Developing a new passive tracer gas test for air change rate measurement

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ABSTRACT

Ventilation is critical in interpreting indoor air quality (IAQ), yet few IAQ assessments report ventilation rates; even when they do, the measurement method is often not fully described. Most ventilation assessments use a tracer gas test (TGT) to measure total air change rate. In a TGT, the indoor air is marked with an easily identifiable gas (tracer) so that the air change rate can be inferred by monitoring the tracer’s injection rate and concentration. Passive sampling (adsorptive/absorptive samplers) is mostly preferred to monitor tracer concentration for its simplicity, practicality and affordability. Such samplers are commercialized by a range of companies and are widely used in IAQ studies to assess pollutants levels. Currently used passive TGTs present some limitations: inadequate tracer gas, disconnection from IAQ analysis (providing ventilation rates in a different time-scale than the pollutant concentrations) and possible bias arising from the perfect-mixing assumption. Thus, this paper proposes a new approach on the passive TGT method, which uses as tracer a suitable gas that can be co-captured and co-analysed using commercial passive samplers employed in common IAQ studies and which includes a more careful planning phase to account for imperfect mixing. A literature review was carried out in pursuit of such a gas. Considering that the most relevant compounds in IAQ studies are volatile organic compounds (VOCs), which are sampled separately from inorganic pollutants, the gases considered as possible tracers were the VOCs capable of being captured by the samplers commercialized by Radiello®, 3M and Gradko. They are composed by activated charcoal, which captures all VOCs in the targeted molar mass range by adsorption. The info-sheets for these samplers were consulted. Two options for alternative tracer gas are currently under consideration: 2-butoxyethyl acetate (EGBEA) and deuterated decane. Both present low-reactivity, usually negligible background indoor concentration, generally low toxicity and no links to chronic health effects. A preliminary field test was carried out in order to check EGBEA’s measurability, and results showed insignificant background EGBEA concentration and good measurability by the Radiello® sampler. Two test chambers were also performed: TCP1 and TCP2. TCP1 tested a first option of tracer source for EGBEA; TCP2 tested a second option of source for EGBEA and decane (as proxy for deuterated decane). Results from both showed that the used sources yielded emission rates higher than targeted, but the concentration curves obtained for EGBEA in TCP1 and decane in TCP2 suggest emission rates stability. Future work includes further chamber testing in pursuit of an adequate source design and computer simulations using CONTAM software coupled to CFD to study the effects of source/samplers positioning on the accuracy of the resulting air change rate calculations.

KEYWORDS
Ventilation, air change rate, indoor air quality, tracer gas test, passive sampling.

1 INTRODUCTION

Air pollution in indoor environments has become a great concern in the last decades. People tend to spend the majority of their time indoors, where numerous known sources of substances with high potential to cause adverse effects to human health are present (Godish, 2005). Exposure to air pollution in indoor environments may be responsible for almost 2 million
premature deaths in developing countries and for about 4% of the global burden of disease (Bruce et al., 2000; Godoi et al., 2009).

A crucial factor in determining the accumulation of pollutants in indoor environments is ventilation, and its impacts on the health and comfort of occupants have long been recognized in standards and regulations (EPA, 1994). Simultaneously, ventilation is closely related to the energy efficiency of a building (Persily and Levin, 2011; Persily, 2015): the higher the building airtightness, the higher is its insulation, which saves heating/cooling costs. However, increased airtightness can also lead to lower total ventilation rates. Evidence shows that buildings with lower ventilation rates tend to present higher concentrations of indoor air contaminants (Flemish Government, 2012; 2014).

Although ventilation is critical in interpreting indoor air quality (IAQ) measurements, only few IAQ field studies report measured ventilation rates (Persily, 2015); and even when they do, the measurement methods are often not described in sufficient detail to evaluate their quality or applicability to the study design (Persily and Levin, 2011). Given the importance of ventilation in estimating pollutant sources impacts and proposing remediation actions if needed, it is crucial that IAQ assessments not only provide information on basic ventilation parameters (e.g. ventilation type, designed air change rate), but also report actual ventilation rate values, measured by means of a reliable and reproducible method.

