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ealth study". In: Sei-
, Ruden, H. and Weg-
ndoor Air '87, Berlin
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SAS Users Guide, Box
Institute.
"Fixation of sulphur
III and subsequent
alytical Chemistry, 28,

6420

Indoor Air, 4, 465-477 (1991)

Total Volatile Organic Concentrations in 2700 Personal, Indoor, and Outdoor Air Samples collected in the US EPA Team Studies

L. Wallace[1], E. Pellizzari[2] and C. Wendel[3]

Abstract

Concentrations of total volatile organic compounds (TVOC) exceeding 1 mg/m^3 have been implicated in the Sick Building Syndrome. Very few measurements of TVOC have been made in homes and buildings in the United States. However, stored gas chromatography-mass spectrometry (GC-MS) data on 12-hour average values of individual *VOCs from 750 homes and 10 buildings were available from EPA's Total Exposure Assessment Methodology (TEAM) Studies (1981-88). An initial study to determine the feasibility of obtaining a TVOC value from stored GC/MS data showed that TVOC estimates could be obtained with adequate precision. Therefore TVOC values were calculated for about 2700 personal, indoor, and outdoor air samples collected in the TEAM Studies.*

More than half of the personal and indoor air samples had TVOC levels exceeding 1 mg/m^3, compared to only about 10% of the outdoor air samples. However, these calculated values may not be directly comparable with values determined using different sampling and analytical techniques. Nonetheless, since all samples were collected on Tenax cartridges, which (like all sorbents) adsorb only a portion of the organic chemicals in the air, these values are likely to be underestimates *of the total volatile organic loading.*

KEY WORDS:
Total volatile organic compounds, TVOC, VOCs, Exposure, Personal monitors, TEAM Study.

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Introduction

We are all exposed to mixtures of hundreds of volatile organic compounds (VOCs) at all times. A number of studies (Mølhave and Moller, 1979; Pellizzari et al., 1987a,b; Wallace 1987; Krause et al., 1987; Sheldon, et al., 1988a,b) have shown that for *individual* VOCs, indoor levels in homes and buildings are typically 2-5 times those of outdoor levels. A few studies (e.g., Mølhave 1986) have indicated that indoor levels of *total* VOCs also exceed outdoor levels. Some researchers have hypothesized that the Sick Building Syndrome may be due in part to reactions to the total mixture of VOCs rather than to individual toxic chemicals (Mølhave, 1986). The level at which reactions occur during an exposure of a few hours was shown to be ≤ 5 mg/m^3 in a clinical study (Mølhave et al., 1986) and the actual threshold level was hypothesized to be around 1 mg/m^3 based on studies of sick buildings (Mølhave, 1987).

If the total concentration of VOCs has an effect on health, information on the frequency distribution of such total concentra-

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tions in people's breathing zones, homes, buildings, and the ambient air would be desirable. EPA's TEAM Study collected information on 20-30 *individual* VOCs for 750 persons and their homes, about 250 outdoor sites in residential areas, and inside and outside 10 buildings in several U.S. cities in the 1980's. Although only the targeted VOCs were quantitated, the information was collected in the form of full scan GC-MS analyses, which were stored in computerized form, thus providing a record that could be analyzed for information on all other VOCs occurring in the sample.

Therefore it was decided to explore whether these records could be analyzed for total volatile organic concentrations (TVOCs). If this proved feasible, a substantial fraction of personal, indoor, and outdoor samples collected in the TEAM Study could be analyzed to provide estimates of people's exposure to total VOCs.

Materials and Methods

About 2700 personal air, indoor air, and outdoor air samples were collected in eight sites across the country between 1980 and 1987 (Table 1). Most of these air samples were collected on Tenax cartridges over two consecutive 12-hour periods (night and day). Flow rates were adjusted to provide a sample volume of about 20 liters (approximately 30 cc/min). All samples were thermally desorbed and analyzed by GC-MS techniques.

All of the samples included in this TVOC calculation were originally analyzed for 20-30 target compounds by full scan (mass range 50 to 250) analysis on a Finnigan 3300 mass spectrometer (MS) located at Research Triangle Institute. The GC and MS hardware and software were the same over the 8-year period (1980-87) of collection. QC/QA procedures were unchanged. Criteria for chemical targets to be considered in control or out of

Table 1 Data Sets used in Study.

Location	No. of Seasons	Year	Sample Type[a]	No. of Persons /Homes	No. of Samples
Homes					
Eliz.-Bayonne[b]	3	1981-3	P, O	350	774
Devils Lake, ND	1	1982	P	25	39
Greensboro, NC	1	1982	O	5	10
Los Angeles, CA	1	1984	P, O	120	268
L.A.-Ant.-Pitt.[c]	1	1984	P, O	120	294
RTP[d], NC[e]	1	1985	P, I, O	7	133
L.A.	2	1987	P, I, O	50	439
Baltimore, MD	1	1987	P, I, O	75	155
Elizabeth, NJ[e]	1	1987	P, I, O	11	315
Buildings					
East Coast[f]	All	'82-85	I,O	10	282
Total				675	2709

[a] P = Personal; I = Indoor; O = Outdoor 12-hour air samples

[b] Elizabeth and Bayonne, NJ

[c] Los Angeles, Antioch, and Pittsburg, CA

[d] Research Triangle Park, NC

[e] These studies were "high-exposure" studies in which participants were asked to carry out activities over periods o 3-5 days that were expected to increase their personal exposures and indoor air concentrations of VOCs.

