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Maximizing Information from Residential Measurements of Volatile Organic Compounds

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SUMMARY

Continually changing materials used in home construction and finishing can introduce new chemicals or changes in the VOC profile in residential air and the trend towards tighter homes can lead to higher exposure concentrations for many indoor sources. However, the complex mixture of VOCs in residential air makes it difficult to discover emerging contaminants and/or trends in pollutant profiles. The purpose of this study is to prepare a comprehensive library of chemicals found in homes, along with a semi-quantitative approach to maximize the information gained from VOC measurements. We carefully reviewed data from 108 new California homes and identified 238 individual compounds. The majority of the identified VOCs originated indoors. Only 31% were found to have relevant health based exposure guidelines and less than 10% had a chronic reference exposure level (CREL). The finding highlights the importance of extending IAQ studies to include a wider range of VOCs.

KEYWORDS

VOC measurements; Sources/emissions; Residential; Emerging contaminants

1 INTRODUCTION

Two recent trends in home construction are expected to impact exposure to indoor air pollutants. The first is the ever-expanding suite of synthetic products and materials used in the construction, finishing and furnishing of homes. This can lead to changes in the profile of chemicals to which occupants are exposed. The second is the drive to reduce air leakage in homes for the purpose of energy efficiency and comfort. As homes are tightened, outdoor air exchange is reduced and concentrations of chemical pollutants emitted inside the homes increase. Detailed measurements of chemical concentrations in homes are critical for identifying sources of indoor pollutants and how exposures in homes might be changing as a result of changing ventilation strategies, aging of homes and/or simply varying across the housing stock.

The majority of published IAQ studies focus on “target compounds” selected to address specific study goals; or based on known toxicological relevance; or selected from a small number pilot measurements. As a result, there is limited information available in the public domain about the full suite of chemical air pollutants present in homes. This data gap makes it difficult to assess trends in indoor air quality; to retrospectively assess risks when a new or long-present chemical is found to present a health hazard; or to assess the effect of different construction techniques or ventilation strategies. Detailed information on the full suite of indoor contaminants is needed but identification and quantification of non-targeted chemicals in air samples requires substantial effort by experienced chemical analysts.

The objective of this study is to develop an approach that will allow analysts to more efficiently identify and quantify a wider range of chemicals in indoor air samples analyzed by gas chromatography and mass spectrometry. The key to the approach is a detailed library of indoor chemical contaminants. We developed the library by analyzing archived chromatograms from air samples collected during the recent California New Home Study, CNHS (Offermann, 2009). The CNHS database includes measurements from 108 conventional homes built in California in 2002-05. We applied the approach to a large set of data files from the CNHS to provide detailed baseline profiles and semi-quantitative pollutant concentrations in new homes.

2 MATERIALS/METHODS

The approach presented in this paper to maximize information from indoor air measurements consists of a detailed searchable library of indoor VOCs and a semi-quantitative calibration.

Identification of indoor chemical

A custom library of indoor VOCs was developed through careful and thorough re-analysis of 140 chromatograms representing indoor air from the CNHS. Full details for the original study design, sample collection and analysis method are provided elsewhere (Offermann, 2009). Each chromatogram from the original study was re-analysed using automated mass spectral de-convolution and identification software (AMDIS), which is publicly available through the National Institute of Standards and Technology (NIST). The project used a commercial package of the software, which combines AMDIS with an interface to the Agilent Technologies chromatographic analysis software (ChemStation[®]). The software identifies co-eluting mass ions that can subsequently be used to search mass spectral libraries for chemical identification. The NIST08 mass spectral library was used for all searches. In addition to VOCs identified in the chromatograms, some compounds that were expected to occur in residences but not detected (e.g., 4-phenylcyclohexene and various dipropylene and tripropylene glycol ether isomers) were added to the library. We excluded some compounds from the library because of co-elution with shared common ions. For example, nonanal and dodecane co-elute with a common ion where nonanal was likely an artefact. Some compounds with a high number of potential isomers were excluded because of difficulty accurately distinguish between isomers without analyzing pure standards. Generally, the C9 and higher alkyl substituted benzenes and C9 and higher branched alkane hydrocarbons were excluded. Normal alkane hydrocarbons through C17 were included. In total, 235 compounds, including those identified in the original CNHS, were identified in one or more of the indoor air samples.

