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Developing a New Passive Tracer Gas Test for Air Change Rate Measurement

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ABSTRACT

This paper describes the ongoing development of a new tracer gas test (TGT) for total air change rates measurement. This new TGT, intended for use in large-scale IAQ assessments and based on constant tracer injection, employs an alternative tracer gas that is more adequate than the currently employed SF_6 *and perfluorocarbons and that can be co-captured and co-analyzed along with commonly assessed VOCs using a commercial passive IAQ sampler. Via literature study and lab testing, decane-*D_{22} *was found to be a suitable tracer substance. Several laboratory tests have been performed under controlled environmental conditions to develop and optimize a passive source of decane-*D_{22}*. The source design ultimately selected provides stable and repeatable emission rates under standard temperature and is unaffected by RH. A series of chamber tests were performed under different temperatures, and a consistent exponential curve was derived for determining the source emission rate from the room temperature. Future work includes field test applications for validation of the new TGT.*

INTRODUCTION

Indoor air quality (IAQ) is a topic of great public concern. Most people tend to spend most of their time indoors, where numerous known sources of harmful pollutants are typically present. The association between poor IAQ and adverse health effects has been shown in numerous studies (Fernandes et al., 2009; Heinrich, 2011; Carrer et al., 2018). A key factor that influences the accumulation of pollutants in indoor spaces and the interpretation of IAQ data is ventilation. However, due to the additional cost and the complexity of aligning ventilation measurements with IAQ assessments, only few IAQ field studies report ventilation rates adequately, i.e. fully describing the measurement method (Persily, 2015). Given the importance of ventilation in understanding IAQ, estimating pollutant sources' impact and

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proposing remediation actions, it is crucial that IAQ assessments report actual ventilation rate values, measured by reliable methods.

Most ventilation assessments use a tracer gas test (TGT) as a method to measure total air change rates (ACH) in indoor spaces (Persily, 2015). In a TGT, the air is marked by the injection of a tracer gas and the ACH is then calculated from the tracer's emission rate and final room concentration. The TGT is the only method capable of measuring the actual airflow between building zones and the outdoors (Lunden et al., 2012). Although the TGT approach may present a relatively higher degree of uncertainty compared to other methods, this is compensated by its greater simplicity, convenience and compatibility to be executed during normal occupancy (Lunden et al., 2012). TGTs are especially suited for large-scale ventilation surveys, in which a lower degree of individual data precision is acceptable in favor of an increased amount of data.

However, TGTs present three important shortcomings: 1) Most TGTs provide instantaneous results (due to the use of online monitors), while the concentrations of indoor pollutants are commonly measured using long-term sampling techniques that report time-averaged values, i.e. IAQ and ventilation data are not directly comparable; 2) Most TGTs employ sulfur hexafluoride (SF_6) or perfluorocarbons (PFTs) as tracer gases, both being potent greenhouse gases with very long lifetimes in the atmosphere (IPCC, 2007); 3) Common TGT applications assume that the air in the assessed indoor space is perfectly mixed (which is in fact rarely observed in real life), meaning that the placement of sources and samplers can influence the measurements of tracer concentration, and potentially lead to severe bias in the calculated ACH values (Van Buggenhout et al., 2009; Lunden et al., 2012; Liu et al., 2018).

Therefore, the main goal of the current project is to develop a new TGT which tackles the three aforementioned shortcomings by: 1) utilizing standard passive samplers commonly used for IAQ assessments to capture the tracer gas simultaneously with other pollutants of interest, matching the timescales of the datasets, 2) using an alternative substance as tracer gas, and 3) including a pre-test planning phase in which the optimal physical placement of sources/samplers in an indoor space is determined by means of computer simulation, in order to minimize bias arising from imperfect mixing. Additional advantages of this new method are its suitability to use during normal occupancy, as it causes no disturbance and employs a harmless tracer at safe air concentrations, and the employment of purely passive techniques, which lowers the costs and broadens the range of buildings where the TGT can be applied.