[f] Includes office buildings in Washington, DC, Fairfax, VA, Cambridge, MA, and Research Triangle Park, NC; a hospital in Martinsburg, WV; an elementary school in Washington, DC; homes for the elderly in Washington, DC (2) and Worcester, MA; and a nursing care facility in Martinsburg, WV.

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control were also consistent over time. The same internal standard, perfluorobenzene, was used in all cases. The external standard, perfluorotoluene, was also used consistently to check the acceptability of the MS tuning performance, the criteria for which were also unchanged over time. The percent recovery of target chemicals and the background level on the Tenax batches varied, but were used to correct measured concentrations in a consistent way. About 5% of the samples were duplicates analyzed at the quality assurance laboratory (IIT Research Institute). The target compounds were quantitated using single ion current (SIC) responses from one or two selected ions for each chemical. Computerized GC-MS records were created and stored for each sample.

About 10% of each batch of Tenax was reserved for blank cartridges, which were not exposed to the atmosphere, but were analyzed at the same time and in the same fashion as the exposed field cartridges. Some of the blank cartridges remained in the laboratory; others were transported to the field and returned unopened. No consistent differences between the laboratory and field blanks were observed, so they were combined in the statistical analysis. In the original TEAM Studies, the mean amounts of the target chemicals observed in the blank cartridges drawn from a particular batch of Tenax were subtracted from the amounts observed on all other cartridges from the same batch. In this study, a similar procedure was followed – a mean TVOC value was calculated for the blank cartridges from each Tenax batch, using the method explained below, and that value was then subtracted from all other cartridges in that batch.

The basic principle of the method explored in this study was the use of an "average response factor," based on the measured response factors of a number of target chemicals drawn from several representative classes (aliphatics, aromatics, and halocarbons), to estimate the TVOC level as a function of the area under the ion current curve. Since response factors vary from one chemical to another, and since no two air samples contain the same mix of chemicals, this approach is not as precise as if standards for each chemical were analyzed to determine recovery efficiencies and precise response factors. However, standards for a large fraction of these chemicals are not available, and it would be impractical to attempt to analyze each sample for scores of organic chemicals in a precisely quantitative fashion. Therefore we decided to investigate whether a less precise but widely useful method could be employed to estimate TVOCs (Norwood and Pellizzari, 1988).

The first step was to examine the single ion current (SIC) relative response factors. A response factor is the ratio of the peak height or area on a graph of ion current for a given chemical to the amount of that chemical. The *relative* response factor (RRF) is that ratio compared to the response factor for a chosen reference standard. SIC RRFs were calculated for 17 target compounds in nine synthetic air samples containing known concentrations of the targets on the Finnigan 3300 instrument using bromopentafluorobenzene as the reference standard compound. The mean SIC RRF over all chemicals was 1.09, with a standard deviation of 0.67, corresponding to a CV of 62%. The mean SIC RRFs over the nine samples varied over an unacceptably wide range, from 0.07 for the 142 ion of *n*-decane to 2.6 for the 91 ion of ethylbenzene (Table 2). This range corresponds to a nearly 40-fold difference in response between different chemicals. Therefore, use of a mean SIC RRF averaged over all these chemicals could give widely differing results for air samples with different chemical constituents.

The next step was to calculate the *total* ion current (TIC) RRFs for the same 17 chemicals on the same spiked samples. (Only eight of the nine samples were utilized because of coelution problems on the ninth sample.)

The area under the TIC curve for the chromatographic region between chloroform and dodecane (scan range from m/z =35 to 350) was integrated and compared to a known amount of a new reference standard, perfluorobenzene. The range of the TIC RRFs was much narrower than for the SIC RRFs – from 0.4 to 1.5 (Table 2). This is smaller than a factor of 4 – about a 10-fold improvement over the SIC RRF. The mean TIC RRF was 0.99 ± 0.41. A second set of seven spiked samples provided a mean TIC RRF of 1.07 ± 0.40. Thus the variability of the TIC RRF across different chemicals appeared to be relatively small, with a CV of about 40% in each group of air samples analyzed – a considerable improvement over the 62% CV of the SIC RRF.

When the variability of the TIC RRF was analyzed by chemical class, it appeared that much of the chemical-to-chemical variability was contributed by the halogenated chemicals (CVs of 50% and 47% for the two sets of air samples). The non-halogenated chemicals had CVs of 21% and 18%. The magnitude of the mean TIC RRF also varied between classes of chemicals, with mean values of 0.80 and 0.92 for the halocarbons, 1.24 and 1.28 for the non-halogens.

Since the calculated mean TIC RRF is based on only 17 chemicals, but is applied to scores of additional chemicals, there is a possibility of a bias in the TVOC estimate. If this mean RRF is not representative of other chemicals in the air samples analyzed, the TVOC levels may be over- or under-estimated.

As a further estimate of the size and direction of the error to be expected in using a mean TIC RRF, three TEAM Study air samples were then analyzed using the mean TIC RRF value of 1.03 to estimate the total amount of *target chemicals only* on each sample. This estimate was then compared with the sum of the levels using the original SIC calculations (Table 3); the relative difference

Table 2 Mean relative response factors (RRF) and coefficients of variation (CV,%) for 17 TEAM Study chemicals based on single ion current (SIC) compared to total ion current (TIC) analyses of nine spiked samples.

