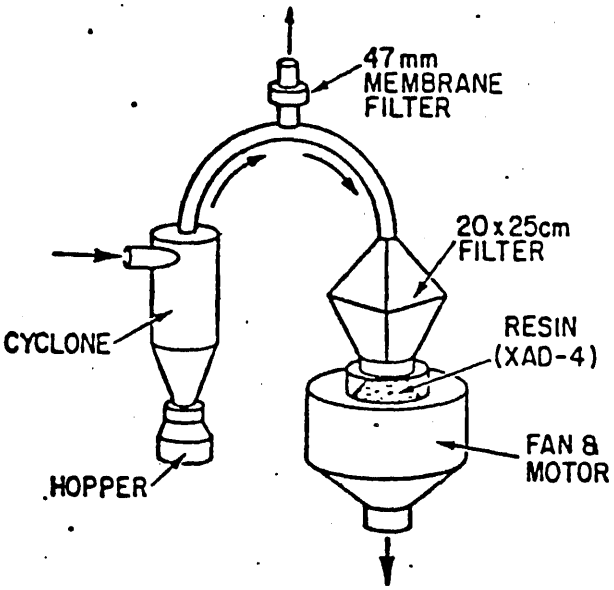

Fig. II-2. Hivol sampler configuration for respirable fraction of rice straw smoke.

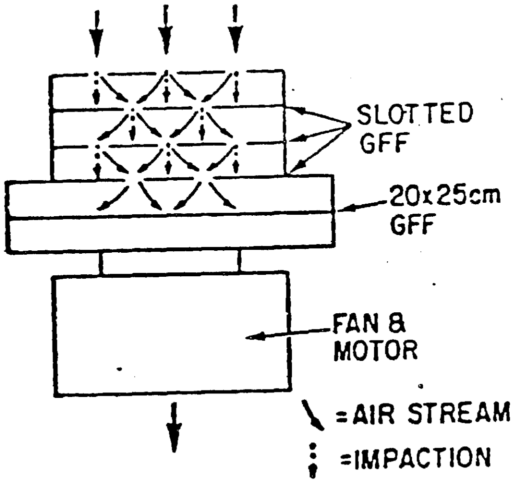

Fig. II-3. Hivol cascade impactor for size fractionation of rice smoke particles.

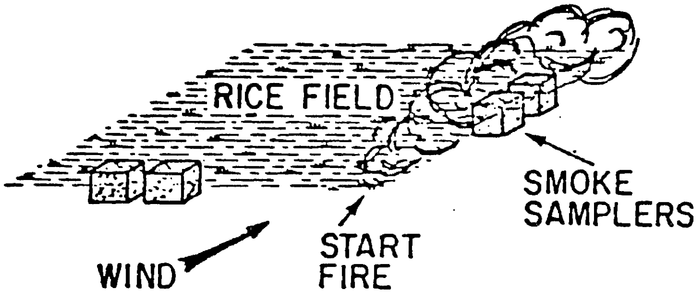

Fig. II-4. A typical deployment of Hivol samplers about a burning rice field.

C. Smoke Sampling

Rice fields. The smoke samplers were deployed about burning rice fields as shown in Figure II-4. For most of the samplers inside the smoke plume there were duplicate samplers upwind to determine contributions from the background air. The upwind samplers remained stationary during the sampling period, while the samplers used for trapping smoke were place on the bed of a truck and moved, when necessary, to keep them within the smoke plume. Four different fields, ranging in size from 32 ha to 61 ha and located in Butte, Sacramento, and Yolo Counties, were back-fired and then monitored during burning 30 to 150 days after harvest. Sampling lasted for about 1-2 hr and air volumes sampled were 2-164 m^3 (Table II-2). Unlike the other three fields, the field burned on December 15, 1978, was monitored by placing stationary samplers at the downwind edge of the field and 402 m and 1609 m downwind. The samplers were of the type shown in Figure 2, except those at the downwind edge which filtered smoke through GFF and XAD-4 at 30-50 L/min. Typical sampling conditions included a prevailing 2 m/sec wind and stable atmospheric conditions which caused the smoke plume to remain close to the ground for some distance from the source. These fields had been treated with the herbicides Ordram, typically at 3-5 kg/ha, and MCPA, typically at 0.5 kg/ha, 120 days to 150 days prior to harvesting. Both straw and ash samples were collected to check for residues of these pesticides. All samples were transported to the laboratory and the filtering media, straw, and ash samples were stored at -10 to -20°C before analysis.

Burn facilitiy at U.C., Riverside. The Statewide Air Pollution Control Research facility at U.C., Riverside, has a burning tower with monitoring equipment which allows for simulation of field burns of agricultural residues, such as rice straw. An earlier study demonstrated that burning rice straw under the controlled conditions of the tower closely approximates actual field burns (Darley et al, 1966). In view of this and the pressing need for substantial amounts of smoke residue per sample so that both the Ames mutagen assay and chemical analysis could be completed, we burned ~6 bales of rice straw and collected >150 samples during three 12-hr days at the end of July, 1980.

The smoke was sampled from the stack at the top of the tower. The samplers were fitted with probes and some were placed on the cat-walk about the stack, while other samplers remained on the ground (Figure II-5). A sampling train consisting of two Greenburg-Smith impingers in series filled with 100 ml ethylene glycol each and chilled in a refrigerated water bath (18°C) was also set up on the cat-walk to trap smoke (at 28 L/min) and protect it against oxidation and the hot reactive gases of the smoke plume. This was done with the intention of determining whether the chemical composition of the smoke changed during dry filtration; these samples have yet to be analyzed. In addition, some of the refrigerated water was pumped through an insulated coil surrounding a filter holder for the purpose of cooling 20 x 25 cm filters. In this way, the filter temperature was maintained near ambient. Upwind, background samples were also obtained on filters, resin, and in ethylene glycol (Figure II-6). The Air Resources Board also monitored the burning tower using a source van; for methodology and results, see attached report.

Each sampling run consisted of burning 9.1 kg of rice straw in the tower and operating the samplers until smoke was no longer visibly produced by the burned straw. On the average, this took about 12-13 min. The straw was placed on a weighing table at an incline of 25% and the higher end was ignited to simulate a back-burn with a 2 m/sec wind; the loss in

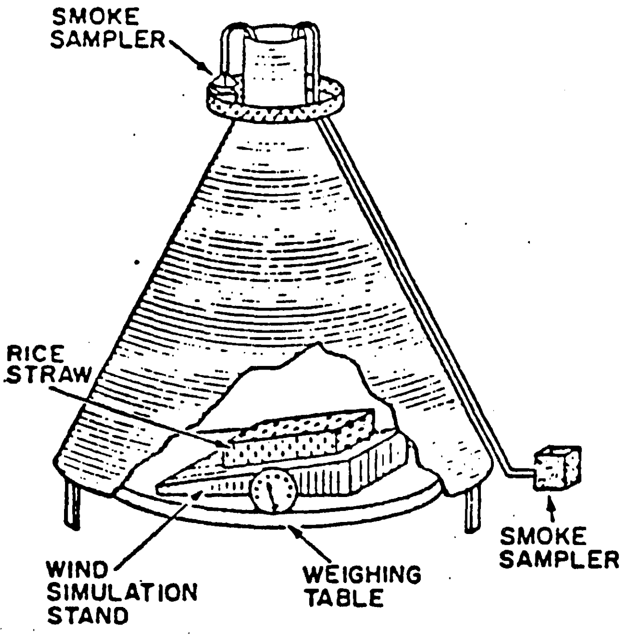

Fig. II-5. Deployment of smoke samplers about the U.C., Riverside, burning tower.

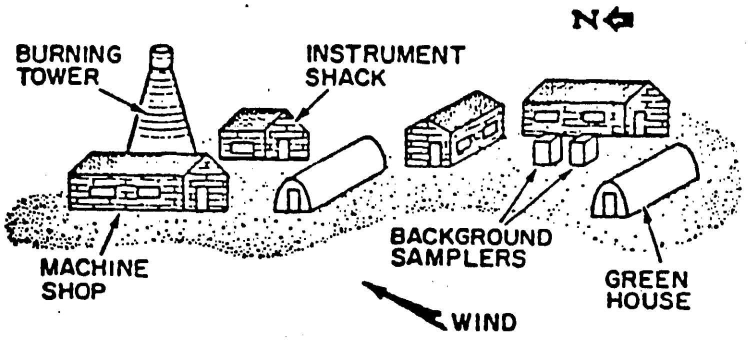

Fig. II-6. The U.C., Riverside, burn facility and location of background samplers.

weight during burning was monitored for a number of the runs (Table II-3). On the average, dry straw (~5% water w/w) lost about 76% of its weight while moist straw (about 18% water w/w) lost about 84%. However, an earlier study has shown that particulate matter made up less than 1% of the lost weight (Baubel et al, 1969). Real time analyses of the burning tower exhaust for CO, CO_2, total hydrocarbon, and temperature are summarized in Tables II-4 through II-6. The filters and XAD-4 resin were usually changed after each run; however, due to the relatively low flow rate of the impinger train, a single charge of ethylene glycol was used to collect a day's series of runs. All trapping media were placed immediately into a freezer for storage while in Riverside, and in dry ice-filled chests for transport back to Davis.

Incinerator samples. (Table II-2). Bales of rice straw were finely ground, transported to the incinerator (By-Dry Feed Products, Rancho Cordova), and continuously fed into the combustion chamber by a conveyor belt. The start-up fuel source was bottled gas; the combustion chamber was water-jacketed to produce steam as a heat source for drying grain; and unburned material was removed from the exhaust stream by using a cyclone separator. About 25% of the stack exhaust was diverted through a baghouse and then to the atmosphere. The baghouse exhaust gases were sampled using the specially designed smoke samplers to filter the exhaust through GFF, VF, MF, and XAD-4 resin (Figure II-7). Baghouse ash samples were also taken by opening the bottom of the baghouse and allowing the ash to drain into 1 L glass containers. The incinerator exhaust gases were at 375°C and by the time the gases passed through the baghouse the temperature dropped to 240°C. Moreover, the baghouse exhaust contained enough water to cause condensation throughout our sampling equipment. Sampling was conducted for a period of 4 hrs after which the samples were stored in dry ice-filled chests for transport back to Davis.

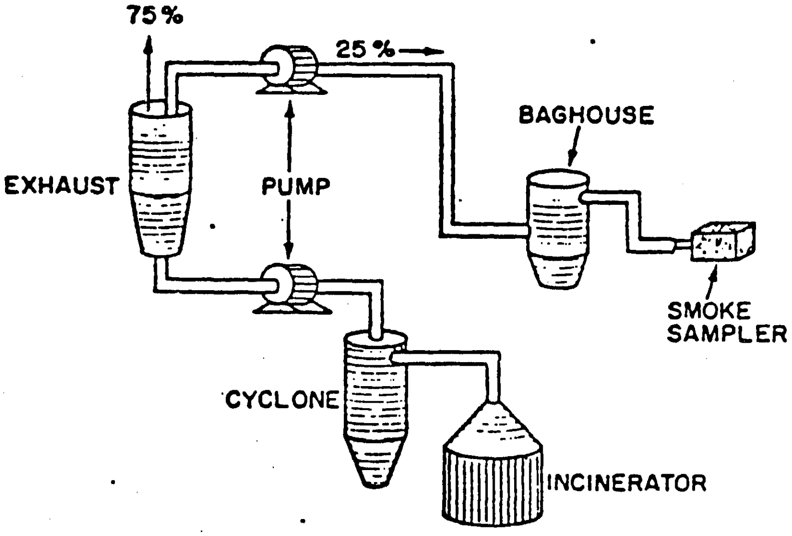

Fig. II-7. Sampling of smoke from the commercial incineration of rice straw.

Table II-3 Rice Straw Weight Loss During Burning

Burn Number[a]	Scale Reading, Kg		Weight Loss, Kg	% Wt. Loss[b]
	Before	After		
8	9.08	2.04	7.04	77.53
9	9.08	2.38	6.70	73.79
10	9.08	2.95	6.13	67.51
11	9.08	2.16	6.92	76.21
12	9.08	2.04	7.04	77.53
13	9.08	2.27	6.81	75.00
14	9.08	1.82	7.26	79.96
15	9.08	1.93	7.15	78.74
*[c]	9.08	2.04	7.04	77.53
M-1[a]	8.85	1.47	7.38	83.39
M-2	8.85	1.25	7.60	85.88
M-3	8.74	1.59	7.15	81.81
M-4	9.19	1.36	7.83	85.20

[a] Burns 8-15 and * had moisture content ≥5%; M-1 through M-4 had average moisture content of about 18%; M = moist.

[b] Average % loss: 75.98 (8-*); 84.07 (M-1 through M-4).

[c] Last burn (not in sequence).