Semi-quantification of individual compounds

In order to quantify compounds in the complex chromatograms, often without fully resolved peaks, it was necessary to base the quantification on extracted ions. A primary extracted ion and at least two qualifying ions were selected for each compound. Commonly occurring ions were not used as primary ions. For each compound, a response factor based on the area of the selected primary ion to the total ion current (TIC) peak area (m/z 30 to 450) was determined either using good quality peaks from the samples or using the full electronic spectra in the NIST08 library. Then, an adjusted calibration curve assuming a linear response and a zero intercept was constructed for each compound based on the TIC to mass relationship for toluene relative to an internal standard at the time of the original analysis. The results were used to create a compound list and quantitative method within the Agilent ChemStation[®] software. To apply the method, each sample or chromatogram is analyzed against the compound list within ChemStation[®] and then repeated using the custom library within the

AMDIS program. In many cases, peaks were detected by both systems. The analysis still requires an experienced analyst to review the automated results and verify that each target hit meets acceptance criteria for match quality and retention time, and if necessary, to make corrections.

Verification of Indoor Chemical Library and Semi-Quantitative Method

The quality of the indoor VOC library was evaluated in several ways. Paired results by compound for primary and duplicate air samples were assessed when available. The noted discrepancies for compounds within sample pairs were generally associated with problems related to co-elution and shared mass ions, or involved masses of less than 5 ng. A second evaluation examined the assigned retention time for each compound across all samples to see if the retention times were stable, as variable retention times are an indicator of possible misidentifications. It was discovered that manual integrations of the primary ions returned the retention times selected by the compound list in ChemStation[®]. In a number of cases, software did not select the correct peak for many of the manually integrated peaks relative to the corresponding AMDIS integrated peaks. This was identified as a software processing anomaly so in these cases, the results were not changed. A third evaluation searched for compounds that have the same retention time (to the second decimal place or hundredths of a minute) by sample. This evaluation can highlight chromatographic peaks that have been assigned to two or more identifications. A small number of problems of this type were identified and corrected.

Application of Chemical Profile Assessment Protocol

The hybrid method described above was applied to a subset of chromatograms from the CNHS including indoor, outdoor and quality assurance samples. The CNHS consisted of 153 indoor, 55 outdoor, 19 field blank and 17 duplicate samples including 18 target compounds quantified using pure standards. The re-analyses consisted of 98 indoor, 40 outdoor, 6 field blank and 7 duplicate samples representing 64 of the 108 homes in the original study. The re-analysis included 3 of the 18 original VOCs (i.e. ethylene glycol, 1, 4 - dichlorobenzene, and n-hexane) providing an opportunity to assess the accuracy and precision of the semi-quantification approach. In addition to the verification experiments described above, quality assurance evaluations included field blanks, comparison of duplicate analyses and comparison of the semi-quantitative mass to the mass based on pure standards. The percent occurrence of each compound in the homes and frequency distributions were constructed for the indoor and outdoor air samples from the CNHS chromatograms and compared to health based exposure guidelines when available.

3 RESULTS

The final indoor VOC library includes 223 compounds plus the 15 additional compounds from the original CNHS. The hybrid chromatographic analysis procedure using ChemStation[®] and AMDIS in parallel allows for the identification and quantification of relatively low chemical masses even in complex chromatograms. Of the 238 compounds identified in the indoor air samples, 105 were also identified in the outdoor air samples (data not shown). The approach was applied to a large set of homes from the CNHS and to test the performance of the hybrid method.

Field Blank Analyses

The identity and semi-quantitative mass of compounds in six field blanks were normalized to concentration using a typical sample volume from the original study (Offermann, 2009) and compared to indoor results. Nineteen chemicals were identified in one or more of the blanks.

Chemicals detected more than 50% of the time included Hexamethylcyclotrisiloxane, 1-Butanol, Trichlorofluoromethane, 1,3,5-Trioxane and Trichloroethylene with ratios of blank to the median indoor concentrations of 0.65, 0.24, 0.21, 1.75 and 1.17, respectively. The last two compounds appear to be primarily an artifact of the sampling media or method.