	Single Ion Current (SIC)						TIC[a]	
Chemical	Ion	RRF	CV	Ion	RRF	CV	RRF	CV
Chlorinated								
vinylidine chloride	96	0.31	40	61	0.65	17	0.42	17
chloroform	83	0.86	9	85	0.57	12	0.47	15
ethylene dichloride	62	0.70	12	64	0.17	12	[b]	
1,1,1-trichloroethane	97	0.67	11	99	0.44	12	0.49	10
carbon tetrachloride	117	0.55	13	119	0.49	13	0.42	11
trichloroethylene	130	0.43	22	132	0.43	21	0.57	23
tetrachloroethylene	164	0.47	8	166	0.56	8	0.86	8
chlorobenzene	77	1.09	9	114	0.56	9	1.13	10
m + p-dichlorobenzene	146	1.53	6	148	0.98	7	1.40	6
o-dichlorobenzene	146	1.59	7	148	1.00	7	1.45	8
Aromatic and Aliphatic								
benzene	78	1.83	15				0.73	17
styrene	104	1.37	23				1.27	9
ethylbenzene	91	2.62	6	106	0.96	8	1.38	7
m + p-xylene	91	1.50	5	106	0.64	12	1.08	9
o-xylene	91	2.22	7	106	0.80	9	1.42	9
n-decane	57	1.14	17	142	0.07	9	1.34	12
n-undecane	57	1.44	20	156	0.08	10	1.50	10

[a] Based on eight of the nine samples – one had coelution problems for a number of chemicals

[b] Coelution problem

Table 3 Sum of target chemicals (nanograms per cartridge) calculated using mean TIC RRF [a] vs. observed using individual SIC RRFs[b].

Sample	No. Chems	Observed (SIC RRFs)	Calculated (TIC RRF)	% Diff.
1	11	1030	1131	+ 9
2	6	565	739	+27
3	5	638	514	− 22

[a] mean TIC RRF = mean total ion current relative response factor calculated for 17 chemicals (see text for further explanation)

[b] individual SIC RRFs = single ion current relative response factors calculated for each of the chemicals on the sample

between the two values ranged between -22% and +29%. Thus the error associated with using a mean response factor instead of individual response factors was on the order of ± 20% for these cases in which the actual concentrations of the chemicals were known.

To estimate the reproducibility of this method when used by other laboratories, the stored GC-MS records for 17 duplicate air samples that had been analyzed by the quality assurance laboratory were reanalyzed for TVOC by that laboratory using the TIC RRF approach outlined above. (The QA laboratory was blind to the TVOC results obtained by the main laboratory.) When the TVOC results from the two laboratories were compared for the 17 duplicate samples, the median relative difference was 24%, with a range of -59% to +55%. A similar level of interlaboratory precision had been observed for individual target compounds in previous TEAM Study samples, indicating that the use of the mean TIC RRF had not greatly worsened the precision attainable with the use of measured individual SIC RRFs.

We concluded that the method appeared feasible for estimating TVOC levels to within ± 30-60%, provided that the mean TIC RRF of the 17 target chemicals does not differ greatly from the mean value of other chemicals commonly found in indoor and outdoor air. (The TIC RRFs of other chemicals could be determined by obtaining the pure chemicals and spiking samples with these standards to determine their recovery efficiencies and TIC RRFs. However, this additional experiment was beyond the scope of this study.)

Results and Discussion

Existing computerized full scan GC-MS analyses of 329 blank samples from 71 batches of Tenax used on 14 previous field trips were reanalyzed using the TIC RRF method to establish the background level of organic contamination on the Tenax cartridges (Pellizzari et al., 1989). Contaminant levels were high during the first 3 years (1980-82) of the TEAM Study, with average levels of 24 ± 10 μg/cartridge. Since about 20 liters of air were pumped across the field cartridges, this corresponds to a background contamination equivalent to a TVOC concentration of about 1.2 ± 0.5 mg/m^3 on the 725 cartridges analyzed from that period. Contaminants decreased sharply during the 1983-88 period, with levels of 5 ± 2 μg/cartridge, corresponding to 0.25 ± 0.1 mg/m^3 on the 1988 cartridges analyzed from those years.

The limit of detection (LOD) for a given batch of Tenax cartridges was set at twice the standard deviation of the blanks. The LODs for the two periods were 1.2 ± 0.8 mg/m^3 and 0.25 ± 0.1 mg/m^3. A total of 558 (20%) of the samples fell below the LOD.

All TVOC values were obtained by subtracting the average blank value for a given Tenax batch from the calculated TVOC value for the sample. For a small number ($<5\%$) of samples, this led to a negative value for the TVOC, as would be expected on a statistical basis for sample concentrations that fall near the LOD. Such negative values were retained when calculating arithmetic means and percentiles of the frequency distribution, but were replaced by values of 1/2 LOD when calculating geometric means. The overall effect of these negative values was

Table 4 Summary statistics for TVOCS (mg/m³).

