HYDROCARBONS, IRRITATING AND TOXIC PHENOLS, AND OTHER BIOLOGICAL TOXINS IN SMOKE FROM BURNING WHEAT STUBBLE

Annual Report
Submitted by:

Candis S. Claiborn, Ph.D.
Laboratory for Atmospheric Research
Department of Civil and Environmental Engineering and
Center for Multiphase Environmental Research
Washington State University
Pullman, WA 99164-2910

and

Jeff Corkill, Ph.D.
Department of Chemistry
Eastern Washington University
Cheney, WA

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INTRODUCTION

The primary objective of this research is to quantitate benzo (a)pyrene (B(a)P) and other selected toxic and carcinogenic polycyclic aromatic hydrocarbons (PAHs), irritating and toxic phenols, and other persistent biological toxins [PBTs] in smoke from burning wheat stubble. A secondary objective is to quantitate the particulate dioxin fraction, in order to allow for dioxin emission factors to be estimated. This also entails quantifying the fine particulate emission factor. The project further measures air quality impacts near burning agricultural fields and in selected nearby communities. These objectives are accomplished by measuring respirable particulate matter and chemical constituents of interest at the sources as well as in nearby communities and surrounding areas during the burn season.

Four tasks were originally envisioned to carry out this work:

(1) conducting small-scale controlled burns (approximately 1 kg biomass) to collect air samples for particulate matter (PM), phenols and PAH analysis;
(2) conducting additional controlled burns in EPA's "burn hut" (approximately 20 kg biomass per sample) to collect air samples for dioxins and PAH analysis as well as to estimate emission factors, along with supporting measurements to determine combustion efficiency;
(3) mobile mapping of particulate and phenols and PAH concentration fields and particulate sample collection in regions near field burns; and
(4) operating one continuous particulate measurement site in Pullman, WA.

Initial small-scale controlled burns were conducted however it was quickly recognized that it would be important to re-create the orientation of the fuel because of its potential effect on combustion efficiency. The controlled burn experiments conducted in the EPA's burn hut facility were designed to allow us to imitate the fuel orientation. Burn hut experiments were conducted on wheat stubble biomass during spring and fall of 2001. Additional burn hut experiments will be conducted during August of 2003 on Kentucky bluegrass stubble.

A continuous particulate measurement site was operated in Pullman, WA, for several burn seasons. In addition, integrated particulate mass concentrations and chemical compositions were also measured in Pullman at that site site, during the summer burn season of 2001. During the fall burn season of 2002, further particulate and semivolatile organic compound (SVOC) samples were collected, by leveraging this work against a health and exposure assessment project funded by the Washington Department of Ecology. That work is aimed

at characterizing the exposure of asthmatic adults to smoke from regional field burning and the health effects associated with such exposures.

Because of detection limit difficulties associated with sampling for PAHs and phenols, the mobile mapping was not conducted; instead, samples were collected downwind of actual field burns, for measuring ambient particulate mass concentrations and chemical compositions in the source areas. Samples were collected downwind of both wheat stubble and grass stubble field burns, during the summer of 2001Also as part of the leveraged work with the WDOE funded exposure assessment project, the variability of PM concentrations in Pullman during agricultural field smoke episodes is being characterized using a network of distributed samples.

The original focus of this project was on wheat stubble smoke, however some initial work is also being conducted on Kentucky bluegrass stubble smoke since that is another agricultural crop of regional significance for which preferred cropping practices include burning the stubble. This project has been conducted as a cooperative agreement with EPA in RTP (Dr. Brian Gullett, PI). Dr. Gullett's interests lie in the quantification of dioxins and furans in biomass smoke. Dr. Gullett's group has provided access to the test burn facility in RTP, NC, and also supported the project with a number of support measurements including temperature, carbon monoxide, hydrocarbons, oxygen, and mass of fuel. Table 1 shows an overview of the experiments conducted and the particulate and vapor phase SVOC samples collected to date.

