Long Term Air Quality Monitoring in a Net- Zero Energy Residence Designed with Low Emitting Interior Products

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Content submitted to and published by: Building and Environment

U.S. Department of Commerce *Penny Pritzker, Secretary of Commerce*



National Institute of Standards and Technology Willie E May, Director

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Abstract

The National Institute of Standards and Technology (NIST) constructed a Net Zero Energy Residential Test Facility (NZERTF) to support the development and adoption of costeffective Net Zero Energy (NZE) designs and technologies. One key design objective was to provide for occupant health and comfort through adequate ventilation and reduced indoor contaminant sources. To improve source control, guidelines were implemented to utilize products with relatively low volatile organic compound (VOC) emissions. Indoor and outdoor concentrations of formaldehyde and 30 other VOCs were measured approximately monthly during the first year of house operation. Indoor temperature and ventilation conditions were relatively constant over the study. Indoor minus outdoor (I-O) concentrations of many VOCs varied with outdoor temperature. Correlation analyses of I-O concentrations versus inverse outdoor temperature (1/*K*) suggested that some building envelope components were an indoor source of aldehydes (but not formaldehyde) and several other VOCs. Floor area specific emission rates were calculated and compared to values from several prior studies of conventional new houses. The average formaldehyde emission factor of 6.7 μ g h⁻¹ m⁻² in this study was lower than literature values (29 μ g h⁻¹ m⁻² to 45 μ g h⁻¹ m⁻²) indicating formaldehyde source control approaches were effective. VOC measurements at other indoor conditions demonstrated that eliminating mechanical ventilation contributed more to an increase in indoor VOC concentrations than an 8 °C increase in the indoor temperature.

Highlights:

- Formaldehyde source control reduced emission factors to ≤ 23 % of typical values
- Mechanical ventilation needs to be operated per relevant consensus standards
- Reduced ventilation can have a larger impact on VOC concentrations than temperature
- Building envelope components may be an overlooked source for some VOCs

Keywords:

Formaldehyde, Emission Rates, Mechanical Ventilation, Volatile Organic Compound (VOC)

1. Introduction

In the United States, residential and commercial buildings account for approximately 41 % of all energy consumption and 72 % of electricity usage [1]. Energy efficiency is widely recognized as an essential strategy for addressing national building energy use both currently and into the future. Federal, state, and local governments, utilities, and many other organizations support energy efficiency in buildings through development and implementation of energy codes and programs that provide incentives for stakeholders to conserve energy. As part of the federal effort, the National Institute of Standards and Technology (NIST) received funding in 2009 to

design, construct, and operate a Net Zero Energy Residential Test Facility (NZERTF) in Gaithersburg, MD. The facility, constructed in 2012, functions as a laboratory to support the development and adoption of cost-effective net-zero energy (NZE) designs and technologies, construction methods, and building codes.

The first principle in developing the NZERTF was to design for the comfort level and functions of presumed occupants [2]. Under this principle, indoor air quality (IAQ) was an essential design element because it directly impacts occupant comfort, health and well-being. To that end, the U.S. Environmental Protection Agency (EPA) has developed the Indoor Air Plus labeling program [3] that supports both EPA and U.S. Department of Energy residential energy efficiency programs. IAQ is also addressed by major high-performance building rating systems and building codes [4, 5]. IAQ in homes is particularly important because U.S. residents, on average, spend approximately 90 % of their time indoors with the majority of this time spent at home [6]. The concentrations of many air pollutants often are elevated in homes relative to outdoor air because many of the materials and products used indoors contain and release a variety of pollutants [7, 8]. With respect to indoor air contaminants for which inhalation is the primary route of exposure, the critical design and construction parameters are the provision of adequate ventilation and the reduction of indoor sources of the contaminants.

2. Building Design and Analytical Methods

The primary design goal of the NZERTF was to achieve net-zero energy performance over an annual period with simulated occupancy of a family of two adults and two children. A complementary goal was to minimize indoor contaminant concentrations, particularly VOCs, by supplying continuous mechanical outdoor air ventilation and implementing source control strategies during product selection prior to construction. The study reported here commenced in May 2013 after sensors, controls and data acquisition systems were installed and tested in the NZERTF. Indoor and outdoor VOC concentrations and mechanical ventilation rates were measured approximately monthly for 15 months, and simulations of infiltration were performed. Total air change rate was measured by tracer gas decay at the end of the study and used in emission rate calculations.

2.1. NZERTF Design and Construction

The design and construction of the NZERTF are described in Pettit et al. [2], and the lighting, appliance, sensible and latent loads, and water usage associated with the simulated family are outlined in Omar and Bushby [9]. The NZERTF is a two-story, detached home with an unfinished basement and attic, both within the building thermal envelope (Figure 1). The garage is not attached. The house is similar in size $(242 \text{ m}^2 \text{ for occupied floors}, 485 \text{ m}^2 \text{ inside the})$ building envelope including the attic and basement) and aesthetics to homes in the surrounding communities. The house is not furnished other than permanently installed cabinetry. Several technologies are employed in the house to achieve the net-zero energy goals including a high efficiency air-to-air heat pump, a solar hot water system, a heat recovery ventilator (HRV), and a 10.2 kW photovoltaic system. To comply with the outdoor air requirements in American Society of Heating, Refrigerating & Air-Conditioning Engineers Standard 62.2-2010 [10], the HRV was sized to deliver 137 m³ h⁻¹ of outdoor air, which is equivalent to an air change rate of 0.11 h⁻¹. To minimize infiltration and conduction losses, special attention was paid to the design and construction of the highly insulated and airtight building envelope. Figure 1 shows the air barrier membrane (rubberized asphalt bonded to high density cross laminated polyethylene film) during construction.

2.2. Product Selection Guidelines

IAQ-based guidelines were developed for this project to guide the selection of interior finishes and insulation. The guidelines were mostly prescriptive requiring use of certain products and avoidance of others. The objective was to reduce common sources of VOC contaminants that may affect health and comfort. Emphasis was placed on substantially reducing sources of formaldehyde emissions based on its known health impacts. In 2004, the International Agency for Research on Cancer (IARC) classified formaldehyde as carcinogenic to humans [11]. In addition, the California Air Resources Board found that one of the major sources of formaldehyde exposure is from composite wood products containing urea-formaldehyde resins.

