Development and field validation of a new diffusive sampler for determination of atmospheric volatile organic compounds

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HIGHLIGHTS

- A new diffusive sampler was developed for determination of VOCs.
- A comprehensive validation study was carried out under field conditions.
- Uptake rates were evaluated together with the meteorological parameters.
- The results of the validation study were satisfactory.
- The diffusive sampler is reliable and applicable for atmospheric VOC sampling.

ARTICLE INFO

ABSTRACT

A tailor-made diffusive sampler was developed for the determination of atmospheric Volatile Organic Compounds (VOCs) and the validation of the sampler was carried out under field conditions. All parts of the diffusive sampler which are reusable after a proper cleaning process were made of plastic material (delrin). The reusability of the sampler brings an important advantage considering its lower cost. Activated carbon was used as adsorbent and VOCs adsorbed on the activated carbon were analyzed by GC—MS (gas chromatography equipped with mass selective detector). A comprehensive validation study including detection limit, precision, bias, recovery, self-consistency, shelf life, storage stability, reusability was carried out in accordance with the related European standards ((EN) 13528-1 (2000) and 13528-2 (2000)). Also, a comparison was performed with some commercial diffusive samplers such as 3 M OVM 3500 and Radiello to test the performance of the new diffusive sampler in different environments such as urban area and road tunnel. Uptake rates for the measured VOCs were determined and they were evaluated together with the meteorological parameters (temperature, humidity, wind speed). According to the validation results; all the parameters evaluated for the sampler comply with the related standards and this is an indication of the reliability of the sampler for the sampling of VOCs in the atmosphere.

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1. Introduction

Volatile organic compounds (VOCs) are among important air pollutants since they can cause short and long-term adverse health effects. Volatile organic compounds emitted from certain anthropogenic and natural sources play an important role in the tropospheric ozone formation. Major sources of VOCs include emissions from petrochemical industries and petroleum refineries in the urban atmospheres. Motor vehicle exhausts, petroleum storage and distribution, solvent use in the industrial processes are also among the important VOC sources (Sawyer et al., 2000; Lanz et al., 2008; Kansal, 2009).

Monitoring of these compounds is essential for several reasons. Most of the VOCs are toxic and carcinogenic and they pose human health risk (Guo et al., 2003; Murray et al., 2007; Wu et al., 2012). Determination of their sources is essential to mitigate risks by controlling their emissions. In some cases, spatial distribution of those VOCs needs to be determined for risk management purposes.

Active and diffusive sampling methods are widely used for the collection and determination of VOCs from indoor and outdoor environments. Both types of methods have their own advantages and disadvantages. For instance, in the case of active samplers, air needs to be drawn with a certain flow rate by a pump which should

be calibrated and checked frequently. Most of the active sampling studies are performed based on sorbent adsorption or by using canisters followed by thermal desorption (TD) preconcentration and analysis by gas chromatography equipped with a mass selective detector (GC–MS) or flame ionization detector (GC-FID) (Koga et al., 2001; Fernandez-Villarrenaga et al., 2004; Kuntasal et al., 2005; Volden et al., 2005; Murena, 2007; Ras et al., 2010; Civan et al., 2012; Yurdakul et al., 2013). Due to their cost, it is not practical to carry out multiple measurements in a certain geographical area by active samplers. In that case, diffusive samplers which are cheap, light, easy to use, do not involve complex operations and do not require electricity to operate can be deployed at many points to collect VOC data with high spatial resolution. In diffusive sampling, the sampling rate is controlled by molecular diffusion process. The concentration of the pollutant is calculated by using Fick's first law (Gorecki and Namiesnik, 2002). According to the Fick's first law, the quantity of the pollutant collected in the sampler is determined by several parameters such as ambient air concentration, diffusion coefficient, dimensions of the sampler and sampling time. Ambient air concentrations are calculated from the quantity of the pollutant collected in the sampler by using the following formula:

$$C = (Q \times z)/(A \times t \times D) \qquad (1)$$

where, C represents the ambient air pollutant concentration measured by the diffusive sampler ($\mu g \ m^{-3}$), Q is the quantity of the pollutant captured in the sampler (μg) and z, A, t and D denote the diffusion length (m), cross-sectional area (m^2), sampling time (s) and diffusion coefficient ($m^2 \ s^{-1}$), respectively.

In most of the diffusive samplers designed for VOCs, activated carbon was used as a collecting medium and adsorbed pollutants were desorbed by carbon disulfide (CS_2) extraction before gas chromatographic analysis (Begerow et al., 1999; Mukarjee et al., 2004; Yamada et al., 2004; Pilidis et al., 2005; Chung et al., 2009; Wu et al., 2012). Sorbents such as Tenax TA, Carbograph 4, Chromosorb 106 were also used as collecting medium and pollutants were thermally desorbed prior to analyses (Brown and Crump, 1998; Bruno et al., 2005; Pekey and Yılmaz, 2011; Walgraeve et al., 2011; Civan et al., 2012). The analyses of the diffusive samples for VOCs were based on well-established methods using GC–MS and GC-FID.