Methods currently used for measuring ventilation rates either involve direct flow rate measurements at vent holes combined with pressurization tests, or a tracer gas dilution/dispersion test (TGT). The first type is used only under very specific circumstances, such as in extremely airtight buildings where all airflows occur mechanically in ductwork (Persily, 2015). Thus, most ventilation assessments use TGT as a method to measure the total air change rate of a building/indoor space (Persily, 2015). In a TGT, the air is marked by the injection of an easily identifiable gas and the air change rate is then inferred by monitoring the tracer emission rate and room concentration. This is a very simple and convenient method that can be carried out in occupied buildings, which allows for a greater accuracy since it takes into account the large effect occupancy has on a building’s air change rate.

However, there are three important shortcomings related to TGTs. The first one is linked to the fact that most TGT techniques provide instantaneous results (due to the use of online monitors), which are very variable over time. The concentrations of indoor pollutants (also variable over time and significantly influenced by air change rate) are usually measured over a longer period using long-term sampling techniques that report time-averaged values, i.e. the link between the IAQ and the ventilation data is not direct, hindering their comparability.

The second shortcoming is connected to the substances currently used as tracer gases. Most TGTs employ sulfur hexafluoride ($\text{SF}_6$) or perfluorocarbons (PFTs) as tracers. Both substances are very potent greenhouse gases mentioned in the Kyoto protocol, with very long lifetimes in the atmosphere (IPCC, 20007). Therefore, even small atmospheric concentrations can have proportionately large effects on global temperatures and the release of any quantity of these substances should be avoided. Hence the importance of proposing alternative tracer gases, as it is possible that efforts to phase-out these substances may be done in the near future.

The third shortcoming is related to the perfect-mixing assumption. The application of a TGT assumes that the air in the assessed indoor space has a homogeneous spatial distribution. However, a perfect-mixing situation is rarely observed in real life, meaning that concentration levels of substances and airflows vary across the indoor space. Therefore, the placement of source/samplers can greatly impact the tracer concentrations measured and consequently the calculated air change rate. Studies show that this assumption can lead to severe bias in the air change rates measured by this method, even in single-zone measurements (Ott et al, 2002; Van Buggenhout et al, 2009; Liu et al, 2018).

Thus, a TGT which provides ventilation rates in the same timescale as the pollutant concentration measurements, uses a more adequate substance as tracer and includes a more
careful planning for placing sources/samplers to account for imperfect mixing would be more appropriate than the ones currently used. Furthermore, it is also important that the new method is suitable for use during normal occupancy, thus the TGT must not cause disturbance and the employed tracer must be scientifically proven harmless to the occupants’ health. Also, a highly desirable characteristic for this new method is the non-dependence on electricity (i.e. a method based entirely on passive techniques for emitting and sampling the tracer), which lowers the utilization costs and broadens the range of buildings where it can be applied.

Taking all these desired characteristics into account, this project aims to develop a reliable and reproducible TGT using as tracer a substance that is safe for use during occupancy and that can be co-captured and co-analyzed with standard passive samplers used for common IAQ assessments. Additionally, this new method proposes the implementation of a pre-test planning phase in which the optimal physical placement of sources/samplers is determined by means of simulations, in an effort to minimize bias arising from imperfect mixing and possibly enabling the assessment of interzonal airflows.

2 MATERIALS AND METHODS

2.1 Selection of a new substance for use as tracer gas

The first step to propose this new TGT consists of finding an adequate substance to be used as a tracer, alternatively to the currently employed SF₆ and PFTs. This initial step was done by means of a comprehensive literature review. The thought process through which the literature review was carried out is explained below.