Duplicate Pair Precision Analyses

Seven duplicate pairs (six indoor and one outdoor) were used to evaluate precision of the estimated concentrations. We calculated both relative precision (standard deviation divided by the average) and the absolute precision (absolute difference) of each sample pair. The relative precision is the more useful metric for assessing performance and when low it always indicates good precision. However, when concentrations are very low, the relative precision values can be inflated. In these cases, the absolute precision is assessed because high relative precisions are only indicative of poor measurement precision if the absolute precision is also high. Taking the average relative precision for each compound across all sample pairs, and then the average for all 187 compounds in the duplicate samples, the overall relative precision is 0.22 ± 0.25 (\pm indicates one standard deviation), with a minimum of zero and a maximum of 1.35. A relative precision that is better than 0.2 is generally considered acceptable. Excluding all of the compounds with fewer than 3 duplicate pairs and having concentrations less than $5 \mu\text{g}/\text{m}^3$ results in a relative precision for 31 remaining compounds, the average of the mean relative precision was 0.12 ± 0.07 , with a minimum of 0.03 and a maximum of 0.29. Only four of the remaining 31 compounds had mean relative precision exceeding 0.20 and the high values for all four compounds were associated with the same sample. Overall, the precision of the peak identification and semi-quantitative method were within an acceptable range.

We also compared the mean relative precision of duplicate samples for 3 compounds that were included in both the original CNHS ($n=17$ pairs) quantified with pure standards and the re-analyses ($n=7$ pairs) using the semi-quantitative method. The mean relative precision from the CNHS versus the re-analysis for ethylene glycol, n-hexane and dichlorobenzene were 0.15 ($n=6$) compared to 0.13 ($n=4$); 0.10 ($n=13$) compared to 0.25 ($n=5$); and 0.01 ($n=1$) compared to 0.12 ($n=5$), respectively. Although the number of comparisons was limited, the overall results indicate that the approach had a similar precision whether using the targeted method with pure standards or the semi-quantitative method.

Compound Occurrence and Concentrations for New California Homes

The 238 compounds in the custom library developed for this study were detected in one or more of the homes studies. Ninety-eight chemicals were detected in 50% or more of the homes tested. These are listed in Table 1 grouped by chemical class. The indoor concentration frequency distributions for the compounds in the re-analyzed samples were calculated and, when available, concentrations were compared to health based exposure guidelines. The primary exposure guideline that was used is the OEHHA Chronic Reference Exposure Levels (CRELs). For compounds without a CREL we used 1% of the Cal/OSHA Permissible Exposure Level (PEL). Of the 238 compounds identified in the indoor air samples, just 75 (31%) have relevant health based exposure guidelines and only 18 had a CREL. The compound in the indoor air with the highest hazard quotient at the median concentration (i.e., ratio of median concentration to exposure guideline value) was acetic acid (0.11). The compounds with the highest hazard quotients at their maximum observed concentration were camphor (0.67) and 1,4-dichlorobenzene (0.64).

