TRANSIENT ANALYSIS OF VOC CONCENTRATIONS FOR ESTIMATING EMISSION RATES

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ABSTRACT
While VOC emissions rates have been obtained for building materials and furnishings in chambers, field measurements are more difficult due to the existence of multiple and time-varying sources, variations in ventilation rates, impacts of adsorption and desorption, and other complexities associated with field testing. Procedures to estimate emission rates and sink parameters using transient analysis of VOC concentrations are applied in a two-story classroom/office building. The analysis is based on semi-real-time VOC concentrations determined with a portable GC/FID and simultaneous air change rate measurements using tracer gas decay. The results of the analysis yield consistent values of emission rates for building materials, but less consistent estimates of emission rates associated with occupant activities and of sink model parameters. The approach can be used in other buildings, and the results indicate that simultaneous air change rate measurements are critical to estimating VOC emission rates in the field.

INDEX TERMS
Emission rates, Field testing, Measurement, Volatile organic compounds

INTRODUCTION
Volatile organic compounds (VOC) are important indoor pollutants based on the wide range of sources and their impacts on occupant health and comfort (Wolkoff 1995). Reliable values of VOC emission rates in actual buildings are needed for design analysis, exposure estimates, evaluations of indoor air quality control technologies and understanding the significance of indoor and outdoor sources. While useful emissions data have been obtained through chamber testing of materials, furnishings and office equipment, fewer emission rate measurements have been made in the field. Field measurements of VOC emission rates are more difficult than chamber or other laboratory tests due to the existence of multiple and time-varying sources, varying ventilation rates, impacts of adsorption and desorption, and complexities of making measurements in real buildings. Nonetheless, reliable measurements of VOC emission rates would be useful and measurement procedures are needed to obtain these data.

VOC emission rates have previously been estimated in buildings, generally by assuming that the VOC concentration is at steady-state and that the air change rate is constant (Dols et al. 1995, Hodgson et al. 1991). More recent work has considered the estimation of emission rates when these assumptions are not valid, but does not present a complete methodology or actual results based on mass balance analysis and real-time air change rate measurement (Kraenzmer 1999, Molhave et al. 1996, Persily 1996). An important motivation for measuring emission rates in the field is to proportion emissions among various indoor and outdoor sources. Some work has been done in proportioning sources, but much of it has been based on indoor-outdoor concentration ratios rather than the use of transient mass balance analysis.

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Procedures using transient analysis of VOC concentrations to estimate emission rates were applied in a two-story classroom/office building in Oberlin, Ohio that was designed to showcase technologies for reducing the environmental impacts of buildings. Some of these features include operable windows, CO$_2$ demand controlled ventilation and ventilation heat recovery. Another design goal was to have low indoor VOC concentrations by using low-emitting building materials. Specifically, “low-VOC” materials, paints and adhesives were specified for the building. However, the emission rates of these materials were not measured prior to or after their selection, and the current status of emission rate measurement data and standards does not necessarily allow one to equate terms like “low VOC” with specific emission rates. In order to evaluate the extent to which this design goal was realized and to investigate procedures for estimating VOC emission rates in the field, indoor VOC concentrations were measured and analyzed to estimate VOC emission rates. More details on the building, measurements and analysis procedure are contained in Nabinger et al. (2002).

**MEASUREMENT METHODS**

VOC concentrations were measured with a portable gas chromatograph (GC) with a sorbent trap (porous polymer resin based on 2,6-diphenylene-oxide plus 30 % graphite) and a flame ionization detector (FID). The total VOC concentration was based on the integrated area under all peaks detected. During the tests, the GC/FID operated continuously with air samples collected and analyzed every 30 min. The system was calibrated with toluene from 5 µg/m$^3$ to 500 µg/m$^3$, with an uncertainty of 5% in the concentration measurements. While the VOC measurement approach only accounts for some of the VOCs in the building, the objective of the effort was to evaluate a procedure for analyzing these concentrations to determine emission rates and not necessarily to account for all VOCs in the building. Building air change rates were measured with the tracer gas decay technique (ASTM 2000) using an automated tracer gas system employing sulfur hexafluoride (SF$_6$) as the tracer gas in the range of approximately 30 µg/m$^3$ to 900 µg/m$^3$. The ventilation system and building configurations made it difficult to achieve uniform tracer gas concentrations as required by the ASTM test method. Given these mixing problems, the measured air change rates are estimated to have an uncertainty of about 25%.