Table II-4 Combustion Parameters for Dry (5%) Tower Burns on July 22, 1980

	Burn #2				Burn #3			
Time, min	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	5	20	<1000	45	15	~ 10	<1000	42
1	30	100	12,500	136	65	120	14,200	151
2	65	200	18,500 (Peak =20,500 2 min. 40 sec	186	95	230	20,000 (Peak)	96 (Peak)
3	150	400	18,000	198 (Peak = 224 2 min 36 sec)	235	500	17,500	188
4	345 (Off-400 4 min 7 sec)	750 (OFF)	9,000	103	505 (Peak)	920 (Peak 970 4 min 10 sec)	7,000	89
5					375	800	5,500	76
6					260	650	4,500	74
7					250	500	3,800	69
8					200	430	3,500	66
9					165	350	3,000	64
10					125	270	2,500	60
11					105	250	2,500	58
12					95	220	2,200	58

Table II-4 (Continued) Combustion Parameters for Dry (5%) Tower Burns on July 22, 1980

	Burn #4				Burn #5			
Time, min	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	10	0	<1000	92	10	0	<1000	42
1	40	100	15,500	158 (max=201 1 min, 36 sec)	100	170	16,000	166
2	150	270	19,500 (Peak= 20,200 1 min,57 sec)	161	120	200	19,000	186
3	182	400	19,200	184 (max=206 2 min 54 sec)	150	300	18,500 (Peak= 19,900 3 min 20 sec)	206 (Peak= 214 3 min 6 sec)
4	450	830 (Peak)	10,500	96	250 (Peak=380 4 min 20 sec)	650 (Peak= 850 4 min -30 sec)	10,000	98
5	455 (Peak=500) 5 min,17 sec)	800	6,000	79	365	800	5,300	76
6	335	720	5,000	69	260	600	4,000	66
7	325	620	4,000	66	165	430	3,300	64
8	230	520	3,200	62	115	450	3,200	60
9	185	470	3,000	62				
10	140	400	3,000	60				
11	110	300	2,500	58				
12	85	270	2,200	58				
13	60	250	2,100	55				
14	40	180	1,900	52				

Table II-4 (Continued) Combustion Parameters for Dry (5%) Tower Burns on July 22, 1980

	Burn #6				Burn #7			
Time, min	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	10	0	<1000	42	10	0	<1000	50
1	65	100	13,000	156	50	100	14,000	154
2	130	260	17,700 (Peak)	176 (Peak=186 2 min,30 sec)	120	220	15,000	161
3	230	400	14,000	176	225	350	13,000 (Peak= 16,500 2 min,45 sec)	178 (Peak=196 2 min,30 sec)
4	650 (Peak=700 4 min,12 sec)	600 Peak= 1,200 4 min, 30 sec)	7,500	86	545	850 (Peak)	7,500	84
5	475	870	4,500	69	510 (Peak=560 5 min,30 sec)	750	4,000	64
6	415	780	4,700	66	430	600	3,500	60
7	265	600	4,000	60	385	650	3,500	58
8	215	550	3,500	60	300	500	3,000	52
9	160	450	3,000	58	245	450	2,800	52
10	125	350	2,800	55	170	420	2,800	50
11	90	280	2,500	52	135	350	2,600	50
12	80	250	2,500	52	90	280	2,300	48

Table II-5 Combustion Parameters for Dry (5%) Tower Burns on July 23, 1980

	Burn #8				Burn #9			
Time, min	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	--	--	<1000	32	<5	~0	<1000	45
1	85	180	10,500	148	60	150	9,000	132
2	105	250	14,000 (Peak=16,000 1 min, 50 sec)	176 (Peak-191 1 min, 36 sec)	150	250	11,000	146
3	145	400	14,300	186	230	500	11,000 (Peak=13,000 3 min, 30 sec)	156 (Peak=178 3 min, 18 sec)
4	430 (Peak=685 4 min, 12 sec)	700 (Peak=1320 4 min, 20 sec)	8,500	94	295 (Peak=470 4 min, 43 sec)	600 (Peak=970 4 min, 50 sec)	11,700	151
5	365	950	4,500	79	395	920	5,500	84
6	145	650	3,500	69	300	770	4,000	74
7	100	470	2,500	60	195	550	3,000	66
8	85	570	2,500	60	160	450	2,500	60
9	55	450	2,000	55	150	420	2,200	60
10	50	350	2,000	52	115	320	2,000	58
11					95	330	2,000	58
12					60	250	1,800	55
13					50	250	1,500	52

Table II-5 (Continued) Combustion Parameters for Dry (5%) Tower Burns on July 23, 1980

	Burn #10				Burn #11			
Time, min	Total Hydrocarbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydrocarbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	10	--	<1,000	45	10	--	<1,000	58
1	95	200	10,400	132	90	200	13,500	151
2	125	250	10,600	151	215	320	15,000 (Peak=17,500 2 min, 10 sec)	201 (Peak=206 1 min, 57 sec)
3	270	500	14,000 (Peak=15,500 3 min, 15 sec)	205 (Peak=206 3 min,9 sec)	300	570	14,300	188
4	540 (Peak=780 4 min, 24 sec)	1,000 (Peak=1,350 4 min,20 sec)	8,000	98	600 (Peak=665 3 min, 43 sec)	1,050 (Peak=1,120 3 min, 40 sec)	6,000	94
5	585	1,030	4,000	77	470	850	4,300	79
6	530	1,000	4,000	74	365	720	3,700	74
7	350	750	3,000	69	305	620	3,000	69
8	280	600	3,000	67	230	550	2,700	65
9	205	520	2,500	64	165	430	2,300	62
10	140	450	2,000	60	125	370	2,000	60
11	95	350	1,800	58	85	270	1,800	58
12					70	270	2,000	58
13					50	200	1,500	55

Table II-5 (Continued) Combustion Parameters for Dry (5%) Tower Burns on July 23, 1980

	Burn #12				Burn #13			
Time, min	Total Hydrocarbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydrocarbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	--	--	--	60	5	--	<500	40
1	190	300	17,000 (Peak=17,800 1 min,10 sec)	231 (Peak)	85	200	20,000	204
2	570	870	9,000	110	240	500	31,000 (Peak)	221 (Peak=261 1 min, 45 sec)
3	560 (Peak=630 3 min, 30 sec)	840 (Peak=930 2 min, 20 sec)	4,800	84	480 (Peak=495 2 min, 40 sec)	770 (Peak=810 2 min, 45 sec)	8,000	106
4	530	750	3,500	74	390	610	5,200	86
5	420	560	3,000	67	440	630	4,500	76
6	355	460	2,400	67	370	550	3,000	66
7	355	450	2,400	64	275	410	2,300	60
8	310	400	2,000	62	290	410	2,500	62
9	250	320	1,800	62	205	300	2,000	58
10	250	300	1,700	60	175	270	1,800	58
11	220	270	1,600	58	130	250	1,800	55
12	190	250	1,600	58	105	210	1,700	55
13	170	250	1,500	58				
14	155	210	1,300	57				

Table II-5 (Continued) Combustion Parameters for Dry (5%) Tower Burns on July 23, 1980

	Burn #14				Burn #15			
Time, min	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	15	--	<500	50	20	--	<500	40
1	105	180	14,100	144	100	170	20,000 (Peak=31,000 1 min, 20 sec)	241 (Peak=251 1 min, 12 sec)
2	320	510	17,800 (Peak=20,000 2 min, 10 sec)	201 (Peak)	375	620	23,000	238
3	650 (Peak=875 3 min 35 sec)	850 (Peak=1,030 3 min,30 sec)	12,000	107	740 (Peak=820 3 min,5 sec)	960 (Peak=1,000 3 min, 10 sec)	8,000	92
4	810	960	7,000	94	715	850	5,000	76
5	670	750	5,300	76	640	700	4,000	69
6	760	700	4,000	66	475	520	3,200	64
7	600	580	3,100	62	395	430	3,000	58
8	500	480	2,600	60	340	460	3,000	60
9	460	520	3,000	60	265	310	2,500	58
10	305	250	2,000	55	210	270	2,300	55
11	245	350	2,500	55	190	270	2,100	55
12	155	230	2,000	52	130	230	2,100	55
13	--	--	--	--	105	200	2,000	52

Table II-5 (Continued) Combustion Parameters for Dry (5%) Tower Burns on July 23, 1980

	Burn #16				Burn #17			
Time, min	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	20	-	<500	35	30	--	<500	32
1	130	220	14,500	146	75	100	10,000	136
2	170	350	22,000	206	180	250	12,000	161
3	300 (Peak=910 3 min, 30 sec)	550 Peak= 1,400 3 min, 30 sec)	18,500 (Peak= 23,000 2 min, 45 sec)	154 (Peak=211 2 min,42 sec)	200	480	18,200 (Peak=19,000 2 min, 55 sec)	181 (Peak=196 2 min, 24 sec)
4	740	1,100	5,200	74	650 (Peak=700 4 min, 30 sec)	980 (Peak= 1,100 4 min,16 sec)	10,000	76
5	630	870	4,300	64	500	990	4,800	64
6	515	700	4,000	62	425	780	3,800	58
7	460	670	3,800	60	320	600	3,000	55
8	340	550	3,100	60	265	550	3,000	50
9	265	500	2,900	58	260	480	2,400	48
10	195	400	2,400	52	220	400	2,100	48
11	160	320	2,000	52	180	350	1,900	47
12					140	300	1,800	43
13					110	240	1,700	40
14					95	250	1,600	38

Table II-6 Combustion Parameters for Moist (18%) Tower Burns on July 24, 1980

	Burn #M-1				Burn #M-2			
Time, min	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	5	--	--	35	20	--	~ 700	28
1	65	~70	9,500	110	110	200	12,000	122
2	235	230	11,500	122	172	280	14,000	124
3	330	480	14,000 (Peak= 17,600 3 min,20 sec)	178 (Peak=181 3 min, 6 sec)	260	450	15,000 (Peak=16,300 3 min, 8 sec)	132 (Peak=161 2 min, 48 sec)
4	440 (Peak 775 4 min,17 sec)	530 (Peak=930 4 min, 20 sec)	11,000	114	480 (Peak=765 4 min,43 sec)	860 (Peak=1,050 4 min,20 sec)	11,500	79
5	680	820	5,200	67	690	880	5,000	55
6	455	600	4,000	58	500	700	4,500	55
7	455	500	3,500	58	415	580	4,000	50
8	350	470	3,200	53	345	470	3,700	48
9	330	430	3,000	52	365	430	3,000	45
10	280	300	2,500	50	300	350	2,700	43
11	250	280	2,300	48	270	350	2,700	43
12	220	270	2,400	48	195	290	2,500	40
13	190	260	2,100	45	145	240	2,200	38
14	140	170	2,000	45	130	210	2,100	36
15	145	200	2,000	45	95	190	2,000	34

Table II-6 (Continued) Combustion Parameters for Moist (18%) Tower Burns on July 24, 1980

	Burn #M-3				Burn #M-4			
Time, min	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C	Total Hydro-carbons, ppm	CO, ppm	CO_2, ppm	Exhaust Temp., °C
0	15	--	--	23	20	--	~600	18
1	55	~50	10,000	94	95	100	2,200	28
2	202	300	13,500 (Peak=14,300) 2 min,27 sec)	124	120	200	8,000	74
3	230	330	13,500	138 (Peak)	155	250	11,600	98
4	380 (Peak=705 4 min,23 sec)	560 (Peak=910 4 min,23 sec)	14,200	132	390	550	10,300	107
5	620	820	5,500	55	345	500	14,700 (Peak=15,500 4 min,50 sec)	132 (Peak=146 4 min, 45 sec)
6	525	630	4,000	48	375 (Peak=625 6 min,17 sec)	600 (Peak=890 6 min,20 sec)	11,000	79
7	425	500	3,200	42	565	800	5,000	48
8	315	320	2,600	38	455	620	4,000	40
9	310	350	2,700	38	385	520	3,500	38
10	270	300	2,600	35	330	450	3,200	35
11	225	270	2,200	33	310	450	3,000	33
12	220	250	2,200	33	260	380	2,800	33
13	195	240	2,200	33	220	330	2,700	30
14	165	200	2,000	30	185	290	2,500	30
15	140	200	2,000	30	145	240	2,200	28
16	140	190	1,900	--	110	200	2,000	27
17	130	150	1,600	--	--	--	--	--

Aircraft samples. (Table II-2). A Boeing Model 26 aircraft equipped and operated by the U.S. Environmental Protection Agency for environmental sampling was used to collect samples inside a rice straw smoke plume some distance above and downwind of the source. The intention was to look for chemical changes in smoke that had been exposed to the atmosphere and to sunlight for some time. The aircraft was operated at about 305-460 m in altitude and made numerous passes through the plume. Smoke residue was collected on GFF, VF, and XAD-4 resin. The samples were shipped to Davis and stored at -10 to -20°C.

D. Smoke samples

The samples from the various sources are listed in Tables II-2 and II-7 through II-11. The samples are listed according to code designations and explanations are provided in each table. The filter samples taken from rice fields were light-gray in color and the average weight recovered was 0.03-0.08g (72-137m^3) for each filter. The incinerator filter samples were also lightly colored and the average weight recovered was 0.075g. In this case, the color was a function of high-temperature incineration and baghouse filtration. Some of the aircraft samples were brown and the average weight of recovered material was about 0.077g. Samples taken at the burning tower were dark-brown to black; average weights of recovered material were in the range 0.4-0.7g (average ~12m^3). Only the last stage of the cascade impactor samples, the 20 x 25 cm GFF, was dark-brown to black in color. The previous stages had little or no color; this implies that most of the rice smoke was in the respirable range (less than 2 um). An earlier study indicated that greater than 90% of the rice smoke particulates had diameters less than 2um (Carroll et al, 1977). The samples cover a range of type and conditions so

Table II-7 Filter Samples - Tower Burns[a] - July, 1980

20 x 25 cm Filters (35 count)

Date	Burn Number	GFF[b]	QFF[b]	VF[b]
7/22	1-7	H03, control	--	--
	1-3	H04, cooled	--	--
	1-3	H05, ambient[c]	--	--
	5-6	H08, ambient[c]	--	--
	5-6	H09, cooled	--	--
	7	H012, cooled	--	--
7/23	8	--	JW2, cooled	--
	8	--	JW3, ambient	--
	8	--	JW4, control	--
	9	--	JW5, ambient	--
	9	--	JW6, cooled	--
	11	--	JW8, ambient	--
	11	--	JW7, cooled	--
	11	--	JW9, control	--
	12	--	JW10, cooled	--
	12	--	JW11, Control	--
	12	--	JW12, ambient	--
	13	--	JW13, cooled	--
	13	--	JW14, ambient	--
	13-14	--	JW15, control	--
	14	--	JW16, cooled	--
	16	--	JW17, cooled	--
	16	--	JW18, control	--
7/24	M-1[d]	F24, control	--	--
	M-1	F27, ambient	--	--
	M-1	F28, cooled	--	--
	M-2	--	JW19, cooled	--
	M-2	--	JW20, control	--
	M-2	--	JW21, ambient	--
	M-3	--	--	JY21, cooled
	M-3	--	--	JY23, control
	M-3	--	--	JY24, ambient
	M-4	--	--	JY25, cooled
	M-4	--	--	JY27, ambient
	M-4	--	--	JY28, control

[a] Smoke samples taken on tower cat-walk (Figure II-5)

[b] GFF = Glass Fiber Filter; QFF = Quartz Fiber Filter; VF = Verapor Filter

[c] Samples used for Ames mutagen assay

[d] M = moist (~18% w/w)

Table II-8 Cascade Impactor Filter Samples - Tower Burns[a] - July, 1980

(6 filters/run - 24 total filters)

Date	Burn Number
7/23	8
	10
	15
7/24	M-1[b]

[a] Smoke samples taken on tower cat-walk (Figure II-5).

[b] Stage 1: Filter #32

" 2: " #31

" 3: " #29

" 4: " #28

" 5: " #27

" 6: " #26 (20 x 25 cm GFF)

M = moist (~18% w/w).