An overall reduction in emissions of VOC solvents was addressed by incorporation of maximum VOC content requirements for wet-applied products. Reduction of odors often associated with new residential construction was another objective. Such odor likely is due in part to emissions of acetic acid, which is commonly emitted by some of the same sources that emit formaldehyde.

Specific guidelines were written for adhesives and sealants, paints and coatings, built-in cabinetry, woodwork, doors, countertops, floor coverings, and insulation. The measures included use of water-base finishes, solid wood and hardwood plywood with no-added formaldehyde resin for cabinetry, hardwood and tile flooring throughout, and mechanical fasteners for gypsum board. Also included was avoidance of insulation produced with formaldehyde resins, composite wood for moldings/trim, acid-catalyzed finishes, and large amounts of silicone sealants. The design team implemented the guidelines using available product information as well as discussions with NIST research staff and their contractors.

2.3. Outdoor Air Change Modeling and Measurement

In order to determine emission rates of the sampled contaminants, outdoor air change rates were obtained using both simulations (infiltration) and measurements of the mechanical ventilation rate of the HRV and the total outdoor air change rate of the building.

Infiltration rates were modeled using the CONTAM multizone airflow model [12]. The modeled building envelope airtightness utilized the results of blower-door tests following ASTM E779-10 [13]. The airflow rate through the building envelope at 50 Pa was 802 m³ hr⁻¹ which is equivalent to an air change rate of 0.60 h⁻¹. The calculated effective leakage area (ELA4) at 4 Pa was 194.2 cm². The HRV and central heat pump were modeled with constant supply and return rates determined from measurements. Kitchen and dryer exhausts were modeled using their actual operation schedules. The CONTAM simulations were performed using weather data obtained from a local weather station approximately 9 km from NIST. In the CONTAM model, balanced mechanical ventilation was modeled using a constant outdoor air intake rate of 171 m³ h⁻¹ and an equal exhaust airflow rate based on measurements described below. Note that the infiltration rate predicted by CONTAM is the rate at which air enters the building through leaks in the building envelope due to weather and system effects, and does not include the air intake rate through the HRV.

Mechanical outdoor ventilation airflow rate through the HRV was measured in the four ducts (supply, return, exhaust, outdoor) using a hot wire anemometer (accuracy ± 3 % of reading). Average velocity was measured using a multipoint traverse as described by the Sheet Metal and Air Conditioning Contractors' National Association [14], and used to calculate the average volumetric flow rate through the HRV. Whole house air change rates were measured by tracer gas decay following

ASTM E-741 [15] in July 2014 with the HRV on and off. These rates reflect the combination of mechanical HRV ventilation and infiltration. An automated tracer gas system with sulfur hexafluoride injection and sampling at multiple locations (seven indoor, one attic and one outdoor) was employed. Measurements were made at each location once every 27 minutes following a one-hour mixing period. The estimated uncertainty in the measured air change rates is 10 %.

2.4. Temperature Monitoring

Indoor and outdoor temperatures were recorded for each sampling event. For the first two events, outdoor temperatures were measured at a nearby local weather station and indoor temperatures were measured with a handheld probe during sampling. Subsequently, temperatures were measured by the house data system every minute at the roof of the house and at multiple indoor locations. Reported temperatures for each monthly sampling event were averages from midnight before the sampling period to the end of the sampling period.

2.5. Air Sampling

During each sampling event, air samples were collected in three locations: first floor kitchen area, second floor landing, and outdoors adjacent to the house. Two types of samples were collected. Formaldehyde and acetaldehyde were collected for 1 hour at 1 L min⁻¹ on 2,4-dinitrophenylhydrazine (DNPH) cartridges according to ASTM D5197 [16]. An upstream ozone scrubber cartridge was used for the outdoor samples. Other VOCs were collected for 1 hour at 0.1 L min⁻¹ on multi-sorbent tubes. At each sampling location ozone concentrations were measured adjacent and concurrent to VOC sampling using a real-time ozone monitor. Average outdoor ozone concentrations are listed in Table 1.

After the 15-month study under normal operating conditions, the role of indoor temperature and ventilation on indoor VOC concentrations was investigated by collecting additional VOC samples under three different operating conditions conducted in the following order: (a) elevated indoor temperature (32 °C), HRV on; (b) standard conditions: i.e., normal temperature setpoint and HRV on; and (c) normal temperature setpoint, HRV off. Table 2 summarizes additional conditions during these sample events.

The emissions of VOCs from a sample of the house air barrier and from other materials were qualitatively assessed in a micro-chamber following ASTM D7706 [17]. The samples were held in the chamber at 40 °C for one hour with nitrogen airflow at 100 mL min⁻¹. VOC air samples were collected from the chamber exhaust port onto multi-sorbent tubes.

2.6. Analytical

Formaldehyde and thirty other individual VOCs (Table 3) were quantified in the indoor and outdoor samples. Formaldehyde and acetaldehyde on DNPH cartridges were analyzed by ASTM D5197 (liquid chromatograph-ultraviolet detection (LC-UV)) [16]. VOCs on sorbent tubes were analyzed by U.S. EPA TO-17 (thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS)) [18]. Target VOCs were selected based on qualitative analysis of total-ion-current chromatograms to include the majority of frequently occurring VOCs above detection limits. Quantitative analyses of target VOCs were performed using multi-point calibrations prepared with pure standards, except acetic acid, which was quantified using toluene as a surrogate. Thus, reported values for acetic acid were underestimated. The method detection limit (MDL) for each calibrated VOC was determined as the confidence interval for repeated analysis of a low standard. For formaldehyde and acetaldehyde, the MDL was 15 ng. For other VOCs, MDLs ranged between 1 ng and 17 ng. Based on sampling volumes, average sample

detection limits (DL) for many VOCs were $\leq 1 \ \mu g \ m^{-3}$ and, for all but two VOCs, DLs were $\leq 2 \ \mu g \ m^{-3}$ (Table 3).