**THEORY AND ANALYSIS APPROACH**

The VOC concentration analysis is based on a single-zone mass balance and a boundary layer, diffusion controlled sink model (Axley 1991). In this approach, the conservation of species is expressed as:

$$M_Z \frac{dC}{dt} = G(t) + QC_{out} - QC + \frac{h\rho A}{K} C_S - h\rho A C$$

where $M_Z$ is the mass of air in the building (air), $C$ is the indoor VOC concentration (mg/mg), $t$ is time (s), $G$ is the VOC emission rate (mg/s), $Q$ is the outdoor air ventilation rate (mg/s), $C_{out}$ is the outdoor VOC concentration (mg/mg), $h$ is the film mass transfer coefficient acting over the sorbent surface (m/s), $\rho$ is the air density (mg/m$^3$), $A$ is the sorbent surface area (m$^2$), $K$ is the equilibrium partition coefficient (mg/mg) and $C_S$ is the VOC concentration in the sorbent (mg/mg). In addition, the mass balance for the sorbent is expressed as:

$$M_S \frac{dC_S}{dt} = -\frac{h\rho A}{K} C_S + h\rho A C$$
where $M_s$ is the mass of the sorbent. Equations 1 and 2 can be solved for the VOC concentrations $C$ and $C_S$ based on parameters that define the air and sorbent system ($M_s, M_z, h, \rho, A$ and $K$) and quantities that generally vary with time ($G, Q$ and $C_{out}$). In this analysis, all of these parameters were measured or estimated except for the emission rate $G$, which was determined using curve fitting routines that compared the measured and predicted values of $C$. The approaches used to estimate these parameters are described in the complete report on this effort (Nabinger et al. 2002).

![Figure 1. Measured and predicted VOC concentrations in a conference room (Test 1)](image)

These mass balance equations were applied to a generic VOC intended to represent the compounds measured with the GC/FID used in this study. Obviously, this GC/FID system, or any measurement approach, will not detect and accurately measure all VOCs present. In addition, the sources, transport properties and sorbent interactions vary for different VOCs. Therefore, the emission rates estimated in this analysis are necessarily only relevant to the compounds captured by this particular measurement system and are subject to uncertainties based on the “lumping together” of the various compounds.

In order to estimate emission rates and sink parameters, the mass balance equations were applied to the measured data in three ways, steady-state, smooth decay/buildup, and full interval. These analysis approaches are described with reference to the data in Figure 1. In steady-state analysis, a period characterized by relatively constant VOC concentration and air change rate is used to estimate the VOC emission rate using a simplified form of equation 1. Under steady-state, the rate of adsorption into the sink equals the rate of desorption from the sink, so the last two terms of equation 1 cancel each other out and the time rate of change of $M_S$ in equation 2 can also be set equal to zero. The emission rate is given by equation 2, where $C_{ss}$ is the average concentration over the steady-state interval.
\[ G = Q(C_{ss} - C_{out}) \]  

Equation 3 can generally be applied only to periods of time when the only active sources are those associated with building materials and furnishings (referred to as \( G_B \)), e.g., during unoccupied periods, such as the first 20 h of the test in Figure 1.

