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ABSTRACT - Three volatile nitrogen-containing compounds, 3-ethenylpyridine (3-EP), pyridine and pyrrole, were investigated as potential tracers for determining the contribution of environmental tobacco smoke (ETS) to concentrations of volatile organic compounds (VOCs) in indoor environments with smoking. The source emission rates of the three tracers and ten selected VOCs in ETS were first measured in a room-size environmental chamber for a market-weighted selection of six commercial cigarettes. The ratios of the emission rates of the tracers to the emission rates of the selected VOCs were calculated and compared among the six brands.

The utility of the tracers was then evaluated in a field study conducted in five office buildings. Samples for VOCs were collected in designated smoking areas and adjoining non-smoking areas, air change rates were measured, and smoking rates were documented. Concentrations of the three tracers in the smoking areas were calculated using a mass-balance model and compared to their measured concentrations. Based on this comparison, 3-EP was selected as the most suitable tracer for the volatile components of ETS, although pyrrole is also potentially useful.

Using 3-EP as the tracer, the contributions of ETS to the measured concentrations of the selected VOCs in the smoking areas were estimated by apportionment. ETS was estimated to contribute 57 to 84 percent (4.1 to 26 μg m^{-3}) of the formaldehyde concentrations, 44 to 69 percent (0.9 to 5.8 μg m^{-3}) of the 2-butanone concentrations, 37 to 58 percent (1.3 to 8.2 μg m^{-3}) of the benzene concentrations, and 20 to 69 percent (0.5 to 3.0 μg m^{-3}) of the styrene concentrations. The fractional contributions of ETS to the concentrations of acetone, toluene, ethylbenzene, xylene isomers and d-limonene were all less than 50 percent.

INTRODUCTION

Building occupants are typically exposed to complex mixtures of volatile organic compounds (VOCs) in air. Sources of VOCs in buildings may include outdoor air used for ventilation, combustion appliances, interior finish materials, office equipment and various occupant activities, such as smoking.

The smoke to which non-smokers are exposed when they are in an indoor environment with smokers is termed environmental tobacco smoke (ETS). The U.S. Environmental Protection Agency's (EPA) has classified ETS as a Group A carcinogen (EPA, 1992). ETS is complex mixture of hundreds of chemicals, including numerous VOCs of which some are individually classified as toxic air contaminants (NRC, 1986). Although certain VOCs in ETS are tobacco specific, many also have other indoor sources. Examples of toxic air contaminants in ETS with multiple indoor sources include formaldehyde, benzene and styrene.

It is difficult to determine or even estimate the contributions of ETS to concentrations of VOCs in buildings because, as noted, many of the compounds of interest have multiple sources. In principle, a source-apportionment approach can be used, if there are appropriate tracer or marker compounds. The National Research Council lists four criteria for an ETS tracer: 1) uniqueness to tobacco smoke; 2) easy detection at low smoking rates; 3) similar emission rates across different tobacco products; and 4) consistent proportions to other ETS compounds for different environments and tobacco products (NRC, 1986). Airborne nicotine has extensively been used as an ETS marker. The majority of nicotine is found in the gas-phase, but nicotine readily sorbs onto surfaces and, therefore, is not an ideal marker for the more volatile components of ETS which have significantly lower deposition rates. For example, the ratios of nicotine to gas-phase components of ETS measured as total VOCs were found in a chamber study to be highly variable with time and ventilation rate (Nelson *et al.*, 1992). When tobacco is burned, 3-ethenylpyridine (3-EP), a compound more volatile than nicotine, is formed by the pyrolysis of nicotine. 3-EP is probably unique to tobacco smoke in indoor environments. In the ETS chamber study referenced above, the ratios of 3-EP to total VOCs were much less variable than those of nicotine to total VOCs indicating that 3-EP is a better predictor of the concentrations of the gas-phase components of ETS. Furthermore, 3-EP can readily be collected and measured in conjunction with the other VOCs. In contrast, a separate sampling and analysis procedure is required for nicotine (Hammond *et al.*, 1987; ASTM, 1990).

Heavner *et al.* (1992) investigated the use of 3-EP as a marker for VOCs in ETS. They first conducted experiments in an 18-m^3 environmental chamber in which reference cigarettes (University of Kentucky 1R4F) were machine smoked. The average ratios of 3-EP to benzene and styrene for a range of ventilation conditions had coefficients of variation of about ten percent, at least partially satisfying the criterion for consistent ratios in different environments. Field measurements were then made in four "smoking" and four "non-smoking" homes. 3-EP was not detected in any of the non-smoking homes, supporting the criterion for uniqueness to tobacco smoke. The ETS apportionment of benzene and styrene in the homes was determined based on the measured concentrations of 3-EP and the chamber data. For the smoking homes, ETS was found to contribute from 0.2 to 39 percent of the benzene and from 1.6 to 49 percent of the styrene.

In a more extensive study, Heavner *et al.* (1995) compared VOC concentrations in 49 homes, smoking and non-smoking. 3-EP exhibited a significant correlation with smoking activity. However, benzene and styrene were not correlated with 3-EP or other smoking related indicators because there are multiple sources of these compounds. An apportionment technique was again used to estimate the contribution of ETS to the total concentrations of benzene and styrene. In the 25 smoking homes, the median percentages of benzene and styrene in air attributable to ETS were both 13 percent. Heavner *et al.* concluded that there was a need for additional data on the ratios of 3-EP to VOCs across a number of commercial cigarette brands.

The study reported here is a laboratory and field evaluation of 3-EP and two additional volatile, nitrogen-containing ETS components (pyridine and pyrrole) as potential tracers for other VOCs in ETS. In addition, the study provides data on the contribution of ETS to the concentrations of a number of common VOCs in smoking areas of office buildings.

EXPERIMENTAL METHODS

Laboratory chamber study

Laboratory experiments were conducted to measure emission factors for selected VOCs in ETS (Daisey *et al.*, 1994). Six commercial brands of cigarettes and a reference cigarette (University of Kentucky 1R4F) were selected for the study. Together, the commercial brands accounted for 62 percent of the market share of cigarettes sold in California in 1990. Filtered, non-filtered, mentholated and low-tar cigarettes were included. Four different manufacturers were represented.

The experiments were conducted in a 20-m^3 environmental chamber with stainless steel interior surfaces and low background concentrations of VOCs. The chamber was operated under static conditions (*i.e.*, no mechanical ventilation) with a minimal air change rate of 0.03 ± 0.003 h^{-1} (air changes per hour) due to infiltration and the removal of air for sampling of ETS constituents. The chamber temperature was $23 \pm 1^\circ$ C, and the relative humidity was 45 ± 5 percent. Diluted sidestream smoke was used to simulate ETS. In each experiment, three cigarettes were sequentially smoked in the chamber by a machine using a standard smoking cycle of one puff per minute of 35-cm^3 volume and 2-sec duration (ISO, 1986). Mainstream smoke was exhausted to the outside of the chamber. The air in the chamber was mixed throughout the entire experiment with six small fans placed along the walls of the chamber. Duplicate chamber experiments were conducted for one cigarette brand. An additional experiment was conducted with one of the commercial cigarettes in which the 8.9-m^2 floor of the chamber was entirely carpeted with a new nylon-pile carpet.