Pairs of collocated indoor samples from one indoor location were analyzed for each sampling event to evaluate the precision of the sampling. The precision of sampling and analysis for each paired VOC measurement was assessed as a relative standard deviation (RSD) for the pair. The average RSD for formaldehyde was 2 % (range = <1 % to 8 %). The average RSDs for other individual VOCs ranged from 1 % to 13 %. Analytical performance tests were conducted for 19 of the target VOCs using solutions prepared by an accredited vendor and spiked onto sorbent tubes. Expanded uncertainties (relative) were estimated for each VOC taking into account scatter in calibration points, day-to-day variation in instrument response, and indicated bias from performance test results. Expanded uncertainty for formaldehyde was 7 %. Expanded uncertainties for other VOCs ranged from 6 % to 43 % (median = 13 %).

For each VOC measurement, four samples were collected and analyzed: two samples from one indoor location, one sample from a second indoor location, and one sample from an outdoor location. An average indoor concentration for the house was calculated as the average of the paired average value from one indoor location and the single value for the other indoor location. Outdoor concentrations were subtracted from the average of the indoor concentrations to determine the concentrations (I-O concentrations) associated with indoor emissions. Associated RSDs were calculated for the average I-O concentrations and reported in Table 3.

2.7. Emission Rate Calculations

To estimate whole-house emission rates (*i.e.*, emission factors) of individual VOCs, the NZERTF was modeled as a single zone with no net sorption or reaction losses:

$$\frac{dC}{dt} = \lambda C_{out} - \lambda C + \frac{E_f A}{V}$$
(1)

where λ is the air change rate (h⁻¹), V is house volume (m³), C is average indoor concentration (μ g m⁻³), C_{out} is outdoor concentration (μ g m⁻³), E_f is the area emission rate (μ g m⁻² h⁻¹) and A_i is area of the material of interest (m²). At steady state, Equation (1) simplifies to:

$$C_{ss} - C_{out} = \frac{E_f A}{\lambda V}$$
(2)

where C_{ss} is the steady state concentration. The steady state area specific emission rate $(E_f, \mu g m^{-2} h^{-1})$ is then:

$$E_{f} = \frac{\lambda V (C_{ss} - C_{out})}{A_{i}}$$
(3)

Emission rates were calculated in two ways. For the monthly sampling events, emission rates were calculated using the corresponding air change rates calculated as the sum of the measured mechanical ventilation and modeled infiltration rates. For the three conditions described in Sec. 2.5, the total air change rate measured by tracer gas decay was used in the calculations. The time required to reach 95 % steady state concentration in the transition from the standard condition (b) to the HRV-off condition (c) in a non-reactive environment was ~150 hours $(3/\lambda)$ for this house. As the time between samples was only 42 hours (time required to reach ~0.5 steady state concentration), a transient mass balance solution was employed (the derivation of Equation 4 is shown in Supplementary Material):

$$C_{No \ Ventilation} = C_{Standard} e^{-\lambda t} + \left(C_{out} - \frac{E_f A}{\lambda V} \right) \left(1 - e^{-\lambda t} \right)$$
(4)

Using the VOC concentrations measured during the standard (b) and HRV-off conditions (c), along with the time between measurements of 42 hours, Equation (4) was solved for the unknown term of $E_f A/\lambda V$.

3. Results

Data on NZERTF energy, HRV performance, air change rates, and VOC concentrations were collected and reported in this section.

3.1. Energy and HRV Performance

Through 12 months (July 2013 to June 2014) of operation, the NZERTF produced more energy through the roof-mounted photovoltaic panels than it consumed (see Supplementary Material, Figure S.1). The airflow provided by the installed HRV was measured on multiple occasions and averaged 196 m³ h⁻¹ (Stdev = 14 m³ h⁻¹), equivalent to an air change rate of 0.15 h⁻¹. This exceeded the outdoor air requirements from ASHRAE Standard 62.2-2010 [10] of 137 m³ h⁻¹ for the NZERTF (equivalent to an air change rate of 0.11 h⁻¹). The average measured sensible heat recovery effectiveness of the HRV was 0.72 (Stdev = 0.05). The HRV consumed approximately 43 kWh/month (Stdev = 3 kWh) of fan energy, which was approximately 4 % of the total annual energy consumed in the house. Further details on the house energy performance can be found in Fanney et al. [19] .

3.2. Air Change Rates

Table 1 presents indoor and outdoor temperatures, CONTAM modeled infiltration rates, and measured HRV mechanical ventilation rates for each sampling date. Combined infiltration and mechanical ventilation at the normal indoor temperature setpoint with the HRV running ranged from 0.14 h⁻¹ to 0.22 h⁻¹. Over two weeks in July 2014, air change rates were measured using tracer gas decay under the three conditions described in Sec. 2.5. The average air change rates for conditions (a), (b), and (c) were $0.22 h^{-1}$ (elevated indoor temperature), $0.15 h^{-1}$ (standard conditions), and $0.02 h^{-1}$ (HRV off), respectively. The test conditions and results are summarized in Table 2. The air change rates for condition (a) were higher than they were under

standard conditions, which was expected due to the greater indoor-outdoor temperature difference. The air change rate for condition (c) with the HRV off was lower, as expected.

3.3. VOC Concentrations

Reported VOC concentrations (I-O) were average indoor VOC concentrations minus corresponding outdoor concentrations. When a VOC was not detected outdoors, the MDL was substituted for outdoor VOC concentration. I-O concentrations reflected the impacts of product and material sources in the unoccupied house.