Table 1: Overview of experiments conducted or to be conducted on this project

Experiment	Duration	No. of SVOC samples
EPA Burn Hut, May 2001	5 days 6 exp'ts, 5 burns each	30 PM samples 5 composited SVOC
EPA Burn Hut, Aug 2001	5 days 5 exp'ts, 6 burns each	31 PM samples 5 composited SVOC
EPA Burn Hut, Aug 2003	5 days planned	
Grass and wheat fields, June 2001	2 days 2 exp'ts 2 burns + 3 burns	3 combined particulate and vapor phase SVOC
Central Site, June 2001	2 days 2 exp'ts	2 combined particulate and vapor phase SVOC

The samples from the burn hut experiments have been analyzed and the data are currently being analyzed and compared to field results from actual field burns conducted by Air Sciences and the Missoula Fire Lab. The samples from the field burns and the central site have been analyzed and the data are also being analyzed. In addition, operation of the fixed site in Pullman and distributed particulate measurements that were leveraged against the study funded by Washington Department of Ecology are still being analyzed and will not be discussed in this report.

METHODS

Burn Hut Experiments

The burn experiments were conducted at the United States Environmental Protection Agency (US EPA) burn facility in Research Triangle Park, North Carolina. A platform was constructed with a screen that permitted orienting the stubble as found in the field. The platform was 1m x 1m and consisted of two woven wire mesh screens. A 1-inch mesh screen (77.4% open area) provided the base of the burn area. The top screen was covered with coarse gravel and dirt to simulate the field surface. Combustion occurred above the top screen. The entire platform was placed on an electronic scale in order to record the stubble mass change during the burn in real time (Figure 1).

The biomass tested was irrigated winter wheat straw (*Triticum aestivum* L., variety Madsen) from Washington State University's Dryland Research Station in Lind, WA, in the arid (<25 cm rainfall/year), central part of Washington State. The stubble density in the field was approximately 38 Mg/ha (17 tons/ acre). Wheat straw collected was categorized according to whether it was standing, semi-upright, laying flat, or partially decomposed litter, and the relative proportion of each category was recorded. Stubble was cut close to the base and approximately 40 kg of biomass was collected. Samples of each of the sorted materials were analyzed for moisture and organic content.

Figure 1: Weighing platform in EPA Burn Hut, showing orientation of wheat straw prior to combustion.

Sample Collection

Fine particulate matter was sampled using low-volume (5 L min^{-1}) air samplers (Airmetrics Inc.) and a DataRam 2000 (MIE, Inc.) nephelometer for bulk integrated samples and continuous particulate measurements, respectively. The low-volume samplers were fitted with $PM_{2.5}$ and PM_{10} inlet heads whereas the DataRam had a $PM_{2.5}$ inlet head. Particulate samples were collected on Teflon filters for mass determination. To determine the particulate organic carbon and elemental carbon content (OC/EC), particulate samples were also collected on quartz filters. In a subset of samples collected during the May 2001 experiments, the quartz filter positive adsorption artifact was measured by deploying quartz filters behind Teflon filters in the lo-volume sampler cassettes. The quartz filters were analyzed for OC/EC by taking a rectangular 1.5 cm^2 punch from the quartz filter and using Thermal Optical Transmission (TOT) (Sunset Labs Inc.) with a modified NIOSH 5040 method (see Table 2).

Table 2: Temperature profile for TOT analysis

Carrier Gas	Hold Temperature for (seconds)	At Temperature (°C)
For OC analysis		
Helium	60	250
Helium	60	500
Helium	60	630
Helium	90	870
Cool Oven		
Helium	30	
Helium	10	500
For EC analysis		
Oxygen	20	600
Oxygen	20	670
Oxygen	20	740
Oxygen	20	810
Oxygen	20	860
Oxygen	120	940

Vapor phase SVOC were sampled using polyurethane foam (PUF) filters that were placed in a glass tube and installed on the low-vol samplers with $PM_{2.5}$ inlets. Some of the PUFs were placed downstream of Quartz filters (to sample gaseous phase SVOC only) and other PUFs had no filters upstream such that they sampled both the particulate and gaseous phase SVOCs.

Prior to deployment, Teflon filters were equilibrated in a humidity chamber (RH ~50%) for 24 hours and pre-weighed. Quartz filters were fired at approximately 800 °C for 12 hours and also equilibrated in a controlled humidity chamber for 24 hours. PUF filters were pre-cleaned by repeated extractions with dichloromethane before use.

At first it was attempted to obtain a gravimetric PM measurement from the quartz filters but this was subsequently abandoned because of the fragile nature of the quartz filters. Quartz filters were either analyzed for organic and elemental carbon (OC/EC) or were extracted and analyzed for SVOC. Detection limits were determined using laboratory blanks of the Teflon and quartz filters. 18% of the Teflon filters used in May and 8% of the Teflon filters used in August

consisted of laboratory blanks. Lab blanks accounted for 5% of the Quartz filters deployed during both sampling periods.