In each experiment, four samples for VOCs were sequentially collected at one-hour intervals starting at times 0, 1, 2, and 3 hours after completion of smoking. They were collected on multisorbent tubes which contained Tenax-TA, Ambersorb XE-340, and activated carbon in series (Part No. ST032, Envirochem, Inc.). Sample volumes were typically 2 L. Two samples were collected for low-molecular weight aldehydes. These were collected during the first and last 100 minutes of the four-hour post-smoking period on silica cartridges impregnated with an acid solution of 2,4-dintrophenylhydrazine (Part No. 37500, Waters Corp.). Sample volumes were 25 L. A single nicotine sample was collected over the four-hour post-smoking period on a XAD-4 sorbent tube (Part No. 226-93, SKC West, Inc.). The sample volume was 0.5 m^3.

Field study

The field study was conducted as part of a larger investigation of 22 city and county office buildings in California (Alevantis *et al.*, 1994; Hayward *et al.*, 1994). Five of the buildings were selected for this investigation. In these buildings, air sampling for formaldehyde and VOCs was simultaneously conducted in a designated smoking area and in two nearby non-smoking areas. The samples were collected over a continuous five-hour period during a typical mid-week work day. Sampling started at approximately 9 am. During this period, the number of cigarettes smoked in the smoking area was observed and recorded in one-half hour increments.

Air sampling for ETS constituents was conducted at a single location in each area. The sampling equipment was designed to be visually and audibly unobtrusive. Samples for VOCs were collected on multisorbent tubes as described above. Samples for formaldehyde were passively collected on badges impregnated with an acid solution of 2,4-dintrophenylhydrazine (Part No. 570, GMD Systems, Inc.); the effective sample volumes were about 9 L.

In each building, the air change rate for the entire building was determined on the same day that air sampling was conducted. Ventilation measurements in the smoking area were made one to three days after air sampling was conducted. In order to minimize any changes in ventilation conditions between the day the air samples were collected and the day the ventilation measurements were made, the building's outdoor air dampers were adjusted to the same fixed position (*i.e.*, either maximum or minimum setting) and any local exhaust fans in the smoking area were operated in the same manner (*i.e.*, either on or off). Ventilation measurements in a smoking area were conducted by releasing sulfur hexafluoride (SF_6), a tracer gas, at a constant rate in this area continuously for two to three hours. SF_6 concentrations in the smoking area and adjacent non-smoking locations were automatically monitored using a computer-controlled, eight-location sampling system with a 90-s sample sequencing time. The steady-state concentration of SF_6 in the smoking area was used to calculate the rate at which SF_6-free air was supplied to the area. The "effective" air change rate of a smoking area was determined by the following steady-state equation:

$$a = \frac{S}{C_{SS} V} \cdot 10^{-9} \tag{1}$$

where a = the effective air change rate for the space (h^{-1}); S = the SF_6 release rate ($m^3\ h^{-1}$); C_{SS} = the steady-state concentration of SF_6 in the smoking area ($\mu L\ m^{-3}$); and V = the volume of the smoking area (m^3).

Analytical methods

The analytical procedures for VOCs collected on multisorbent tubes have previously been described (Hodgson and Girman, 1989). In brief, the samplers were thermally desorbed, and the samples were introduced into a Hewlett-Packard 5970B gas chromatograph/mass spectrometer (GC/MS) system using a UNACON 810 concentrating system (Envirochem, Inc.). Prior to analysis, an internal standard was added to each sample. The GC/MS was operated to scan a mass range of *m/z* 33-300. For quantitative analyses, target mass ions were extracted from the total-ion-current chromatograms. For calibration, standard gas mixtures of the more volatile compounds were prepared in static dilution bottles; standard solutions of the less volatile compounds were diluted in a suitable low-boiling solvent and injected directly onto all-Tenax samplers.

The aldehyde samples were analyzed using the method of Fung and Grosjean (1981). The silica cartridges were extracted with acetonitrile. The extracts were analyzed for the formaldehyde hydazone derivative with a high-performance liquid chromatograph (HPLC) equipped with a diode-array ultraviolet detector (Model 1090, Hewlett-Packard Co.). Peak-height responses were measured at a wavelength of 365 nm. The formaldehyde passive badges were similarly analyzed by the supplier (GMD Systems, Inc.).

The nicotine samples were extracted with ethyl acetate modified by the addition of 0.01 percent v/v triethylamine. The extracts were analyzed by capillary GC equipped with a nitrogen-phosphorous detector.

Data analysis

The concentrations of the ETS tracer VOCs in a study area over the five-hour monitoring period divided into ten intervals, 0.5 h each, were modeled using a time-dependent mass-balance equation:

$$C_i(t) = C_{i-1}(0.5) \cdot e^{-at} + \frac{S_i\,[1 - e^{-at}]}{a\,V} \qquad (2)$$

where $0 \leq t \leq 0.5$ h for each interval; $C_{i-1}(0.5)$ = the airborne concentration of the compound ($\mu g\ m^{-3}$) at the end of interval i-1; the starting point, $C_0(0.5) = 0$; S_i = the ETS source strength ($\mu g\ h^{-1}$) during the i^{th} interval, obtained by multiplying cigarette consumption during that interval by the emission factor; and a and V are defined as in Equation 1. Therefore, the assumptions that there was no smoking prior to the initiation of sampling, that smoking was constant for each 0.5-h interval, and that the concentration of the compound in the incoming air was zero are incorporated into the model. The model further assumes that the air change rate was constant and that the air in the space was perfectly mixed. As written, the model neglects possible losses of a compound through chemical reactions or sorption onto interior surfaces. Justification for this omission is based on the observation that the effective air change rates for the smoking areas were relatively high compared to the expected loss rates of the selected compounds to surfaces (see below).

RESULTS AND DISCUSSION

ETS emission factors

Emission factors were experimentally determined for target VOCs, three nitrogen-containing, ETS tracer compounds, and nicotine produced by the six commercial brands of cigarettes and the 1R4F cigarette (Daisey *et al.*, 1994). The ten target VOCs selected for this study are formaldehyde, 2-propanone (acetone), 2-butanone, benzene, toluene, ethylbenzene, combined meta- and para- isomers of xylene, ortho-xylene, styrene and d-limonene. Acetone and d-limonene were included because they are frequently found indoors at elevated concentrations. The other target compounds are either classified or are being reviewed for classification as toxic air contaminants in California. The ETS tracer compounds are pyridine, pyrrole, and 3-EP.