Table II-9 Ethylene Glycol Samples - Tower Burns[a] - July, 1980

Date	Burn Number	Number of Samples[b]	
		Burn[c]	Control
7/22	1-7	1 cooled	1 ambient
7/23	8-16	1 cooled	1 ambient
7/24	M-1 through 4[e]	1 cooled	1 cooled[d]

[a] Smoke samples taken on tower cat-walk (Figure II-5).

[b] Each sample consisted of two impingers in series (100 ml ethylene glycol each); contents of impingers were combined for each sample.

[c] The glass wool used to trap aerosols of ethylene glycol was saved as a sample; in addition, XAD-4 was placed downstream of the glass wool for two of the samples (7/23 and 7/24).

[d] Control impingers were placed in ice baths.

[e] M = moist burns (~18% water w/w/).

Table II-10 XAD-4 Resin Samples - Tower Burns[a] - July, 1980

Date	Burn Number	Samples (39 total)[b]			
			Ambient		
		Cooled[c]	Backup	Alone	Controls[d]
7/22	1-3	+	+	+	+
	5-6	-	+	+	+
	6-7	+	-	-	+
7/23	8	-	++	-	+
	9	+	+	-	-
	10	-	+	-	-
	11	-	+	-	+
	11-12	+	-	-	-
	12	-	+	-	+
	13	-	+	+	-
	13-14	+	-	-	+
	15	-	+	-	-
	16	+	-	-	+
7/24	M-1-M-2[e]	+	-	-	-
	M-1	-	++	-	+
	M-2	-	+	+	+
	M-3-M-4	+	-	-	-
	M-3	-	+	+	+
	M-4	-	+	+	+

[a] Smoke samples taken on tower cat-walk (Figure II-5).

[b] Number of samples indicated by +.

[c] XAD-4 used as back-up to cooled filters.

[d] One control sample was run for burns 1-7.

[e] M = moist burns (~18% water w/w).

Table II-11 Filter and XAD-4 Samples - Tower Burns[a] - July, 1980

Date	Number	Filters (49 count) GFF[b]	VF[b]	MF[b]	XAD-4 Resin
7/22	1	H02	JY2	32	--
	2	H02	JY2	32	--
	3	H02	JY2	--	--
	4	H06	JY4	34	--
	5	H06,10	--	35	+[c]
	6	H010	JY5	33	+
	7	H010	JY7	36	+
7/23	8	H011	--	--	--
	9	H011	--	--	--
	10	H011	--	--	--
	11	H011,14	--	--	--
	12	H015,16	--	--	--
	13	H018	JY3[d]	--	--
	14	H019	JY3,11[e]	37	--
	15	H019	JY3,13[e]	25	--
	16	H021	JY3,15[e]	27	--
	17	H020	--	--	--
	18	H020	--	--	--
7/24	M-1[f]	H031,32	JY9[d],17[e]	27,29	+ +[c]
	M-2	H033,38	JY9,19[e]	28,M5	+ +
	M-3	H034,39	JY9,20[e]	30,M8	+ +
	M-4	H036,37, 40,42	--	M4,M10	+ +

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[a] Smoke samples taken with samplers on the ground (Figure II-5).

[b] GFF = Glass fiber filter; VF = versapor filter; MF = membrane filter.

[c] + indicates samples taken; same resin charges used for burns 5-7 and M-1 - M-4.

[d] JY3 and JY9 = Background samples and macrophage controls.

[e] Samples evaluated in macrophage assay.

[f] M = moist burns (~18% water w/w).

that analysis should provide a fairly complete picture of the nature of rice straw smoke and its impact on human and animal health. So far, chemical analysis for higher molecular weight compounds and the Ames mutagen assay have both been done on only one burning tower sample (HO#5; Table II-7). In addition, the Ames assay and macrophage assay only have been performed on other burning tower samples (Tables II-7 and II-11) and on aircraft, incinerator, and field samples (Table II-2).

E. References

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III. CHEMICAL ANALYSIS

A. Introduction

There has been much current interest in the formation, biological activity, and detection of organic pollutants and toxicants present in emissions from combustion of organic matter. These products of combustion range from relatively simple hydrocarbons, olefins, aldehydes, esters, acids, and mercaptans--materials of particular interest as primary air pollutants and from their involvement in photochemical smog--to more complex, higher molecular weight phenols, polynuclear aromatic hydrocarbons (PAH), heterocyclic compounds, and their derivatives. The complexity of primary combustion products, compounded by their further transformation by oxidative and photochemical reactions during residence in the atmosphere, accounts for the difficulty in ascribing a specific biological effect to a discrete chemical or chemical class. Some success in the area of cause-effect has been achieved with the carcinogenic PAH's (Bjorseth and Dennis, 1980) in cigarette smoke (refs. in Schmeltz and Hoffmann, 1976) and in the effluent of fossil fuel combustion--coal (Natusch, 1978), diesel (refs. in Rappoport _et al_ 1980), and gasoline (Grimmer, 1977). Many members of this chemical class, such as benzo[α]pyrene, are potent animal carcinogens (Gelboin and Ts'O, 1978) and associated with the particulate fraction (< 1 μm) that can be inhaled and retained in lungs of humans (Miguel and Friedlander, 1978). However, even with this relatively well characterized class of pollutants, there is a growing realization that PAH derivatives--oxides (Pitts, Jr. _et al_ 1980), nitro derivatives (Pitts, Jr. _et al_ 1978), and anhydrides (Rappoport _et al_ 1980)--may contribute substantially to mutagenic activity.

Work with the combustion products of vegetative matter--with the exception of cigarettes--has been much less extensive than for fossil fuels. Nevertheless, there is compelling evidence that smoke from such sources as leaf burning (Friedman and Calabrese, 1977) and wood burning (Hall and DeAngelis, 1980; Cooper, 1980) also contain PAH's, polynuclear heterocyclics, and related chemicals. Friedman and Calabrese (1977) reviewed the carcinogenicity of 19 such products and generic classes isolated and identified from the smoke of burning leaves. Hall and DeAngelis (1980) quantified emissions of 33 specific and generic PAH's and heterocyclics from wood-fired residential equipment. Anthracene and phenanthrene, and their methyl derivatives, constituted nearly 50% of the polynuclear organic matter, although several potent animal carcinogens (benzopyrenes, benzofluoranthenes, dibenzopyrenes, methylcholanthene, methylchrysene, and dibenzocarbazoles) were also measurably present.

With this background of candidate chemicals in mind, we set out to identify the major organic compounds present in rice straw smoke. Although a gross characterization of effluent from field combustion of rice straw has been made previously (Miller, Jr. _et al_ 1976; Boubel _et al_ 1969; Darley _et al_ 1966; Carroll _et al_ 1977; Darley, 1979) no detailed analysis of constituent chemicals has been reported to date. While we assumed that PAH's would very likely be present, and contribute to the mutagenic activity of smoke particulates, our plan during this chemical screening was to identify organic compounds of several classes (not restricted to PAH) present in fractions which exhibited activity in the Ames assay. It was our view that a more complete characterization would logically follow based upon this chemical screening, and the methods of sampling, fractionation, and identification developed in conjunction with the screening.

Extraction. There are a number of methods in the literature for extracting organic constituents and particularly POM from air filter samples. Many of these are based on extended (18-24 hr.) Soxhlet extraction with refluxing solvents such as benzene, hexane, methanol or solvent mixtures. This is a time-consuming process and may lead to degradation of more reactive constituents. We thus focussed our attention on more rapid extraction procedures which could be carried out at lower temperatures.

Golden and Sawicki (1978) used an ultrasonic (sonifier) extraction with 35% methylene chloride in cyclohexane as solvent. Soluble materials were worked up under nitrogen to avoid oxidation. The recovery of benzo[α] pyrene from glass fiber filters was claimed to be better with this procedure than by Soxhlet extraction with hexane. Royer *et al* (1979) used an ultrasonic bath and methylene chloride or 1:1 toluene-propanol for glass-fiber filter extraction. Recovered mutagenic activity was comparable to that obtained by Soxhlet extraction. Griest *et al* (1980) employed a sonibath with benzene for extraction of several radiolabelled hydrocarbons and PAH's spiked to coal fly ash. Recoveries of saturated hydrocarbons was higher than for PAH's, indicating adsorption or poor solubility of the latter under the extracting conditions. It would appear that a more polar co-solvent is needed to improve PAH extraction efficiency when sonication is used--a modification which we have employed in our analyses of rice straw smoke.

Fractionation. The extract of smoke condensate produces too complex a mixture for direct constituent analysis. Thus a cleanup or fractionation scheme is employed with constituent analysis proceeding with individual fractions. Approaches to fractionation include the classical acid-base partitioning, yielding neutral (hydrocarbons, aldehydes, esters, etc.), basic (amines, N-heterocycles), and acidic (carboxylic and sulfonic acids) fractions (Shriner et al 1964). A major disadvantage is that the neutral fraction is still a complex mixture, in which the constituent analysis of, for example, PAH's is confounded by the presence of non-PAH neutrals. Another approach to fractionation is based upon chromatography, using adsorption, gel permeation, or partition columns (Snyder and Kirkland, 1979).

Hsieh et al (1969) used Sephadex LH-20 (hydroxpropylated dextran polymer) eluted with THF to achieve a gel permeation fractionation of some coal carbonization products and related liquids. Fractions enriched in paraffins, olefins, and aromatic hydrocarbons were obtained in sequential order, with some separation within each class occurring based upon molecular weight. In a related area, Streuli (1971) showed that Sephedex LH-20 eluted with THF allows for separation of PAH's into classes and their resolution from paraffins. Furthermore, oxygenated, sulfonated, and nitrated PAH's and some heterocyclic aromatics are resolved from unsubstituted hydrocarbons by hydrogen-bonding to Sephadex LH-20, and can then be eluted with a more polar solvent such as methanol.

Royer et al (1979) applied Sephadex LH-20 eluted with THF and methanol to the fractionation of diesel combustion particulate extracts. Use of Ames assay and GC-MS analysis supported an elution pattern, in increasing fraction number, of aliphatic hydrocarbons (fractions 1 and 2, THF), PAH's (fractions 3-5, THF), and more polar constituents--phthalate esters, methyl quinolone, and THF degradation products (fraction 6, methanol). This was essentially the technique we applied to the fractionation of rice straw smoke extracts.

Resolution. High performance chromatography, principally by liquid and gas chromatography (Snyder and Kirkland, 1979; Lee and Wright, 1980), affords the most practical and useful approach to resolution of polycyclic aromatic compounds. Among these two techniques, gas-liquid partition chromatography using glass capillary columns gives the more complete resolution of individual PAH's and heterocyclic compounds in complex mixtures of isomers and homologues. The development of glass capillary columns stable at the relatively high temperatures (>250°) required to elute PAH's containing four or more rings is a notable advance; several liquid phases are now available, with SE-52 and SE-54 the most useful for this application. A comprehensive review of the subject of glass capillary gas chromatography of polycyclic aromatic compounds has been published very recently (Lee and Wright, 1980), and includes operating conditions and retention data upon which our analyses of rice straw smoke polynuclear aromatics was based.

Identification. GC retention data and comparison with the retention of standards is generally not sufficient for identifying constituents in complex mixtures such as exist in smoke condensate. For such applications use of a gas chromatograph interfaced to a computerized mass spectrometer is essential. Many examples of the application of GC-MS to environmental samples may be found in the literature. An example is the work of Lee et al (1976) in identifying and quantitating over 150 PAH's in tobacco and marijuana smoke condensates by capillary GC-MS analysis of fractions from Sephadex LH-20 and HPLC separation. Many close, yet toxicologically important, isomers of alkyl PAH derivatives were successfully resolved and identified as to parent ring structures and type of alkyl substituents. GC-MS was also the principal technique used by Hall and DeAngelis (1980) to identify and quantify POM's in wood combustion emissions.

Summary of methods. Summarizing the methods reviewed in the preceeding sections, our approach to analyzing for POM's and other organic compounds in rice straw smoke emissions consisted of the following:

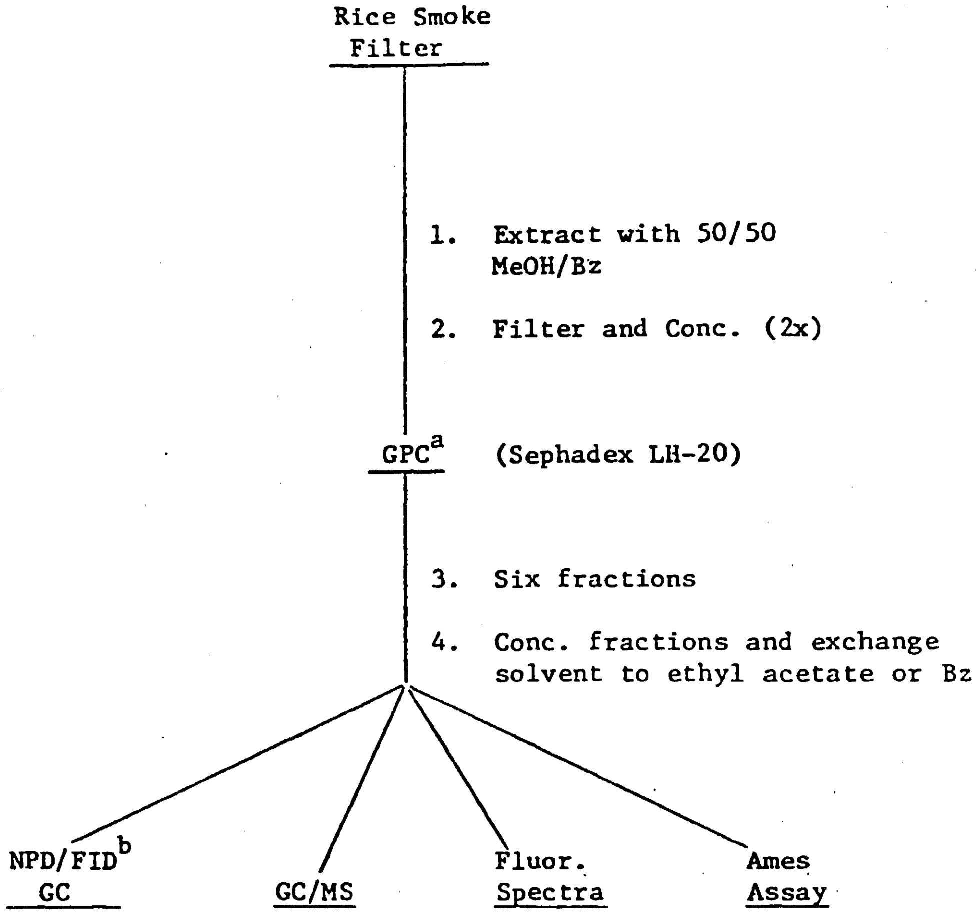
1. Extraction at room temperature by sonification with benzene-methanol (1:1) mixture.
2. Fractionation of extractables by gel permeation chromatography on Sephadex LH-20 eluted with THF followed by methanol.
3. Resolution of individual chemicals in liquid chromatographic fractions by capillary GC on SE-54.
4. Identification of major constituents by computerized GC-MS.