The EPA personnel in RTP operated CO, CO_2, O_2, and Total Hydrocarbon [THC (=CH_4 + non-methane hydrocarbons)] analyzers, dioxin samplers, and a dilution sampler. They also provided continuous fuel mass measurements and temperatures in the flame, hut, and exit stack.

A set of experiments was conducted in the spring (May 2001), and another was conducted in the late summer (August 2001) (Table 3). Each experiment consisted of 5 to 7 separate burns. In the spring, a total of 25 burns were conducted over a period of 4 days. In order to examine the effect of fuel orientation on emissions, one set of 5 burns was conducted by combusting randomly piled stubble. In the August 2001 experiments the air flow rate through the hut was reduced to 75% of the volumetric rate employed in May, to lower the combustion efficiency of the burns. A total of 31 burns were conducted in August.

In all cases sampling was carried out for about 20 minutes to capture both the flaming and smoldering stage emissions. Field blanks were obtained by operating the samplers in the empty burn hut on the last day of the sampling session. In May, no other experiments were conducted on the last day, but in August the field blank was taken after 7 burns had been conducted earlier in the day. An inventory of samples is summarized in Table 4.

Table 3: Experimental conditions during May and August 2001 trial burns.

	May 2001	August 2001
Standing stubble, % (w/w)	45	45
Semi upright stubble, % (w/w)	15	15
Flat stubble, % (w/w)	25	20
Partially decomposed stubble, % (w/w)	15	20
Average stubble organic content, % (w/w)	86	86
Average stubble water content, % (w/w)	7.5	6.6
Total number of burn experiments	6 (5 burns each)	5* (6 burns each)
Mass of stubble combusted per burn, kg	0.8	0.8
Flowrate of air into burn hut, m^3/hr	13.85	10.39

*31 burns were conducted over 4 days (4 experiments of 6 burns each and 1 experiment of 7 burns).

Table 4: Inventory of samples collected with lo-vol samplers during burn hut experiments

	May 2001	August 2001
$PM_{2.5}$ samples on Teflon filters	30	31
$PM_{2.5}$ samples on Quartz filters	30	31
PM_{10} samples on Teflon filters	4	31
Quartz filter artifacts	4 behind Teflon 20 behind quartz	-
PUF samples with no front filter ($PM_{2.5}$ inlet)	-	4 (composited, 1/day)
PUF samples with front quartz filter ($PM_{2.5}$ inlet)	-	4 (composited, 1/day)
Gas phase samples collected on XAD/ PUF trap ($PM_{2.5}$ inlet)	30 (10 behind quartz 20 behind Teflon)	
Combined gas and particulate phase samples collected on XAD/PUF, with $PM_{2.5}$ inlet		4 (composited 1/ day)
$PM_{2.5}$ field blank on Teflon filter*	1	1
PM_{10} field blank on Teflon filter*	-	1
$PM_{2.5}$ field blank on Quartz filter*	1 (with backing Quartz filter)	1
$PM_{2.5}$ measurements using DataRAM (1s time resolution)	Real-time data for 27 burns	Real-time data for 23 burns
Temperature above flame, in hut and at exit (time resolution 5 s)	Real-time data for 31 burns	Real-time data for 32 burns
O_2, CO_2, CO and THC data (time resolution varies between 5s–5 min)	Real-time data for 30 burns	Rel-time data for 31 burns
Stubble mass remaining (time resolution 5- 15s)	Real-time data for 30 burns	Real-time data for 31 burns

*Teflon and Quartz field blanks were analyzed for PM mass as well as for SVOCs.

After each sampling campaign the individual filters were wrapped in aluminum foil, placed in sealed plastic bags, stored in cooler boxes that contained frozen cooler packs and transported back to the laboratory at Washington State University, where they were stored in a walk-in freezer. Exposed Teflon filters were equilibrated for 24 hours in a humidity chamber before weighing on a microbalance. The mass concentration was determined from the mass gain on

each filter divided by the total standard volume of air sampled. For each experiment, the combustion efficiency was also computed.