For each chamber experiment, emission factors in µg of compound produced per cigarette were calculated for all of the VOCs by applying a time-dependent mass-balance model to the concentration data. For the model, it was assumed that the only source of the VOCs was cigarette smoking (concentrations were corrected for any measured chamber background) and that the concentrations followed a first-order decay with time due to infiltration and the removal of air from the chamber for sampling.

All of the time-averaged VOC concentrations decayed as predicted by the model, except the concentration of 3-EP which decayed faster. A second decay term was added to the model to account for the loss of 3-EP to chamber surfaces. The additional loss rate for 3-EP in the stainless-steel chamber was determined to be 0.09 ± 0.02 h^{-1}, which is three times higher than the combined infiltration and sampling rate of 0.03 h^{-1}. Accounting for this deposition to chamber surfaces with the model allowed the correct derivation of the emission factor for 3-EP. Formaldehyde concentrations measured at the beginnings and ends of the experiments agreed within experimental uncertainties as predicted by the model.

Emission factors for vapor-phase nicotine were calculated from the time-averaged nicotine concentrations in the chamber (data not shown). These ETS nicotine emission factors were only 15 - 22 percent of sidestream emission factors for total nicotine as reported by Daisey *et al.* (1994). Thus, only about one-fifth of the total emitted nicotine persisted in chamber air over the four-hour post-smoking period. These data demonstrate that nicotine has a high tendency for deposition to surfaces and support the assertion that nicotine is not an ideal tracer for vapor-phase components of ETS.

The average emission factors and ranges of the target VOCs and ETS tracer compounds in µg per cigarette are shown in Table 1 for the six commercial cigarette brands. These emission factors were normalized to standardized cigarette lengths which ranged from 46 to 65 mm (ISO, 1986). It should be noted that these emission factors exclude the minor contributions from exhaled mainstream smoke and, therefore, are expected to be slightly lower than emission factors for real smoking environments. The precisions for these data are expressed as coefficients of variation (CVs). These CVs ranged from 11 percent for d-limonene to 29 percent for pyridine. A portion of this variation was due to differences in the lengths of the cigarettes since the CVs for emission factors expressed in ng of VOC produced per mg of tobacco consumed ranged from only 5 to 20 percent among the six brands (Daisey *et al.*, 1994). The emission factors for the reference cigarette are shown in Table 1 for comparison. Although the 1R4F values all exceed the corresponding average values for the commercial brands, they fall within the indicated ranges for the commercial brands.

The good precisions demonstrate that the emission factors expressed as µg of compound produced per cigarette are remarkably consistent across the dominant brands of cigarettes sold in California. Differences among the cigarettes with respect to mentholation or tar content had little effect on the ETS emission factors for these compounds. Also, cigarette filtration had no effect since mainstream smoke was excluded.

The emission factor ratios of 3-EP to the ten target compounds (µg per cigarette/µg per cigarette) are given in Table 2. Emission factor ratios for pyridine and pyrrole, the two other possible tracers for the volatile components of ETS, are also shown in the table. Generally, the variations in the emission factor ratios among the target compounds, as indicated by the normalized ranges in Table 2, are similar for all three ETS tracer compounds. The CVs for the average ratios were, with one exception, in the range of 7 to 16 percent with the pyrrole/VOC ratios generally having somewhat lower variability than the 3-EP/VOC and the pyridine/VOC ratios. Thus, the emission factor ratios have even better precisions than the emission factors for individual compounds. These results demonstrate the high degree of uniformity in the ETS tracer/target VOC ratios across the dominant brands of cigarettes sold in California.

Heavner *et al.* (1992) reported average 3-EP/benzene and 3-EP/styrene emission factor ratios of 1.3 (range 1.1 to 1.6) and 3.3 (range 2.8 to 4.0), respectively, for a chamber study of the effect of ventilation rate on the ETS emissions of reference cigarette 1R4F. The chamber ventilation rates varied from 0.05 to 2.11 h^{-1}. There was a small but statistically significant effect of ventilation on the ratios. For the ten experiments conducted at ventilation rates of 1.4 h^{-1} and higher, the average 3-EP/benzene and 3-EP/styrene ratios were 1.4 (range 1.3 to 1.6) and 3.6 (range 3.0 to 4.0), respectively. This result is consistent with the fact that losses of 3-EP to the surfaces of the chamber will be a larger fraction of the total removal rate (ventilation plus deposition) at the lower ventilation rates.

In the study reported here, the average 3-EP/benzene and 3-EP/styrene ratios for the six commercial brands of cigarettes were 1.6 (range 1.2 to 1.9) and 4.5 (range 3.4 to 4.9), respectively. The 3-EP/benzene ratios for the two studies are in reasonable agreement (within 12 to 19 percent) while the 3-EP/styrene ratios are somewhat more divergent (20 to 27 percent). The differences may be attributable in part to the differences in the chamber ventilation rates and the way in which the emission rates were calculated.

An additional chamber experiment was conducted with one of the commercial cigarettes to assess the deposition losses of the three ETS tracer compounds to a carpeted floor. In this experiment, the concentrations of all three compounds decayed faster than predicted solely by infiltration and the removal of air for sampling. The mass-balance model was fit to the data as described above using an additional decay term to account for losses to the carpet. The calculated decay rates attributable to sorption losses to the carpet were 0.085, 0.20 and 0.25 h^{-1} for pyridine, pyrrole and 3-EP, respectively. In buildings, the significance of this effect on airborne concentrations will depend on the types and areas of the surface materials and on the magnitudes of the sorption losses relative to the rate of compound removal by ventilation. For example, the sorption losses to the carpet were substantially lower than the effective air change rates of the smoking areas included in this study (see below). In addition, it is likely that compounds sorbed onto surfaces will be released when the air concentrations are low.

Building measurements

The field study was conducted to evaluate the utility of the three ETS tracers for apportioning the concentrations of VOCs from ETS. The physical descriptions of Smoking Areas 7, 8, 9, 10 and 11 in the five office buildings included in the study are summarized in Table 3. The buildings, study areas and ventilation systems are described in detail in a report on the parent study of 22 office buildings (Hayward *et al.*, 1994). The smoking areas in the 22 buildings were divided into three groups based on the degree to which they were isolated from nearby non-smoking areas (Alevantis *et al.*, 1994). Group I, of which Smoking Areas 9 and 11 are examples, were enclosed lounges with local mechanical exhausts to the outside. Group II, of which Smoking Areas 7 and 8 are examples, were enclosed lounges but without separate exhausts to the outside. Group III, of which Smoking Area 10 is an example, were open smoking/non-smoking locations.