Ames assay analysis and fluorescence spectrophotometry were used to characterize fractions from liquid chromatography. Additionally, standard PAH's were employed to determine recoveries through the method and for matching, via retention times and mass spectra, with components of rice straw smoke. As subsequent sections of this chapter will show, a number of PAH's, heterocycles, and other organic compounds were identified from rice straw smoke using this methodology.

B. Experimental

Extraction and Column chromatography (Figure III-1). One-half of a 20 x 25 cm GFF, that had been used to trap rice straw smoke at the U.C. Riverside burning tower, (H05; Sampling Section, Table II-7), was placed in a 1 L Teflon® beaker, in a bed of ice, covered with a 50/50 mixture of methanol(MeOH) and benzene(Bz), and sonified with a Branson Model J-32A sonifier for 2 min. The probe was positioned just below the surface of the liquid to achieve good cavitation. The contents of the beaker were then filtered through Whatman #1 filter paper and the paper and glass filters were combined and sonified again using fresh solvent. After filtration, the two extracts were combined and reduced in volume on a rotary evaporator shielded with aluminum foil against illumination by both sunlight and fluorescent lighting. The smoke extract was then transferred to a 50 ml centrifuge tube and reduced further in volume under a stream of dry nitrogen. When substantial precipitate formed, the mixture was filtered through a 25 mm diameter GFF and the filter was washed with 50/50 MeOH-Bz until the washes were essentially colorless. The filtrate and washes were combined and reduced in volume under a stream of dry nitrogen for column chromatography. If necessary, the mixture was filtered again.

A thin paste slurry of Sephadex LH-20 (Pharmacia, Inc.) in tetrahydrofuran (THF) was poured at one go into a 2.5 x 100 cm glass column (Pharmacia, Inc.). Fresh THF was allowed to drain through the column at about 4 ml/min until the Sephadex reached maximum bulk density. Final Sephadex dimensions were 2.5 x 70 cm. In preparation for chromatography, the solvent was allowed to drain until it reached to just



[a] Gel permeation chromatography

[b] NPD = nitrogen/phosphorus thermionic detector

FID = flame ionization detector

Fig. III-1. Scheme for Extraction and Fractionation of Rice Smoke from Glass Fiber Filter the top of the Sephadex column. Using a pipet, a 5 ml aliquot of a total of 10 ml of whole smoke condensate was added slowly to the top of the column so as not to disturb the bed. After the sample was allowed to drain into the Sephadex, fresh THF was added and the glass column was connected to a reservoir containing THF. Five THF fractions were collected while fraction 6 was eluted with 50/50 THF/MeOH (see Table III-1 for volumes of the individual fractions). All fractions were concentrated to approximately 5 ml and the solvent exchanged to ethyl acetate for gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) or to benzene for the Ames mutagen assay. Chromatography was repeated on the same column with a fresh sample of smoke condensate, the fractions were concentrated, 3 ml aliquots were removed from each fraction, and the aliquots were taken to dryness in preweighed vials to determine weight recovery for each fraction. Moreover, a mixture of about 500 μg each of 16 different polyaromatic hydrocarbons (PAH) (Table III-2) was also chromatographed on the same Sephadex column to determine percent recovery and distribution among the fractions.

<u>GC and GC/MS</u>. GC of the smoke fractions was accomplished using a Hewlett-Packard Model 5710-A gas chromatograph equipped with either a flame ionization detector (FID) or a nitrogen/phosphorus thermionic detector (NPD) and a 30 m x 0.25 mm i.d. fused silica capillary column coated with SE-54 (J & W Associates) in conjunction with a variable split valve (25:1). Conditions for the FID were as follows: Injector and detector temperatures were 250°C and 300°C, respectively; gas flows were 200, 20, 20, and 1 ml/min for air, hydrogen, make-up gas (nitrogen), and carrier gas (helium), respectively. Conditions for the NPD were the same as for the FID except that the air and hydrogen flows were 60 and 3 ml/min, respectively, and the

Table III-1 Fractionation of Whole Smoke Condensate on Sephadex LH-20

Fraction No	Eluting Solvent, ml
1	THF[a], 60
2	THF, 30
3	THF, 30
4	THF, 30
5	THF, 190
6	1:1 THF/MeOH[b], 300

a) THF = tetrahydrofuran

b) MeOH = methanol

Table III-2 Polyaromatic Hydrocarbons (PAH) used to Determine Recovery off Sephadex LH-20

(1) Naphthalene
(2) Acenaphthene
(3) Dibenzothiophene
(4) Phenanthrene
(5) Anthracene
(6) 5,6-Benzoquinoline
(7) Carbazole
(8) 4,5-Methylenephenanthrene
(9) Fluoranthene
(10) Pyrene
(11) 1,2-Benzanthracene
(12) Chrysene

(13) Benz(a)anthracene-7,12-dione
(14) Benzo(e)pyrene
(15) Benzo(a)pyrene
(16) Perylene

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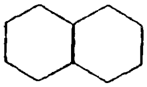
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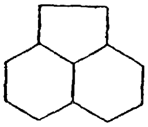
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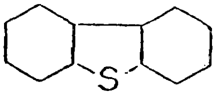

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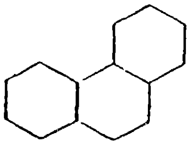
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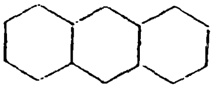
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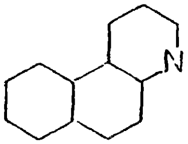

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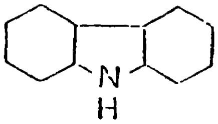

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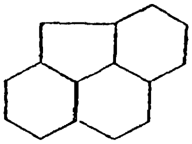
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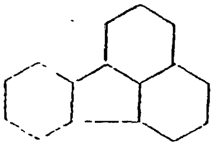
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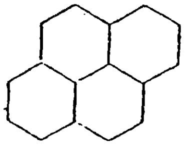
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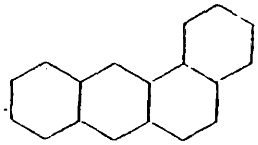
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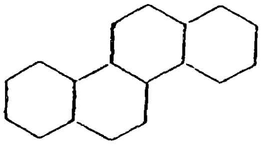
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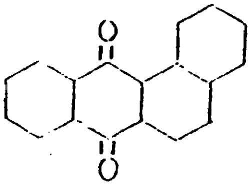

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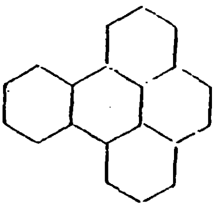
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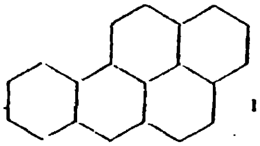
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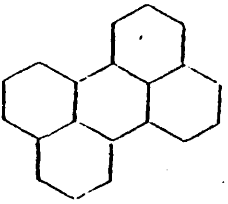

detector voltage was set at about 21 VDC. Column temperature programs were typically 80-260°C at 8°/min and 120-240°C at 4°/min.

GC/MS was performed using a Finnigan Model 3000 mass spectrometer interfaced with a Finnigan Model 9500 gas chromatograph and a Finnigan Model 6000 data system. The gas chromatograph was equipped with a 30 m x 0.25 mm (i.d.) fused silica column coated with SE-54; column head pressure was 20 lbs and carrier gas (helium) flow was about 1 ml/min. Injector port temperature was 250°C, column temperature program was 80-260°C at 8°/min, and the data system scan rate was 3 sec/scan. The mass spectrometer ionizer was operated at 70 ev.

Elemental analysis. Versapor (acrylic polymer) filter (VF) samples of rice straw smoke were irradiated with alpha particles, generated by a cyclotron, and VF, rice straw, and ash samples were irradiated with thermal neutrons and the characteristic x-rays emitted by the various elements in the samples were read. For alpha particle-induced x-ray emission (PIXE), the emission from a clean VF was computer-subtracted from the sample emissions. For neutron activation, two readings per sample were made: Immediately after a 9 sec activation for elements with large cross-sections for neutrons, and 1-2 weeks after a 90 sec activation to allow background impurities to decay so that more accurate readings could be made of elements with small cross-sections for neutrons. This method was not capable of seeing emissions from silicon. Corrections were not made for contributions from the VF itself; however, a clean VF was activated and read. The analysis was performed by the Crocker Nuclear Laboratory (PIXE), University of California, Davis, and the Los Alamos Scientific Laboratory (neutron activation), Los Alamos, New Mexico.

Fluoresence Spectra. Smoke fractions 3-5 were combined and the solvent for this mixture and that of fraction 6 was changed to methylene chloride. The samples were placed in quartz cuvettes and the excitation and emission spectra were scanned individually at 60 nm/min in order to determine the maximum wavelength for the excitation and emission spectra.

C. Results

Column chromatography. After addition of the dark brown-black whole smoke condensate to the Sephadex column, the sample spread from 5 cm into a pale-brown band of about 30 cm in width that was highly fluorescent under long-wavelength ultra-violet light. This band no doubt represented the bulk of the sample; it moved slowly down the column during elution (4 ml/min) and some color began to appear in fraction 4 with the remainder eluting in fraction 5. After fraction 5 was collected, some color remained on the entire length of the column and it was removed only by eluting with 50/50 THF/MeOH. The MeOH caused the column to swell by about 7% causing the flow to drop to about 0.5 ml/min; by pressurizing the column to 12 psi with nitrogen head pressure the flow rate was raised to about 3 ml/min. The eluate was designated as fraction 6 which was assumed to contain the polar components of the smoke concentrate. When the fractions 4-6 were concentrated to equal volumes (2-3 ml) and briefly exposed to long-wavelength ultra-violet light, they all fluoresced with fractions 5 and 6 exhibiting the greatest fluorescence.

Table III-3 lists the amounts of smoke condensate recovered in each fraction. The column was loaded with 140.4 mg of material and 101.9 mg (73%) total material was recovered. Of the material recovered, fraction 5 contained the bulk of it (57%) followed by fraction 6 (20%). The percent recoveries through the Sephadex column of the components of a PAH standard mixture are listed in Table III-2. The recoveries ranged from 68-105% with an average of 92.5 ± 10.2%. All 16 of the PAH were found exclusively in fraction 5 as determined by FID-GC (Figure III-2).

Table III-3 Recovery of Smoke Residue from Sephadex LH-20

Fraction No.	Amount Smoke Residue, mg[a]	%
1	2.7	2.0
2	6.3	4.5
3	1.8	1.3
4	12.2	8.7
5	58.5	41.7 (57)[b]
6	20.4	14.5 (20)[b]
	Σ 101.9	72.7

[a] Amount loaded on column = 140.4 mg

[b] Values in parantheses based on recovered material

Table III-4 Recovery of Polyaromatic Hydrocarbon (PAH) Standard from Sephadex LH-20

PAH No.[a]	% Recovery	PAH No.	% Recovery
2	99.6	11	78.7
3	105.0	12	67.5
6	99.6	13	94.3
7	90.5	14	93.2
8	101.8	15	85.7
9	102.8	16	88.9
10	95.4		

[a] See Table III-2 for identification of PAH No.

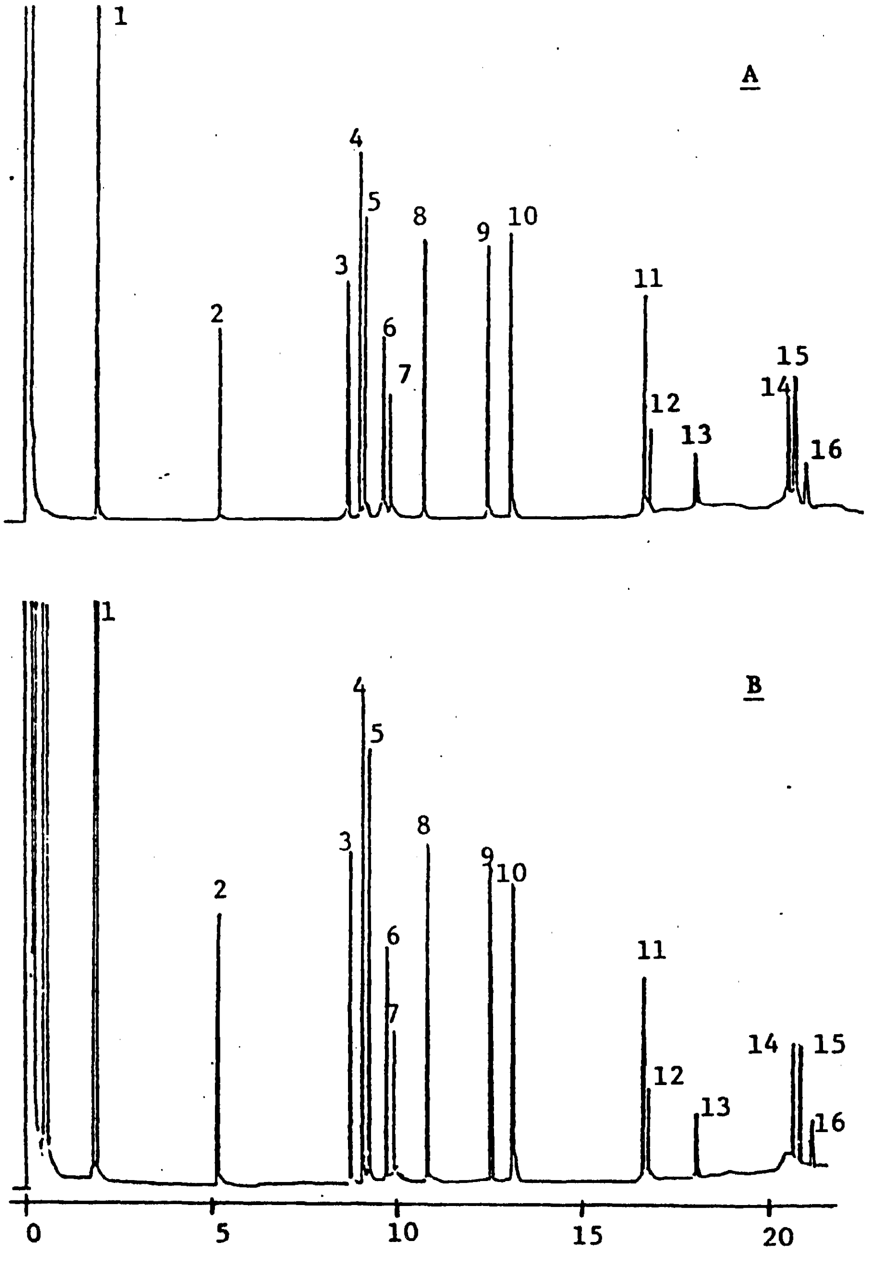

Fig. III-2. FID capillary gas chromatograms of a PAH mixed standard (A) and fraction 5 of mixed standard off Sephadex column (B). See Table III-2 for number designations.