This paper focuses specifically on the work executed to select an alternative substance for use as tracer gas and to develop a suitable emitting source design for this new tracer. The issues related to air mixing and planning of physical sources/samplers' placement will be dealt with in future field tests and will be reported in future papers.

MATERIALS AND METHODS

As mentioned above, this paper focuses on the processes of selecting an alternative substance for use as tracer gas and of developing a suitable emitting source design for the selected tracer. Both processes are described in detail below.

Selection of an alternative substance for use as tracer gas

A comprehensive literature review was performed to propose an adequate substance to be used as a tracer in the new proposed TGT, alternatively to the currently employed SF_6 and PFTs. To help guide this process, 6 determining criteria for a suitable tracer gas were set:

1. The tracer gas should be quantifiable by means of a commonly used passive air sampling method
2. The tracer gas should be able to be analyzed together with common IAQ pollutants
3. The tracer gas should have negligible presence in typical indoor environments, thus having no significant known indoor sources
4. The tracer gas should present no significant health impact, thus being suitable for use indoor during normal occupancy (including most vulnerable populations)
5. The substance selected as tracer gas must be financially adequate, considering the amount needed for running a complete test

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6. The tracer gas should not be susceptible to physical and chemical parameters of the indoor environment

Criteria 1 and 2 are directly aimed at eliminating the issue of time-scale discrepancy between indoor pollutants measurements and ACHs measured by this new TGT. The approach proposed by these two criteria also saves time and resources, as only one sampler and one analysis provide all the information needed to infer both the ACH and the IAQ level of the assessed space. Since volatile organic compounds (VOCs) are the most relevant gaseous contaminants in IAQ studies, they were selected as the group of substances from which the alternative tracer was to be drawn. The VOCs considered for use as tracer were those capable of being captured by the passive VOC samplers commercialized by Radiello® (Radiello, 2007).

Initially, paraffins were considered as candidates for their high stability, inertness and low toxicity. However, paraffins do not fulfill criterion 3, as they commonly present considerably high background concentration in most indoor environments. Therefore, the use of paraffins as tracer gases was considered inadequate.

An effective way found to circumvent this issue was the use of stable isotope labeling, more specifically of deuterated compounds. These compounds are not naturally present in the atmosphere or in any household product. Stable isotopes are analytically distinguishable yet chemically and functionally identical to their original correspondent compounds (Wilkinson, 2016). Thus, the substances considered as alternative tracer gas are the deuterated paraffins in the C8-C12 range. In this range, decane-D_{22} was selected for its combination of lower flammability and higher volatility.

To ensure the fulfillment of criterion 4, the advice from VITO's Exposure Modelling and Risk Assessment (Environmental Risk and Health Unit, BREM-G) on safe exposure to decane-D_{22} levels was sought. Decane-D_{22} safety information is considered as the same as for n-decane, for which there is no harmonized classification. DNELs (derived no effect level) values, threshold concentrations for toxicity below which exposure is safe, have not been derived as n-decane is not hazardous for quantifiable effects (EC, 2006). There is also no derived OEL (occupational exposure limit) for n-decane. Nevertheless, the final advice from VITO's Exposure Modelling and Risk Assessment is: decane-D_{22} concentration must not exceed 250 mg m^{-3} during generation of a stable airborne concentration for 1 day. The peak (<15 minutes) concentrations should not exceed 500 mg m^{-3}. Also, as the substance is flammable, there must be no open flames, no sparks and no smoking during a TGT using decane-D_{22} as tracer. Above 46°C explosive vapor/air mixtures may be formed; thus, temperatures must be kept below this limit.

Regarding criterion 5, an ampule containing 5 g of decane-D_{22} is sold by Sigma-Aldrich® for €491.00. Considering that the intended emission rate of the tracer source is in the magnitude of 1 mg h^{-1}, a 5 g ampule should provide enough tracer for more than 6 months of continuous emission. Therefore, for the purposes of the present paper, it is considered that decane-D_{22} meets criterion 5 as well.

