



Diffusive sampling of 25 volatile organic compounds in indoor air: Uptake rate determination and application in Flemish homes for the elderly

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ABSTRACT

Passive sampling of volatile organic compounds (VOCs) in air has received increasing attention in recent years. However, in order to use passive sampling as a reliable sampling technique a compound and sampler specific uptake rate is needed. Therefore, the scope of our study was threefold. First, uptake rates for 25 VOCs were determined under real indoor and outdoor conditions using axial-sampling tube-type samplers filled with Tenax TA, and active (pumped) sampling as a reference technique. Secondly, the mechanisms of passive sampling were investigated by comparing the experimentally determined uptake rates ($0.13\text{--}0.46\text{ ml min}^{-1}$) to the ideal uptake rates, calculated based on Fick's first law of diffusion and sampler geometry. Sampling efficiency SE, defined as the ratio between the experimental and ideal uptake rate, was introduced as a correction factor and showed that ideal uptake rates may underestimate VOC concentrations by a factor up to 4. This compound dependent SE is explained in terms of the partitioning coefficient K , i.e. the compound's Tenax TA to air concentration equilibrium ratio. Compounds with a low K -value showed the most pronounced non-ideal sorptive behavior. Third, the experimentally determined uptake rates were used to determine VOC concentrations (between 12 and $311\text{ }\mu\text{g m}^{-3}$) in 6 homes for the elderly in Antwerp (Belgium). This study provides unique data for indoor air quality at care centers in Flanders.

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1. Introduction

Indoor air quality has received increasing attention mainly because it has been estimated that people spend more than 90% of their time indoors (Jia et al., 2008). Volatile organic compounds (VOCs) represent an important group of indoor air pollutants as their concentration levels are frequently elevated indoors (Edwards et al., 2001a, 2001b; Parra et al., 2008). Emission from building materials (Brown et al., 1994; Horemans et al., 2008), cigarette smoke (Kuusimäki et al., 2006), cars (Batterman et al., 2006; Gallego et al., 2008), home renovations (Herbarth and Matysik, 2010), indoor activities such as cooking (Viegi et al., 2004), and inadequate ventilation (Chan et al., 2009) are well-known contributors to the indoor air quality. Exposure to high VOC concentrations is related to negative health effects and the sick building syndrome (SBS) (Sakai et al., 2004). From all VOCs, benzene, toluene, ethylbenzene, and xylenes (BTEX) are most often monitored (Zalé et al., 2008; Buczynska et al.,

2009), most probably because of their toxicity, their ubiquity in indoor and outdoor air and their easiness to monitor (Skov et al., 2001). The annual average ambient benzene concentration is regulated by the EU directive 2000/69/EC to $5\text{ }\mu\text{g m}^{-3}$ (Legislation, 2000). However, guideline values for indoor air quality exist only for a few countries or regions: Germany, Norway, Flanders (Belgium), China and Canada (Stranger et al., 2007). For Flanders guideline values exist for six individual organic compounds, being acetaldehyde ($\leq 4600\text{ }\mu\text{g m}^{-3}$), benzene ($\leq 2\text{ }\mu\text{g m}^{-3}$), formaldehyde ($\leq 10\text{ }\mu\text{g m}^{-3}$), tetrachloroethylene ($\leq 100\text{ }\mu\text{g m}^{-3}$), toluene ($\leq 260\text{ }\mu\text{g m}^{-3}$), trichloroethylene ($\leq 200\text{ }\mu\text{g m}^{-3}$) and two groups of compounds, i.e. TVOCs ($\leq 200\text{ }\mu\text{g m}^{-3}$) and total aldehydes ($\leq 20\text{ }\mu\text{g m}^{-3}$, without acetaldehyde) (Binnenmilieubesluit, 2004). It has to be noted that the Flemish guidelines do not specify the measuring time and a definition of TVOC concentration.

In order to sample trace concentrations of airborne VOCs, two main sorbent enrichment techniques are used: active (Demeestere et al., 2007) and passive (or diffusive) sampling (Batterman et al., 2002; Martin et al., 2003; Strandberg et al., 2005; Bruno et al., 2008). Passive sampling does not make use of pumps but is based on the analyte's molecular diffusion, which can be described by Fick's first law.