From an IAQ point of view, volatile organic compounds (VOCs) are the most relevant contaminants, since they are ubiquitous in indoor spaces, specially occupied ones, and several of them are knowingly harmful to human health (Uhde and Salthammer, 2009). This group of compounds is truly extensive and its constituents vary greatly in characteristics and properties. In IAQ assessments, such gases are sampled separately from inorganic pollutants due to their different physicochemical characteristics. The vast majority of researchers utilize passive sampling (i.e. purely diffusion-based, involving no pumps) to measure average VOCs concentration in common IAQ studies, for its simplicity, accuracy, practicality and suitability for use during normal occupancy. As one of the aimed characteristic for the new TGT is the matching timescale for air change rate and pollutant concentration measurements, the best option for a tracer is a gas which can be captured simultaneously by commercial passive VOC samplers. This approach also simplifies the process of ventilation measurement in IAQ studies, since only one sample simultaneously provides the information needed to infer both the air change rates and the indoor VOCs levels. Thus, the gases considered for use as tracer were the VOCs capable of being captured by the commercial passive VOC samplers most widely employed in common IAQ assessments. These samplers are composed by activated charcoal, in which organic gases are captured by adsorption. This process is essentially non-specific, meaning that any VOC in the targeted molar mass range may be captured and later analyzed in lab by applying the adequate extraction and analytical processes.

The information sheets for commercial passive VOC samplers were consulted. Radiello® and 3M samplers capture VOCs in the range C2-C12, and Gradko samplers capture compounds up to C28. Among the numerous VOCs in this range, paraffins initially stood out as possible candidates for use as tracer gas.

Paraffins are linear acyclic saturated hydrocarbons (alkanes). First four alkanes (methane to butane) are colorless, odorless gases at ambient conditions, C3 to C17 are colorless, nearly odorless, volatile liquids and higher alkanes are wax-like solids. Alkanes are the simplest class of organic compounds, extremely stable and inert, as they contain only carbon and hydrogen atoms (small electro negativity difference) and have no functional groups (Bano, 2007). C5-
C15 alkanes present no significant toxicological effects to humans, with the exception of n-pentanes, trimethylpentanes and n-hexanes. Alkanes of >C15 have lower vapor pressures, hindering their application as passive tracer gases (HSPA, 2015).

There is however a major problem regarding the applicability of paraffins as tracers. An ideal tracer should be absolutely absent in the ambient it is being placed. Alternatively, a tracer with non-zero background may be used provided that such background is stable and that the additional tracer concentration is significantly larger than it. Both background and added concentrations should be as low as possible in order not to oversaturate the passive sampler (when the adsorbed mass of analyte reaches the maximum capacity of the adsorbing medium, resulting in underestimation of the actual air concentration). Paraffins do not meet either of this criteria: they are largely present in the composition of a range of household products, thus their typical background concentration is significant in most indoor environments.

The option currently under consideration for use as tracer gas is the solvent 2-butoxyethyl acetate (also called ethylene glycol monobutyl ether acetate or EGBEA), mentioned by Radiello® in the VOC CS₂-desorption sampler info-sheet. EGBEA is a compound of the family of glycol ethers and has a relatively high production volume. Although EGBEA is present in various household products (ATSDR, 1999), its background indoor concentration is usually very low. A national survey for IAQ carried out in 490 French dwellings found EGBEA concentrations below the detection limit in 97% of the assessed houses (Billionnet et al, 2011). A similar assessment, carried out as part of the HABIT’AIR Nord – Pas de Calais program, monitored the presence of glycol ethers in 60 homes located in northern France, finding no trace of EGBEA in any of the assessed houses (Plaisance et al., 2008). More recently, Derbez et al. (2014) performed a field survey in 7 newly built energy-efficient houses, also in France, measuring a range of IAQ indicators and environmental parameters both before and during the first year of occupancy; EGBEA was not detected in any sample from any of the assessed houses. Regarding human health, EGBEA has generally low toxicity and has not been linked to any chronic effects (ATSDR, 1999; ECETOC, 2005; SCHER, 2006).