Maximum and average I-O VOC concentrations over the 15 sampling events at standard indoor conditions are shown in Table 3. Average RSDs for individual VOC measurements made at the two indoor locations generally exceeded corresponding average RSDs for collocated indoor samples indicating spatial variation of sources and/or imperfect air mixing. VOCs with the highest average I-O concentrations (*i.e.*, $\geq 10 \ \mu g \ m^{-3}$) were ethanol, 2-propanol, acetaldehyde, pentanal, hexanal, octanal, nonanal, toluene, propylene glycol, ethylene glycol, acetone, and α -pinene. The average formaldehyde concentration was 7.7 $\mu g \ m^{-3}$ (range = 5.1 $\mu g \ m^{-3}$ to 11 $\mu g \ m^{-3}$). Concentrations of formaldehyde, acetaldehyde, hexanal, propylene glycol, acetone and α -pinene are plotted versus time in Figure 2 (see Figure S.2 to Figure S.5 for plots of other VOCs). The temporal data revealed two general trends. Concentrations of many VOCs were higher during the first summer of sampling than during the second summer, indicating that building product and material emissions decreased with time. Additionally, concentrations of many VOCs increased throughout the warmer summer sampling events and decreased during cooler winter sampling events (see Sec. 4 Discussion).

Maintenance of the ground source heat pump in the basement was the likely source of ethanol, which had the highest average concentration. Toluene concentration increased by a

factor of 400 in May 2014 due to the use of an adhesive for modifying the heat pump. Ethanol, 2-propanol, acetone, and 2-butanone concentrations also spiked during this sampling event.

4. Discussion

Long term sampling and monitoring in an unfurnished house operated with simulated occupancy provided a unique opportunity to investigate sources of indoor VOCs and the dynamics of their concentration behavior.

4.1. VOC Concentration Temperature Dependence

The observed seasonal variation in I-O VOC concentrations at nearly constant indoor temperature and air change rate suggested a dependence on outdoor temperature. Chemical vapor pressure relates to temperature via the Clausius Clapeyron equation and to concentration by the ideal gas law as follows:

$$C \propto P \propto e^{\left(\frac{\Delta n}{RT}\right)}$$
 (5)

where *P* is the vapor pressure (Pa), *T* is the absolute temperature (K), *R* is the universal gas constant, and ΔH is the enthalpy of vaporization. Hence, if a VOC concentration is purely controlled by evaporative primary emissions, a plot of $\ln(I-O)$ versus 1/T will exhibit a linear inverse relationship. Correlations of $\ln(I-O)$ versus indoor and outdoor 1/T were calculated for all VOCs. Average outdoor temperatures varied from -1 °C to 23 °C. Correlation coefficients (r²) for the linear fits are shown in Table 3. VOCs with r² \geq 0.7 are hexanoic acid; 1-butanol; the aldehydes: acetaldehyde, pentanal, heptanal, octanal, and nonanal; styrene, and 1,2,4trimethylbenzene. Formaldehyde was poorly correlated (r² = 0.2).

Figure 3 illustrates the linear trend of concentration $(\ln(I-O))$ versus average outdoor 1/T for aldehydes with generally higher indoor concentrations and moderate to strong correlations. Formaldehyde (low correlation) is also shown in Figure 3. Due to emissions decaying over time, the last three samples from summer 2014 were omitted in Figure 3 (all samples and chemicals are included in Figures S.6 through S.9). Correlations between $\ln(I-O)$ and inverse indoor temperature, which only varied over 4 °C during standard indoor conditions, were not as strong as correlations between $\ln(I-O)$ and inverse outdoor temperature (Figure S.10).

The observed relationship with outdoor temperature, with nearly constant indoor temperature, suggests that emissions of a number of VOCs were related to building envelope temperature. The NZERTF's unique building envelope, highlighted by Pettit et al. [2], contains plywood sheeting and 15 cm of cellulose insulation, which may be primary emission sources for the aldehydes. In addition, the rubberized asphalt air barrier emits n-pentadecane, n-hexadecane, and n-heptadecane (see below).

4.2. Evidence for Primary Emissions of Aldehydes

Formaldehyde and other aldehydes in indoor air can be the result of primary emissions from products/materials or as secondary byproducts of ozone reacting with other primary emitting chemicals [20, 21]. Ozone concentrations generally increase in summer months [22] and initiate a range of chemical reactions that can result in aldehyde formation [23, 24]. If ozone initiated reaction is a dominant source of aldehyde concentrations in the house, aldehyde concentrations should correlate with ozone concentration. However, there was minimal correlation between aldehyde concentrations and outdoor (Figure S.11) or indoor (Figure S.12) ozone concentrations for the measured ozone concentrations below 50 ppb_v (based on eight of ten sampling events when outdoor ozone concentration was measured). These observations plus the lack of seasonality in formaldehyde concentrations support the hypothesis that primary indoor emissions of aldehydes were predominant.

4.3. Effects of Varying Air Change Rate and Indoor Temperature

To evaluate the relative roles of indoor temperature and air change rate on indoor VOC concentrations, the NZERTF was operated over two weeks in July 2014 at the three conditions described in Sec. 2.5: (a) elevated indoor temperature, HRV on; (b) normal temperature, HRV on; and (c) normal temperature, HRV off.

The ratio of steady state VOC concentrations for the elevated temperature condition relative to the standard condition (a)/(b) for 15 illustrative VOCs are shown in Figure 4 (all chemicals are shown in Figure S.14). On average, the 8 °C increase in temperature resulted in a factor of 2.6 (Stdev = 1.1) increase in steady state VOC concentration. However, the steady state concentrations are a function of the both changing emission rates and air change rates as shown in Equation 7:

$$\frac{\left(C_{ss}-C_{out}\right)_{Elevated Temp}}{\left(C_{ss}-C_{out}\right)_{Base}} = \frac{\left(\frac{E_{f}A}{\lambda V}\right)_{Elevated Temp}}{\left(\frac{E_{f}A}{\lambda V}\right)_{Base}} = \frac{E_{f,Elevated Temp}}{E_{f,Base}} \left(\frac{\lambda_{Base}}{\lambda_{Elevated Temp}}\right)$$
(7)

The air change rates were not consistent for the base and elevated temperature conditions. Using the measured air change rates (Sec. 3.2), the 8 °C temperature increase alone resulted in an average 3.8-fold increase in VOC emissions rates.

