LBL-33686
UC-407

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

To be presented at the Indoor Air '93, The Sixth International Conference on Indoor Air Quality and Climate, Helsinki, Finland, July 5–8, 1993, and to be published in the Proceedings

Volatile Organic Compounds in Twelve California Office Buildings: Classes, Concentrations and Sources

J.M. Daisey, A.T. Hodgson, W.J. Fisk, M.J. Mendell, and J.Ten Brinke

January 1993

ENERGY & ENVIRONMENT DIVISION

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

To be Published in Proceedings of
Indoor Air '93, the 6th International
Conference on Indoor Air Quality
and Climate, July 5-8, 1993, Helsinki, Finland

LBL-33686

Volatile Organic Compounds in Twelve California Office Buildings: Classes, Concentrations and Sources

Joan M. Daisey, Alfred T. Hodgson, William J. Fisk,
Mark J. Mendell and JoAnn Ten Brinke

Indoor Environment Program
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

January 1993

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division, and by the Director, Office of Energy Research, Office of Health and Environmental Research, Human Health and Assessments Division, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

VOLATILE ORGANIC COMPOUNDS IN TWELVE CALIFORNIA OFFICE BUILDINGS: CLASSES, CONCENTRATIONS AND SOURCES

J. M. Daisey, A. T. Hodgson, W. J. Fisk, M. J. Mendell and J. Ten Brinke
Indoor Environment Program, Energy and Environment Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720 U.S.A.

ABSTRACT

Volatile organic compounds (VOCs) measured in 12 Northern California office buildings were investigated with respect to variability in overall chemical composition by class and major indoor sources common to these buildings. Chemical composition varied substantially among the buildings. Wet process photocopiers in two buildings increased total VOC levels by factors of about 5 and 13 relative to the other buildings. Motor vehicle emissions from outdoor air accounted for 70 to 90% of seven aromatic and five alkane compounds in most of the buildings. There was evidence of freon leaking from HVAC and/or refrigeration systems in several of the buildings.

INTRODUCTION

As part of the California Healthy Building Study (1,2,3) concentrations of total volatile organic compounds (TVOC) and of 39 individual volatile organic compounds (VOCs) were measured in 12 office buildings in the San Francisco Bay Area in Northern California. The major purpose of the overall study was to investigate the prevalence of various occupant symptoms and perceptions of thermal comfort in office buildings selected without regard to worker complaints, and to determine if there was a difference in symptom prevalences as a function of ventilation type (2,3). Indoor concentrations of VOCs were measured in each building to characterize indoor air exposures, to investigate inter-office variations in chemical classes and concentrations, and to identify major sources of VOCs. This paper presents the VOC results.

METHODS

Twelve buildings, with a non-smoking policy, were selected for the study: 3 naturally ventilated (NV), 3 mechanically ventilated (MV) with operable windows and no air conditioning, and 6 mechanically ventilated with sealed windows and air conditioning (AC). Buildings were selected from lists of city-or county-owned buildings in the San Francisco Bay area; all eligible buildings to which access was granted were included. One of the AC buildings was a classic "sick building" with a long history of occupant complaints, cause(s) of which were never clearly identified. Environmental measurements were made in 32 study areas within the 12 buildings. The VOCs were collected on multisorbent samplers for 8-hr work day periods and were analyzed for TVOC using a flame-ionization detector and for individual compounds using a capillary gas chromatograph-mass spectrometer (4). TVOC values were multiplied by 1.19 to convert ug C/m^3 to ug/m^3 for comparison to the sums of the concentrations of the individual VOCs (VOC). Outdoor samples were also collected and analyzed for comparison. Duplicate samples were collected and analyzed for each site. The

lower limits of detection for the individual VOCs ranged from 0.1 to 0.4 ppb. Temperature, relative humidity, and the difference between indoor and outdoor CO_2 concentrations (CO_2), which serves as an indicator of occupant-adjusted ventilation, were also measured (1,2,3).

The geometric mean concentrations of VOCs and TVOC were calculated for each building from the average concentrations at the one to four sampling sites within each building. The two sampling areas within building 5, located on the 2nd and 6th floors and designated 5.2 and 5.6, were treated as separate buildings because the two floors had separate ventilation systems and only one was affected by the presence of liquid process photocopiers. This gave an effective total of 13 buildings.