An alternative for EGBEA may be the use of stable isotope labeling, more specifically using deuterated compounds, not naturally present in the atmosphere or in any household product. Stable isotopes are chemical elements that occupy the same position in the periodic table, but differ in mass due to a different number of neutrons within the atomic nucleus. This difference makes isotopes analytically distinguishable yet chemically and functionally identical to the original compound (Wilkinson, 2016). Deuterium (D) is one of the most commonly used stable isotopes for tracing purposes. This approach allows revisiting the initial idea of using paraffins as tracers. Thus, the second option under consideration consists of deuterated paraffins in C8-C15 range. Deuterated decane (D-decane) is initially considered for its combination of lower flammability and higher volatility. Due to the high purchase cost of D-decane compared to EGBEA, its use as tracer gas has been considered as a backup plan in this project.

2.2 Preliminary test

A preliminary test was carried out in order to test EGBEA’s measurability by Radiello® samplers in simplified field conditions. The Radiello® samplers were used to measure this compound’s concentration in one room before and after the placement of a recipient containing the solvent. The room used was an office which was unoccupied at that time, although fully furnished (two desks with two chairs, two PCs, one wall cabinet and plastic blinds in the windows). Three sampling cartridges were used in total for this test: one as a lab blank, i.e. analyzed right out of the package; a second cartridge was used to measure the background EGBEA concentration in the office; the third and last cartridge was used to measure the air concentration of EGBEA after the placement of a source of this solvent in liquid phase. This so-called source consisted of a simple glass beaker filled with approximately 11 ml of EGBEA.
(9.536 g) left uncapped so the solvent could freely volatilize into the room air, acting therefore as a completely passive source. Both these samplers were exposed in the room for a period of consecutive 4 days. Figure 1 shows the setup of the experiment.

![Figure 1: Preliminary test setup](image)

### 2.3 Chamber tests

To this date, two chamber tests (TCP1 and TCP2) were performed to evaluate the behavior of EGBEA when released from a source to the air under standard and constant conditions. From that baseline, it will then be possible to compare the substance’s behavior under varying conditions and circumstances in future chamber tests. Testing under standard/constant conditions also enables the determination of the concentration curve of the tracer, allowing to know when it will reach steady state.

Efforts for determining this baseline started in the Test Chamber Phase 1 (TCP1), in which liquid phase EGBEA was added to a glass recipient with an adjustable cap and then used as tracer source inside the test chamber. The test chamber used in TCP1 was a 117 dm³ steel chamber, with temperature, relative humidity and air change rate set to constant standard conditions (23°C, 50% and 0.5 h⁻¹, respectively, according to ISO 16000-9). Three different measurement methods were used simultaneously to measure EGBEA concentrations in the chamber: passive sampling (Radiello® tubes, solvent desorption), active sampling (Tenax® tubes, thermal desorption) and online monitoring (with a flame ionization detector - FID). Figure 2 shows the chamber setup right before the beginning of the experiment. TCP1 had a whole duration of 8 hours, during which the FID was used to monitor the EGBEA concentration.

The FID measures the air concentration of total hydrocarbons (THC). In TCP1, since the airflow provided to the chamber was completely clean of THC and there was no other source of VOCs inside the chamber, the THC concentration measured was equivalent to the EGBEA concentration originating from the source placed inside the chamber. In order to determine specifically the absolute EGBEA concentration as the experiment proceeded, Tenax® tubes were used to collect one air sample each hour, and 2 Radiello® samplers were placed together inside the chamber. Both Tenax® and Radiello® samplers were analyzed by means of gas chromatography with mass spectrometry detection, which allows to differentiate between different VOCs and thus to confirm that the signal detected by the FID is in fact due to exclusively EGBEA presence. While the Radiello® sampler is passive and provides long-term averages, the Tenax® tubes need a pump for sampling and provide short-term averages. In TCP1, Tenax® samples were taken in 8 moments (the first before the source placement, for a chamber baseline concentration), one per hour, for a period of around 30min each. This sampling period was determined by the sampling pump flow and by the maximum volume of air that can be sampled by the tube. The Radiello® samplers, on the other hand, were placed
inside the chamber at the same time as the source and remained there until the chamber was opened, 3 days later.