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$$m = D \cdot A/L \cdot (C - C_0) \cdot t \quad (1)$$

The mass m collected on a passive sampler after a certain exposure time t is equal to the product of a compound specific diffusion coefficient D ($\text{cm}^2 \text{s}^{-1}$), a geometry factor GF ($GF = A/L$, with A : cross sectional area (cm^2); L : length of the stationary air layer (cm)), and a driving force being the concentration gradient in the stationary air layer between the air to be sampled (concentration C) and the primary air layer above the sorbent (concentration C_0). In the theoretical case of an ideal sorbent (acting like a perfect sink), the concentration C_0 can be assumed to be 0 and can be eliminated from Equation (1). The time weighed average concentration C (TWA) is then calculated from the ideal uptake rate UTR_{ideal} ($D \cdot A/L$), the exposure time t and the sorbed mass m . However, the assumption $C_0 = 0$ might not hold for relatively weak sorbents, like e.g. Tenax TA that is commonly used in passive tube-type axial-sampling devices designed for thermal desorption (Krol et al., 2010; Zabiegala et al., 2010). Consequently, the use of UTR_{ideal} for VOCs quantification may lead to underestimations. Therefore, there is a need for real uptake rates applicable for VOCs monitoring at indoor air conditions. Literature data, however, are scarce (Markes, 2006) and most often, if passive sampling is used, it is not clearly reported if TWA concentrations are calculated from theoretical or experimental uptake rates, and at which conditions the latter have been determined.

Laboratory experiments conducted in the study of Walgraeve et al. (2011), Roche et al. (1999) and Oury et al. (2006) indicated that considering the uptake rate as one single numerical value to be used in all conditions may lead to important errors, particularly for compounds that have a rather low affinity for the sorbent. Although new insights were gained from these laboratory studies, it is not fully understood yet how passive samplers behave in real environmental conditions and to what extent experimental uptake rates determined under controlled and constant laboratory conditions are valid in complex multi-compound environments (Brown et al., 1992, 1993; Brown, 1999; Langlois, 2008; Martin et al., 2010). At least two points of attention should be considered. First, when measuring in real environments fluctuations in concentrations are likely, and back diffusion of the compounds may occur whenever the concentration in the primary air layer C_0 is higher than the concentration C in the air to be sampled. As a result, using lab-scale uptake rates may result into an underestimation of the concentration. Second, in real environments several hundreds of VOCs are present, which could have an effect on the uptake rate behavior of other compounds. Some authors have studied the performance in real environments in a qualitative way, i.e. without the determination of the real uptake rate (Brown et al., 1992; Bradshaw and Ballantine, 1995; Tolnai et al., 2001) or in a quantitative way (Ballach et al., 1999; Wideqvist et al., 2003; Andrietta et al., 2010) for a limited set of compounds, mostly focusing on BTEX-compounds.

Given these considerations, the scope of this work is threefold. First, real environmental uptake rates for a wider set of 25 VOCs belonging to different chemical classes were determined for prolonged exposure times at both indoor and outdoor locations in (sub)urban regions in Flanders. Active sampling was used as a reference technique to determine ambient VOC concentrations. Secondly, the mechanisms of passive sampling were investigated by comparing the experimental uptake rates with the ideal one, and by explaining deviations between them in terms of relevant physical–chemical properties. Third, the experimentally determined uptake rates were used to quantify VOCs concentrations in homes for the elderly located in the province of Antwerp, Belgium. As far as we know, there are no data available on VOC concentrations in this type of indoor environment.