The building air change rates and the effective air change rates for the five smoking areas are given in Table 4. The effective air change rates of the smoking areas ranged from 3.7 to 21 h^{-1}. The highest rate was measured in Smoking Area 10 which was part of an open cafeteria. Smoking areas 9 and 11 had variable air volume (VAV) heating, ventilating and air conditioning (HVAC) systems. A VAV system varies the amount of air supplied to a building zone in response to the thermal requirements of the zone. In addition, the outdoor air supply rate varies according to the outdoor air temperature. Consequently, it is possible for there to be undetermined differences in the effective air change rates for study areas 9 and 11 between the days in which air samples were collected and the days in which the effective air change rates for the smoking areas were determined if the heat loads in these areas and/or the outdoor air temperatures varied significantly over the two-day intervals. Smoking areas 7, 8 and 10 had constant volume HVAC systems. In these buildings, it is likely that the air change rates for the smoking areas remained relatively constant.

The numbers of cigarettes smoked in the five-hour study periods ranged from 21 to 103 (Table 5). Specific average smoking rates in cigarettes smoked per m^2 of floor area per hour ranged from 0.08 to 0.38 with the lowest and highest values occurring in Smoking Areas 11 and 9, respectively.

Measured concentrations of the target and ETS tracer compounds in the smoking areas are presented in Table 6. The uncertainties in the measurements were estimated using propagation of errors. The relative percent uncertainties in the concentrations due to the variability in sampling and analysis were typically about ten percent, with the exceptions of the uncertainties for styrene, pyridine and pyrrole which were higher. The concentrations of the ETS tracer compounds were all below the indicated lower limits of detection (LODs) in Smoking Area 7 and near or below their LODs in Smoking Area 10. In the three other areas, the concentrations of

3-EP ranged from 5.0 to 13.3 μg m^{-3}, well above the LOD of 1.5 μg m^{-3}. The corresponding concentrations of pyridine and pyrrole in these areas were lower than the concentrations of 3-EP.

The concentrations of the three ETS tracer compounds in the adjoining non-smoking areas were below their LODs in all of the buildings.

Evaluation of Tracers

Equation 2 was used to model the concentrations of the three ETS tracer compounds in Smoking Areas 8, 9 and 11. Smoking area 7 was omitted from this analysis because the ETS tracer compounds were below their LODs in the sample from this location. Smoking area 10 was omitted because this area was not enclosed, and it was, therefore, impossible to accurately determine an effective air change rate. The average emission factors of the three ETS tracer compounds from the chamber experiments, the observed smoking rates, the effective air change rates and the measured room volumes were used in the calculations. The modeled concentrations were calculated using both an average, constant smoking rate for the five-hour study period (total number of cigarettes smoked divided by five hours) and a time-dependent smoking rate based on the observations made every one-half hour. The constant and time-dependent smoking rates gave comparable five-hour time average concentrations that were within ± two percent of each other except for Smoking Area 8 (Figure 1). In that area, the time average concentrations for the time-dependent source were about 12 percent lower than the concentrations for the constant source primarily due to a large amount of smoking in the final observation period.

The averages of the concentrations of 3-EP, pyridine and pyrrole, which were modeled for Smoking Areas 8, 9 and 11 using the time-dependent smoking rates, are compared to their corresponding measured concentrations in Figure 2. There are substantial uncertainties in these ratios of modeled to measured concentrations due to the individual uncertainties in the ETS emission rates, the measured concentrations and the effective air change rates. An estimate of the uncertainties in the ratios was made by propagation of errors assuming, for the purposes of this analysis, that steady-state conditions had been reached and that the air change rate measurements had relative uncertainties of 25 percent. The average CV for the emission rates of the three ETS tracer compounds was about 25 percent (Table 1), and the relative uncertainty in the concentrations of these compounds in the smoking areas was about 15 percent (Table 6). Combining these uncertainties produces an average uncertainty in the ratios of modeled to measured concentrations of approximately 38 percent. It is possible that the ratios for Smoking Area 8 have lower uncertainties than the ratios for the other two smoking areas because this is the only smoking area of the three (*i.e.*, Smoking Areas 8, 9 and 11) that was served by a constant-volume HVAC system.

Despite these uncertainties, there was generally good agreement between the modeled and measured concentrations for all three compounds. For 3-EP which had a small loss to the surfaces of the stainless-steel chamber and the highest loss to the carpet, the good agreement between modeled and measured concentrations suggests that losses of this compound to interior surfaces in the study areas may not have been a significant factor compared to the high removal rates by ventilation. In all three buildings, 3-EP and pyrrole had similar ratios of modeled to measured concentrations, while pyridine had correspondingly higher ratios. This suggests that there may have been some selective loss mechanism for pyridine.

3-EP was chosen as the most suitable tracer for the volatile components of ETS because of its higher emission factor and resulting airborne concentrations and the lack of evidence for significant deposition of 3-EP to surfaces in buildings at least at higher ventilation rates. In addition, 3-EP is unlikely to have other indoor sources besides tobacco smoke. The usefulness of pyridine as a tracer is questionable since it has been found at low concentrations in a number of non-smoking homes (Heavner *et al.*, 1992, 1995). Pyrrole is a structural subunit of many important biological molecules. It is not known if there are indoor sources of gas-phase pyrrole besides ETS. If no other sources are found, pyrrole would also be a suitable tracer.

ETS Apportionment

The contributions of ETS to the measured concentrations of the selected VOCs in Smoking Areas 8, 9, 10 and 11 were estimated by apportionment using 3-EP as the tracer. The fraction of a target compound attributable to ETS is given by the equation:

$$\text{Fraction VOC}_{\text{ETS}} = \frac{C_{3-\text{EP}} \ / \ C_{\text{VOC}}}{E_{3-\text{EP}} \ / \ E_{\text{VOC}}} \qquad (3)$$

where $C_{3\text{-EP}}/C_{\text{VOC}}$ is the ratio of the concentration of 3-EP to the concentration of the target compound in the building, and $E_{3\text{-EP}}/E_{\text{VOC}}$ is the ratio of the emission rate of 3-EP to the emission rate of the target compound from the chamber study (Table 2).