GC and GC/MS. The Sephadex fractions of the whole smoke condensate were examined using both FID and NPD-GC. Only fractions 5 and 6 showed a myriad of peaks with both detectors (100-200 peaks) (Figures III-3 and III-4). The mass spectral analysis of fraction 5 indicated the presence of many different classes of compounds. Table III-5 summarizes compounds tentatively identified. They include cresols, phthalates, PAH's, and long-chain hydrocarbons. While similar classes of compounds were observed in fraction 6, specific identifications were not made due to the lack of appropriate standards. Many compounds were at levels too low to quantitate accurately.

Fluoresence spectra. Table III-6 lists the maximum wavelength for the excitation and fluorescence spectra obtained for mixed fraction 3-5 and fraction 6. Figure III-5 shows the profiles of the scans; Figure 15 shows the scan of a mixed PAH standard. Fraction 6 was 10-30 nm higher than mixed fraction 3-5 for both excitation and fluorescence wavelength maxima.

Elemental analysis. The elements found and their amounts are listed in Tables III-7 and III-8 for each sample examined. Using PIXE, the elements of greatest abundance for most of the samples were potassium and calcium; the heaviest element observed was barium which appeared in only one sample. The element of greatest abundance for the samples irradiated with thermal neutrons was sodium; there were also traces of the rare-earth elements. The limit of detection for the PIXE method ranged from about 1000 ng/cm^2 for bromine to about 140 ng/cm^2 for copper. The limit of detection for neutron activation ranged from about 8000 ppm for potassium to less than 0.01 ppm for uranium. In general, the detection limit was lowest for the higher atomic number elements using this method.

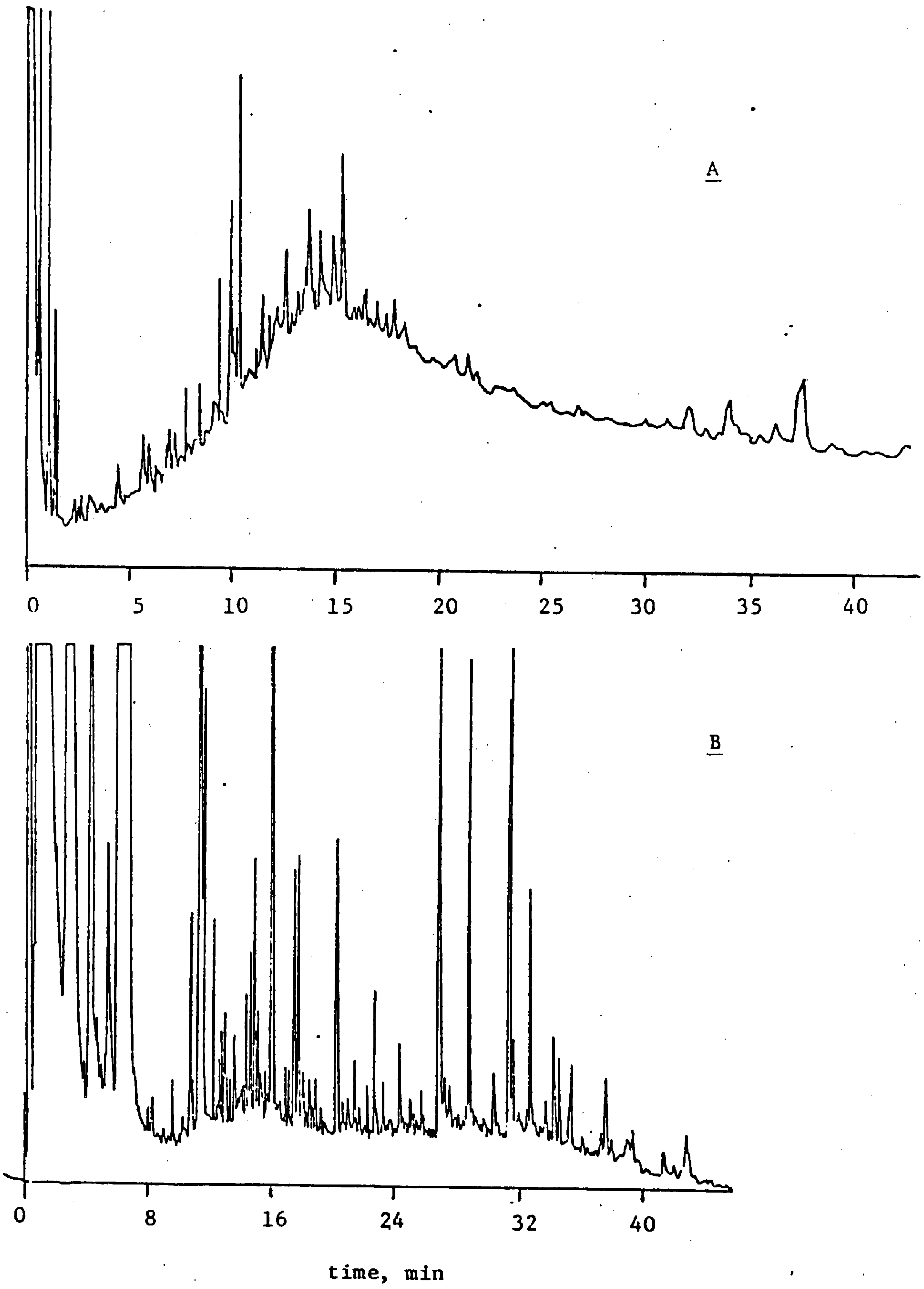

Fig. III-3. FID capillary gas chromatograms of fractions 5 (A) and 6(B) of rice smoke condensate off Sephadex column.

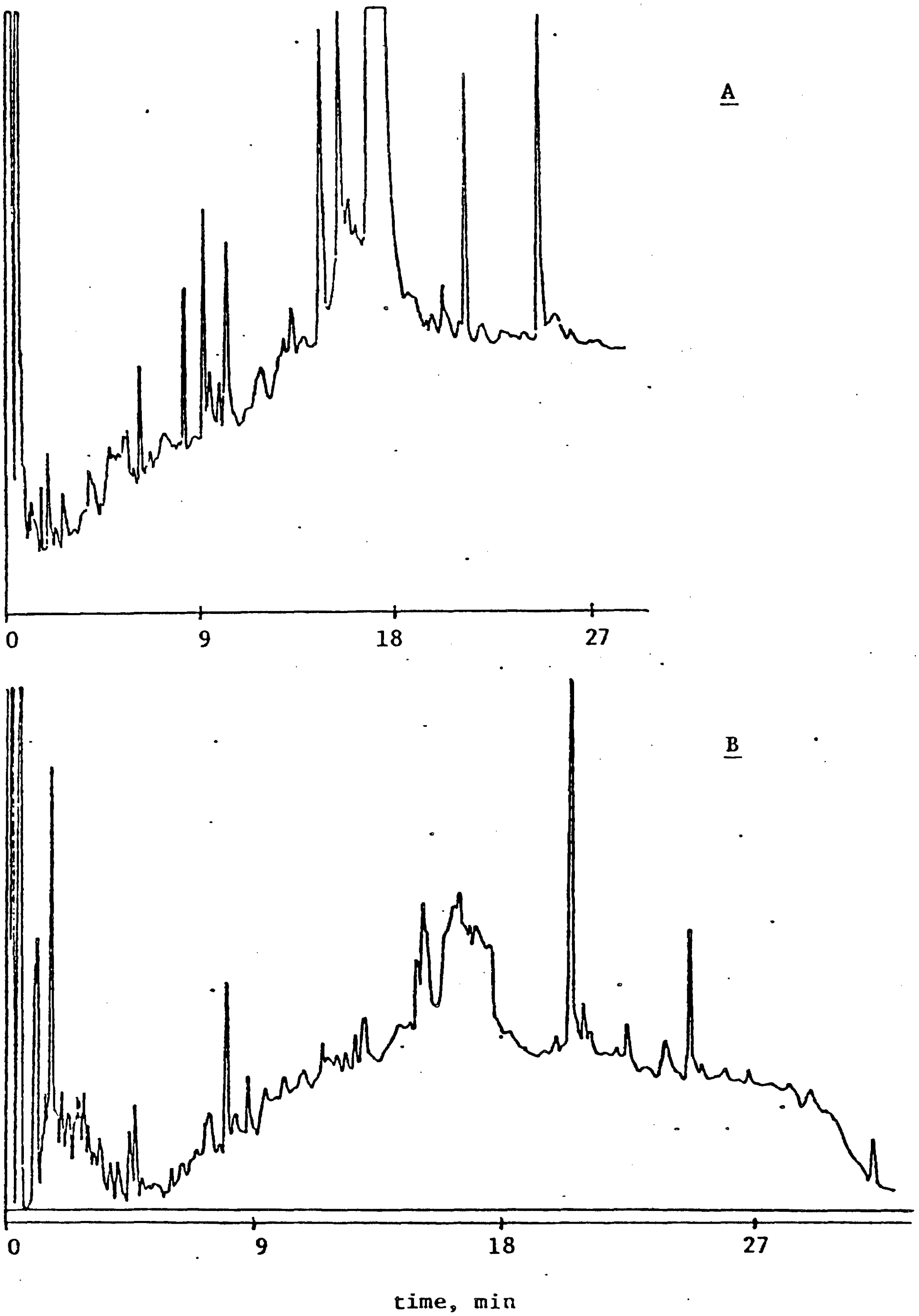

Fig. III-4. NPD capillary gas chromatograms of fractions 5 (A) and 6 (B) of rice smoke condensate off Sephadex column.

Table III-5 Compounds Identified in Rice Straw Smoke

1. cresol isomers
2. xylenol isomers
3. methyl benzaldehyde
4. styrene
5. cresol acetate
6. coumaran
7. acenaphthene
8. biphenyl
9. methylbenzothiophene isomer
10. dimethylnaphthalene isomer
11. trimethylindene isomer
12. fluorene
13. carbazole
14. phenanthrene
15. anthracene
16. methylphenanthrene
17. cyclopentanophenanthrene
18. fluoranthene
19. pyrene
20. 1,2-benzanthracene
21. chrysene
22. triphenylene
23. 3Hbenzo(e)indole-2-carboxylic acid
24. thiazole[5,4d]pyrimidine-5-ethylamino

Table III-5 (cont'd)

Substituted Aromatics

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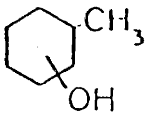

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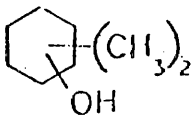

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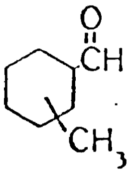

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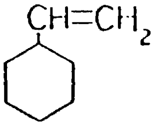

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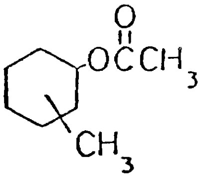

Polynuclear Aromatic Hydrocarbons

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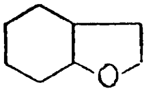

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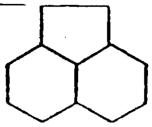

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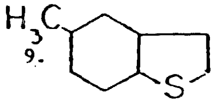

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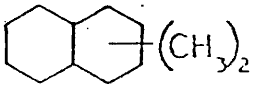

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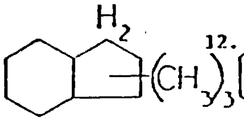

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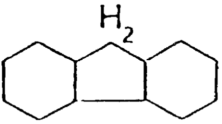

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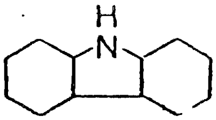

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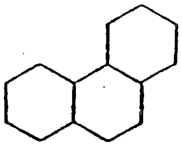

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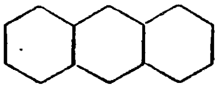

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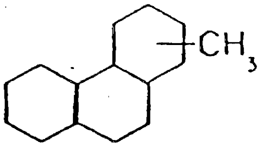

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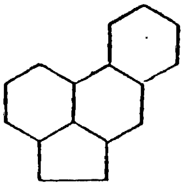

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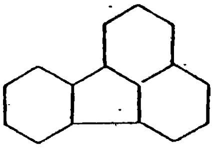

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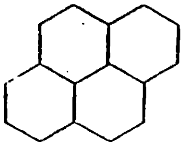

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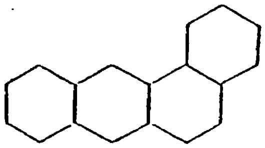

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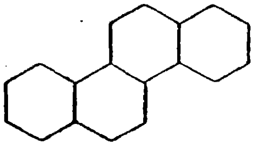

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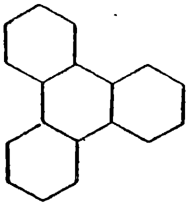

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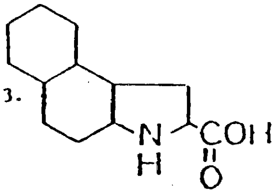

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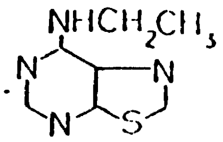

Table III-6 Maximum Wavelength for Excitation and Fluoresence for Smoke Fraction 5 and 6 and a Mixed Standard

	Maximum Wavelength, nm	
Sample	Excitation	Fluoresence
Mixed Fraction 3-5	381	425
Fraction 6	390 (410)	436
Mixed Standard	373 (385)	435

D. Discussion

The binary solvent system consisting of MeOH and Bz appeared to be quite adequate in removing condensed smoke from GFF during sonification. Two extractions of the same filter left it essentially colorless; even the carbonaceous material, which is often difficult to recover, was either dissolved or suspended as very fine particulates. MeOH was chosen for its polarity and its ability to dissolve heterocycles and Bz was selected because of its affinity for pi-electron density, such as that in PAH. While dimethyl sulfoxide has been recommended by others as an excellent solvent for condensed smoke and ash, and especially for PAH (Butler, 1979), we rejected it because its high boiling point (189°C) would make concentration of samples difficult. By contrast, MeOH and Bz form a low boiling azeotrope (58.3°C).