A second phase of chamber testing was then carried out as a re-test of TCP1, under the same conditions. This re-test was called Test Chamber Phase 2 (TCP2) and its planning took into account some shortcomings observed in TCP1. The setup of TCP2 is shown in Figure 3.

There were four main differences between TCP1 and TCP2: 1) the glass recipient used as source in TCP1 was substituted by a different one in TCP2 (Figure 3), in an attempt to lower the tracer emission rate; 2) a bigger chamber was used in TCP2 (WEISS chamber, 1000 dm³), to enable an increase in the airflow rate (to dilute more the tracer, in case the emission rate from the new source remained high) while still maintaining the same air change rate from TCP1; 3) the FID monitor yielded results below the detection limit due to a misconfiguration, thus no continuous FID data is reported for TCP2; and 4) two tracer options were tested, first EGBEA and then D-decane (in fact, normal decane was used as a proxy for D-decane, as an economy measure).

The EGBEA source was tested first, and then the decane source. Both tests lasted 3 days, with 8 Tenax® samples taken for each. In the EGBEA test, 1 sample was taken as blank, the following 6 were taken one per hour on the first day, and 1 was taken after 72h. In the decane test, 1 sample was taken as blank, the following 5 were taken one per hour on the first day, 1 was taken after 51h and 1 was taken after 70h. One Radiello® sample was taken per test, for a period starting with the tracer source placement and running until the reopening of the chamber at the end of the tests.

3 RESULTS AND DISCUSSION

3.1 Preliminary test
Results from the preliminary experiment are presented in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sampling start</th>
<th>Sampling finish</th>
<th>EGBEA mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab blank</td>
<td></td>
<td></td>
<td>0.067</td>
</tr>
<tr>
<td>Background</td>
<td>15/01 – 17h25</td>
<td>19/01 – 17h39</td>
<td>0.059</td>
</tr>
<tr>
<td>With EGBEA source</td>
<td>19/01 – 17h40</td>
<td>23/01 – 17h34</td>
<td>3.324</td>
</tr>
</tbody>
</table>

Based on the values presented in Table 1, the background EGBEA concentration in the assessed room can be considered insignificant: the EGBEA mass desorbed from the cartridge placed before the recipient placement (background) was very similar to the mass desorbed from the blank cartridge, even slightly lower, meaning that virtually no EGBEA was adsorbed onto the cartridge. Furthermore, the relatively low volatility of EGBA (0.23 g evaporated in 4 days) did not hinder its measurability by the Radiello® sampler: the cartridge placed in the room after the addition of the EGBEA source adsorbed an EGBEA mass two orders of magnitude higher than the blank and background cartridges. The calculated average concentration in air corresponding to the adsorbed mass after 4 days exposure to the EGBEA source was 14.1 µg m$^{-3}$. The results observed in this primary experiment can be interpreted as clear indications of the potential suitability of EGBEA as tracer for the purposes of a new TGT approach: its background concentration in the assessed room was negligible and it was successfully captured by a commercial VOC sample at a measurable level.

3.2 Chamber tests

Figure 4 shows the results measured by the FID monitor during TCP1. Note that the FID acquisition started running approximately 30 minutes before the source placement, in order to have a background measurement.

Results measured by the FID monitor presented a high noise signal even after smoothing (10 points moving average line), as it can be seen in Figure 4. The most likely reason for that is the fact that the sampling flow from the chamber to the FID had to be combined with another (clean) airflow in order to reach the working FID inlet flow. To reach the intended air change rate in the chamber, the inlet flow to the chamber had to be set at 1 l min$^{-1}$, the exact same as the inlet flow needed in the FID. Since the outlet flow from the chamber must correspond to less than 80% of the inlet flow, in order to maintain the equilibrium conditions inside the chamber (ISO 16000-9), the addition of an “extra” flow had to be done. This combination of flows implicates in 2 additional uncertainties: 1) the mixing may not be perfect and 2) the resulting concentration may be too diluted for the FID monitor. Nevertheless, the FID measurements followed the theoretical concentration trend quite well. The theoretical concentration ($C(t)$) of an emitted substance in a test chamber is given by:
\[ C(t) = C_0 (1 - e^{-Nt}) \]  

(1)

In which \( C_0 \) is the substance concentration when it reaches steady state and \( N \) is the air change rate. Thus, even though the FID response was noisy, it can be considered realistic.