Smooth decay/buildup analysis is applied to periods when the concentration build up or decay is fairly smooth, such as the last eight hours in Figure 1. During such a period, one assumes that the source strength and ventilation rate are both constant and uses the data to estimate the sink parameters \( hA, K \) and \( M_S \). (Note that the parameters \( h \) and \( A \) always appear as a product in equations 1 and 2, and therefore their individual values cannot be determined by curve fitting.) During the decay at the end of the test in Figure 1 one can assume that only the building source term is active, using the value of \( G_B \) determined from the steady-state analysis and solving for the sink parameters. In full interval analysis, the solution of equations 1 and 2 is applied to a full test or a significant portion of such a test where multiple sources are active. Using values of the building source \( G_B \) and sink parameters from steady-state and smooth decay/buildup analyses, other “non-building” emission rates are determined.

RESULTS AND DISCUSSION

Table 1 shows estimated source strengths and sink parameters obtained in the building for three tests. The first three columns of results are the estimated values of the emission rates associated with the building \( G_B \) and with occupant activities \( G_{o1} \) and \( G_{o2} \). Note that these emission rates, despite being in the same column, were measured in different spaces at different times, and will not necessarily be close in value for the different tests. The last three columns contain the estimated sink parameters \( K, hA \) and \( M_S \). In all the tests, it was assumed that the building-related source \( G_B \) was constant throughout the test period. One or more of the occupant-related sources was assumed to exist during each of the tests, based on the patterns observed, in particular elevated concentrations during periods of the day. These emission rates were assumed to be constant over such periods, though they are the result of varying emissions and are best considered as average values. For example, during Test 1 in the conference room (see Figure 1), two sources associated with occupant activities were assumed to exist during the periods of elevated concentration around hours 30 and 55.

In the analysis of Test 1, steady-state analysis was applied to the first 20 h of the test period, resulting in an estimated value of the emission rate \( G_B \) of 7.0 mg/h. Dividing by the conference room floor area yields a normalized emission rate of 0.28 mg/m\(^2\)•h. A curve fit to the entire test, without consideration of sinks, yielded the two values shown for the sources related to occupant activities, 1.33 mg/m\(^2\)•h and 0.67 mg/m\(^2\)•h. The value of \( G_{o1} \) is relatively high, but that source was associated with the opening of several liquid marker pens. Based on a 25 % uncertainty in the air change rates, the estimated values of the emission rates also have an uncertainty of 25 %. The predicted concentrations based on the no-sink values are shown in Figure 1 by the solid line.

In order to obtain estimates of the sink parameters for the conference room, the decay at the end of the measurement period was analyzed with adsorption/desorption effects included. Initial estimates of \( hA, K \) and \( M_S \) were applied to the decay using the value of \( G_B \) determined by steady-state analysis. Analysis of this decay period yielded a value of \( K = 0.62 \). Using this estimate of \( K \), the last decay interval was reanalyzed to estimate \( hA \) and \( M_S \), which yielded
$hA = 5.3 \text{ m}^3/\text{h}$ and $M_s = 6.8 \times 10^8$. Based on a value of $h$ of 0.105 m/h (derived from correlations described in Axley 1991), this estimate of $hA$ corresponds to a sorbent area of 50 m$^2$, which corresponds to 200 % of the conference room floor area and a surface-to-volume ratio of 0.66 m$^{-1}$. These estimated sink parameters were then used in a full interval analysis with sinks to estimate the two occupant activity source terms. The results of this analysis are shown in Table 1, and are not significantly different from those estimated without sinks. Figure 1 also contains a plot of the predicted concentrations in the conference room (open circles) based on the inclusion of sink effects. The inclusion of sink effects has only a minor impact on the predicted concentrations, and there is no indication that the predictions are any more accurate with the inclusion of sinks.