Few previous studies report emission factors as a function of combustion efficiency (Turn et al., 1997; Air Sciences Inc, 2002; Ward et al., 1992). Combustion efficiency (CE) is defined as the percentage of carbon emitted during the combustion process that has been completely converted to its fully oxidized form (i.e., CO2). For these experiments, the CE was computed from the mass of C in CO_2 as a percentage of the total C released during combustion, as measured in the form of CO_2, CO, total hydrocarbons (THC) and fine particulate carbon (Turn et al., 1997, Ward et al., 1992). Stated mathematically:

$$CE, \% = \frac{CO_2 - C}{(CO_2 - C) + (CO - C) + (THC - C) + (PM_{2.5} - C)} \times 100 \qquad \text{--- (1)}$$

where $CO_2 - C$ = the mass of carbon released as CO_2
CO – C = the mass of carbon released as CO
THC – C = the mass of carbon released at total hydrocarbons
$PM_{2.5} - C$ = the mass of carbon released as fine particulate carbon.

The burn hut was assumed to behave as a well-mixed chamber. The air flow through the hut was provided by pumping air into the chamber so that the chamber operated at a positive pressure. The air flow rate was measured by measuring the velocity of the air in the inlet to the chamber, along with the cross-sectional area (Q = V*A). All concentrations were measured in the vicinity of the exit of the chamber. The mass of carbon released as CO2 was calculated from the CO2 concentration in the burn hut (mg/m3) times the ratio of the MW of C to the MW of CO2 (or 12/44) times the burn hut air flow rate (m3/min). The mass of carbon released as CO was calculated similarly, from the CO concentration times the ratio of MWs (12/28) times the burn hut air flow rate.

For determining the amount of carbon emitted as gas-phase hydrocarbons, THC was assumed to have an average composition of C_3H_8 (M. Schaaf, Air Sciences Inc, personal communication). And according to Turn et al. (1997), 66% of biomass combustion-related $PM_{2.5}$ (w/w) is made up of carbon (Turn et al., 1997); this appears to be consistent with our own measurements and so the particulate carbon was estimated from 66% of the $PM_{2.5}$ mass.

Emission Factors (in units of pollutant mass/mass of biomass burned) were

calculated using two different methods.

EF calculation based on the assumption of a well-mixed combustion chamber:

$$EF_x = (\chi_x . Q_{hut} . t_{run}) / (m_{burned}) \quad \text{--- (2)}$$

EF_x = Emission factor in mg of pollutant X per kg stubble burned
χ_x = Concentration of the pollutant X in excess of the background, in mg/m^3
Q_{hut} = Flow rate of dilution air into the burn hut in m^3/min
t_{run} = Run time in min
m_{burned} = Mass in kg of biomass burned over the run.

This method of calculating EFs will be abbreviated as EF(total) through the rest of this document. The underlying assumption is that the measured average pollutant concentration is representative of all air passing through the burn hut, so that the concentrations measured at the sampling locations represent the concentrations in the exit gas.

EF calculation based on carbon balance

This method calculates the pollutant specific emission factors by assuming that the carbon in the biomass can be accounted for during the combustion process by measuring CO2, CO, THC, and particulate carbon, and then apportioning the emissions according to the relative concentrations of the species of interest to the total carbon. This requires a knowledge of the carbon content of the biomass before and after the combustion process. For our purposes, the EF based upon the carbon balance was found by dividing the pollutant concentration by the total airborne carbon concentration times the residue mass to carbon ratio, assumed to be 2 (Air Sciences 2002, Andreae and Merlet, 2001):

$$EF_x \ (\text{g kg fuel}^{-1}) = \frac{\chi_x \big|_{Fire} \ (1{,}000 \text{ g kg}^{-1})}{2.0 \cdot \left(\chi_{C\text{-}CO_2} \big|_{Fire} + \chi_{C\text{-}CO} \big|_{Fire} + \chi_{C\text{-}THC} \big|_{Fire} + \chi_{C\text{-}PM2.5} \big|_{Fire}\right)} \quad \text{--- (3)}$$

where χ_x and EF_x are as defined above. $\chi_{C\text{-}CO2} \big|_{Fire}$ is the carbon concentrations in mg/m^3 emitted in the form of CO_2, etc., for all C containing species. The factor 2.0 in the denominator stems from the estimate that half the stubble consists of carbon on a w/w basis (Air Sciences Inc., 2002). Jenkins et al. (1996) report that 44.3% of biomass consists of C and Ortiz de Zarate et al (2000) report 44 ±1.6 % C.