Using a sonifier for extraction was preferred over Soxhlet extraction because of the low time investment and greater extraction efficiency afforded by sonification (Golden and Sawicki, 1978; Roger et al, 1979). Soxhlet extraction requires 12-16 hrs for quantitative recovery, while four min (two extractions) of sonification will accomplish the same task. Moreover, the relative mass extraction efficiency of a sonifier is 1.14, where Soxhlet extraction is 1.00. Also, compounds may be lost through thermal decomposition at the boiling points of solvents commonly used in a Soxhlet extractor. However, a sonifier fragments a GFF so that during the concentration step the sample must be filtered several times; but, this is not viewed as a serious drawback.

Many methods have been devised for separating complex mixtures of organic compounds into separate classes. Classically, acid/base/neutral extractions have been used to accomplish this (Shriner et al, 1964). However, such extractions are time consuming and there is no guarantee that a particular class of compounds (eg PAH) will not appear in more than one fraction. In addition, if care is not taken there are many opportunities for sample loss and overall low recovery using extraction techniques. Gel permeation chromatography (GPC) appeared to be the most attractive alternative (Snyder and Kirkland, 1979). We adopted a method used by the Inhalation Toxicology Research Institute, Albuquerque, New Mexico, to analyze for mutagens in diesel exhaust particulates (Roger et al, 1979). For GPC, they used a hydroxpropylated dextran (Sephadex LH-20) column to fractionate the diesel exhaust material into six fractions. They claimed that the column could separate long-chain hydrocarbons from PAH, and fractionate the PAH according to molecular weight (Streuli, 1971). Furthermore, the larger PAH would appear first in the eluate because of their inability to fit into the pore spaces of the gel. The only modifications we made to the method were to use a larger column (about 2x) and proportionately larger volumes of eluting solvent, except for fraction 6 which was kept the same. The larger column was necessary to accommodate larger loadings of smoke extract so that each fraction would have enough material for the Ames mutagen assay. However, in view of the fact that all of the PAH standards appeared in one fraction and that the mass spectrometer detected both long-chain hydrocarbons and PAH in the same fraction our column did not operate efficiently. This may have been partly due to column flow rate (4 ml/min). Hsieh et al (1969) claim that for GPC to work well, flow rates should be less than 0.5 ml/min; but even so, they still had overlap of low molecular weight hydrocarbons with high molecular weight PAH. Operating our column at 0.5 ml/min would require over 20 hrs to collect all of the fractions. A more attractive alternative which is yet to be investigated is reversed-phase high performance liquid chromatography; this method promises to give efficient separation with a low time investment.

Many constituents of rice straw smoke are reactive and, therefore, require special handling techniques. Phenolics, for example, in an oxidizing environment will polymerize. We observed that in fractions 5 and 6, which contained the bulk of the smoke extract, dark-brown precipitates formed within a few days after the fractions were isolated and concentrated (<1 ml). Without chemical confirmation, we assumed the precipitates were polyphenolics. While the solvent properties of THF made it attractive as an eluting solvent for GPC, its ability to autooxidize and form peroxides probably contributed to precipitate formation. The rate of precipitate formation could be decreased by diluting the fractions with non-oxidizing solvents such as Bz. PAH are light sensitive and will photooxidize in the presence of ultra-violet radiation. The wavelengths at which many PAH are excited (290-400 mu) are comparable to chemical bond energies. For example, an excitation wavelength of 290 mu is equivalent to an energy of 98.6 kcal/mole. Thus, the observed conversion of PAH to quinones, for example, may be explained in terms of photoexcitation followed by oxidation with molecular oxygen. Sunlight and common fluorescent lighting contain wavelengths down to 290 mu; lifetimes of some PAH under these types of illumination have been shown to be only a few hours. (Tebbens et al, 1966). It is important, then, to exclude light altogether or work under red or yellow light when handling smoke extracts. We excluded light by wrapping the Sephadex column and all glassware with aluminum foil; samples were also stored in a refrigerator. Handled in the ways described, our smoke fractions remained essentially unchanged for 2-3 weeks, as indicated by physical appearance and GC peak profile.

The gas chromatograms and fluorescent spectra of fractions 5 and 6 indicated that they consisted of complex mixtures of compounds. The most economical approach to the analysis of these mixtures and a method with the greatest probability of success included the use of a GC/MS with data system. The worth of such a system has been proven in the analysis of tobacco and marijuana smoke condensates (Lee et al, 1976) and wood combustion emissions (Hall and DeAngelis, 1980). As far as we know, little or no work has been done on rice straw smoke. So faced with a unique analytical problem we spent much of our time adapting the GC/MS system to the analysis of rice straw smoke, and, therefore, most if not all of the compound identifications are tentative. A limiting factor was the data system whose small disc storage capacity held us to short analysis times (40 min) and, therefore, to only two analyses per disc; however, the installation of a Finnigan INCOS data system which has a much greater data storage capacity should remedy this situation in the future.

Compound identification was done in part by comparing mass spectral fragmentation patterns and relative GC retention times with those of standards. When standards were not available, a mass spectral data reference work (Cornu and Massot, 1966) was consulted to compare fragmentation patterns and relative abundances of fragments. Moreover, identifications were also made using the computerized NIH-EPA Chemical Information System (CIS) which contains about 33,000 mass spectral entries. In some cases, it was not possible to decide between isomers (eg, anthracene and phenanthrene).

Many of the compounds found in our rice smoke extract (Table III-5) have been observed in other types of smoke resulting from the pyrolysis of plant materials (Schmeltz and Hoffmann, 1976; Friedman and Calabrese, 1977; Darley, 1979; Hall and DeAngelis, 1980; Cooper, 1980). Pyrosynthetic pathways have been suggested for the formation of the many and varied compounds observed in smoke. PAH can form from long-chain hydrocarbons and small condensed ring compounds; steroids are also implicated. In addition, flame temperature is important in determining relative amounts of different PAH (Schmeltz and Hoffmann, 1976). While phthalic acid and phthalic anhydride could be formed in an oxidizing flame, the presence of higher molecular weight phthalic esters, such as di-n-butyl and di-2-ethyl hexyl phthalates, in our rice smoke samples was probably due to contamination from synthetic plastic materials used in the smoke samplers and present throughout the environment.

Benzo(a)pyrene, pyrosynthesized from various plant constituents such as dotriacontane (Schmeitz and Hoffmann, 1976) is commonly found associated with the particulate matter in smoke. This PAH has been established to be both mutagenic and carcinogenic; it is a frame-shift mutagen which causes errors in DNA replication. However, its presence in our rice smoke extract was below the detectable limits of our analytical methodology. This may be partly due to low recovery. Griest et al (1980) found that by spiking coal fly ash with ^{14}C-benzo(a)pyrene and extracting the material with pure Bz using a sonifier, recovery was less than 10%; on the other hand, recovery of naphthalene and phenanthrene was quantitative. Another possibility is that the flame temperature was not optimum for efficient formation of benzo(a)pyrene (Schmeltz and Hoffmann, 1976). A third possibility is that this PAH is less stable than some other PAH and degrades rapidly (Thomas et al, 1968). The use of THF for GPC may contribute to the degradation of benzo(a)pyrene because of the formation of reactive peroxides by THF. A suitable replacement for THF is under investigation.

The fluorescence spectra of the smoke fractions were broad, almost Gaussian, curves with little or no fine structure (Figure III-5). This characteristic, combined with the excitation-emission wavelengths, indicates a complex mixture of fluorescent compounds which includes PAHs as contributors to fluorescence; this also points out the poor separation of the compounds during GPC. By using a smaller diameter column and taking smaller fractions (<10 ml) the probability of seeing fluorescence spectra of individual compounds should be greatly enhanced. The excitation band for fraction 6 showed some fine structure where the most prominent maxima were at 390 nm and 410 nm. Splitting of an absorption band can be due to a highly asymmetric polycyclic hydrocarbon (Clar, 1964). Also, the longer wavelength maxima exhibited by fraction 6 may be due to oxidized and nitrated compounds. Although definite conclusions cannot be made from the fluorescent spectra without further refinement of the samples, the observed results further support the presence of PAHs in Fractions 5 and 6 of the Sephadex column.

The elements listed in Tables III-7 and III-8 are commonly found in soils and in plant materials through uptake from soil. A characteristic marker for airborne soil dust is the potassium/calcium ratio which is typically less than 0.5 for soil from the Sacramento Valley. On the other hand, the ratio in smoke particles resulting from pyrolysis of plant residues is greater than 1.0 through enrichment of potassium. We observed

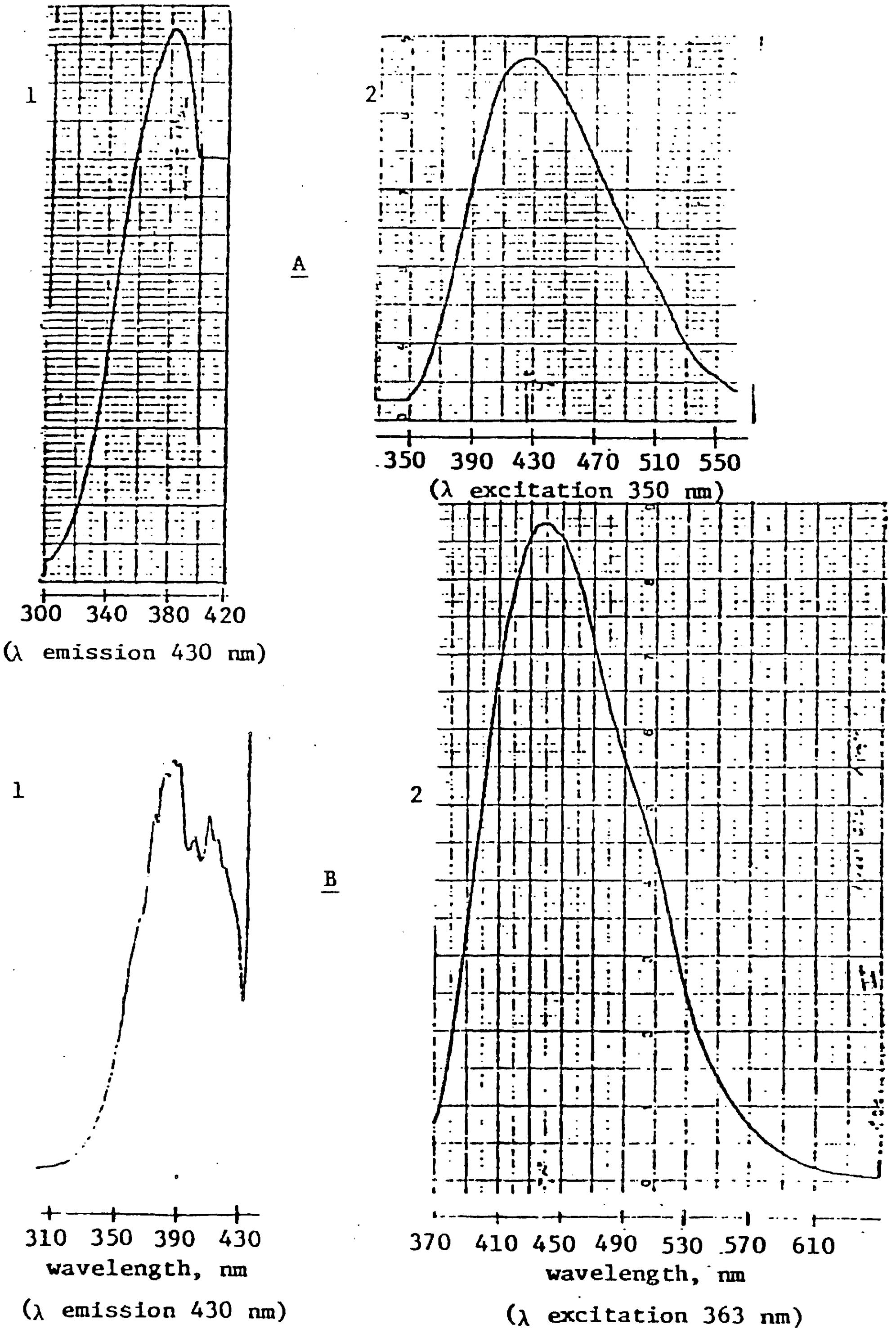

Fig. III-5. Fluorescence spectra of fractions 3-5 (A) and 6 (B) of rice smoke condensate off Sephadex column. Both excitation (1) and fluorescence (2) are shown.