Table 1. Results of Emissions Rate Analysis

<table>
<thead>
<tr>
<th></th>
<th>$G_B$</th>
<th>$G_{o1}$</th>
<th>$G_{o2}$</th>
<th>$K$</th>
<th>$hA$, m$^3$/h</th>
<th>$M_s$, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Test 1: Conference room</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Steady state</td>
<td>0.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Full interval, no sinks</td>
<td>1.33</td>
<td>0.67</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Decay, sinks</td>
<td>0.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Decay, sinks, $K = 0.62$</td>
<td></td>
<td></td>
<td></td>
<td>5.3</td>
<td>$6.8 \times 10^8$</td>
<td></td>
</tr>
<tr>
<td>Full interval, sinks</td>
<td>1.39</td>
<td>0.70</td>
<td></td>
<td></td>
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<tr>
<td><strong>Test 2: Atrium</strong></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Steady state</td>
<td>0.34</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Full interval, no sinks</td>
<td>0.37</td>
<td>0.19</td>
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<tr>
<td>Decay, sinks</td>
<td>13.9</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Decay, sinks, $K = 13.9$</td>
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<td></td>
<td></td>
<td>35.2</td>
<td>$1.7 \times 10^{13}$</td>
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<tr>
<td>Full interval, $K = 13.9$</td>
<td>0.40</td>
<td>0.21</td>
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<tr>
<td><strong>Test 3: Atrium</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Full interval, no sinks</td>
<td>0.38</td>
<td>0.34</td>
<td>0.11</td>
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<td></td>
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<tr>
<td>Full interval, sinks</td>
<td>0.41</td>
<td>0.33</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 also shows results for Tests 2 and 3 in the building atrium. In Test 2, the value of $G_B$ was determined using steady-state analysis, and is similar to that seen in Test 1 for the conference room. Two occupant activity sources were also estimated for the atrium, but there is no reason to expect them to correspond to the values for Test 1. A smooth decay at the beginning of Test 2 was used to estimate $K$, and this value of 13.9 was subsequently used to estimate the other sink parameters and then the values of the two occupancy sources. The estimated value of $hA$ corresponds to a sorbent area equal to 210 % of the floor area of the atrium and a surface-to-volume ratio of 1.71 m$^{-1}$. Again, the inclusion of sinks did not affect the determination of $G_{o1}$ and $G_{o2}$ significantly. The data from Test 3 was analyzed without sinks and with the sink values determined in Test 2. The value of $G_B$ was slightly higher than in Test 2. Values of the occupant activity sources were also determined for Test 3, and again there is no reason for them to be the same as for Test 2. Again, the inclusion of sink effects did not impact the results significantly. In only one of the tests, described in Nabinger et al. (2002), did sink effects appear to have an impact. That test included a weekend during which the ventilation system was off and the sources were assumed to be relatively constant. Under those conditions, the long time constant associated with the sink appeared to impact the predicted concentrations, but more analysis of that data is needed.
CONCLUSION AND IMPLICATIONS
Simultaneous measurements of indoor VOC concentrations and air change rates enable the use of transient mass balance analysis to estimate indoor emission rates from building-related sources as well as from occupant activities. Transient analysis is essential for estimating these values when sources and air change rates vary, as is generally the case in buildings. The application of transient analysis to a classroom/office building yielded emission rates for the building on the order of 0.3 mg/m²•h, which is relatively low (Levin 1995), consistent with the building design goal. However, sources associated with occupant activities increased the total emission rate to above 1.0 mg/m²•h, a value consistent with more typical buildings.

While these procedures may help to improve our understanding of VOC sources, more work is needed in understanding the significance of sink effects. These results indicate that sinks may have a secondary effect on the estimation of emission rates, but additional measurements are needed. The measurements and analysis were complicated by the layout of the building and its air handling system, and it would be valuable to repeat these tests in a simpler building with better mixing of the indoor air. Such tests would presumably also enable more accurate proportioning of VOC emissions among building materials, furnishings, occupant activities and other sources. Difficulties associated with the measurement of air change rates point out that reliable air change rate measurements are required to estimate emission rates in the field.

REFERENCES