Source designing

In practice, the application of a TGT requires the placement of a source (or several sources) that injects the tracer gas in the air of the assessed space and a sampler (or several samplers) that monitors the concentration of the tracer gas. As explained above, the type of sampler to be employed in the new proposed TGT was pre-determined: commercial adsorptive samplers for passive long-term sampling. Given this project's focus on simplicity and inexpensiveness, it was decided that the employed source should also be passive and based on the constant emission approach (Persily and Levin, 2011). In this approach, the source emits tracer gas at a constant rate until the room concentration reaches a steady state (assuming a constant ACH), from which the total ACH can be inferred using Equation 1.

$$q = \frac{G}{VC_S} \tag{1}$$

where q is the ACH (h^{-1}), G is the source emission rate (μg h^{-1}), V is the total volume of the assessed space (m^3) and C_s is the steady-state tracer concentration (μg m^{-3}). (If q is not constant, the final concentration measured by the passive sampler will not be C_s, but rather the average concentration over the sampling period. Thus, Equation 1 is still

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valid, but in that case the calculated *q* represents the average ACH over the total period).

Several options were tested in pursuit of the most adequate source design, i.e. one that allows a stable, repeatable and significant tracer emission rate using a small amount of liquid solvent. Figure 1 shows the different types of source design that were considered at the beginning of the testing process.

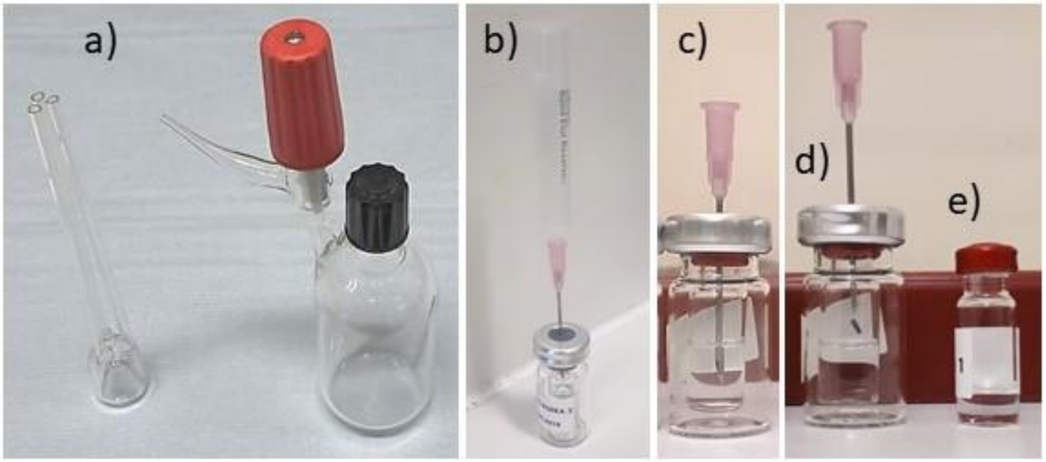

Figure 1 Different source designs that have been tested: a) Larger glass flasks, b) source design based on Shinohara et al. (2010), c) adapted from Shinohara et al. (2010), with submerged needle tip, d) adapted from Shinohara et al. (2010), with the needle tip in headspace, and e) original design.