For examination of chemical composition variability among buildings, VOCs were grouped into five chemical classes: alkanes, aromatics, oxidized hydrocarbons, chlorinated hydrocarbons and terpene (limonene). Indoor to outdoor concentration ratios (I/O) were calculated for 12 buildings (Bldg.6 was omitted because of the loss of the outdoor sample). Principal components factor analysis with a varimax rotation (5) was used on the VOC data, with and without CO_2, and on some sub-sets of these data to try to find compounds and sources common to these buildings.

RESULTS

Table 1 presents geometric mean concentrations, geometric standard deviations (GSD), and ranges of TVOC and of VOC. Indoor TVOC ranged from 230 ug/m^3 to 7,000 ug/m^3 and, with one exception, were higher than outdoor air concentrations. The highest TVOC values (> 2000 ug/m^3) were measured in buildings with liquid-process photocopiers (Bldg.4 and 5.6). If these values are excluded, the median TVOC concentration was 410 ug/m^3 for the remaining areas.

Table 1. Geometric mean indoor concentrations (ug /m^3) of TVOC, VOCs and their ranges in San Francisco Bay Area office buildings

Volatile Organic Compounds	Geometric Mean*(GSD)	Range of Concentrations**
TVOC	420 (1.3)	270 - 7,000
VOC	270 (1.3)	170 - 460

* Buildings with wet-process photocopiers omitted; n=11; **n = 13

The individual VOCs, grouped into five chemical classes, are presented in Table 2.

Table 2. VOCs included in each chemical class

Chemical Class	VOCs in Chemical Class
Alkanes	n-pentane, n-hexane, methylcyclopentane, n-heptane, methylcyclohexane, 3-methylhexane, n-octane, 2,2,5-trimethylhexane, n-nonane,n-decane, n-undecane, n-dodecane
Aromatic Hydrocarbons	benzene, toluene, ethylbenzene, styrene, m,p-xylene, o-xylene, 2-ethyltoluene 3- & 4-ethyltoluene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene
Oxidized Hydrocarbons	ethanol, ethyl acetate, 2-propanol, acetone, butyl acetate, 2-butoxy-ethanol, pentanal, hexanal, benzaldehyde, 1-phenylethanone
Chlorinated Hydrocarbons	dichloromethane, trichlorofluoromethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene,
Terpenes	limonene

DISCUSSION

The indoor concentrations of TVOC and VOCs measured in these northern California office buildings were generally low, with the exceptions of Bldgs. 4 and 5.6, which had liquid process photocopiers. For these buildings, TVOC levels were 2,700 and 7,000 ug/m^3, respectively. The impacts of such office equipment on TVOC levels has been reported previously (4). The average concentrations of TVOC (excluding the buildings with the liquid-process photocopiers) did not differ significantly among the three types of building ventilation: 460 $\pm$ 270 ug/m^3 (NV); 400 $\pm$ 120 ug/m^3 (MV); 450 $\pm$ 130 ug/m^3 (AC). Concentrations of TVOC in Bldg. 2, the "sick building," did not differ from concentrations in other buildings. The sums of the 39 individual VOCs which were quantified accounted for 35 % to 90 % of the TVOC values, excluding the buildings with liquid-process photocopiers (Bldgs. 4 & 5.6). Concentrations of both TVOC and individual VOCs were generally consistent with what has been reported by others for office buildings (4,6).

Although there was relatively little variation in the overall levels of TVOC and VOC among these buildings (excepting Bldgs. 4 and 5.6), there was considerable variation in the chemical composition of the VOC mixtures, as shown in Figure 1. The oxidized hydrocarbons accounted for the greatest proportion of the VOCs for almost all of the buildings. Ethanol contributed substantially to the oxidized hydrocarbon class in many buildings; concentrations ranged from 12 to 239 ug/m^3. Concentrations of chlorinated hydrocarbons were highly variable among buildings and even within buildings, ranging from a few percent of the sum of the VOCs to as much as one-third. In Bldgs. 2, 5.2, 8, and 12, the chlorinated hydrocarbons were the second most abundant class of VOCs. For Bldgs. 1, 3, 7, 9, and 11, the alkanes or aromatic hydrocarbons were the second most abundant class of VOCs. Terpenes accounted for the smallest fraction of the total in all of the buildings; however, this class consists of a single compound, limonene.