Changes in house ventilation were predicted to have direct impacts on indoor VOC concentrations at steady-state conditions. The ratio of "HRV-off" VOC concentration to concentration at the standard ventilation condition, i.e., (c)/(b), was calculated as:

$$\frac{\left(C_{ss}-C_{out}\right)_{No ventilation}}{\left(C_{ss}-C_{out}\right)_{Base}} = \frac{\left(\frac{E_f A}{\lambda V}\right)_{No ventilation}}{\left(\frac{E_f A}{\lambda V}\right)_{Base}} = \frac{\lambda_{Base}}{\lambda_{No Ventilation}}$$
(8)

Using the average measured air change data for conditions (c) and (b) and assuming constant VOC emission rates (*i.e.*, no mass transfer effects) and steady-state conditions, the predicted ratio was 9.2 (right side of Equation (8)). The measured ratios for 15 VOCs are shown in Figure 4. Concentration ratios of eight of these 15 VOCs responded approximately as predicted. However, the concentration ratios of formaldehyde, phenol, acetic acid, ethylene glycol, TMPD-MIB, and n-pentadecane were considerably lower, approximately \leq 3. TMPD-MIB and n-pentadecane have relatively low vapor pressures. Emissions from building materials for chemicals with low vapor pressures can be limited by mass transfer coefficients [25], which was likely the case with the reduced airflow when the HRV was off. The reduced airflow and corresponding mass transfer coefficient may have extended the time needed for TMPD-MIB and n-pentadecane to reach steady state concentrations [25] to longer than the time between the sampling events. Hence, their bulk air concentrations may have not have reached equilibrium as assumed in the ratio calculations. It is also possible that sorption and desorption from surface sinks and particles may have prevented the six chemicals from reaching steady-state concentration between sampling events. Finally, the concentrations for some of the six chemicals were near the detection limits for standard conditions, possibly influencing the observed ratio.

For a number of VOCs, the impact of substantially decreased outdoor air change rate associated with the HRV being off had a larger impact on indoor VOC concentrations than an 8 °C temperature change. This highlighted the importance of maintaining continuous operation of the HRV consistent with recommendation ventilation rates (in this case ASHRAE 62.2-2010) in a house with very low infiltration rates.

4.4. Product Area VOC Emission Rates

Several VOCs were likely emitted by single product sources within the house. As examples, the only known source of styrene was the extruded polystyrene insulation in the basement, and 2,2,4-pentane-1,3-pentanediol monoisobutyrate (TMPD-MIB), a coalescing aid in water-based paint, likely was emitted only from painted surfaces. For these two VOCs, the projected surface areas of their probable sources were measured and used to calculate productarea emission factors (μ g h⁻¹ m⁻²) and plotted in Figure 5. Due to emissions decaying over time, the last three samples from summer 2014 were omitted in Figure 5 (but are included in Figure S.13). The inference for styrene's association with a material in the external wall was reinforced by the 0.69 r² correlation of its concentration and emission factor with outdoor temperature (Table 3 and Figure 5). Concentrations of TMPD-MIB, on the other hand, showed no correlation with outdoor temperature, consistent with a source exposed entirely within the building envelope and subjected to nearly constant temperature.

Microchamber testing of a sample of the air barrier showed that it emitted n-pentadecane, n-hexadecane, and n-heptadecane. Other insulating materials found throughout the house were sampled in micro-chambers, and no other potential sources of n-pentadecane, n-hexadecane, and n-heptadecane were found. For these VOCs, product area specific emission rates were calculated using the surface area of the air barrier (Figure 5) and appear to exhibit a temperature dependence.

4.5. Floor Area Specific VOC Emission Rates

Floor area VOC emission rates were calculated using Equation (3) separately for Phase 1 of monitoring (8 months, June through December, 2013) and for Phase 2 (7 months, January through July, 2014). These two phases were chosen to highlight changes in VOC emission rates

over time. The calculations used the areas and volumes of the first and second floors (242 m^2 and 773 m^3 , respectively). All of the measured mechanical and modeled infiltration flow was assumed to occur in the first and second floors, i.e., no flow into the attic or basement. This was done so the average floor area emission rates could be compared to other studies that used occupied floor areas. Average floor area emission rates (*i.e.*, emission factors (EFs)) for the two phases are shown in Table 4. For many VOCs, EFs decreased from Phase 1 to Phase 2. Exceptions included ethanol and toluene (discussed in section 3.3), the common solvents 2-propanol, acetone, and 2-butanone (possible cleaning product sources with elevated concentrations in May 2014), and formaldehyde, for which average EFs remained constant.

4.6. Comparisons with Previous Studies

Several studies have reported VOC concentrations and whole-house VOC emission factors for newly or recently constructed, detached single-family houses in the United States. The available comparison houses include both conventional site-built and manufactured construction. While the VOC sampling and analytical methods used in the studies were comparable, the data were reported in different ways, somewhat complicating the comparisons. Additionally, the conditions of the houses at the time of sampling varied with respect to completion date, decorations and furnishings, presence of attached garages, and occupancy.

In the design and interior construction of the NZERTF, considerable effort was made to reduce emission sources of formaldehyde. The importance of controlling formaldehyde sources was illustrated by a study of 108 new single-family, detached houses in California (CA) [7]. These houses were built to the 2005 CA energy code and were occupied at the time of the study. Most had attached garages. None were reported to be designed specifically for low VOC emissions. When tested, the homes ranged in age from 1.7 years to 5.5 years. All homes were

furnished and occupied at the time of the study. In occupant surveys, 22 % of the households reported that some new furniture was installed within the six months preceding the sampling dates in the respective homes. Of the 22 measured VOCs, formaldehyde had the highest median volume-specific emission rate of 11 μ g h⁻¹ m⁻³. Using an assumed average 2.6 m ceiling height, this is equivalent to a floor area-specific emission rate of 29 μ g h⁻¹ m⁻², roughly four times the values measured in the unfurnished and unoccupied NZERTF. The median formaldehyde concentration modeled for the houses with ventilation in compliance with ASHRAE Standard 62-2 [10] was 39 μ g m⁻³.