The results of the apportionment are presented in Figure 3 which shows the total concentrations of the these compounds along with the concentrations that are attributable to ETS and in Figure 4 which shows the relative contributions of ETS to the concentrations of the target compounds. The dominant target compounds in at least three of the spaces were formaldehyde, acetone, toluene and d-limonene (Figure 3). These are dominant compounds in many indoor environments. The apportionment technique estimates that ETS contributed 57 to 84 percent (4.1 to 26 µg m^{-3}) of the formaldehyde concentrations in the four areas, 43 to 69 percent (0.9 to 5.8 µg m^{-3}) of the 2-butanone concentrations, 37 to 58 percent (1.3 to 8.2 µg m^{-3}) of the benzene concentrations, and 20 to 70 percent (0.5 to 3.0 μg m^{-3}) of the styrene concentrations. The fractional contributions of ETS to the concentrations of acetone, toluene, ethylbenzene, m-,p-xylene, o-xylene and d-limonene were all less than 50 percent. Using apportionment, Heavner *et al.* (1992) estimated that ETS contributed up to 39 and 49 percent, respectively, of the benzene and styrene concentrations in four homes with smokers; the absolute contributions of ETS to benzene and styrene concentrations ranged up to 2.2 and 0.9 μg m^{-3}, respectively. For their larger study, Heavner *et al.* (1995) reported that: a) the median estimated contributions of ETS to benzene and styrene concentrations in 25 homes with smokers were both 13 percent; b) the maximum relative ETS contributions for benzene and styrene were 63 and 58 percent, respectively; and c) the maximum absolute contributions for benzene and styrene were about 4 and 2 μg m^{-3}, respectively. Thus, in indoor environments with smoking, ETS can add significantly to the concentrations of and exposures to toxic air contaminants including formaldehyde, benzene and styrene. The amounts contributed will depend on the smoking rates, the air volumes in which ETS is mixed, and the air change rates of these spaces.

It was not possible to assess the potential impacts of ETS on the sampled non-smoking locations because, as reported, the concentrations of 3-EP and the other two ETS tracer compounds were all below their LODs in these locations.

CONCLUSIONS

This study demonstrated that there was consistency in the ETS emission factors of target VOCs and nitrogen-containing tracer compounds across the dominant commercial brands of cigarettes sold in California and that there was no obvious effect of cigarette filtration, mentholation, or tar content on these emission factors. In addition, the emission factors determined for reference cigarette 1R4F fell within the ranges of the factors for the commercial brands.

The tobacco-related compound, 3-EP, was evaluated as a tracer for the volatile components of ETS. The relatively low variations in the ratios of its emission rate to the emission rates of the individual target VOCs across dominant brands of commercial cigarettes supports the use of the apportionment technique to determine the contribution of ETS to concentrations of VOCs in indoor environments, such as residences and office buildings. Others have demonstrated the consistency of 3-EP/VOC ratios for different ventilation conditions (Nelson *et al.*, 1992) and the absence of 3-EP in non-smoking houses which satisfies the criterion for uniqueness to tobacco smoke (Heavner *et al.*, 1992). In this study, a limited evaluation was made of the potential for loss of 3-EP to interior surfaces in buildings. 3-EP was the only one of the three ETS tracer compounds studied which showed a measurable loss to the bare stainless-steel surfaces of the chamber. The loss rate increased when the floor of the chamber was carpeted.

However, the loss rate of 3-EP onto the carpet was substantially below the effective air change rates for the smoking areas included in this study suggesting, that for at least these areas, sorption losses of 3-EP were not a significant factor. In environments in which air change rates are low, any selective loss of 3-EP to surfaces will result in an over estimation of the contribution of ETS to the concentrations of other more volatile VOCs. In general, the mechanisms of sorption losses and re-emissions of VOCs on surfaces in buildings need to be further investigated as they can have significant impacts on exposures and on the selection and use of tracer compounds to estimate these exposures.

In this study, the concentrations of 3-EP in areas surrounding the smoking areas were all below the limit of detection. Since the emission rate of 3-EP in ETS is similar to the rates for a number of the target compounds, an improvement in the detection limit for this compound is needed. This would extend the usefulness of 3-EP as a tracer to areas which are less impacted by ETS than indoor environments with substantial smoking activity. Sensitivity can be improved by using larger sample sizes and by increasing the sensitivity of the analysis.

With source apportionment modeling using 3-EP as the tracer, it was demonstrated that ETS can have a significant impact on concentrations of toxic VOCs in smoking environments. In the majority of the five study areas, which included four smoking lounges and an open cafeteria, ETS contributed one-half or more to the concentrations of formaldehyde, 2-butanone, benzene and styrene.

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Table 1. Average emission factors of target VOCs and ETS tracer compounds for six commercial brands of cigarettes and reference cigarette 1R4F.

	Emission Factor, µg cig^{-1}			
	Six Commercial Brands			Reference
Compound	**Average**	**Range**	**CV[a]**	**1R4F**
Target				
Formaldehyde	1,310	960 - 1,880	27	1,330
Acetone	1,190	930 - 1,560	18	1,180
2-Butanone	290	240 - 390	19	380
Benzene	410	320 - 530	18	420
Toluene	660	570 - 860	16	730
Ethylbenzene	101	83 - 142	22	113
m-,p-Xylene	300	260 - 400	17	330
o-Xylene	67	53 - 98	24	75
Styrene	147	122 - 191	17	162
d-Limonene	410	340 - 480	11	390
ETS Tracer				
3-Ethenylpyridine[b]	660	450 - 890	23	680
Pyridine	430	340 - 670	29	640
Pyrrole	400	330 - 570	22	530

[a] CV = Coefficient of variation in percent (mean/standard deviation * 100).

[b] Emission factors were corrected for losses to chamber surfaces.

Table 2. Average emission factor ratios of 3-ethenylpyridine (3-EP), pyridine and pyrrole to target VOCs for six commercial brands of cigarettes (μg per cigarette/μg per cigarette).

	3-EP/VOC		Pyridine/VOC		Pyrrole/VOC	
Compound	**Average**	**Rel. Range[a]**	**Average**	**Rel. Range[a]**	**Average**	**Rel. Range[a]**
Formaldehyde	0.51	0.93 - 1.19	0.33	0.86 - 1.08	0.31	0.87 - 1.11
Acetone	0.56	0.74 - 1.11	0.36	0.85 - 1.19	0.34	0.87 - 1.12
2-Butanone	2.3	0.74 - 1.23	1.46	0.78 - 1.17	1.38	0.82 - 1.15
Benzene	1.63	0.73 - 1.18	1.05	0.81 - 1.20	0.99	0.84 - 1.11
Toluene	1.00	0.77 - 1.13	0.64	0.87 - 1.20	0.61	0.91 - 1.09
Ethylbenzene	6.5	0.82 - 1.13	4.2	0.84 - 1.11	4.0	0.88 - 1.08
m-,p-Xylene	2.2	0.80 - 1.13	1.41	0.86 - 1.19	1.34	0.89 - 1.08
o-Xylene	9.9	0.80 - 1.18	6.4	0.87 - 1.10	6.0	0.91 - 1.11
Styrene	4.5	0.75 - 1.09	2.9	0.86 - 1.21	2.7	0.89 - 1.10
d-Limonene	1.61	0.78 - 1.16	1.04	0.77 - 1.34	0.98	0.84 - 1.23

[a] Relative range was calculated for each compound by dividing the limits by the mean emission factor ratio for that compound (unitless).