Crutzen and Andreae (1990) report that the average chemical composition of dry plant biomass corresponds closely to the formula CH_2O, implying 40% C on w/w basis. Hurst et al. (1994) reports that 96 ± 2% of the stubble carbon is evolved as atmospheric C-containing species.

The carbon balance method of calculating the emission factors assumes that the amount of pollutant sampled/ amount of pollutant produced is the same for all pollutants, i.e. the same representative fraction of all pollutants has been sampled. Differences in the location of the samplers' inlets might lead to inaccuracies if the extent of mixing is not the same. \

Brian Gullett of the National Risk Management Research Laboratory, USEPA, in RTP, also made measurements of polychlorinated dibenzo dioxins and dibenzofurans (PCDD/F) with the use of a Graseby™ PS-1 sampler, which consists of an open-faced filter holder followed by PUF filter surrounding an XAD-2 sorbent. To obtain detectable amounts of sample, burns conducted during a full day were composited onto a single sample media. This implied sampling times from 75 - 500 min. The combined filter and PUF/XAD-2 module were analyzed using high resolution gas chromatography and mass spectrometry. The PCDD/F emission factors from this study are reported elsewhere, as is the analysis of the SVOCs. The results of these measurements are presented elsewhere (Gullett and Touati, submitted to Atmospheric Environment).

The results of the burn hut trials were compared to emission factors obtained during field burns conducted by Air Sciences Inc and the USDA Forest Service's Missoula Fire Sciences Laboratory. These field experiments were conducted in Dayton, Columbia County, WA, in fields of both high and low pre-burn residue loading during the Spring and Fall of 2000 (Air Sciences, 2002).

Analytical Methods and QA/QC

After sample collection the filters were individually wrapped in aluminum foil, placed in sealed plastic bags, stored in cooler boxes and transported to WSU. Pending analysis, the filters were stored in a walk-in freezer. Prior to analysis the filters were brought to room temperature and placed in 10 mL ethyl acetate and sonicated for 15 minutes. This ensured the temperature of the ultrasonic bath did not exceed 40 ºC. The extracts were then transported to EWU, where they were reduced to ~ 1 mL with the use of a rotary evaporator. The exact volume was estimated as accurately as possible, with the aid of a microsyringe. 375 μL of the sample + 25 μL of an internal standard was placed in a GC vial. Internal

standards consisted of 6 deuterated PAHs, selected to cover the molecular mass range of the PAHs. The ratios of concentrations of the sample: internal standard were used to compensate for variations in sample sizes and instrument response.

Calibration standards were prepared from a Supelco Semivolatile Calibration Standards Mixture (64 SVOCs, each at 1000 μg/ mL). These standards were run each time the GC was turned on. For determining the extraction efficiencies, Teflon, Quartz and PUF filters were spiked with 50 μL of the Semivolatile Calibration Standards Mixture. After air-drying the filters were extracted with ethyl acetate, rota-vaped down to ~ 1 mL and prepared for GC-MS analysis. The tests were done in quadruplicate.

Since SVOCs tend to adhere strongly to glass, all glassware was silanized to deactivate the silanol groups on the surfaces. After boiling in $Si(CH_3)_3Cl$ the glassware was washed with methanol and oven dried at 120C for 12 hrs.

Samples were analyzed on a Hewlett- Packard 6890 gas chromatograph and mass spectrometer (GC/MS) equipped with an auto sampler. The column was a J&W DB-5MS: 30m x 0.32mm ID, 1microm film thickness. The analysis protocol used was EPA Method 8270 (protocol for analyzing samples of agricultural smoke for 16 PAHs and some phenols). The GC/MS was operated with a constant helium flow rate of 0.6 mL/min. The temperature program called for the initial temperature of 45C to be held for 3.5 mins, then ramped to 290C at 12C/min, held for 6 mins and then ramped to 325c at 20C/min, and held at 325C for 5min. HP EnviroQuant target software was used for data analysis and peak identification.