A study of new, unoccupied site-built and manufactured houses conducted in the late 1990's reported floor area-specific emission rates for 28 VOCs including many of the compounds measured in this study [8]. The four manufactured houses were contained previously used furniture and the quantity of furniture was sparse relative to typical occupied homes. The seven site-built houses were not furnished. The geometric emission factors of formaldehyde for site-built and manufactured houses were 31 μ g h⁻¹ m⁻² and 45 μ g h⁻¹ m⁻², respectively. For the NZERTF, the average formaldehyde emission factor based on floor area was 6.7 μ g h⁻¹ m⁻². Differences in house occupancy conditions and possible general reductions in formaldehyde emissions from building products over a period of 15 years between the studies may have contributed to the differences. However, the magnitude of the differences suggests that the formaldehyde source control measures employed in the NZERTF were effective. The major contributing factors were likely avoidance of conventional composite woods for built-in cabinetry, shelving, doors and other woodwork and trim, and avoidance of other known sources such as acid-cured finishes. In addition to formaldehyde, floor area emission factors for 19 other VOCs in the NZERTF are compared in Table 3 to values reported for the unoccupied site-built and manufactured houses [8]. Of these, nine VOCs had emission factors in Phase 2 that were $\leq 20 \%$ of the corresponding emission factors reported for the unoccupied site-built and manufactured houses. These VOCs were acetic acid, n-undecane, TMPD-MIB, ethylene glycol, 2-butanone, and the three terpenes – α -pinene, β -pinene, and d-limonene. Two VOCs (ethylene glycol, and α -pinene) measured in the NZERTF exceeded the previously reported values for either study [7, 8], but only during Phase 1. Three chemicals (hexanoic acid, styrene and 1,2,4-trimethylbenzene) measured in the NZERTF exceed the values reported in the literature during both phases of sampling.

5. Conclusions and Residential IAQ Specification

The NIST NZERTF achieved the project's goals for energy performance and VOC source reduction. Throughout an annual period with simulated occupancy of a family of four, the house produced more energy through its solar panels than it consumed. The carefully designed and constructed air barrier reduced uncontrolled air infiltration to ≤ 0.05 h⁻¹ based on multizone airflow simulations. The HRV supplied continuous ventilation meeting the requirements of ASHRAE Standard 62.2-2010. Implementation of formaldehyde source control guidelines reduced formaldehyde emission factors to ≤ 12 % of typical formaldehyde emission factors in conventional site-built and manufactured houses.

The emission factors for other VOCs, although not emphasized to the same degree in the construction specifications, were generally less than previously reported values. Analysis of the VOC concentration and physical data provided evidence that the materials and products in the building envelope were impacting indoor VOC concentrations. The implication is that the air

barrier and everything inside the air barrier need to be considered when developing VOC source control strategies. This supports the current California Department of Public Health material emission test standard (California Specification 01350) that regards the emission from insulation materials the same as if it was an indoor surface in model scenarios [26]. Another important implication of this study is that mechanical ventilations systems in houses with very low infiltration rates need to be highly reliable and operated according to consensus standards, such as ASHRAE Standard 62.2, in order to control the concentrations of air pollutants generated indoors.

The guidelines for low-emitting interior sources developed for the NZERFT proved to be somewhat difficult for the design team to implement due to insufficient product data and because they existed outside of the building contract documents. Based on the lessons learned, the original guidelines have been updated and formalized into architectural specification language [27]. This residential IAQ specification, which is designed for general use and modification by architects, contractors and other building professionals, differs from the original guidelines used to selected products for the NZERTF. The specification emphasizes a more performance-based approach than these guidelines. This change is made possible by the existence today of considerably more product data on VOC emissions generated by manufacturers interested in demonstrating compliance to low-emitting materials credits and the requirements of highperformance building standards and codes.

Acknowledgements

The authors would like to acknowledge the assistance of Matthew Schlegel and Angelica Connor, NIST, in collecting the samples and Na Li, Berkeley Analytical, for chemical analysis. This work was funded by the National Institute of Standards and Technology.

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List of figures and tables

Sampling date ^a	Average outdoor temp (°C ±0.2 °C) ^b	Average indoor temp (°C ±0.3 °C) ^b	Modeled infiltration (h ⁻¹) ^c	Mechanical ventilation $(h^{-1}, \pm 10 \%)$	Average Outdoor Ozone Concentration (ppb _v)
5/2/2013	9	21	0.03	0.16	NA ^d
6/12/2013	23	23	0.02	0.13	NA ^d
7/3/2013	22	24	0.01	0.13	NA ^d
8/7/2013	21	24	0.02	0.15	NA ^d
9/5/2013	20	25	0.02	0.14	NA ^d
10/22/2013	12	22	0.03	0.15	18.0
11/19/2013	7	21	0.04	0.16	33.0
12/17/2013	1	21	0.04	0.16	11.6
1/27/2014	2	21	0.05	0.16	40.6
2/25/2014	-1	21	0.05	0.17	36.4
3/19/2014	3	21	0.05	0.15	26.1
4/16/2014	1	22	0.05	0.14	44.3
5/22/2014	21	24	0.02	0.15	59.2
6/24/2014	22	24	0.02	0.15	50.8
7/29/2014	19	24	0.02	0.15	35.9

Table 1. Temperature, ventilation rates and ozone concentrations on sampling dates.

^a All dates are in the American date format of month/day/year. ^b Temperature was averaged from midnight to end of sampling period, typically 12 h.

^c Infiltration modeled in CONTAM with balanced mechanical system supplying outdoor air and exhausting at 0.13 h^{-1} .

^dNA. Not applicable, ozone concentration not measured.

Average Duration Average Outdoor Average T_{in}-HRV Outdoor Indoor of Air change rate $(h^{-1})^{I}$ Condition Wind Temp T_{out} status Temp Condition (on/off) (°C) Speed (°C) (days) $(^{\circ}C)$ (m/s) 32.0 5 On 0.22 24.2 1.6 7.8 (a) 4 24.7 0.15 22.8 3.6 2.0 On (b)

0.02

20.1

1.9

3.4

Table 2. House conditions and measured air change rates as a function of HRV operation and indoor temperature.