Table 3. Physical descriptions of the five smoking areas.

Smkg. Area	Description	Group[a]	Floor Area (m^2)	Volume (m^3)
7	Smoking lounge	II	16	53
8	Smoking lounge	II	24	66
9	Smoking lounge	I	54	146
10	Cafeteria	III	80	219
11	Smoking lounge	I	74	188

[a] Group I = enclosed area with separate exhaust to outside; Group II = enclosed area without separate exhaust to outside; Group III = open area.

Table 4. Ventilation characteristics of the five smoking areas.

Smkg. Area	Event	Day of Event[a]	Building ACH[b] (h^{-1})	Smkg. Area Effective ACH[c] (h^{-1})	HVAC System Type[d]	Position of OA Dampers[e]
7	VOC sampling/ Bldg. ACH	1	2.3	NM[f]	Constant vol.	Maximum
	Smkg. area ACH	3	NM	17	---	Maximum
8	VOC sampling/ Bldg. ACH	1	1.5	NM	Constant vol.	Minimum
	Smkg. area ACH	2	NM	3.7	---	Minimum
9	VOC sampling/ Bldg. ACH	1	0.43	NM	VAV	Minimum[g]
	Smkg. area ACH	3	NM	4.8	---	Minimum[g]
10	VOC sampling/ Bldg. ACH	1	1.5	NM	Constant vol.	Maximum
	Smkg. area ACH	2, 3, 4	NM	21[h]	---	Maximum
11	VOC sampling/ Bldg. ACH	1	0.76	NM	VAV with induction boxes	Minimum[i]
	Smkg. area ACH	3	NM	5.1	---	Minimum[i]

[a] VOCs were sampled and building air change was measured on Day 1; smoking area effective air change was subsequently measured on indicated day(s) relative to Day 1.

[b] ACH = Air change rate.

[c] Calculated as a, using Equation 1.

[d] Smoking areas had either constant volume or variable air volume (VAV) systems.

[e] Position of outdoor air (OA) dampers was fixed.

[f] NM = Not measured.

[g] Smoking area exhaust fan was off.

[h] Average value for days 2, 3 and 4.

[i] Smoking area exhaust fan was on.

Table 5. Cigarette smoking in the five smoking areas.

Smkg. Area	Location	No. Cigs. Smoked in 5 h	Specific Smkg. Rate (cig m^{-2} h^{-1})
7	Smoking lounge	21	0.26
8	Smoking lounge	32	0.27
9	Smoking lounge	103	0.38
10	Cafeteria	51	0.13
11	Smoking lounge	29	0.08

Table 6. Measured concentrations of target VOCs and ETS tracer compounds in the five smoking areas.

Compound	Concentration, µg m^{-3} Smkg. Area 7	Smkg. Area 8	Smkg. Area 9	Smkg. Area 10	Smkg. Area 11	Relative Uncertainty (%)	Estimated Lower LOD[a] (µg m^{-3})
Target							
Formaldehyde	11.7	39	42	4.9	17.2	10	4.0
Acetone	16	111	60	21	31	8	2.0
2-Butanone	<1.0	10.1	8.0	2.1	4.4	8	1.0
Benzene	4.7	14.8	13.4	3.5	5.8	7	0.5
Toluene	12.6	37	30	7.6	49	6	0.5
Ethylbenzene	2.0	8.7	5.2	1.3	3.0	7	0.5
m-,p-Xylene	7.9	32	16.9	3.9	11.4	7	0.5
o-Xylene	2.4	10.0	4.8	1.3	3.5	5	0.5
Styrene	1.2	4.3	5.2	1.0	5.6	15	0.5
d-Limonene	7.0	82	43	11.7	24	7	0.5
ETS tracer							
3-EP	<1.5	13.3	12.5	2.1	5.0	10	1.5
Pyridine	<1.5	7.1	5.0	<1.5	1.8	18	1.5
Pyrrole	<1.0	9.4	7.4	2.1	2.5	16	1.0

[a] LOD = Limit of detection.