Results

Extraction Efficiency Tests

Extraction efficiencies for various SVOC on the PUF, Teflon, and quartz sampling media are summarized in Table 5. The PUF extraction efficiencies were the highest, approaching (and sometimes exceeding) 100%. The data here represent an average of 4 measurements (i.e., 4 Teflon filters, 4 quartz filters, and 4 PUFs were spiked with the SVOC standards). It should be noted that, in Table 5, we have not yet determined the SDs or range of values because we are in the process of determining the repeatability of the volumes from the micropipette. In the case of two of the Teflon filter samples, 4-chloro 3 methyl phenol and chyrsene had average recoveries of 102 and 104% respectively, although the recoveries of

other SVOCs in those samples were more plausible. One of the quartz filter samples has 10 SVOC's whose extraction efficiencies range from 106- 137%. Another six SVOCs in the same sample have recoveries ranging from 92- 99%. This is possibly due to uncertainties in the micropipette volume. Similarly, two of the PUF samples have efficiencies ranging from 101- 165% - only six SVOCs in those two samples have efficiencies < 100%. The results of the extraction efficiency tests are shown in Figures 2a through 2c, below. The large error bars shown in Figure 2b are due to the samples that have recovery efficiencies > 100%. In Figure 2c, we first removed those samples for which the recovery efficiencies were over 100% for more than one compound were considered suspicious, possibly due to inaccuracies in the micropipette volumes.