The two designs shown in Figure 1a were discarded early on because they would require a relatively high volume of liquid decane-D_{22} compared to the other designs. The design shown in Figure 1b (design B) is based on the source used in a previous study by Shinohara et al. (2010), which consists of a 1 ml glass vial filled with the tracer in liquid state and placed inside a 5 ml glass vial, both capped with metal caps. The tracer emission is initiated by piercing a needle (0.4 mm diameter, 20 mm length) through both caps to reach the headspace of the smaller vial. The needle is then attached to a plastic syringe (9mm diameter and 7.5 cm length), which acts as the tracer diffusion path, where a polyethylene (PE) sintered filter disk is placed to help maintain the emission rate. This design (originally intended for PFTs emission) yielded too low decane-D_{22} emission rates. A few adaptations were then made to that design aiming to increase the emission rate. In the designs shown in Figure 1c and 1d (designs C and D, respectively), the use of the syringe and PE filter was discarded, and the needle size was increased (1.2 mm diameter, 40 mm length). In design C, the needle tip was submerged in the liquid tracer, but test results indicated lack of repeatability between sources (>50% std. error, n = 8). The design shown in Figure 1e (design E) consists of one single 1ml vial filled with ~0.5 ml of decane-D_{22} capped with a metal cap, with the rubber stop substituted by a PE disk.

To compare the different source designs emission rates, repeatability and leakage rates, gravimetry tests were executed using a micro-balance (accuracy: 0.01 mg). A climate chamber of 117 dm^3 (Figure 2), made of stainless steel, was employed to control T, RH and ACH in which the sources were kept in between the weighing moments.

In each gravimetric test, several replicate sources (a number varying from 4 to 12 simultaneous sources, depending on the tracer availability at each test) were kept in specified T, RH and ACH conditions inside the chamber for a period of 5 up to 10 days, depending on the test. The replicates are weighed in intervals of 24 to 72h to observe the stability of their emission rates. The average weight loss of the replicates was then plotted against time, and the average emission rate of the sources in each test is equal to the slope obtained by linear regression.

RESULTS AND DISCUSSION

Figures 3 and 4 show the average weight losses of the decane-D_{22} source replicates over time for source designs

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D and E, respectively. In each figure, results for two different tests are shown, one under 25% RH and the other under 75% RH. Moreover, both figures include the results of a leakage test for each type of source design.

Figure 2 Climate chamber used for source design testing.

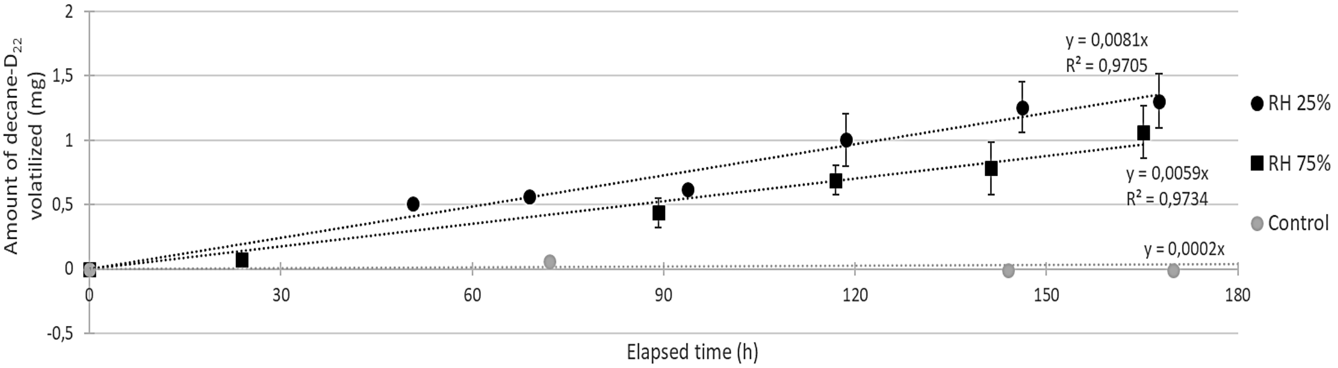

Figure 3 Results from two gravimetry tests comparing the average weight loss of the design D sources over time under 25% and 75% RH (both under constant T = 23°C, n = 6).