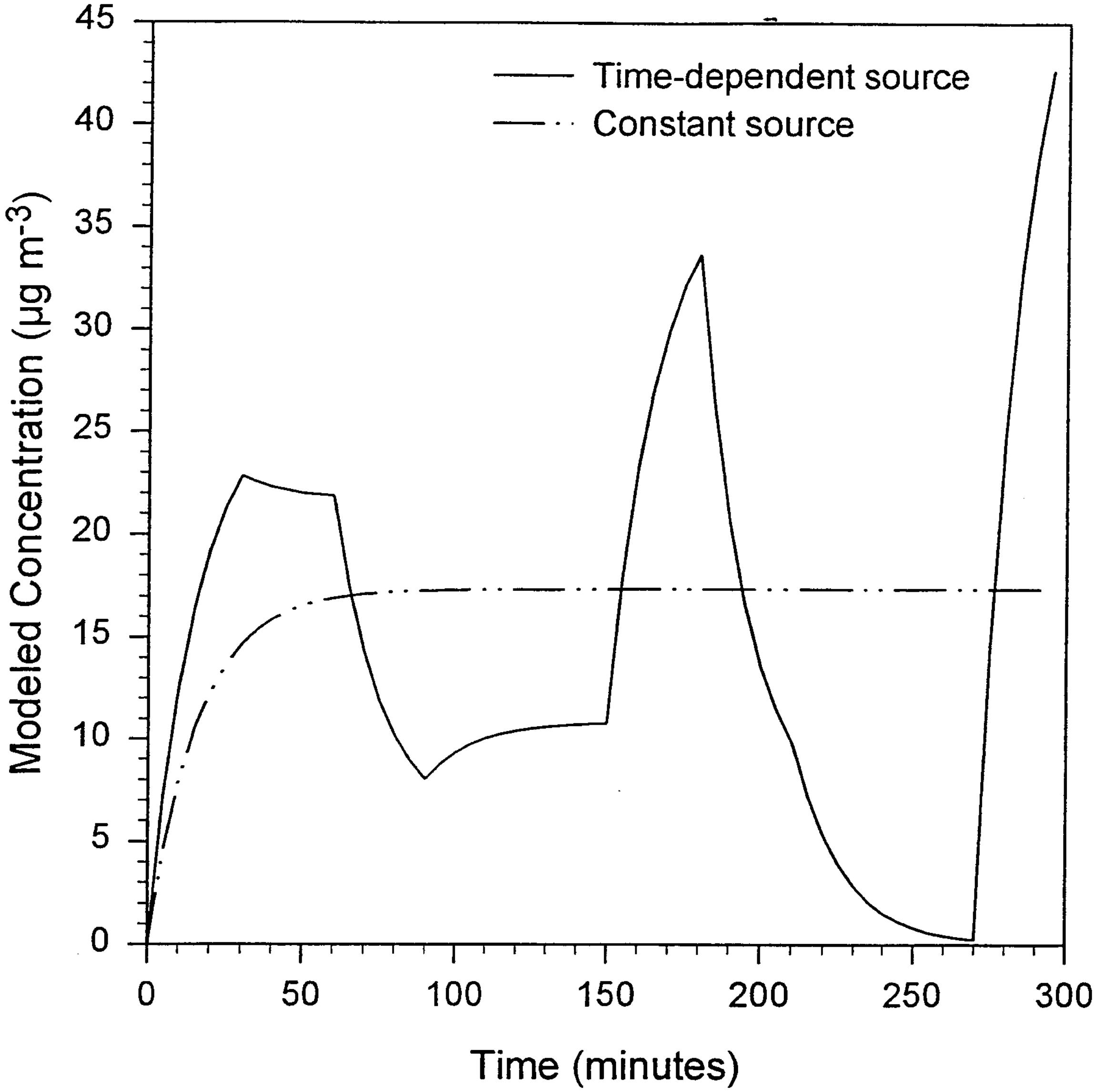
Figure Captions

Figure 1. Temporal concentration profiles for 3-EP in Smoking Area 8 modeled with Equation 2 using both time-dependent and constant smoking rates.

Figure 2. Ratios of modeled to measured concentrations of 3-EP, pyridine and pyrrole for Smoking Areas 8, 9 and 11.

Figure 3. Measured concentrations of target VOCs in Smoking Areas 8, 9, 10 and 11 compared to concentrations attributed to ETS by source apportionment using 3-EP as the tracer.

Figure 4. Fractional contributions of ETS to concentrations of target VOCs in Smoking Areas 8, 9, 10 and 11 estimated by source apportionment using 3-EP as the tracer.



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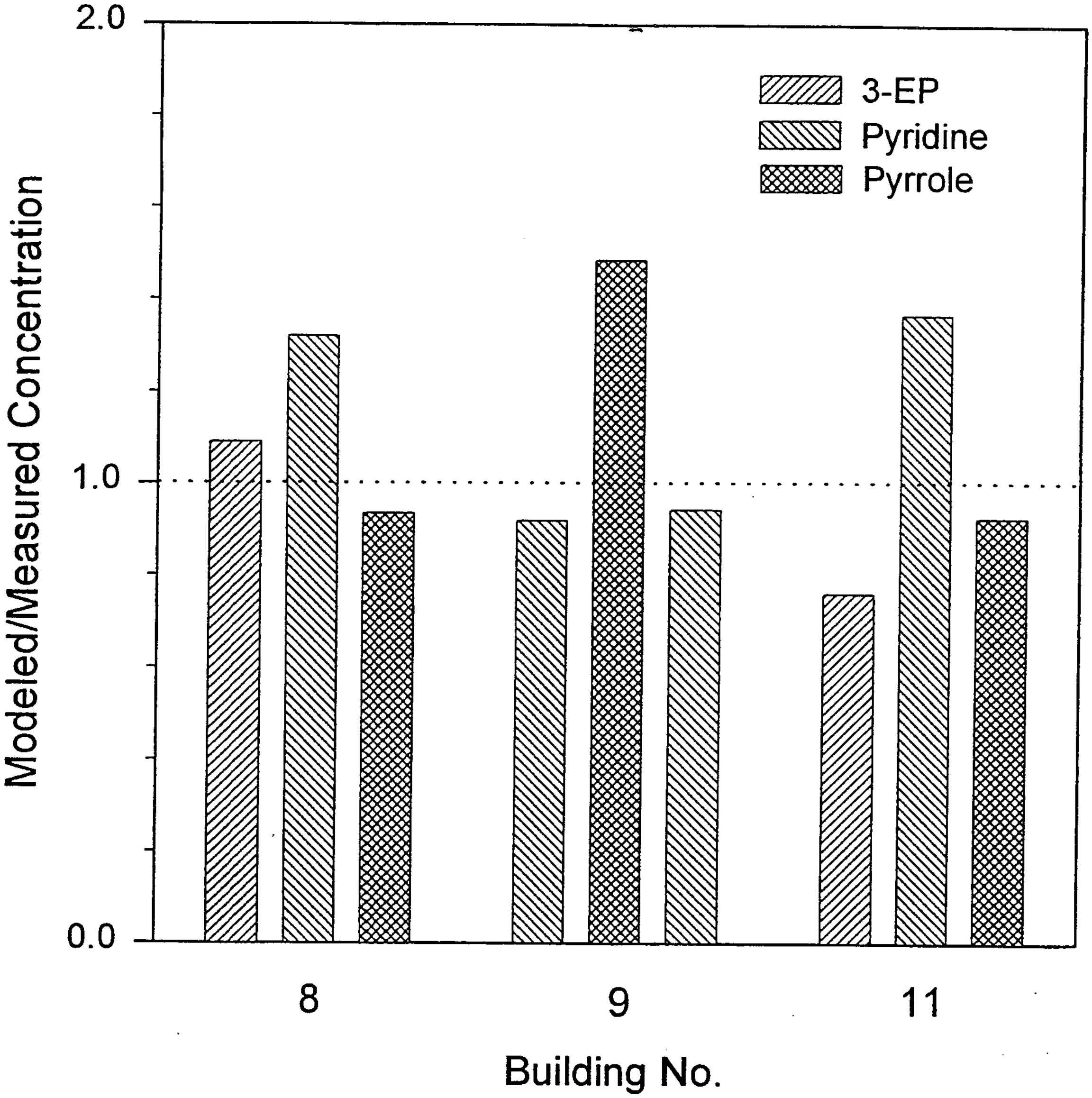