2. Experimental

2.1. Chemicals

A set of 64 LC–MS grade VOCs, purchased at Acros Organics (Geel, Belgium) or at Sigma–Aldrich (Bornem, Belgium) and all having a purity of at least 99.8%, were used as standard compounds. Several classes of VOCs representing a relevant set of indoor air pollutants were included. These compounds involve (i) alkanes (cyclohexane; n-decane; n-dodecane, n-heptane, n-hexane, methylcyclopentane; n-nonane; n-octane, n-undecane), (ii) aromatic hydrocarbons (1,2,4-trichlorobenzene; 1,2,4-trimethylbenzene; 1-bromo-4-fluorobenzene; benzaldehyde; benzene; benzylchloride; benzonitrile; chlorobenzene; ethylbenzene; methyl benzoate; phenol; propylbenzene; styrene; toluene; xylenes (o, m, p)), (iii) oxygen-containing hydrocarbons (1,3-dioxolane; 1-butanol; 1-hexanol; 1-octanol; 1-pentanol; 1-phenylethanone; 2-ethyl-1-hexanol; 2-heptanone; 2-hexanone; 2-methyl-1-butanol; 2-methyl-1-butanol; 2-octanone; 3-methyl-1-butanol; 3-methyl-1-butanol; 5-nonanone; ethyl acetate; hexanal; ethyl propionate; heptanal; methyl acrylate; methylmetacrylate; propyl acetate; tetrahydrofuran), (iv) chlorinated hydrocarbons (1,1,1,2-tetrachloroethane; 1,1,2-trichloroethane; 1,2-dichloroethane; 1,2-dichloropropane; tetrachloroethene; trichloroethene), (v) terpenes (1-methyl-4-prop-1-en-2-yl-cyclohexene (limonene); 3,7-dimethylocta-1,6-dien-3-ol (linalool); alpha-pinene), and (vi) compounds that could not be attributed to the previous groups (dimethyl disulphide; hexamethyldisiloxane; thiophene; triethylamine; trimethoxymethylsilane; tripropylamine).

[$^2\text{H}_8$]Toluene (Tol-d8; 99.5 + atom%D; Acros Organics, Geel, Belgium) was used as an internal standard. Methanol (LC–MS grade, 99.95%, Biosolve, Valkenswaard, The Netherlands) served as a solvent for all standard compounds. Clean and dry nitrogen and helium gases ($[\text{H}_2\text{O}] < 3.0$ ppmv; $[\text{O}_2] < 2.0$ ppmv; $[\text{C}_x\text{H}_y] < 0.5$ ppmv) were provided by Air Liquide (Luik, Belgium).

2.2. Sampling and sample preparation

Six measuring campaigns were conducted between 2007 and 2009 at homes for the elderly located in the Antwerp city center (S1, June 2007) and at several sub-urban cities: Broechem (S2, February 2008; S6, October 2009), Borsbeek (S3, September 2008), Hove (S4, February 2009) and Bonheiden (S5, June 2009). At each home for the elderly, 4 resident's rooms, a recreational room and the garden were sampled passively (at least 2 passive samples + 1 blank) during 6–9 days using Markes stainless steel sorbent tubes (3.5 inch long, 0.25 inch O.D., 4 mm I.D.) filled with 200 mg Tenax TA (35/60 mesh) (Markes, Llantrisant, United Kingdom). At the sampling side, passive samplers were equipped with aluminum diffusion caps (Markes, Llantrisant, UK) to minimize the effect of air movement (resulting in a stationary air gap of 1.5 cm). Blank samples were closed at both ends with 0.25 inch brass long term storage caps, and served as a control. In order to determine VOC uptake rates, valid at the sampling sites, active and passive sampling was performed simultaneously in the recreational rooms of the homes for the elderly (S3–S6) and at a sub-urban outdoor location (S7). Therefore, a MTS-32 multiple tube field sampler (Markes, Llantrisant, UK) equipped with a GilAir3 (Sensidyne, FL, USA) pump was used and allowed for unattended multiple consecutive active samples to be collected via a timing mechanism (4–5 h per sample). The pump was calibrated before and after the sampling campaign (relative standard deviations less than 4%) by a liquid film meter and the average flow was used for calculations ($9\text{--}11 \text{ ml min}^{-1}$ depending on the sampling campaign). The same type of sorbent tubes were used as in passive sampling, but in the field sampler they were closed with an inert difflock cap (Markes)

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