In Turkey, VOCs are not continuously measured within the national ambient air monitoring network. Inexpensive, simple and reliable methods are urgently needed for the expansion of the monitoring network. In this case, diffusive samplers gain much more importance in the large scale monitoring of VOCs since they have many advantages, mentioned above, compared to active samplers. Commercial diffusive samplers have been used in several research projects for measurement and monitoring of ambient VOC concentrations in Turkey (Pekey and Yılmaz, 2011; Civan et al., 2012; Yurdakul et al., 2013).

In this study, a new tailor-made diffusive sampler was developed and validated for the determination of atmospheric VOCs. The sampler has been named "Anadolu diffusive sampler" and this name was used in this manuscript. The results of the extensive field validation of the sampler were presented. All the parameters included in the validation were investigated in accordance with the European Standards (EN) 13528-1 (2000) and 13528-2 (2000) under field conditions and the performance of the new sampler was evaluated for the monitoring of atmospheric VOCs. As it will be explained later in the manuscript, Anadolu diffusive sampler has reusable parts which reduce its cost. Most parts of the sampler can be used many times after a proper cleaning process. This property brings an important advantage for the sampler. The cost of the commercial diffusive samplers (excluding analysis price) is much

higher than the Anadolu diffusive sampler.

2. Experimental section

2.1. Description and preparation of the diffusive samplers and active samplers used in the validation studies

Anadolu diffusive sampler (new developed tailor-made diffusive sampler): After field validation studies were completed and successful results were obtained, the developed diffusive sampler was registered as Utility Model by Turkish Patent Institute and named as "Anadolu diffusive sampler" by our group. Anadolu diffusive sampler and its main parts are made from plastic (Delrin) material. Glass was not preferred due to its fragile structure. The sampler has 2.5 cm length and 2.0 cm inner diameter. The diffusion path length and sampling cross-sectional area of the sampler are 2.5 cm and 3.14 cm^2, respectively. The schematic diagram of the sampler is shown in Fig. 1a. The parts of the diffusive sampler are (Fig. 1b); (1) sampler body, (2) stainless steel mesh barrier, (3) closed cap, (4) pressed glass wool, (5) fixer ring, and (6) activated carbon.

Granular activated carbon (18–35 mesh) supplied by Merck (Darmstadt, Germany) was used as adsorbent. 200 ± 1 mg activated carbon was weighed in a clean environment and placed at the bottom of the sampler. Then, pressed glass wool was fixed on the activated carbon with a plastic ring to avoid the spilling over of the activated carbon during transportation and sampling. The inlet end was closed with a plastic cap. During the sampling period, to minimize turbulence effect of wind inside the sampler, a stainless steel mesh barrier was placed at the open end, and the barrier was replaced with a closed cap during the transportation of the sampler.

Commercial diffusive samplers: Different brands of diffusive samplers (3 M OVM 3500 and Radiello) were used for comparison purpose. During the validation studies, commercial diffusive samplers and Anadolu diffusive sampler were deployed together for performance evaluation.

3 M OVM 3500 diffusive sampler (by 3 M, Neuss, Germany) is an axial batch-type diffusive sampler consisting of a permeable membrane and an activated charcoal pad (180 mg) assembled in a disk-shaped plastic holder. The cross sectional area of the sampler is 7.07 cm^2 and the diffusion length is approximately 1.0 cm.

Radiello diffusive sampler (Fondazione Salvatore Maugeri, Padova, Italy) is a radial sampler that consists of an adsorbent cartridge inserted in a micro porous polyethylene membrane and filled with 530 ± 30 mg of 35–50 mesh activated carbons. The length of micro porous diffusive membrane is 60 mm, the diameter is 16 mm and the pore size is 25 μm.

Active air samplers: Anadolu diffusive samplers were exposed parallel to active sampling to determine the bias for the samplers and also to calculate the uptake rates for VOCs during validation experiments. Active sampling was performed according to ASTM D 3686–08 reference method (Standard Practice for Sampling Atmospheres to Collect Organic Compound Vapors, Activated Charcoal Tube Adsorption Method) (ASTM, 2007a). Active air samples were collected using SKC activated charcoal tubes (SKC, PA, USA) which are mainly composed of two parts with 100 and 50 mg coconut shell based activated charcoal loadings. SKC tubes were connected to an SKC AirChek 2000 pump (SKC, PA, USA) and the air flow rate was adjusted to 25 ml min^{-1}. The flow rate of the pump was controlled by a Bios Defender 510 calibrator with DryCal® Technology (Bios International, NJ, USA) (flow range of 5–500 mL min^{-1}) at the beginning and at the end of each sampling period and recorded in the datasheets. For all the samples, ± 5% change in flow rate, which is allowed in ASTM method, was not exceeded during the validation study.