Type of sample	N	Arith. Mean	Geom. Mean	Median	Maximum	GSD[a]
Residences						
Personal air	1500	2.9	1.1	1.4	108	3.6
Indoor air	198	1.0	0.7	0.7	11	2.4
Outdoor air	371	0.5	0.3	0.3	5	2.6
Buildings						
Indoor air	220	3.0	1.9	1.9	42	2.3
Outdoor air	62	0.7	0.6	0.7	2	1.7
High-exposure Activities						
Personal air	135	3.8	2.5	2.1	46	2.4
Indoor air	224	2.4	1.8	1.6	28	2.2

[a] Geometric standard deviation

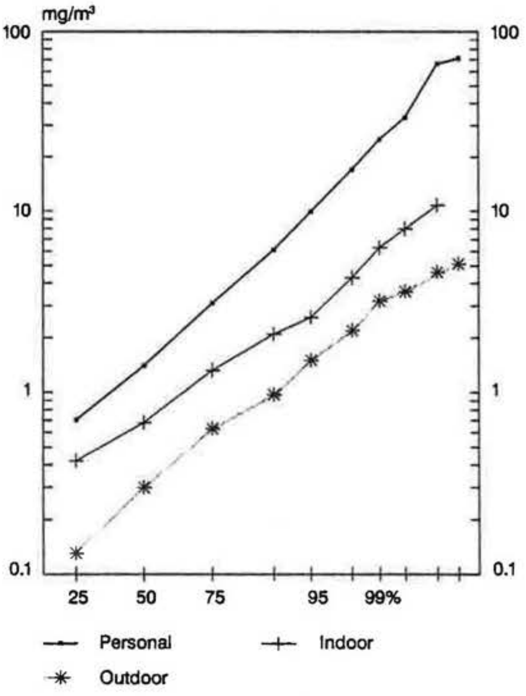

Fig. 1 Frequency distribution of 12-hour average TVOC concentrations for personal (N = 1500 samples), indoor (N = 198) and outdoor air samples (N = 326) collected from about 600 people representing about 600.000 residents of six geographic areas in the U.S. About half of all personal exposures exceed 1 mg/m³, compared to less than 10% of outdoor air concentrations. Presentation is on log-normal probability paper. Unlabelled tic marks in this figure and Figs. 2 and 3 refer to the 90th, 98th, and 99.5, 99.8, and 99.9 percentiles. The distributions appear log-normal.

small except for the second (summer) visit to New Jersey, when all samples were severely contaminated by being stored in a recently renovated hotel.

Concentrations of TVOCs

A total of 2709 samples were analyzed for TVOCs. The samples were divided for this analysis into three groups: personal air, indoor air, and outdoor air. These three groups were further subdivided into residences and buildings (no personal air samples were collected in the buildings). Finally, since two of the TEAM Studies (Wallace, et al., 1989; Lioy et al., 1991) had required participants to carry out activities (smoking, driving, auto repair, visiting dry cleaners, use of room air fresheners, taking hot showers, etc.) suspected of elevating exposure to VOCs, personal and indoor air samples from these studies were treated as separate "high-exposure" subgroups. Since outdoor air samples collected during these studies were not expected to be affected by personal activities, these outdoor samples were combined with the outdoor samples in the other residential studies. Summary statistics for the resulting seven subgroups are provided in Table 4.

Frequency distributions of TVOC concentrations for each of the subgroups are dis-

Maximum	GSD[a]
108	3.6
11	2.4
5	2.6
42	2.3
2	1.7
46	2.4
28	2.2

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played in Figures 1-3. Figure 1, which includes personal, indoor, and outdoor air samples in about 650 residences, shows clearly that personal exposures to TVOCs exceed indoor air concentrations, which in turn exceed outdoor air concentrations. More than 50% of personal air samples exceeded 1 mg/m^3, compared to less than 10% of outdoor air samples. The indoor air TVOC levels were intermediate between the personal and outdoor air concentrations.

The distributions appear to be log-normal, as indicated by the nearly straight lines on the log-normal probability chart. Statistical tests on the nature of the distributions were carried out for each locality, season, type of sample (personal, indoor, or outdoor) and time of day collected (day or night). A total of 54 distributions were thus available for analysis. Tests for log-normality were not rejected for 42 of the 54 distributions. (Five of the 12 cases that did not display log-normal distributions were drawn from the "high-exposure" studies, in which normal exposures were artificially heightened by increasing the number of high-exposure activities.) Geometric standard deviations (GSD) ranged between 2 and 4 for a majority of cases. The overall GSD of 3.6 for the 1500 personal air samples considerably exceeded the GSD of 2.4 for the 433 outdoor air samples.

Figure 2 presents indoor and outdoor TVOCs at 10 buildings. Three of these buildings were new, with some samples being taken within a week of the time they were completed. At all three of these buildings, seven or eight individual organics were measured at 50-100 times concurrent outdoor levels. Repeated samples at these buildings several months later indicated a decline in concentrations to a level intermediate between the very new buildings and the older

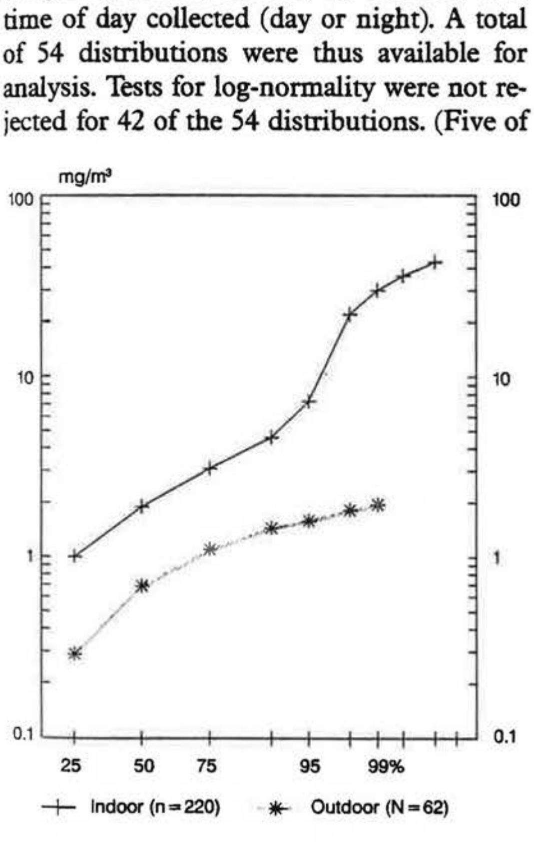

Fig. 2 Frequency distribution of 12-hour average TVOC concentrations for samples collected inside and outside 10 buildings. Three of the buildings were new, and were visited 1 week, 3-4 months, and 6 months after completion. These new buildings account for the high-concentration part of the distribution.