24.0 ¹Air change rates reported in this table were measured using a tracer gas system.

Off

2

(c)

		I-O Concentration (µg m ⁻³)				
Compound	Chemical class	Maxim um concent ration	15- Month average concentr ation	Detecti on Limit	RSD ¹	$\frac{\ln(I-O)}{\text{vs. }1/T}$ r^2
Acetic Acid	Acid	57	35	2.0	0.14	0.39
Hexanoic acid	Acid	12	7.5	0.7	0.10	0.77
Ethanol	Alcohol	450	110	2.0	0.21	0.02
2-Propanol	Alcohol	130	19	1.1	0.18	0.08
1-Butanol	Alcohol	17	8.1	0.7	0.13	0.83
Phenol	Alcohol	3.6	1.6	0.2	0.13	0.49
Formaldehyde	Aldehyde	11	7.7	0.2	0.14	0.19
Acetaldehyde	Aldehyde	34	18	0.3	0.11	0.90
Pentanal	Aldehyde	36	14	0.6	0.11	0.73
Hexanal	Aldehyde	190	58	0.8	0.09	0.63
Heptanal	Aldehyde	14	5.5	1.0	0.09	0.74
Octanal	Aldehyde	28	13	0.9	0.10	0.88
Benzaldehyde	Aldehyde	16	5.7	0.6	0.14	0.66
Nonanal	Aldehyde	23	12	0.9	0.10	0.76
n-Undecane	Alkane	2.6	0.8	0.4	0.12	0.14
n-Pentadecane	Alkane	5.5	2.5	0.2	0.12	0.50
n-Hexadecane	Alkane	9.0	3.0	1.0	0.21	0.45
n-Heptadecane	Alkane	12	3.9	1.4	0.24	0.33
Toluene	Aromatic	250	18	0.1	0.12	0.07
Styrene	Aromatic	9.7	3.3	0.3	0.08	0.69
1,2,4- Trimethylbenzene	Aromatic	7.4	3.9	0.3	0.13	0.75
Cyclohexanone	Cyclic	19	1.5	1.2	0.27	0.08
TMPD-MIB ²	Ester	7.3	5.1	1.1	0.12	0.02
Propylene glycol	Glycol	40	21	1.5	0.16	0.35
Ethylene glycol	Glycol	35	17	2.2	0.15	0.25
Acetone	Ketone	150	29	1.9	0.22	0.07
2-Butanone	Ketone	28	3.1	1.1	0.35	0.13
Decamethylcyclo pentasiloxane	Siloxane	18	6.2	0.6	0.15	0.08
α-Pinene	Terpene	29	17	0.3	0.14	0.39
β-Pinene	Terpene	12	6.3	0.3	0.13	0.51
d-Limonene	Terpene	4.6	1.8	0.3	0.13	0.48

Table 3. Average indoor minus outdoor (I-O) VOC concentrations at standard conditions for entire study. Also shown are correlation coefficients (r²) for natural log I-O concentrations versus inverse temperature.

¹Average relative standard deviation of concentrations at two indoor locations on each sampling date. ²1,2,4-Trimethyl-1,3-pentanediol monoisobutyrate, combined isomers

	Floor Area Emission factor						
	$(\mu g h^{-1} m^{-2})$						
	Phase 1	Phase 2	CNHS ¹	Site-	Manufa		
Compound	(8 mon)	(7 mon)	n = 108	Built ²	ctured ²		
	average	average	n - 100	n = 7	n = 4		
Acetic Acid	39	21		95	310		
Hexanoic acid	7.5	4.9		3.8	1.8		
Ethanol	95	95					
2-Propanol	11	21					
1-Butanol	8.5	4.8		23	8.5		
Phenol	2.1	0.8	0.8	2.1	9.6		
Formaldehyde	7.1	6.2	29	31	45		
Acetaldehyde	18	7.4	14	25	17		
Pentanal	17	4.1					
Hexanal	79	14	5.8	84	77		
Heptanal	6.7	2.2		7.2	7.7		
Octanal	14	6.9		11	14		
Benzaldehyde	7.1	2.1					
Nonanal	13	3.8		13	15		
n-Undecane	1.2	0.1		18	7.3		
n-Pentadecane	2.9	1.3					
n-Hexadecane	4.3	0.4					
n-Heptadecane	6.0	0.2					
Toluene	1.4	33	3.4	26	3.9		
Styrene	3.3	2.0	0.5	8.3	4.1		
1,2,4-	2.4	2 1	0.5				
Trimethylbenzene	5.4	5.1	0.5				
Cyclohexanone	0.2	2.6					
TMPD-MIB	4.0	4.9		64	24		
Propylene glycol	25	11		19	11		
Ethylene glycol	24	4.3	10	170	64		
Acetone	23	30					
2-Butanone	1.9	3.8		19	22		
Decamethylcyclo	5.3	5.8					
pentasiloxane	17	11 2	7.6	100	100		
α-Pinene		11.6	/.6	120	100		
β-Pinene	7.0	3.7		51	28		
d-Limonene	2.0	1.1	6.8	23	19		

Table 4. Average VOC emission factors for NZERTF with values reported by other studies.

¹California New Homes Study [7], median volume-specific emission rates multiplied by 2.6 m typical ceiling height. Houses were occupied. ²Geometric mean value for new unoccupied houses [8].





Figure 1. Construction of NZERTF showing the air barrier (top) and completed structure (bottom).



Figure 2. I-O concentrations of selected VOCs over 15 sample periods at standard conditions. Dates are in the American date format of month/day/year.



Figure 3. Arrhenius Relationships between ln(I-O) concentration and inverse outdoor temperature (1/T) for selected aldehydes. Due to emissions decaying over time, the last three samples from summer 2014 were omitted but are included in Figure S.6.