In order to identify major VOC sources common to the buildings, the I/O ratios were first examined. VOCs for which the I/O ratio was greater than 1.35 for 8 or more of the buildings were identified as coming predominantly from indoor sources. VOCs for which the I/O ratio was less than 1.35 for 8 or more of the buildings were identified as coming predominantly from outdoor sources. The remainder were classified as coming from mixed indoor and outdoor

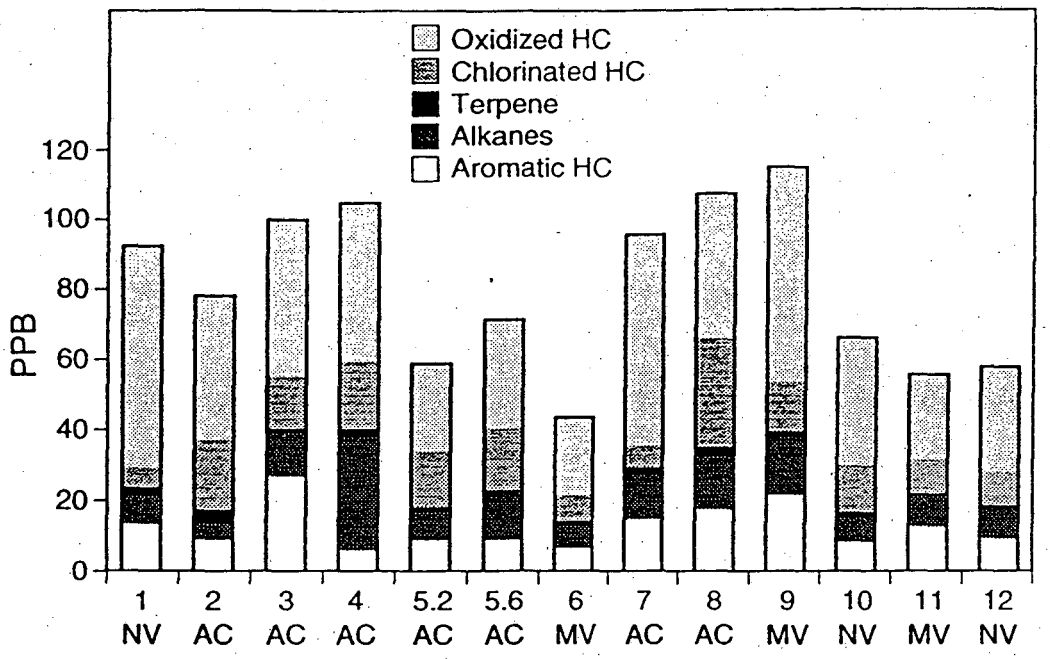

Figure 1. Average concentration of 5 chemical classes of VOCs in 13 Northern California buildings

sources. Those coming predominantly from indoor or from outdoor sources are shown in Table 4, grouped by categories of known indoor sources.

Table 4. VOCs categorized by source types across buildings and grouped by possible sources

Predominantly from Indoor Sources (I/O >1.35)
Cleaning/Degreasing: dichloromethane, trichloroethene, 1,1,1-trichloroethane
Bioeffluents/Bldg.Material: ethanol, 2-propanol, acetone
Products/Bldg. Materials: n-dodecane, n-pentanal, n-hexanal, limonene
Predominantly from Outdoor Sources (I/O < 1.35)
Motor Vehicle Emissions: benzene, m/p-xylene, o-xylene, 2-ethyltoluene, 3-& 4-ethyltoluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, n-pentane, 3-methylhexane
Dry Cleaning: tetrachloroethylene
Other: benzaldehyde, 1-phenylethanone, n-decane

The factor analyses consistently gave a first factor which had high loadings on the aromatic hydrocarbons and a few other VOCs associated with motor vehicle exhaust, specifically, those listed for this source in Table 4, plus ethylbenzene, methylcyclopentane, n-hexane and 1,2,3-trimethylbenzene. Table 5 gives the ratios of the concentrations of these VOCs to benzene for a motor vehicle emissions profile from Chicago (7) and for the outdoor air samples from this study. The ratios for outdoor air and motor vehicle emissions are very similar. The motor vehicles emissions profile for California would be expected to differ somewhat from the Chicago profile because of differences in the mix of catalyst and non-catalyst vehicles and in fuel composition. The California outdoor air concentration profile was used to estimate the contribution of motor vehicle emissions to the total indoor concentrations of these VOCs for 9 of the 13 buildings. For this calculation, benzene was used as the reference compound since its I/O ratio was generally less than one; that is, it was assumed that all of the benzene in a building was from outdoor air/motor vehicle emissions. The motor vehicle contribution to the remaining compounds was calculated from our outdoor air/motor vehicle ratio. These are presented in Table 5 as the average for 9 of the buildings and range from about 70 to 90%.

Table 5. Comparison of ratios of VOCs to benzene in motor vehicle emissions and in outdoor air samples and estimated contribution of motor vehicle emissions to indoor concentrations for 9/13 of the office buildings[a].