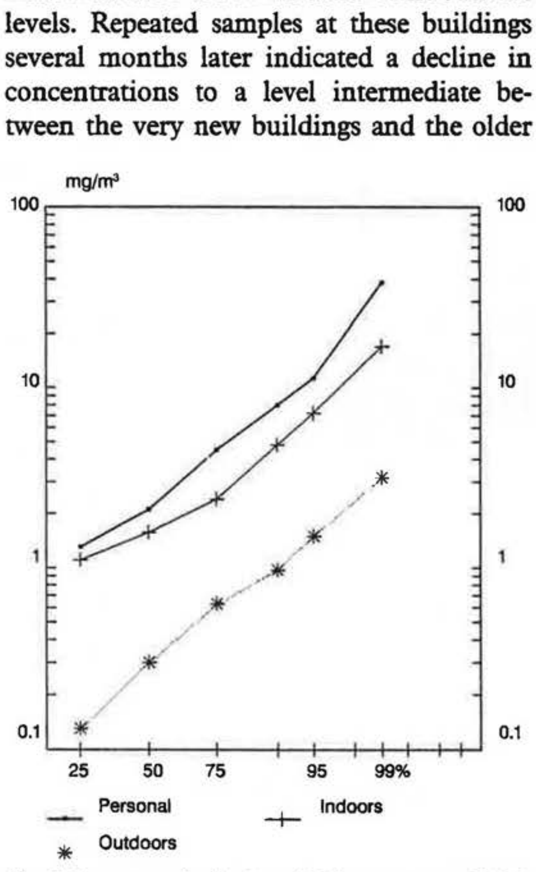

Fig. 3 Frequency distribution of 12-hour average TVOC concentrations for personal (N = 135), indoor (N = 224) and outdoor air samples (N = 45) collected from 18 people carrying out high-exposure activities.

buildings. Thus the distribution shown of indoor air TVOCs probably reflects two or more distributions (very high levels of TVOCs at new buildings vs. low levels at old buildings, with intermediate levels from the buildings of 3-6 months in age).

Figure 3 provides TVOC results from those studies in which 18 persons in 15 homes were asked to perform activities expected to result in higher exposures to the target chemicals. The personal exposures and indoor air concentrations of TVOCs were elevated, with more than 75% of each type of sample exceeding 1 mg/m^3. There is an indication of a convergence of the personal and indoor air levels, due perhaps to the intensive nature of the "high-exposure" activities, which resulted in greatly increasing the indoor air levels.

Geographic, Seasonal, and Diurnal Variation

Median values for personal and indoor air samples ranged from 0.6 to 1.5 mg/m^3 in Los Angeles and Baltimore, with higher values of 1.5 to 4.1 mg/m^3 in New Jersey. Median values for outdoor air were much smaller (0.1 to 0.9 mg/m^3) in all locations. Mean values for each locality were 50-100% greater than medians, reflecting the right-skewed nature of the distributions.

The maximum TVOC value was 108 mg/m^3 for one daytime personal air sample (collected from a cabinetmaker in New Jersey). Other high values included values of 72, 71, and 62 mg/m^3 for personal air samples in New Jersey, 24, 17, 17, and 15 mg/m^3 in Los Angeles and Baltimore, and 42 and 17 mg/m^3 in indoor air samples in one new building in North Carolina. By contrast, the maximum TVOC value among 388 outdoor samples was 5 mg/m^3 in Los Angeles.

Multiple field sampling trips were made to two areas, allowing seasonal and multi-year comparisons. Elizabeth and Bayonne, New Jersey were visited in the fall of 1981, summer of 1982, and February, 1983. Los Angeles was visited in February and May of 1984 and February and June of 1987. Mean values for personal exposures ranged from 2-8 mg/m^3 in New Jersey, whereas mean outdoor values ranged from 0.2 to 0.8 mg/m^3 (Figure 4). The outdoor values for the fall of 1981 were unavailable for analysis, since they had been measured on a different mass spectrometer which had been subsequently decommissioned; thus the mean TIC RRF could not be calculated for this machine.

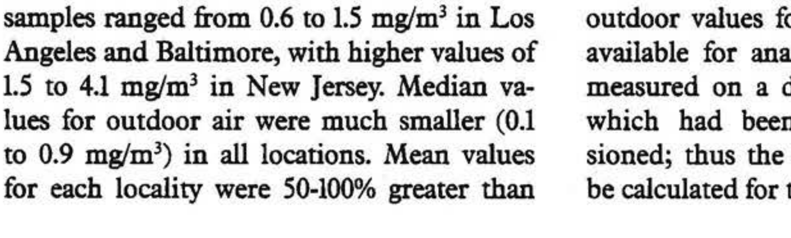

Fig. 4 Arithmetic mean daytime and overnight personal and outdoor air TVOC concentrations in Bayonne and Elizabeth, NJ during the winter of 1983, fall of 1981, and summer of 1982. No outdoor samples were available for analysis from the fall 1981 period.