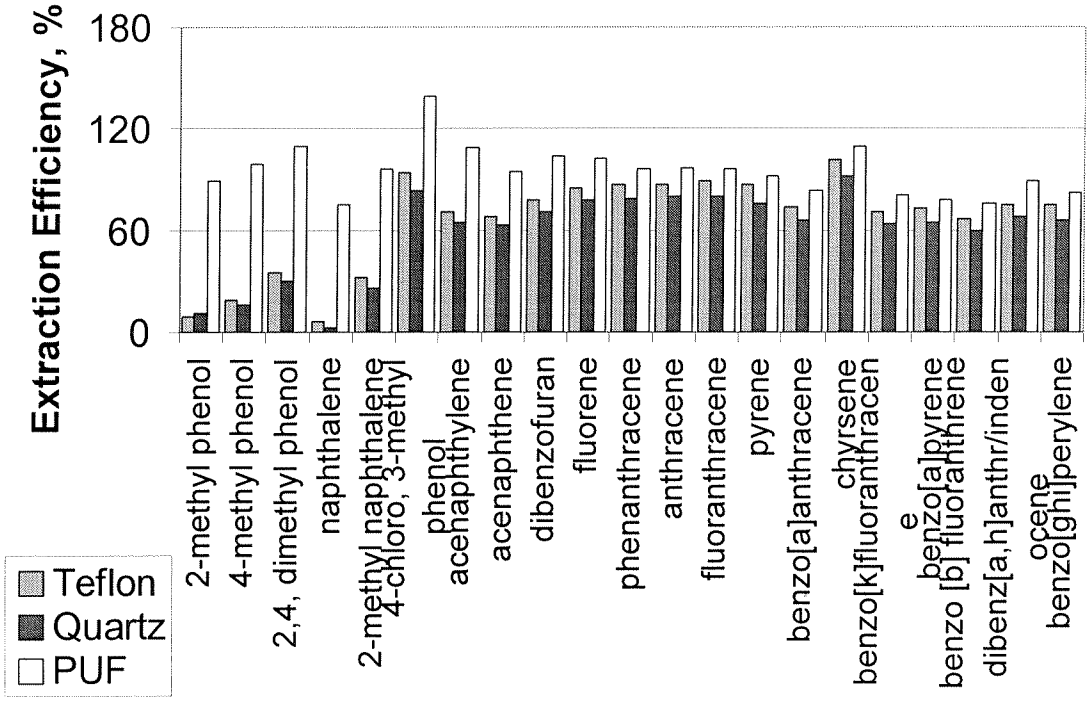

Fig (2a): SVOC extraction efficiencies, based on all samples

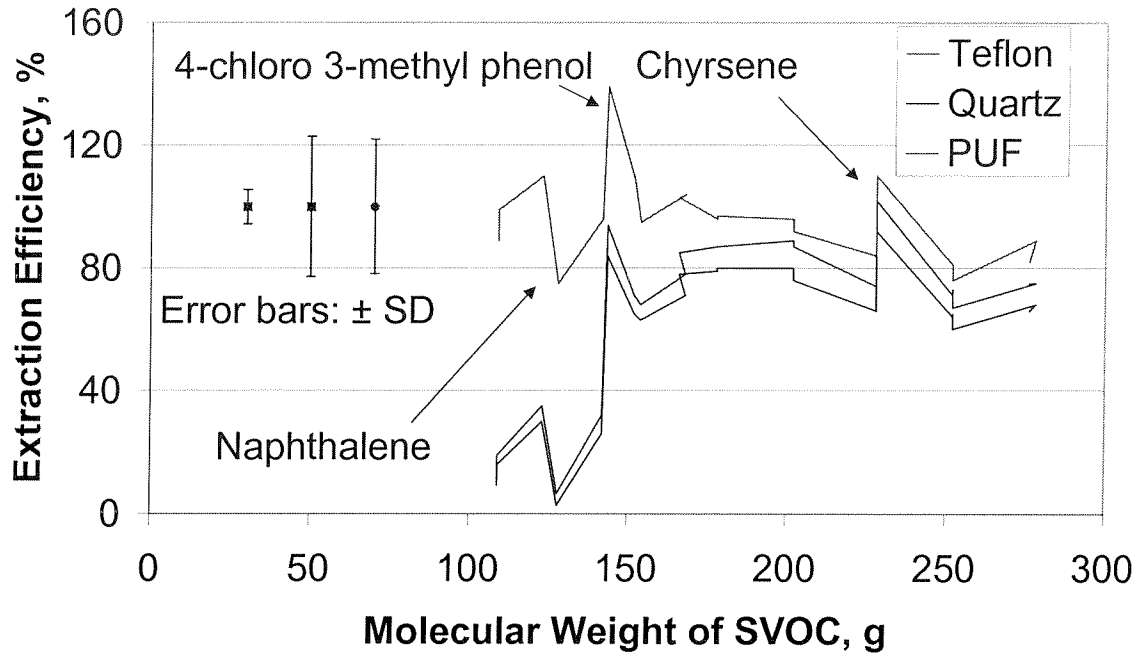

Fig (2b): Same as Fig (a1) but includes error bars, calculated based on results of all samples.

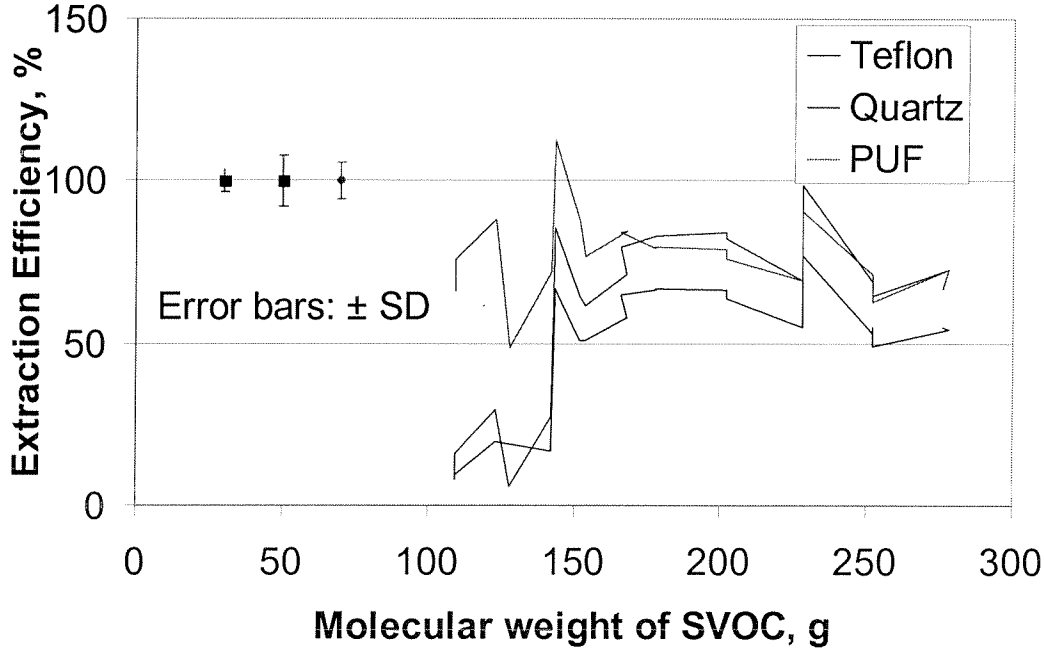

Fig (2c): SVOC extraction efficiencies, calculated by removing the "suspect" samples – see text. Even after removing these samples, there is still one SVOC - 4-chloro, 3-methyl phenol- that appears to be recovered at 112%. This could be due to a standard-related problem or an instrument response problem.