Figure 4. Ratios of I-O VOC concentrations when indoor temperature was increased ≈ 8 °C (blue bars) compared to standard conditions. Ratios of calculated steady state VOC concentrations when HRV was turned off (red bars) compared to standard conditions.

Figure 5. Relationships between product area specific emission factors and outdoor temperature (TMPD-MIB: paint; Styrene: polystyrene insulation; alkanes: air and vapor barrier). Due to emissions decaying over time, the last three samples from summer 2014 were omitted but are included in Figure S.13.

Supplementary Material

The supplementary material includes the derivation of Equation 4 and supporting figures to show the complete data set.

5.1. Derivation of Equation 4

Equation 4 is derived from Equation 1 in the following manner. All parameters are defined in the main document.

$$\frac{dC}{dt} = \lambda C_{out} - \lambda C + \frac{E_f A}{V}$$
(3)

$$\frac{dC}{\lambda C_{out} + \frac{E_f A}{V} - \lambda C} = dt$$
(S.1)

When the terms *a* and *b* are defined as follows:

$$a = \lambda C_{out} + \frac{E_f A}{V}$$
(S.2)

$$b = \lambda$$
 (S.3)

Equation (S.1) becomes:

$$\frac{dC}{a-bC} = dt \tag{S.4}$$

When the terms *u* is defined as follows:

 $u = a - bC \tag{S.5}$

$$du = -bdC \tag{S.6}$$

$$\frac{du}{-b} = dC \tag{S.7}$$

Equation (S.4) becomes:

$$\frac{du}{-bu} = dt \tag{S.8}$$

$$\frac{du}{u} = -bdt \tag{S.9}$$

$$\ln(u) = -bt \tag{S.10}$$

Intergrating Equation (S.11) from time zero with an initial concentration of $C_{t=0}$: $\ln[a - bC]_{C_{t=0}}^{C} = -bt|_{0}^{t}$ (S.11)

$$\ln\left[\frac{a-bC}{a-bC_{t=0}}\right] = -bt \tag{S.12}$$

$$\left[\frac{a-bC}{a-bC_{t=0}}\right] = e^{-bt}$$
(S.13)

$$a - bC = \left[a - bC_{t=0}\right]e^{-bt}$$
(S.14)

$$bC = a - [a - bC_{t=0}]e^{-bt}$$
(S.15)

$$bC = bC_{t=0}e^{-bt} + a(1 - e^{-bt})$$
(S.16)

$$C = C_{t=0}e^{-bt} + \frac{a}{b}\left(1 - e^{-bt}\right)$$
(S.17)

$$C = C_{t=0}e^{-\lambda t} + \left(C_{out} + \frac{E_f A}{\lambda V}\right)\left(1 - e^{-\lambda t}\right)$$

(S.18)When $C_{t=0}$ equals the standard condition concentrations ($C_{Standard}$) and C equals the $C_{No \ Ventilation}$ case, the result is Equation 4:

$$C_{No \, Ventilation} = C_{Standard} e^{-\lambda t} + \left(C_{out} - \frac{E_f A}{\lambda V} \right) \left(1 - e^{-\lambda t} \right)$$
(4)

5.2. Supporting Figures

This section includes detail figures for all chemicals measured during this study. All dates in this section are in the format month/day/year. Figure S.1 demonstrates the net energy used in the NZERTF over one year of testing. Figure S.2 through Figure S.5 illustrate the VOC concentrations throughout the 15 sampling events. Figure S.6 through Figure S.10 highlight the potential Arrhenius relationship between the VOC concentrations and temperatures. Figure S.11 and Figure S.12 show the lack of correlation between aldehyde concentrations and ozone concentration. Figure S.13 illustrates the temperature dependence of the product specific emission factors. Figure S.14 highlights the relative impact of elevated indoor temperature and lack of mechanical ventilation on all chemicals.

Figure S.1. Daily net energy use (bars) and cumulative net energy use (line) in NZERTF [28].

Figure S.2. Aldehyde and ketone concentrations over 15 sample periods following the completion of NZERTF.

Figure S.3 Acid and alcohol concentrations over 15 sample periods following the completion of NZERTF.

Figure S.4. Alkane and aromatic concentrations over 15 sample periods following the completion of NZERTF.

Figure S.5. Terpene and other chemical concentrations over 15 sample periods following the completion of NZERTF.

Figure S.6. Arrhenius Relationships between I-O Concentration and Inverse Outdoor Temperature for Aldehydes.

Figure S.7. Arrhenius Relationships between I-O Concentration and Inverse Outdoor Temperature for Acids and Alcohols.

Figure S.8. Arrhenius Relationships between I-O Concentration and Inverse Outdoor Temperature for Aromatics and Alkanes.

Figure S.9. Arrhenius Relationships between I-O Concentration and Inverse Outdoor Temperature for Terpene and other chemicals.

Figure S.10. Arrhenius Relationships between I-O Concentration and Inverse Indoor Temperature for Aldehydes.

Figure S.11. Relationships between I-O Aldehyde and Ketone Concentrations and Outdoor Ozone Concentration.

Figure S.12. Relationships between I-O Aldehyde and Ketone Concentrations and Indoor Ozone Concentration.

Figure S.13. Relationships between product area specific emission factors and outdoor temperature (TMPD-MIB: paint, Styrene: polystyrene insulation, alkanes: air and moisture barrier). Above 18 °C there are seven values for each VOC, the four higher values were taken in the summer of 2013, the three lower values were measured in the summer of 2014.

Increased Temperature/No Ventilation to Base Condition

Figure S.14 Ratio of NZERTF concentrations when indoor temperature was increased 8 °C (blue) compared to standard conditions. Ratio of NZERTF calculated steady state concentrations when ventilation was eliminated by turning off the HRV (red, infiltration still present) compared to standard conditions. Vertical dashed lines illustrate the expected ratios for the conditions. Aldehydes (except formaldehyde), ketones, alcohols, aromatics, and terpenes are highlighted with green. N-alkanes, gylcols, acids, and formaldehyde are highlighted with purple.