	Ratios of VOC	to Benzene	Average Estimated % of Indoor Air Concentration from Motor
Compound	Motor Vehicle[b.]	Calif. Outdoor Air[c.]	Vehicle Emissions
n-Pentane	1.11	1.75	79
n-Hexane	0.62	0.34	73
Methylcyclopentane	0.36	0.30	82
3-Methylhexane	0.37	0.23	91
n-Heptane	0.22	0.23	82
Benzene	1.00	1.00	100 (Reference)
Toluene	1.67	1.77	76
Ethylbenzene	0.30	0.31	88
m/p-Xylene	1.05	1.30	82
o-Xylene	0.38	0.41	82
3-& 4-Ethyltoluene	0.44	0.50	86
1,2,4-Trimethylbenzene	0.14	0.53	84
1,3,5-Trimethylbenzene	0.27	0.23	81

a. Bldgs. 5.2 and 5.6 omitted due to high I/O ratio for benzene; building 6 omitted due to lack of outdoor sample; building 4 excluded due to very low benzene value (<0.1 ppb) and consequent large uncertainties in the ratio.
b. Reference 7; c. This study

Factor analysis also consistently yielded a freon factor with a high (>0.9) loading for trichlorofluoromethane; acetone and CO_2 were generally associated with the freon on this factor. The CO_2 is an indicator of occupant- adjusted ventilation. The association of acetone with CO_2 suggests that the acetone is also largely a bioeffluent. Acetone has been reported as a bioeffluent (8). The association of these two variables with freon is suspected to be a time-dependent one, i.e., the HVAC systems are typically in operation during the same period as buildings are occupied. For many of the buildings, the indoor and outdoor concentrations of the freon were very similar. For 4 of the 7 AC buildings, 2 of the MV buildings, and 1 NV building, the I/O ratio of this compound was greater than 1.9 and reached as high as 16. This compound is commonly used as a refrigerant and is probably leaking from the HVAC systems or from some refrigeration system in these buildings. The MV and NV buildings which had excess freon are all physically connected to AC buildings. Although the source strength for a building can only be estimated, it may be of the order of grams per day.

A factor with tetrachloroethene loaded at a level of > 0.9 was also observed in these analyses and identified as a "dry cleaning" source, which is the major source of this compound in both indoor and outdoor air. Ten of the 12 buildings had I/O ratios for this compound that were less than 1.35 indicating that most of it originated from outdoor air in these buildings. In the remaining two buildings, the I/O ratio was 2 or less, indicating that even in these building, outdoor sources contributed significantly.

Finally, ethanol was always found on a separate factor and did not seem to be significantly associated with the bioeffluent/bldg. materials sources (CO_2, acetone). This suggests that there may be an additional source(s) of this compound common to these buildings, possibly baked goods made with yeast.

ACKNOWLEDGMENTS

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division, and by the Director, Office of Energy Research, Office of Health and Environmental Research, Human Health and Assessments Division, U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

Daisey, JM, Fisk, WJ, Hodgson, et al. The California Healthy Building Pilot Study. I. *Study* Design and Protocol. LBL-29851, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA, December, 1990.

Mendell, MJ *Risk Factors for Work-related Symptoms in Northern California Office Workers.* LBL-32636. Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA, October, 1991.

Fisk, WJ, Mendell, MJ, Daisey, et al. The California Healthy Building Study, Phase 1: A summary. Proceedings of the 6th International Conference on Indoor Air Quality and Climate. Helsinki, Finland, July 4-8, 1993.

Hodgson, AT, Daisey, JM, and Grot, RA. Sources and source strengths of volatile organic compounds in a new office building. J. Air Waste Manage. Assoc., 1991;41: 1461-1468.

Norusis, MJ, SPSS Base System User's Guide. SPSS Inc., Chicago, 1990.

DeBortoli, M, Knoppel, H, Peil, A, et al. Investigation on the contribution of volatile organic compounds to air quality complaints in office buildings of the European parliament. Proceedings of the 5th International Conference on Indoor Air Quality and Climate. Vol. 2, pp. 695-700. Toronto, Canada, July 29-Aug. 3, 1990.

Dosky, PV, Porter, JA, Scheff, PA. Source fingerprints for volatile non-methane hydrocarbons. J. Air Waste Manage. Assoc., 1992; 42: 1437-1445.

Wang, TC. A study of bioeffluents in a college classroom. ASHRAE Transactions, 1975, 81(part 1): 32-44.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720