Figure 3 shows that the weight loss of an unpierced source is insignificant over more than 10 days (last weighing result not shown), thus leakage of design D is negligible. Both tests showed a good linearity in the average measurements, indicating that Design D can keep a stable emission rate under different RH conditions. However, observing the linear regression slopes, the emission rate under drier conditions is slightly higher than under more humid conditions (decrease from ~8 to ~6 μg h^{-1}, corresponding to a relative difference of 27%), which indicates that the effect of RH over design D's emission rate cannot be neglected. The average repeatability error among the replicate sources was 11% for 25% RH and 25% for the 75% RH.

Similarly to what was observed with design D, results shown in Figure 4 indicate that leakage from a design E control source (i.e. source capped with a rubber stopper instead of a PE filter disk) is negligible for over 10 days (last weighing result not shown). Regarding the replicate sources participating in the emission tests, design E provided average emission rates two orders of magnitude higher than design D. Higher emission rates are desirable in order to ensure that the steady state tracer concentration during a TGT will be above the detection limit provided by the passive samplers. Linearity in both tests is almost perfect, indicating a high stability in the emission rates provided by design E

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sources. Moreover, the effect of varying RH over design E's emission rate can be considered insignificant (decrease from ~379 µg h^{-1} under 25% RH to ~371 µg h^{-1} under 75% RH, corresponding to a relative difference of only 2%). The average repeatability error among the replicate sources was 3% for the test under 25% RH and 4% for the test under 75% RH. Therefore, based on the higher emission rate value, stability and repeatability, design E has been selected as the most suitable design source of decane-D_{22} for the proposed TGT.

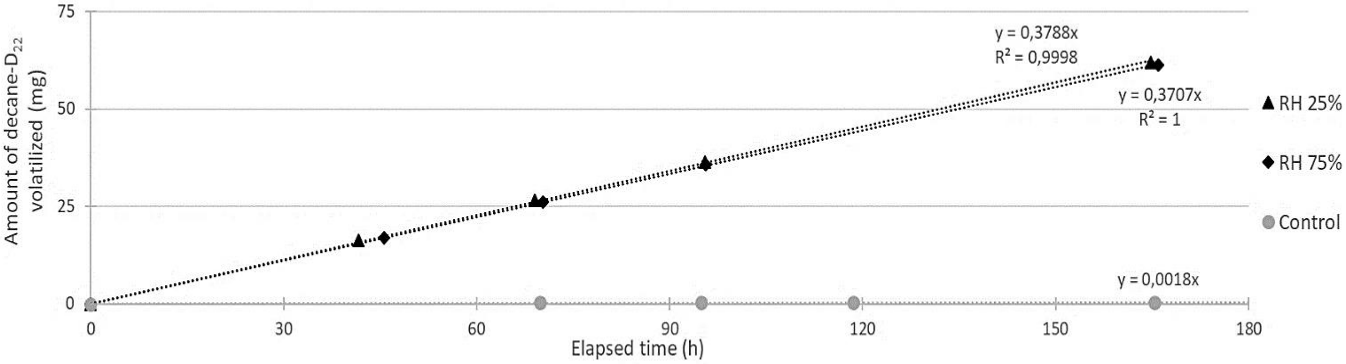

Figure 4 Results from two gravimetry tests comparing the average weight loss of the design E sources over time under 25% and 75% RH (both under constant T = 23°C, n = 6).

Once the source design was selected, the next set of tests were intended to observe the effect of T over the source emission rates. Differently from RH, it is expected that T will have a significant impact on the tracer volatility, since it is known that the vapor pressure of a compound increases with increasing T, especially for VOCs. Figure 5 shows the graph of the emission rates achieved by the sources as a function of the temperature. As expected, the relationship is an exponential function, thus the exponential regression equation fit to the obtained data can be used to determine the emission rate from the average ambient temperature.