Some seasonal variation in TVOC levels was observable for the New Jersey locations, with a very high mean daytime personal exposure noted in February 1983; the mean overnight personal exposures, which represented mainly indoor concentrations at home, were lower than the mean daytime exposures but showed a similar seasonal variation (highest in winter, lowest in summer).

The Los Angeles results (Figures 5 and 6) indicated somewhat greater seasonal variation, with the February visits in both 1984 and 1987 showing higher overnight personal exposures (≈1.4 mg/m³) and overnight outdoor concentrations (≈0.6 mg/m³) than the May and June visits in those years (≈0.8 mg/m³ and 0.2 mg/m³, respectively). This is a reflection of both the unfavorable meteorology in the Los Angeles Basin during the winter (nocturnal inversions and stagnant air) and the decreased air-exchange due to fewer open windows. Once again the daytime personal exposures (1.5-2.5 mg/m³) exceeded the overnight exposures (0.7-0.9 mg/m³), confirming previous observations of the importance of personal activities in exposure to

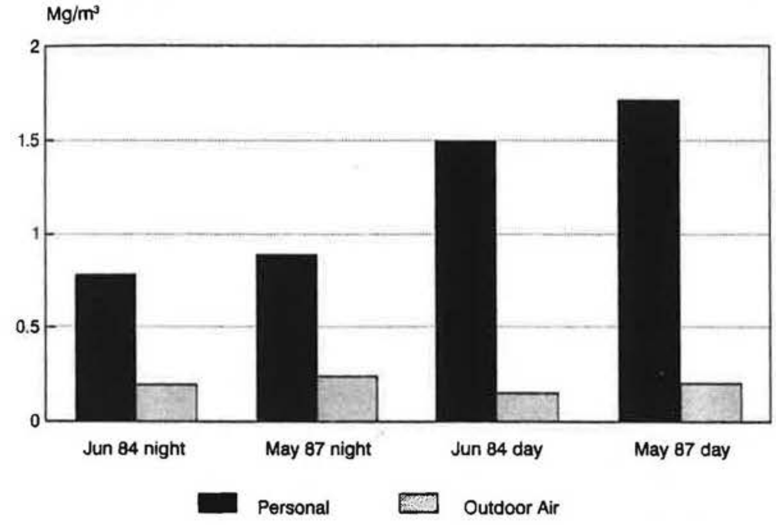

Fig. 5 Arithmetic mean daytime and overnight personal and outdoor air TVOC concentrations in Los Angeles in June 1984 and May 1987.

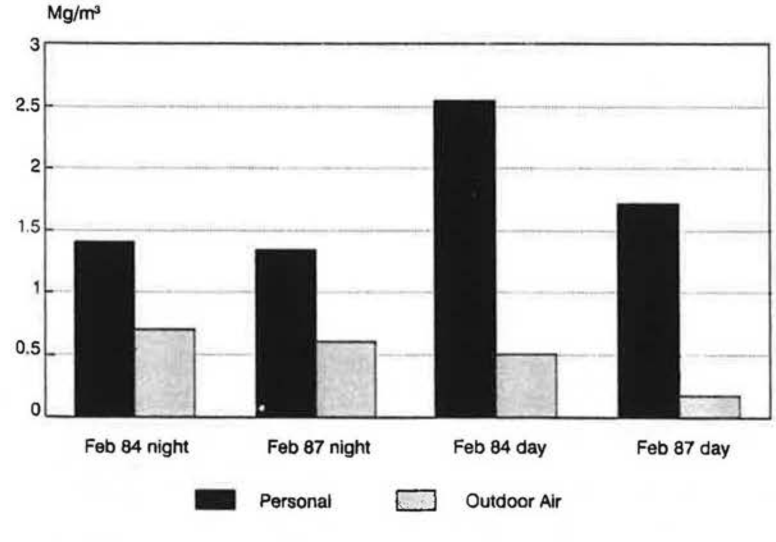

Fig. 6 Arithmetic mean daytime and overnight personal and outdoor air TVOC concentrations in Los Angeles in February 1984 and February 1987.

VOCs (Wallace et al., 1989) and extending those observations to apply to TVOCs.

A question of interest is what proportion of TVOCs was represented by the TEAM Study target compounds. Eleven compounds were often present in the New Jersey studies, and 19 in the 1987 Los Angeles and 1984 L.A.-Antioch-Pittsburg, CA studies. The proportion of TVOCs due to the 11 target compounds in New Jersey ranged from 3% to 20%, and the proportion due to the 19 compounds measured in L.A. and the other California cities ranged from 10% to 20% (Table 5).