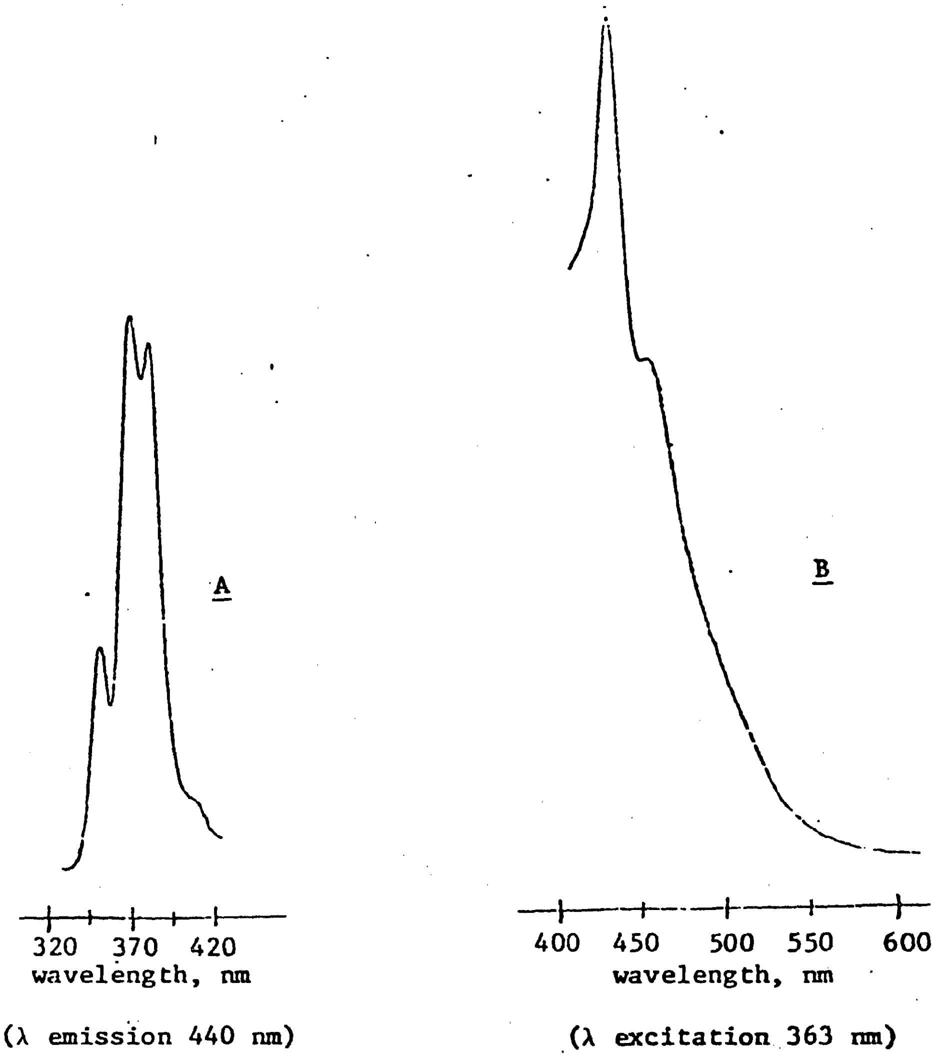

Fig. III-6. Fluorescence spectra for PAH mixed standard (Table III-2). Excitation (A), fluorescence (B).

Table III-7 Elemental Analysis by Particle Induced X-Ray Emission

Source[a] of Sample	Elements Found, ng/cm^2											
	Al	Si	P	S	K	Ca[b]	Ti[b]	Mn	Fe[b]	Cu[b]	Br	Ba[b]
1	--	--	--	--	--	594.8 ±166.7 3193.1 ±1733.6	--	--	<199.0	--	<915.0	--
2	--	--	--	--	2482.6 ±400.0	1098.3 ±153.1	--	--	<199.0	--	2275.8 ±361.7	5169.3 ±689.1 1481.0 ±394.0
3	--	--	--	--	1327.3 ±186.5	--	<279.0	--	338.8 ±89.2	--	<1080.0	--
4	--	<636.0	--	--	1277.9 ±166.3	--	--	--	--	<149.0	--	--
5	--	--	--	<2448.0	--	--	366.5 ±88.2	<201.0	--	--	1298.9 ±280.7	--
6	--	<652	<740.0	<2512.0	1418.6 ±187.5	527.3 ±186.3	367.1 ±90.9	--	--	804.6 ±106.3 987.0 ±288.7	--	--
7	<717.0	3538.6 ±399.5	<768.0	<2604.0	7454.4 ±762.9	1849.4 ±207.4 3654.9 ±633.3	848.8 ±120.8 844.9 ±562.4	325.4 ±86.8	1279.2 ±152.8	--	1431.1 ±303.7	--
8	<722.0	4054.5 ±460.9	<774.0	--	2620.2 ±293.9	1331.4 ±162.7	874.1 ±128.7 874.1 ±0.0	315.7 ±103.5	2990.2 ±316.0 2961.9 ±494.5	1120.6 ±138.8 1568.4 ±320.6	1468.1 ±307.1	--

Table III-7 (Continued)

	Elements Found, ng/cm^2											
Source[a] of Sample	Al	Si	P	S	K	Ca[b]	Ti[b]	Mn	Fe[b]	Cu[b]	Br	Ba[b]
9	--	--	--	2741.7 ±471.4	1968.2 ±230.2	--	--	--	--	<200.0 314.5 ±306.2	--	--
10	--	--	1422.8 ±295.0	--	--	--	--	--	--	--	--	--
11	--	--	--	--	1882.8 ±215.5	--	--	--	--	<139.0	--	--

---

[a] 1 = Yolo Co. burn, 11/8/79; upwind

2 = Yolo Co. burn, 11/8/79; downwind

3 = Sacramento Co. burn, 11/9/79; upwind

4 = Sacramento Co. burn, 11/9/79; downwind

5 = Sacramento Co. burn, 11/21/79; upwind

6 = Sacramento Co. burn, 11/21/79; downwind

7 = Aircraft, 10/24/79 (See sampling section)

8 = UCD Trial burn, 10/4/79

9 = UCD Trial burn, 10/4/79

10 = Butte Co. burn, 3/28/80; upwind

11 = Butte Co. burn, 3/28/80; downwind

[b] $\frac{Ka}{Kb}$, except for Ba which was $\frac{La}{Lb}$.

Table III-8 Elemental Analysis by Neutron Activation

Sample[a] No.	Wt., g	Na	Mg	Al	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Zn	Rb	Sr
		Elements Found, ppm[b]															
1	0.46	1,893	<4,065	<2,635	7,118	15,920	<3,147	<0.1	<1,625	<20.3	<18	879	<1,754	<3.6	<80	<57	<694
2	1.37	7,435	<5,391	<3,596	71,580	151,100	27,320	1.0	<1,895	<26.3	60	1,967	59,270	7.9	1,307	168	<790
3	0.81	429	<1,601	<2,987	58,780	<7,380	<1,589	<0.1	<1,169	<22.3	<11	<3	<1,122	<2.3	<59	<37	<470
4	0.79	447	<1,548	<2,935	62,830	<7,325	<1,572	<0.1	<1,099	<21.8	<10	5	<1,093	<2.2	< 3	<37	<435
5	0.87	441	<1,745	<3,349	62,380	<8,101	<1,615	<0.1	<1,198	<24.3	<10	<3	<1,086	<2.1	<56	<37	<480
6	0.92	395	<1,675	<2,941	58,070	<7,358	<1,344	<0.1	<1,246	<21.9	<11	<3	<1,037	<2.0	<55	<33	<492
7	0.88	346	<1,604	<3,148	71,500	<7,636	<1,471	<0.1	<1,198	<23.4	<11	<3	< 986	<2.1	<52	<33	<479
8	0.84	406	<1,463	<2,859	61,560	<7,009	<1,381	<0.1	<1,040	<20.7	<10	6	< 883	<1.9	< 4	<34	<422

Sample[a] No.	Wt., g	Sb	Cs	Ba	La	Ce	Sm	Eu	Tb	Dy	Yb	Lu	Hf	Ta	Au	Th	U
1[a]	0.46	<3	<2.3	<374	<15	<10	<1.1	<0.5	0	<2.3	<2.6	<0.2	<1	<3	<0.1	<2.2	0.06
2	1.37	<2	3.4	<440	< 6	< 8	<0.9	4.1	0	<2.5	<2.0	<0.1	<1	<1	<0.1	<1.6	0.32
3	0.81	<2	<1.5	<308	< 9	< 7	<0.7	5.5	0	<2.1	<1.8	<0.1	<1	<2	<0.1	<1.3	0.00
4	0.79	<2	<1.4	<273	< 8	< 6	<0.7	<0.3	0	<1.9	<1.6	<0.1	<1	<2	<0.1	<1.3	0.00
5	0.87	<1	<1.4	<300	< 9	< 5	<0.6	6.6	0	<2.1	<1.7	<0.1	<1	<2	<0.1	<1.3	0.00
6	0.92	<2	<1.4	<315	< 8	< 7	<0.7	5.0	0	<1.9	<1.7	<0.1	<1	<2	<0.1	<1.4	0.00
7	0.88	<2	<1.5	<313	< 8	< 6	<0.6	6.0	0	<2.2	<1.7	<0.1	<1	<2	<0.1	<1.3	0.00
8	0.84	<2	<1.4	<260	< 8	< 6	<0.6	<0.3	0	<1.8	<1.6	<0.1	<1	<2	<0.1	<1.3	0.01

[a] 1 = Unburned rice straw from Sacramento Co.
2 = Baghouse rice straw ash (See sampling section)
3 = Smoke sample from Sacramento Co. (11/9/79)
4 = Aircraft smoke sample (See sampling section)
5 = Yolo Co. smoke sample, downwind (11/8/79)
6 = Yolo Co. smoke sample, upwind (11/8/79)
7 = Versapor filter blank
8 = Yolo Co. smoke sample

[b] Values above the detection limits are ± 10%.
All values below detection limit are listed as "less than."

for many of the filter samples analyzed by the PIXE method (Table III-7) that the ratio was greater than 2.0; furthermore, the ratio in unburned rice straw and rice straw ash was greater than 5.0 (samples 1 and 2, Table III-8). These data indicate that each filter sample consisted almost entirely of plant-related residues. The detection limits for neutron activation were too high to allow a similar evaluation of the filter samples in Table III-8. However, it is interesting to observe, with regard to samples 1 and 2, that many elements (sodium to uranium) concentrated in the ash during pyrolysis. The relatively high concentration of iron in sample 2 (straw ash obtained from an incinerator) may be partly due to contributions from corroded iron and steel surfaces of the incinerator.

E. Conclusions

This report, concerned with the chemical analysis of rice straw smoke, is just part of a first-look at the whole area of the impact on human health of agricultural burning. Initial results indicate that rice straw smoke, like other types of smoke, contain a complex mixture of organic compounds, many of which are mutagenic. Only about 10-15% of the observed GC peaks in fraction 5 have been tentatively identified and a few compounds in fraction 6 have only been classified and not actually identified. It is obvious that much work remains in order to thoroughly characterize rice straw smoke.

The development of a rapid and efficient sonifier extraction system, was a notable improvement over the traditional Soxhlet method, benzene: methanol (1:1), which forms a low boiling azeotrope, allows for rapid solvent exchange, and is efficient in extracting PAHs and aromatic heterocyclic compounds was used as the extracting solvent. In addition, the use of a sonifier decreased the time invested in each sample as well as improving the percent recovery of particulate mass from the filter.

The gel permeation chromatography fractionation step was also workable however interfering straight chain hydrocarbons were not completely separated from the PAH and aromatic heterocyclic classes of compounds. The development of a separation step based on high performance liquid chromatography may prove successful in eliminating straight chain hydrocarbon interferences as well as providing enough material for the Ames Assay with a minimum time investment.

The fluorescence spectra of Ames-active fractions 5 and 6 indicated a complex mixture of highly fluorescent compounds typical of PAHs. Their presence in these fractions was confirmed by GC/MS and a number of individual PAHs and heterocyclic compounds were tentatively identified.

The elemental analyses showed that the material trapped on the air filters consisted almost entirely of plant related materials as indicated by the potassium to calcium ratio--evidence that there was little or no contamination by suspended field soil dust.

In summary, an analytical method was developed involving extraction by sonification, liquid chromatographic fractionation, and GC/MS. By improving the efficiency of the liquid chromatographic fractionation, by expanding the storage and processing capacity of the GC/MS data system, and by using on-site libraries such as the NIH/EPA Chemical Information System (CIS), in addition to computerized data bases, chemical characterization of rice straw smoke and smoke from other agricultural wastes could become fairly routine.

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IV. PESTICIDE RESIDUES

A. Introduction

It is possible that pesticide residues may be present in smoke from the burning of rice straw. In order for residues to occur in rice smoke, there must be residues on the straw--a function of application timing, weather conditions, and chemical stability--and these residues must survive combustion so that volatilization and/or entrainment in smoke particulate matter can take place. Furthermore, in order to attach significance to residues released during burning, the levels must be above the background of these chemicals in air and also within the magnitude of air levels associated with measureable biological effects.

Pesticide use on rice in California is approximately known as to types of materials, amounts, and locations by virtue of the State's Pesticide Use Reports (State of California, Annual Summaries dating from 1970). An example of use data for MCPA is in Figure IV-1. Furthermore, the application rates and timing of application are also known, through registration information (EPA, 1974, with more recent updates) and UC publications dealing with suggested pesticide use practices on rice (University of California, 1976 and 1979). Summaries for annual use in California, and labelled or suggested application rates and timing are in Tables IV-1 - IV-4 (Seiber, 1981).

Among the major pest control chemicals are three organophosphorus insecticides (malathion, methyl parathion, and ethyl parathion), three N-methylcarbamate insecticides (bufencarb, carbaryl, and carbofuran), three phenoxy herbicides (MCPA, 2,4-D, Silvex), one aniline-based herbicide

Table IV-1 Reported Uses of Major Pesticides on California Rice

(All numbers are rounded, in thousands)

(Pesticide Use Reports, State of California, 1977-9)

	1977		1978		1979	
Insecticides	lbs	acres	lbs	acres	lbs	acres
Bufencarb (Bux)	58	58	140	140	132	137
Carbofuran	21	43	18	37	29	57
Me Parathion	17	27	45	67	66	101
Parathion	23	105	25	155	19	127
Herbicides and Fungicides						
Betazon	-0-	-0-	6	8	25	36
Blue vitriol	109	11	202	20	182	17
2,4,-D (total)	1	1	11	5	4	2
MCPA dimethylamine salt	363	233	388	364	448	394
MCPA sodium salt	3	6	6	15	19	21
Molinate	548	207	1277	352	1408	374
Propanil	25	6	52	12	101	17
Silvex	4	3	5	4	1	0.7
Totals[a]	1,263 lbs		2,226 lbs		2,524 lbs	

[a] All chemicals, including some not tabulated above.