Quartz filters yielded the lowest recoveries and we suspect this is caused by the active –OH groups on the filter more strongly holding the PAHs and phenols. In Figure 3, the extraction efficiencies are plotted as a function of molecular weight (MW). The collection efficiencies for the low MW SVOCs are low for both the Teflon and quartz filters. The lower molecular weight species have higher volatilities and evaporate more readily from the Teflon and quartz filters after they have been spiked, while the PUF media is more effective at capturing vapor phase SVOC. As the molecular weight increases, the collection efficiencies for all three media increase and become more similar.

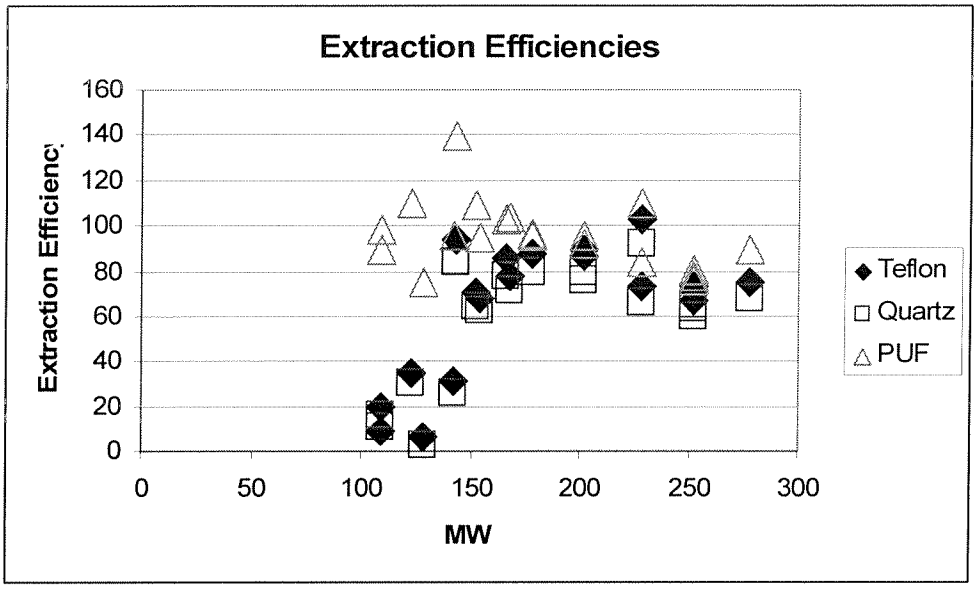

Figure 3: Extraction efficiencies as a function of molecular weight, for PUF, Teflon and quartz filter media.

Table 5: Extraction efficiencies of PAHs and phenols

SVOC*	Molecular weight, g	Filter media		
		Teflon	Quartz	PUF
2-methyl phenol	109	9.27	10.95	89.0
4-methyl phenol	109	19.45	16.21	98.5
2,4, dimethyl phenol	123	34.89	30.18	109.8
naphthalene	128	6.55	2.77	74.9
2-methyl naphthalene	142	31.66	25.74	95.6
4-chloro, 3-methyl phenol	143.5	93.75	84.42	139.0
acenaphthylene	152	71.01	64.79	109.3
acenaphthene	154	67.63	62.70	95.1
dibenzofuran	168	77.75	71.10	103.8
fluorene	166	85.37	78.01	103.1
phenanthracene	178	87.40	79.25	95.9
anthracene	178	87.23	79.94	96.9
fluoranthracene	202	89.17	79.61	95.8
pyrene	202	87.01	76.19	92.1
benzo[a]anthracene	228	73.50	66.31	84.0
chyrsene	228	102.48	91.75	110.3
benzo[k]fluoranthracene	252	71.28	63.47	80.8
benzo[a]pyrene	252	73.27	65.41	78.2
benzo [b] fluoranthrene	252	67.03	59.97	76.3
dibenzo[a,h]anthr/indenocene	278	74.77	67.50	89.2
benzo[ghi]perylene	276	74.87	66.31	82.3

*SVOCs in bold text are PAHs. Others are phenols.