Table 5 Proportion of total VOCs due to targeted VOCs

Site	No. of targets	Mean values (mg/m^3) targets	total VOCs	% of Total
Personal				
NJ fall	11	0.34	3.8	9%
NN summer	11	0.20	3.2	6%
NJ winter	11	0.22	5.8	4%
L.A. winter	19	0.24	2.0	12%
CA summer	19	0.11	1.1	10%
Outdoor				
NJ summer	11	0.06	0.3	20%
NJ winter	11	0.025	0.76	3%
L.A. winter	19	0.12	0.6	20%
CA summer	19	0.024	0.17	14%

Discussion

Methodological

Several methods exist for measuring total organic concentrations; however, no single reference method is accepted, and the relationships between different methods are not well characterized. Compounds more volatile than hexane and chloroform will break through Tenax cartridges under the sampling conditions employed in the TEAM Studies (20 l at room temperature, using 1.5 g Tenax). Low molecular weight polar compounds ($< C_4$) will not be collected by Tenax either, nor will semivolatile compounds less volatile than tetradecane. Therefore Tenax collects only a fraction of the total spectrum of organic compounds. Activated charcoal collects a different fraction of organics, and other sorbents have still different collection characteristics. Evacuated canisters collect very volatile organics, but adequate recoveries are not obtained for compounds less volatile than dodecane. Also, present methods of analysis of samples collected in evacuated canisters require that water vapor be removed prior to analysis, thus losing other polar compounds. For these reasons, it is inappropriate to compare TVOC measurements using one method to those using another.

In this study, we have developed and tested a new method of measuring total organic concentrations. The main advantage of this method is that it allows returning to any full scan GC-MS record of an air sample collected on Tenax to calculate total organic concentrations. Thus we have been able to make further use of some 2700 air samples collected over the past decade.

A second advantage of this method, compared to the common use of GC-FID, is that it is equally sensitive to chlorinated hydrocarbons as well as nonchlorinated hydrocarbons. The GC-FID response is depressed by chlorine atoms; therefore if an appreciable fraction of the organic mixture is composed of chlorinated molecules, the GC-FID method will yield an underestimate of the total concentration. Chlorinated chemicals are widely used in the United States. For example, tetrachloroethylene is used in most dry cleaning shops, and tetrachloroethylene vapors are emitted while the clothes are being worn and/or stored in homes (Wallace, 1990); p-dichlorobenzene is widely used as a room air freshener, bathroom deodorant, and moth repellant, and is found in about a third of American homes (Wallace, 1990); and chloroform, a byproduct of water disinfection, is emitted when clothes and dishes are washed in hot water (Wallace, 1987). Our experience with indoor air samples indicates that homes with moth balls or air fresheners can have

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concentrations of para-dichlorobenzene *alone* in the neighborhood of 1 mg/m^3; yet a GC-FID measurement of this atmosphere would yield a value below this. We have also found correspondingly high levels of 1,1,1-trichlorethane in many homes, and high levels of tetrachloroethylene and trichloroethylene in a smaller number. In New Jersey, for example, six chlorinated compounds accounted for an average of 68% of the total personal air exposure to the 20 or so target chemicals. Therefore we believe that estimates of total organic concentrations made using the common GC-FID method may have considerably underestimated actual concentrations in any case where chlorinated chemicals may be present in substantial quantities.

At present, the method employed here has not been tested side by side with any other method of calculating total organic concentrations; therefore we are unable to say how these values compare with what would be found using GC-FID techniques. Thus it is not possible to compare our finding that >50% of personal and indoor samples exceed 1 mg/m^3 with the Mølhave estimate (based on GC-FID measurements) that 1 mg/m^3 may be the threshold value for the development of the Sick Building Syndrome. For the reasons mentioned above, it seems possible that GC-FID analyses of these samples would have resulted in generally smaller TVOC values. How much difference there is would depend on the sorbent used and on the specific mixture of chemicals being sampled, particularly on the level of chlorinated compounds in the mixture.

TVOC Concentrations

TVOC concentrations seemed surprisingly high, with more than half of the personal and indoor air concentrations exceeding 1 mg/m^3. Several European studies have reported values that are generally below this level except in "problem" buildings. For example, Valbjorn and Skov (1987) reported a mean value of 0.5 mg/m^3 in samples collected on Tenax in 13 Danish town halls. As explained above, one possible reason for the higher values observed in this study is that the GC-FID methods generally employed in European studies are not sensitive to chlorinated chemicals, and that these chlorinated chemicals are found widely in the United States.

Median TVOC values for personal and indoor air were 3-5 times corresponding values for outdoor air. This observation confirms and extends to a substantial number of new chemicals the previous TEAM Study findings that median levels of 20-30 target chemicals were 2-5 times higher in personal and indoor air than outdoor air (Wallace, 1987). These observed indoor air TVOC levels are likely to be due to emissions from consumer products and building materials.

Personal TVOC exposures generally exceeded indoor concentrations during the day but not at night; this probably represents the increased exposure occurring during normal daytime activities, such as commuting, cleaning house, etc. (Wallace et al., 1989).

TVOC levels in new buildings greatly exceeded those in older buildings. This is likely to be due to greatly increased emissions from freshly applied paint and adhesives and new carpet, drapes, cables, and other building materials (Sheldon et al., 1988a,b).

Conclusions and Recommendations

We have developed and tested a new method for determining total organic concentrations from samples analyzed by GC-MS. The method can be used *de novo* on newly collected air samples or can be applied retroactively to computerized GC-MS records of previously analyzed samples.

The method was applied to 2700 personal, indoor, and outdoor air samples collected over the last decade in several U.S. cities. Median TVOC values for personal and indoor air ranged between 0.8 and 2.1 mg/m^3, several times greater than the outdoor air medians of 0.3-0.5 mg/m^3. These findings, in conjunction with the fact that the previously targeted VOCs account for only 3-20% of the total organic concentration, extend the previous TEAM Study findings of higher personal and indoor air values for selected VOCs to a large number of additional VOCs.