The analysis of the Tenax® and Radiello® tubes showed that the concentration of EGBEA inside the chamber was too high for the calibration curve ranges normally used. In the case of the Radiello® samples, it was possible to dilute them for reanalysis, which revealed a very high 3-day average EGBEA concentration in the chamber (1690 µg m\(^{-3}\)). The Tenax® samples could not be diluted for reanalysis due to the destructive nature of the thermal desorption process. The results obtained from both types of passive samplers cannot be trusted because 1) the calibration curve used was in a much lower range and 2) it is likely that the samplers oversaturated during the sampling period, incurring in the breakthrough effect (in which target substances present in the subsequent inlet flow are not captured by the sampler, yielding a result lower than the real one). These high passive sampling results, along with the also very high FID results (which reached values surpassing 13000 µg m\(^{-3}\)), indicate that the emission rate of the used source was too high for a TGT. Thus, the planning for TCP2 included the substitution of the source.

Figure 5 shows the results obtained with the Tenax® samplers in both test, with the EGBEA source and then with the decane source.

![Figure 5: Results obtained with Tenax® samplers in TCP2.](image)

In TCP2, the concentration levels reached inside the chamber were much lower than in TCP1. However, the EGBEA concentration curve deviated considerably from the expected pattern, raising rapidly in the initial 7 hours and then decreasing also rapidly in the following couple of hours. The last sample, taken after 2 days, shows that the concentration decrease deaccelerated, but the lack of samples in this in-between period does not allow to determine if a steady state was reached. Nevertheless, the shape of the EGBEA concentration curve itself indicates that either the emission rate of the source was not constant or there was a strong and variable sink system inside the chamber. Since the WEISS is a standard stainless-steel chamber specifically developed for source testing and the same problem was not observed in the decane test, it is more likely that the recipient used as EGBEA source was not able to hold a constant emission rate. The recipients used as decane and EGBEA sources were initially considered to be identical, but the different concentration curves show that in fact they are not.

The Radiello® samplers yielded average 3-day concentrations of 71.8 and 949 µg m\(^{-3}\) for EGBEA and decane, respectively. The EGBEA result makes sense if we assume that the last Tenax® sample represents the steady state concentration and that such concentration was reached not long after the 7\(^{th}\) sample was taken. On the other hand, the decane concentration was extremely high compared to the Tenax® results, indicating a possible contamination of the Radiello® sample. Moreover, the analysis results from the GC-MS showed that the Radiello®
samples yielded peaks with areas above the linearity range of the calibration curve, meaning that the calculated concentrations should be considered with care, similarly to TCP1. Next chamber tests will employ a different source to lower the emission rate even more, and will use actual D-decane instead of decane as a proxy, to avoid possible contamination.

4 CONCLUSIONS

A TGT employing as tracer a harmless gas which is not commonly present in background indoor air, can be passively captured by commonly used commercial passive samplers and then co-analysed along with common IAQ pollutants is close to an ideal method to measure total average air change rate. Currently, EGBEA solvent and deuterated decane are considered as possible tracer candidates. A preliminary field test and two chamber tests were performed to evaluate the applicability of these substances as tracers, with promising results. Efforts will be continued with further chamber tests in pursuit of an adequate source design. Future work also includes simulation of TGTs in imperfectly-mixed zones using CONTAM software coupled to CFD, in order to study the effects of source/samplers positioning on the accuracy of the resulting air change rate calculations.

5 REFERENCES


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