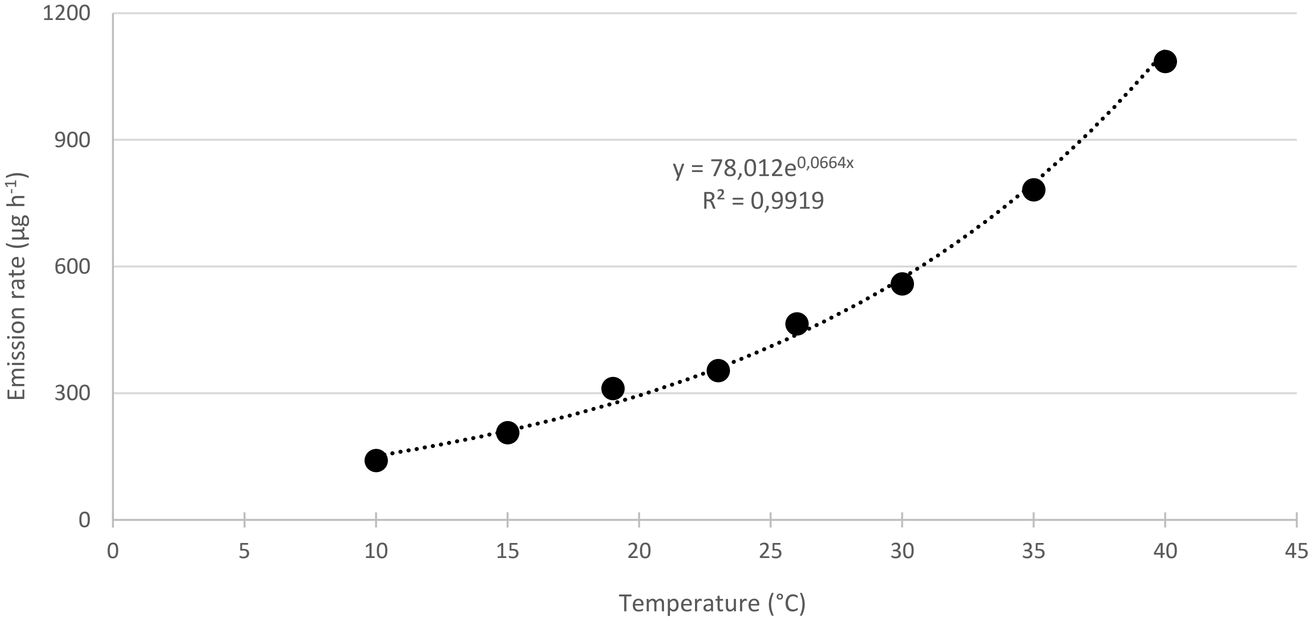

Figure 5 Source emission rate as a function of room temperature. The regression equation and linearity are also presented.

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CONCLUSION

This paper describes an ongoing project dealing with the development of a new TGT, with the motivation of providing an ACH measurement method as simple, practical and accurate as possible. The ultimate goal is to provide an easy-to-use method that will encourage IAQ researchers to include ventilation assessments in their IAQ studies. This new TGT focuses on tackling 3 major issues commonly related to TGT applications: differing timescale between ACH and IAQ data, inadequate substances used as tracers and perfect-mixing-assumption bias. The present paper deals specifically with the efforts made to address the first two shortcomings. Via extensive literature review, decane-D_{22} was chosen as a suitable alternative tracer gas. Several gravimetry experiments, using a climate chamber to control T, RH and ACH, were executed to test a few different options of source design. The option that provided a higher and more stable emission rate with best repeatability and lower susceptibility to varying RH was chosen. The source emission rate was quantified under various T conditions, and a prediction curve for emission rates based on average room T was derived. Future work will include the application of the new TGT to controlled field tests and computer simulated TGTs to study the role of sources and samplers physical positioning in the accuracy of TGT results.

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NOMENCLATURE

ACH = Air change rate (h^{-1})
IAQ = Indoor air quality
PFTs = Perfluorocarbon tracers
RH = Relative humidity (%)
SF_6 = Sulfur hexafluoride
T = Temperature (°C)
TGT = Tracer gas test
VOCs = Volatile organic compounds

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