These measurements provide a baseline for TVOCs in indoor air in homes and buildings in several U.S. cities that may prove useful in future studies of personal exposure or the Sick Building Syndrome. If these VOCs cause the Sick Building Syndrome, this is further objective evidence that the conditions exist both in homes and in buildings for development of the Sick Building Syndrome. However, we caution that the absolute TVOC values reported here are a function of the method employed, and cannot be unambiguously compared to TVOC values calculated by other methods.

We recommend that existing methods of calculating total organic concentrations (sorbent collection or collection in evacuated canisters followed by GC-FID or GC-MS analysis) be compared side by side for several "typical" atmospheres (indoors in homes and buildings, indoors following renovations, outdoors in urban and rural areas, near roadways, etc.) to establish relationships that can be used to compare past measurements using different methods.

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References

Krause, C., Mailahn, W., Nagel, R., Schulz, C., Seifert B. and Ullrich, D. (1987) "Occurrence of volatile organic compounds in the air of 500 homes in the Federal Republic of Germany". In: Seifert, B., Esdorn, H., Fischer, M., Ruden, H. and Wegner, J. (eds) *Proceedings of Indoor Air '87*, Berlin (West), Institute of Water, Soil and Air Hygiene, Vol. 1, pp. 102-106.

Lioy, P.J., Wallace, L. and Pellizzari, E. (1991) "Indoor/outdoor and personal monitor and breath analysis relationships for selected volatile organic compounds measured at three homes during New Jersey TEAM - 1987," *Journal of Exposure Analysis and Environmental Epidemiology*, **1**,45-61.

Maggs, R.J. In: *Column*, **1**, 2-9, 1966.

Mølhave, L. and Moller, J. (1979) "The atmospheric environment in modern Danish dwellings: measurements in 39 flats". In: Fanger, D. and Valbjorn, O. (eds), *Indoor Air*, Copenhagen, Danish Building Research Institute, pp. 171-186.

Mølhave, L. (1986). "Indoor air quality in relation to sensory irritation due to volatile organic compounds." *ASHRAE Transactions*, **92**, 2954.

Mølhave, L., Bach, B. and Pedersen, O.F. (1986) "Human reactions to low concentrations of volatile organic compounds", *Environment International*, **12** (1-4), 167-175.

Mølhave, L. (1987) "The sick buildings – a sub-population among the problem buildings?", In: Seifert, B., Esdorn, H., Fischer, M., Ruden, H. and Wegner, J. (eds) *Proceedings of Indoor Air '87*,Berlin (West), Institute of Water, Soil and Air Hygiene, Vol. 2, 469-474.

Norwood, D.L. and Pellizzari, E.D. (1988) *Total Exposure Assessment Methodology (TEAM) Feasibility Assessment for Total Organic Load Calculation*. Final report, EPA Contract # 68-01-6826.

Pellizzari, E.D., Perritt, K., Hartwell, T.D., Michael, L.C., Whitmore, R., Handy, R.W., Smith, D. and Zelon, H. (1987a) *Total Exposure Assessment Methodology (TEAM) Study: Elizabeth and Bayonne, New Jersey; Devils Lake, North Dakota; and Greensboro, North Carolina, Vol. II*. Washington, DC, United States Environmental Protection Agency (EPA 600/6-87-002b).

Pellizzari, E.D., Perritt, K., Hartwell, T.D., Michael, L.C., Whitmore, R., Handy, R.W., Smith, D., and Zelon, H. (1987b) *Total Exposure Assessment Methodology (TEAM) Study: Selected Communities in Northern and Southern California, Vol. III*, Washington, DC, United States Environmental Protection Agency, (EPA 600/6-87-002c).

Pellizzari, E., Smith, C., Perritt, R. and Hartwell, T. (1989) *Total Organic Levels in TEAM and HEAL Air Samples*, US Environmental Protection Agency, Washington, DC, Final Report, Contract # 68-01-7350.

Sheldon, L.S., Handy, R.W., Hartwell, T.D., Whitmore, R.W., Zelon, H.S. and Pellizzari, E.D. (1988a) *Indoor Air Quality in Public Buildings: Vol. I*, Washington, DC, USEPA, (EPA 600/6-88/009a).

Sheldon, L.S., Eaton, C., Hartwell, T.D., Zelon, H.S. and Pellizzari, E.D. (1988b) *Indoor Air Quality in Public Buildings. Vol. II*. Research Triangle Park, NC, USEPA, (EPA 600/6-88/009b).

Valbjorn, O. and Skov, P. (1987) "Influence of indoor climate on the Sick Building Syndrome prevalence", In: Seifert, B., Esdorn, H., Fischer, M., Ruden, H. and Wegner, J. (eds) *Proceedings of Indoor Air '87* Berlin (West), Institute of Water, Soil and Air Hygiene, Vol. 1, 102-106.

Wallace, L.A. (1987) *Total Exposure Assessment Methodology (TEAM) Study: Summary and Analysis, Vol. 1*, Washington, DC, United States Environmental Protection Agency (EPA 600/6-87-002a).

Wallace, L.A., Pellizzari, E.D., Hartwell, T.D., Davis, V., Michael, L.C. and Whitmore, R. (1989) "The influence of personal activities on exposure to volatile organic compounds", *Environment Research*, **50**,37-55.

Wallace, L. (1990) "Major sources of exposure to benzene and other volatile organic chemicals", *Risk Analysis*, **10**,59-64.