Table IV-2 E.P.A. Limitations on the Use of Chemicals Suggested in the UC publication "Pest and Disease Control Program for Rice"

Chemical	Interval between last application and harvest	Tolerance in parts per million	Dosage in pounds of actual material per acre
Bux	Only one application per season. Preplant--after seedbed preparation but prior to flooding and seeding. Postplant--within 8 weeks after planting after draining the field.	0.05 ppm (rice and straw)	1.0 lb/A (G)
Captan	Seed treatment (slurry). Do not use treated seed for food or feed.	NF	3.75 oz/100 lb.
Carbofuran	Preplant soil treatment. One application per season. Apply to soil surface prior to flooding.	0.2	0.5 (G)
Copper sulfate (pentahydrate)	Postflood.	Exempt	15.0
Difolotan	Seed treatment (slurry). Do not use treated seed for food, feed, or oil. For planting in flooded fields.	NF	3 oz. active/ 100 lb seed
Malathion	7 days	8	1.6
Parathion	Restrict spill for 2 days following application. Do not apply over canals or laterals.	1	0.1
Sevin (carbaryl)	14 days. Foliage application. To avoid plant injury do not apply within 15 days of propanil.	5 (grain) 100 (straw)	2.0

Table IV-3 Suggested Herbicides in the UC Publication "Weed Control in Rice" and Precautions for Use

Herbicide	Application rate of active ingredient (lb/acre)	Remarks	Tolerance in parts per millio
Molinate (Ordram)	3	Preplant application of liquid molinate applied by ground sprayer. Must be incorporated immediately. Granular can be applied by either ground or air, but must be incorporated within 6 hours.	0.1 (grain and straw)
	3 to 5	Postplant application of either liquid or granular should be applied by air. Single or split applications of the 10% granular formulation may be used but no less than 3 pounds or more than 5 pounds active ingredient may be applied per application, with a maximum total of 9 pounds active ingredient per acre allowed per growing season. Split applications must be made 14 days apart and at least 90 days before harvest.	
Propanil[a]	4 to 5	Postplant application can be applied by either ground or air in 10 to 15 gallons of water. Use higher volume for large grass or dense populations.	2.0 (rice) 75.0 (straw)
MCPA[a]	0.75 to 1.25	Postplant application can be applied by either ground or air in 10 to 30 gallons of water. Use higher rate on old weeds or weeds that are difficult to control.	0.1 (rice) 2.0 (straw)
Bentazon (Basagran)	1	Use at least 10 gallons of spray solution per acre by air equipment (airplane) or 20 gallons per acre by ground equipment. It is critical that complete thorough coverage be obtained.	---
Endothall (Hydrothol 191 Granular)	2 to 3	Postplant application can be made either by ground equipment or aircraft. Small patches of submersed weeds may be spot treated providing static water is maintained for 5 days following treatment. Use the higher rate in water deeper than 6 inches or in dense weed stands.	---

Table IV-3 (Continued)

Herbicide	Application rate of active ingredient (lb/acre)	Remarks	Tolerance in parts per milli
Copper sulfate	10 to 15	Apply higher rate in deeper water (6 inches or greater).	Exempt
2,4-D[a,b]	1.25	Tiller to boot. If granules are used, apply 3 lbs. when rice is 2 weeks old.	0.1 (rice and straw)
	1.7	After flooding (3-21 days). Do not apply after seed stalks have emerged.	

[a] Restricted herbicide; permit from County Agricultural Commissioner required for possession or use.

[b] Not included among UC-suggested herbicides.

[c] From EPA "Compendium of Registered Pesticides".

Table IV-4 Results From Analysis of Rice

Straw for Three Pesticides

			---Residues in ppm---		
Grower/other	Date sample taken	Residue lab ID code	MCPA	molinate	parathi
Yolo County	11/8/79	5955B	<0.04	<0.04	<0.01
Yolo County	11/8/79	5955C	<0.04	<0.04	<0.01
Sacramento Co.	11/9/79	5955D	<0.04	<0.04	<0.01
Sacramento Co.	11/21/79	5955E	<0.04	<0.04	<0.01
Butte Co.	4/8/80	5955F	<0.04	<0.04	<0.01
Butte Co.	4/8/80	5955G	<0.04	<0.04	<0.01
UCR					
2nd bale	7/23/80	5955H	<0.04	<0.04	<0.01
3rd run UCR	7/24/80	5955I	<0.04	<0.04	<0.01

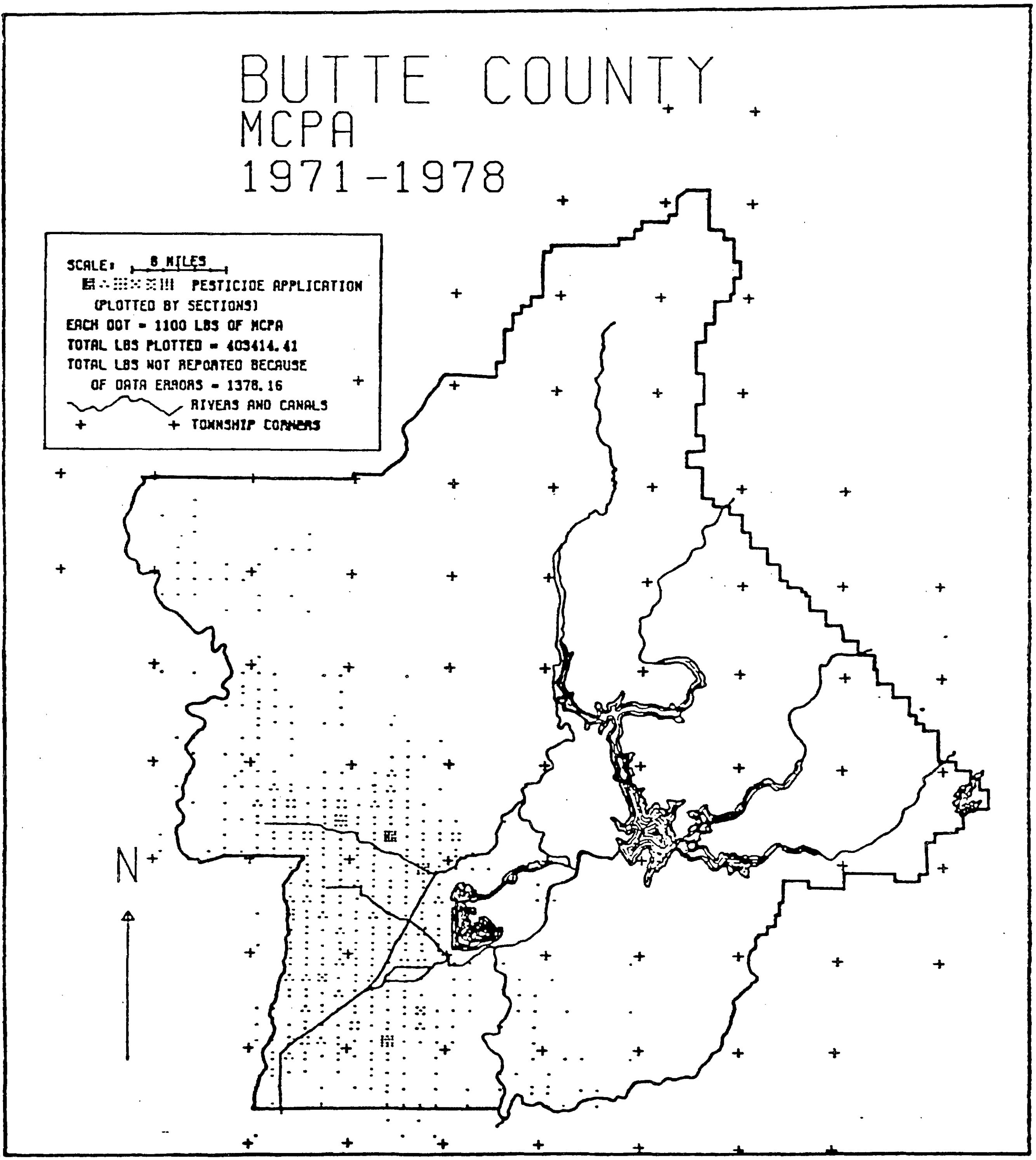

Figure IV-1. Reported Uses of MCPA in Butte County, California, 1971-1978.

Courtesy of M.-Y. Li, Department of Environmental Toxicology, UC Davis.

(propanil), one thiocarbamate herbicide (molinate), one relatively new thiadiazin herbicide (bentazon or basagran), one inorganic herbicide/ fungicide (copper sulfate), and two phthalimide-based fungicides (captan and difolatan). Of these chemicals, only four insecticides (bufencarb, carbofuran, methyl parathion, and ethyl parathion) and four herbicides (bentazon, MCPA, molinate, and propanil) are of sufficiently widespread use to be of interest from an atmospheric contamination viewpoint. Of these eight, propanil is not used north of Interstate 80. Two of the insecticides (bufencarb and carbofuran) and two herbicides (bentazon and molinate) are of insufficient persistence to lead to any significant straw contamination considering that they are used only early in the season. It is only with applications of the two parathions and MCPA made later in the season (after July 1) that potential for observable residues exists for straw from the Butte-Sutter-Sacramento County area, and with these three chemicals published information indicates that the level of contamination should not exceed 1 ppm (Seiber, 1981).

There is thus no reason to believe that the contamination of rice straw by pesticides is particularly noteworthy in terms of amounts or extent. Certainly it would be far less for rice straw than for cotton gin wastes; the latter are known to have high levels (1-500 ppm) of residues of relatively persistent insecticides and harvest-aid chemicals used late in the season in California cotton culture (Seiber et al, 1979).

Nevertheless, measureable residues of some chemicals may exist in some fields of rice straw, and the effect of open burning on these residues, either the parent chemicals or their environmental conversion products, is unknown. Therefore, we proposed to analyze some smoke samples collected as described elsewhere in this report for pesticides known to have been applied to the rice in question. Only two chemicals--molinate and MCPA--were in fact used on rice from which our samples were taken. And neither was measureably present in the rice straw before burning (results below). Thus it was not considered necessary to analyze these air samples for pesticide residues. We instead calculated expected emission rates based upon our negative findings, rice straw residue data in the literature, and several assumptions.

B. Analytical Methods and Results

Samples of rice straw were obtained from four fields and from baled straw used in combustion trials at UC Riverside. These samples were analyzed for MCPA, molinate, and parathion by Mr. Wray Winterlin and Mr. Charles Mourer of the UC Environmental Toxicology Residue Analysis Facility. Summaries of the analytical methods are as follows:

1. MCPA--An aliquot of rice straw was blended and shaken with ethyl acetate and 1N hydrochloric acid. The ethyl acetate solution was dried and filtered. An aliquot representing 12.5 g of straw was taken to dryness and treated with diazomethane solution. Excess diazomethane was removed by evaporation and the concentrated solution was analyzed for MCPA methyl ester by gas-liquid chromatography (10% DC 200 and 1.5% QF-1 mixed phase on Gas Chrom Q at 165°) using a Cl-selective microcoulometric detector. This method, an adapation of ones reported in the literature (St. John, Jr., 1967), has a limit of detection of 0.04 ppm.
2. Molinate--A chopped sample of straw was blended with water, and the mixture distilled. The distillate was acidified with hydrochlor

acid and extracted with hexane. The hexane was dried, concentrated, and analyzed for molinate by gas-liquid chromatography (12% SE-30 on Gas Chrom Q, 160°) using an S-selective flame photometric detector. This method, an adaptation of one in the literature (Zweig, 1972), has a limit of detection of 0.04 ppm.

3. Parathion--Ground up rice straw was blended with ethyl acetate. An aliquot of the ethyl acetate extract representing 12.5 g of straw was dried, evaporated to dryness, and constituted in hexane. Analysis was by gas-liquid chromatography (12% SE 30 on Gas Chrom Q) using a P-selective flame photometric detector. This is a standard method, with a detection limit of 0.01 ppm.

The results are in Table IV-4. It is clear that residue levels of these three chemicals were below the analytical detection limit of the method used. This is not inconsistent with literature data. For molinate, the tolerance for straw used as animal feed is 0.1 ppm (Table IV-2) indicating very little likelihood of residues surviving to the straw. For MCPA, straw residues were less than 0.1 ppm for applications made before July 1 in California in studies cited elsewhere (Seiber, 1981). All MCPA applications to rice from which our analytical samples reported above were taken, had been made before July 1. And there were no reported applications of parathion to any of the rice fields sampled; parathion analyses were conducted because of a laboratory finding of this chemical in one smoke sample--found later to be the result of in-lab contamination.

C. Potential Emission Calculations

Of the chemicals frequently used in California, MCPA is perhaps of greatest interest in relation to straw contamination. The straw tolerance is 2 ppm (Table IV-3) indicating that this level of residue may be encountered (though infrequently) in a given field at harvest. Assuming 2 ppm contamination at rice harvest, no further dissipation in straw from harvest of rice to burning, and that there are 3 tons (2720 kg)/acre of straw in a 100-acre field (272,000 kg of straw), we may calculate that a maximum of 540 g of MCPA may become airborne during burning if all of the MCPA survives combustion and winds up in the smoke. This must be considered rather extreme, and more than a worst-case situation. Taking just the volume of air present at a 10 m height above 100 acres ($4,047\ m^2$/acre x 100 acres x 10 m = $4 \times 10^6\ m^3$), one may calculate a maximum residue level of 5.4×10^5 mg/$4 \times 10^6\ m^3 \simeq$ 0.14 mg/m^3 in the air just above the field with no air dilution occurring by wind movement. Comparing this value, 140 μg/m^3, with the threshold limit value (TLV) of 10,000 μg/m^3 established by the American Conference of Governmental Industrial Hygenists for 2,4-D (a close relative of MCPA; we found no TLV for MCPA) it can be seen that the worst case situation is, at most, only 1% of the threshold level where no effect is expected during an 8 hr. exposure. Thus even under the very worst situations one can envision, MCPA will not occur in air within a factor of 100 (at most) of TLV. It should be borne in mind, however, that TLV's were developed for 8 hr exposure in workplace environments; its utility for estimating hazard for the general population in the ambient environment is questionable. However, it is the only air standard available for pesticides, imperfect though it is.

Using data from our analyses, that is, that less than 0.04 ppm of MCPA was present in our straw samples, and the same assumptions as above, we can further calculate a maximum air level of 3 μg/m^3 if this straw were contaminated at the limit of detection (0.04 ppm).

The analytical methods we employed are also used for analysis of pesticide residues in food based on their reliability and sensitivity. For MCPA the limit of detection of 0.04 ppm provides detection of MCPA levels in straw, approximately one ten-thousandth of those needed, giving this analysis a margin of safety.

It should be noted that MCPA is not considered to be a volatile chemical; during aerial application we found no residues in excess of 10 $\mu g/m^3$ just downwind of application to rice (Seiber and Woodrow, unpublished). Furthermore, MCPA is a relatively reactive chemical which is very likely to be degraded substantially, if not completely, during combustion.

We feel that the chance of finding MCPA at levels in excess of 1 $\mu g/m^3$ in the air just above a burning rice field is remote. The same reasoning may be extended to other pesticides used on California rice.

It should be noted, however, that the long-term health consequences of inhaling pesticide residues in smoke is largely unknown; that even small levels of residue in smoke cannot be assumed to be safe; and no systematic survey of pesticide levels in air near open rice burning sites (where these sites are known to contain residues) has yet been undertaken. It is our belief that an effort should be made in the future to analyze air samples near a burning rice field where chemical residue contamination in the straw exists.

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