Table 1: Most Commonly Occurring Indoor VOCs in New Conventional Homes

Compound Name	Class	Occ	Compound Name	Class	Occ
Acetic acid	acid	99%	TMPD-MIB	alkox	90%
Hexanoic acid	acid	92%	7-Octen-2-ol, 2,6-dimethyl-	alkox	83%
Propanoic acid	acid	78%	Methyl salicylate	alkox	83%
n-Butyl acetate	ace	90%	Propylene glycol	alkox	76%
Ethyl acetate	ace	89%	1,3,5-Trioxane (<i>likely artifact</i>)	alkox	72%
Acetic acid, phenylmethyl ester	ace	89%	TMPD-DIB	alkox	65%
Isobutyl acetate	ace	53%	5-Hepten-2-one, 6-methyl-	alkox	62%
Isobornyl acetate	ace	50%	2-Pentanone, 4-hydroxy-4-methyl-	alkox	61%
Acetic acid, methyl ester	ace	48%	Ethylene glycol	alkox	59%
1-Butanol	alc	98%	2-Propanol, 1-butoxy-	alkox	59%
Ethanol	alc	97%	1-Methoxy-2-propyl acetate	alkox	57%
1-Hexanol, 2-ethyl-	alc	93%	1-Butanol, 3-methyl-, acetate	alkox	54%
Isopropyl alcohol	alc	87%	Toluene	arom	100%
2-Butoxyethanol	alc	86%	m,p-Xylene	arom	97%
Menthol	alc	86%	Styrene	arom	93%
3-Octanol, 3,7-dimethyl-, (ñ)-	alc	72%	Ethylbenzene	arom	91%
Benzyl alcohol	alc	71%	o-Xylene	arom	91%
1-Octanol	alc	70%	1,2,3-Trimethylbenzene	arom	87%
1-Pentanol	alc	67%	Naphthalene	arom	82%
1-Propanol, 2-methyl-	alc	65%	Indane	arom	77%
1-Hexanol	alc	52%	Benzene	arom	73%
Benzaldehyde	ald	100%	Benzene, propyl-	arom	72%
Decanal	ald	100%	Trichloromonofluoromethane	halo	72%
Hexanal	ald	99%	Carbon Tetrachloride	halo	66%
Octanal	ald	91%	1,1-Dichloro-1-fluoroethane	halo	64%
Heptanal	ald	86%	Benzene, 1,4-dichloro-	halo	57%
Furfural	ald	82%	Trichloroethylene (<i>likely artifact</i>)	halo	52%
Tetradecane	alka	86%	Methylene chloride	halo	49%
2-Methylbutane	alka	97%	Acetone	ket	93%
Undecane	alka	84%	2-Butanone	ket	82%
Octane	alka	84%	Cyclohexanone	ket	79%
Tridecane	alka	83%	2-Heptanone	ket	76%
Heptane	alka	83%	Methyl isobutyl ketone	ket	63%
Decane	alka	83%	D5 Siloxane	silox	100%
Cyclohexane, methyl-	alka	83%	D3 Siloxane	silox	100%
Nonane	alka	80%	D4 Siloxane	silox	97%
Pentane, 2,2,4-trimethyl-	alka	77%	D6 Siloxane	silox	93%
Hexane, 3-methyl-	alka	74%	α -Pinene	terp	99%
Cyclohexane	alka	72%	d-Limonene	terp	93%
Pentane, 2-methyl-	alka	64%	β -Pinene	terp	87%
n-Hexane	alka	62%	Camphor	terp	83%
Cyclopentane, methyl-	alka	61%	alpha-Terpineol	terp	75%
Hexane, 2-methyl-	alka	61%	Linalool	terp	66%
Pentadecane	alka	58%	Myrcene	terp	61%
Pentane, 2,3-dimethyl-	alka	58%	gamma-Terpinene	terp	59%
Hexadecane	alka	53%	Limonene oxide, cis-	terp	55%
1,3-Butadiene, 2-methyl-	alke	55%	3-Carene	terp	51%
Acetophenone	alkox	97%			

TMPD-MIB = 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate; TMPD-DIB = 2,2,4-Trimethyl-1,3-pentane diol diisobutyrate; DX Cyclic siloxane where X = number of siloxane units

4 DISCUSSION

An early review of indoor air VOCs by Shah and Singh (1988) identified 66 compounds, with 35 VOCs having enough information to report distributions of indoor concentrations. Holcomb and Seagrook (1995) reported concentration distributions for 18 of 85 chemicals identified in homes and Brown et.al (1994) reported 90 indoor VOCs. More recently, Hodgson and Levin reported 106 indoor VOCs with 57 having enough information to construct concentration frequency distributions. Previous studies compiled data on indoor VOCs from a range of different sources so estimating concentration frequency distributions for all compounds identified in a specific building type was difficult. This project describes an approach for maximizing the information gained from both new and archived indoor air measurements. We used the approach to construct a comprehensive listing of indoor VOCs from a large set of conventional new homes. Over 200 VOCs were identified in samples of indoor air. The full list of compounds along with concentration frequency distributions will be published in a forthcoming report. Less than 8% of the identified compounds had published chronic reference exposure level values highlighting the need for a more comprehensive approach to characterizing and reporting indoor air quality measurements.

5 CONCLUSIONS

The hybrid method of analysing GCMS data from indoor samples that includes automated identification using a custom indoor VOC library along with expert review dramatically reduces analysis time and costs and allows quantitation of compounds that would otherwise not be resolvable in complex mixtures. The approach identifies and labels the majority of peaks in complex chromatograms of indoor air allowing the analyst to focus on any remaining unidentified peaks. The library of indoor VOCs developed in this project provides a baseline set of chemicals and concentrations facilitating a significant increase in the amount of information gained from both new and archived samples of indoor air.

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