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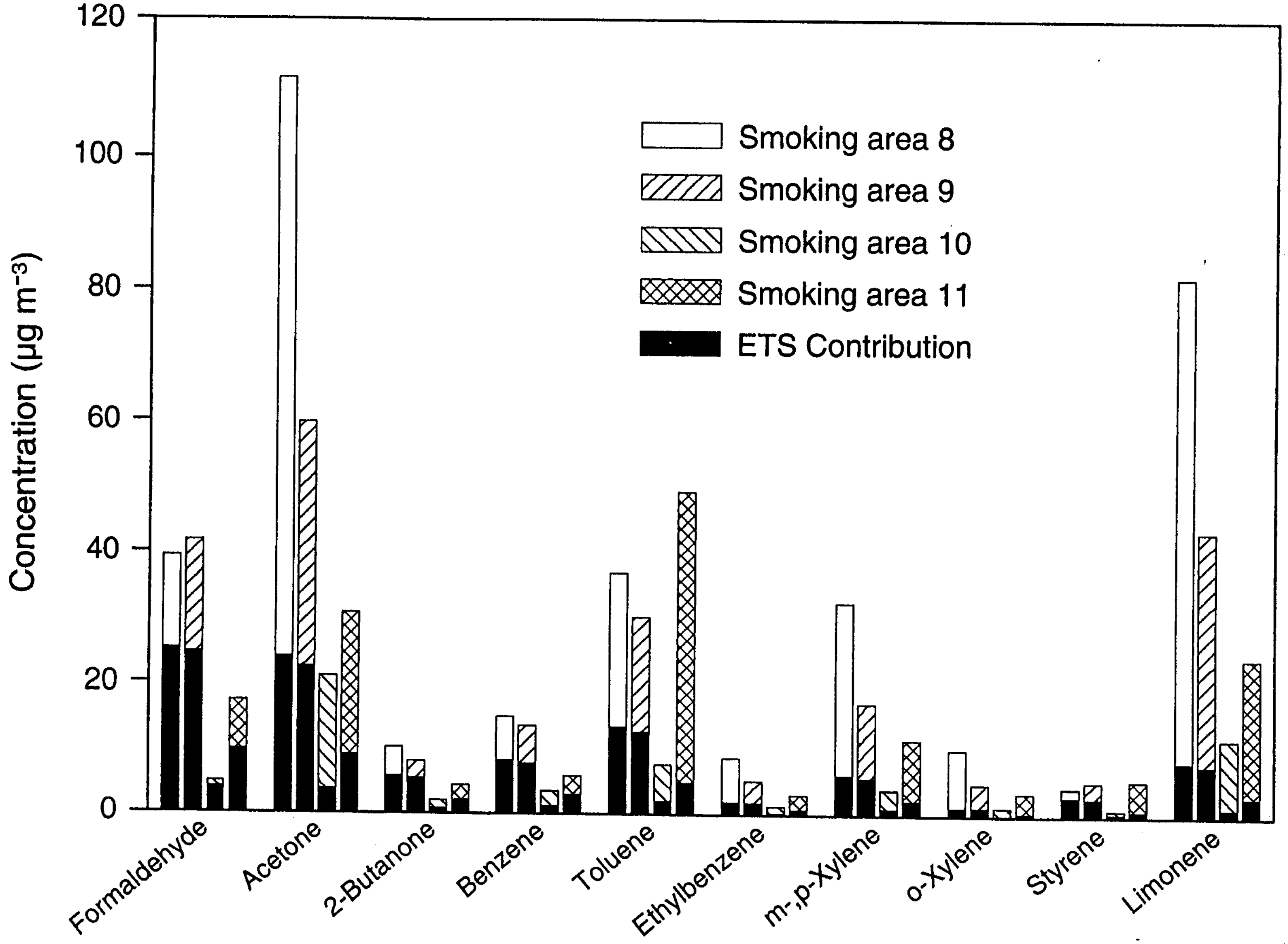

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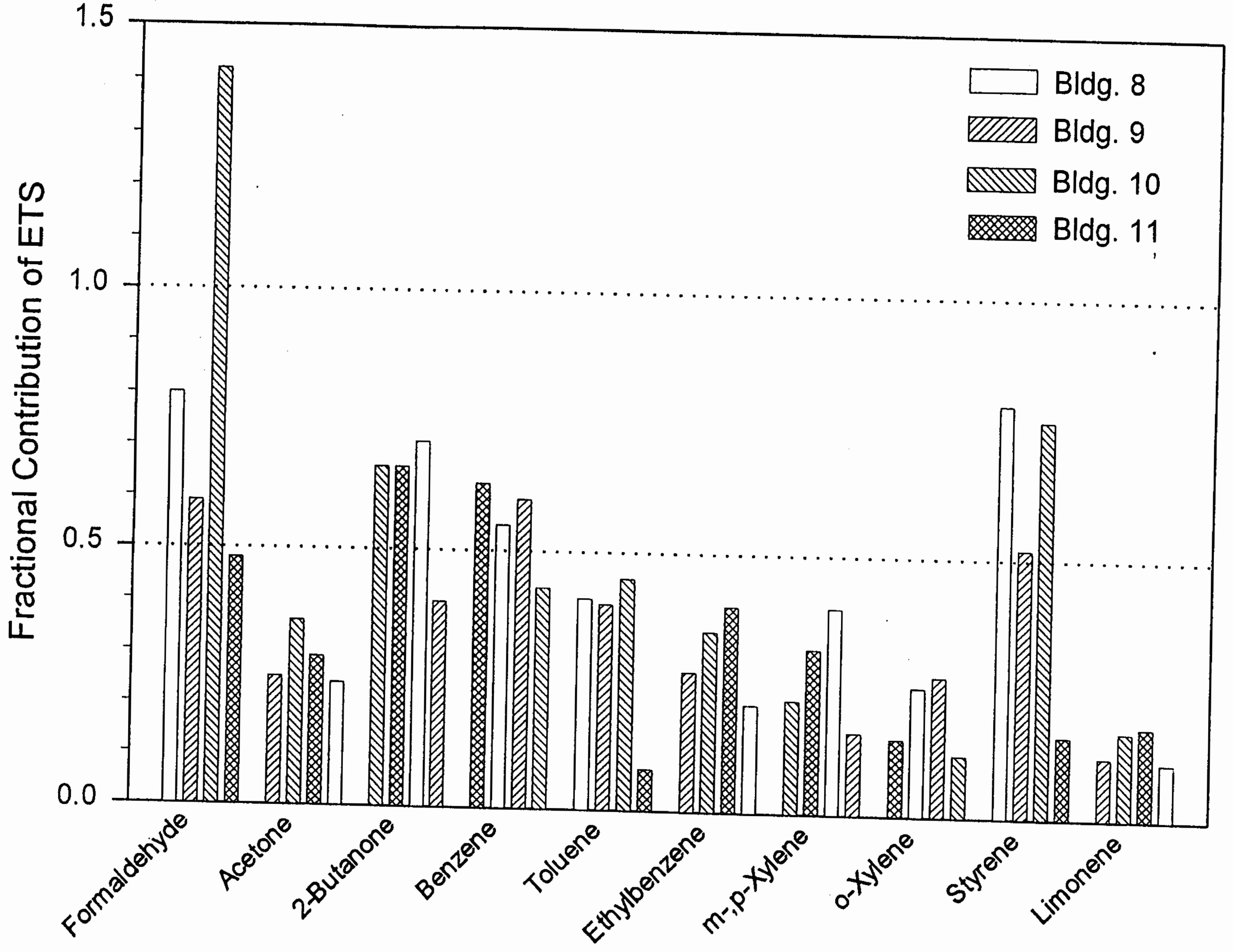

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