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Impact of formaldehyde and VOCs from waste treatment plants upon the ambient air nearby an urban area (Spain)

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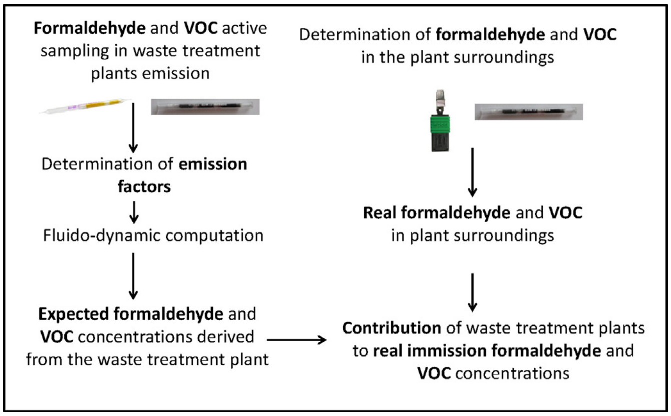
HIGHLIGHTS

- Emission factors of formaldehyde and VOCs were determined for waste treatment plants.
- Formaldehyde and VOC were sampled using DNPH-coated and multi-sorbent tubes.
- Formaldehyde emission factors from biogas engines were between 0.001–0.04 g s$^{-1.}$
- The contribution of waste treatment plants to formaldehyde immission was around 2%.
- The contribution of waste treatment plants to VOC immission was around 0.3 ± 0.9%.

GRAPHICAL ABSTRACT



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ABSTRACT

Emission factors of formaldehyde and VOCs were determined for two waste treatment plants (WTP) located in the metropolitan area of Barcelona city. Formaldehyde emission factors were determined from the biogas engines exhausts and the process chimneys (after the biofilter process), and VOC emission factors were determined in the process chimneys. Formaldehyde and VOC were dynamically sampled using DNPH-coated adsorbent tubes with ozone scrubber and multi-sorbent bed tubes (Carbotrap, Carbopack X and Carboxen 569), respectively, using portable pump equipment. Formaldehyde emission factors from biogas engines were found between 0.001–0.04 g s^{-1}. Additionally, formaldehyde and VOC emission factors from process chimneys were found to be between 0.0002–0.003 g s^{-1} and 0.9 ± 0.3 g s^{-1}, respectively. Employing real emission factors, the expected concentrations derived from the WTPs in their nearby urban areas were calculated using The Atmospheric Pollution Model (TAPM, CSIRO), and impact maps were generated. On the other hand, ambient air formaldehyde and VOC concentrations were determined in selected locations close to the evaluated waste treatment facilities using both active and passive samplers, and were between 2.5 ± 0.4–5.9 ± 1.0 μg m-3 and 91 ± 48–242 ± 121 μg m-3, respectively. The concentrations of formaldehyde and VOC derived exclusively from the waste treatment plants were around 2% and 0.3 ± 0.9% of the total formaldehyde and VOC concentrations found in ambient air, respectively.

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1. Introduction

Waste Treatment Plants (WTP) can be a source of pollution to the environment and affect negatively human health (Bono et al., 2010; Vilavert et al., 2014) and deteriorate personal well-being (Ryu et al., 2011). Formaldehyde and volatile organic compounds (VOC) are among the most important pollutants emitted by WTP. VOC are generated in WTP from biochemical reactions related to degradation processes of organic matter and/or volatilization of different materials treated in the plant (Gallego et al., 2012; Kumar et al., 2011), and are responsible in great part of the odorous nuisance derived from these facilities (Font et al., 2011; Gallego et al., 2009a, 2014; Vilavert et al., 2014). On the other hand, formaldehyde can be evaporated from products managed in the plant and also be emitted by biogas combustion engines due to intermediate reactions, where it is formed by an incomplete reaction of the gas mixture (Heikkilä, 2014; Naegele et al., 2013). It has to be taken into account that between 200–300 VOCs can be found in urban air samples (Gallego et al., 2011; Vega et al., 2011) and that formaldehyde is an ubiquitous irritant contaminant in ambient air (Bono et al., 2010; Kim et al., 2011; Salthammer, 2013). Additionally, formaldehyde has been classified as 1B category carcinogen and 2 category mutagen by 605/2014 European Union Commission Regulation, amending Regulation (EC) 1272/2008, and also been classified as Category 1 carcinogen by IARC. This compound is emitted by WTP but can also be emitted to the atmosphere from incomplete combustion of fossil fuels, production of resins and other chemical compounds, and the use of disinfectants and preservatives (Bono et al., 2010; Zhang et al., 2009).

Generally, industrial emission values are estimated, real measurements being only determined in a few cases. Hence, the absence of emission data restricts the real evaluation of the impact of specific emission sources (Yu et al., 2014). In this line, the present paper describes the evaluation of formaldehyde and VOC impacts (derived from channelled emissions) in the surroundings of two WTPs (also known as Ecoparcs in Spain), determining their real emission factors and calculating the impact maps that showed WTPs derived concentrations. This point aimed to improve the knowledge of the sources and distribution of pollutants originating from WTPs. Furthermore, real VOC and formaldehyde concentrations were monitored in WTPs surroundings. Real concentrations were compared to expected concentrations exclusively originated from WTPs. Additionally, formaldehyde concentrations were also determined in several locations from Barcelona city, in order to determine the typical concentrations that can be found in a 3 million people metropolitan urban area affected by an important traffic density, several industries and a harbour with a total traffic of 47 million tons (2015).

The simplicity, high sampling versatility, high concentration power, easy portability, low cost and easy storage of sorbent tubes (Gallego et al., 2009b; Ribes et al., 2007) led us to adopt a sorbent-based method for sampling VOCs in the process chimneys (which emit the air coming from the biofilters) and for ambient air samplings. Thermal Desorption (TD), coupled with Gas Chromatography/Mass Spectrometry (GC/MS), was the chosen instrumental technique. TD-GC/MS methodology has been widely used in VOC analysis (Gallego et al., 2009a, 2012). It is a selective methodology which allows good chromatographic separation, identification and quantification of target analytes through their characteristic mass spectrum and quantification ion, respectively (Ribes et al., 2007). Formaldehyde emission, both from biogas engines and process chimneys, and immission concentrations were determined using the 2,4-dinitrophenylhydrazine methodology, and analysed using HPLC.

2. Materials and methods

2.1. Chemicals and materials

Standards of VOCs with a purity ≥98% were obtained from Aldrich (Milwaukee, WI, USA), Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). Methanol and toluene for gas chromatography (SupraSolv®) with a purity ≥99.8%, and acetonitrile for liquid chromatography (LiChrosolv®) with a purity ≥99.9% were obtained from Merck (Darmstadt, Germany). Methanol HPLC gradient grade was obtained from J.T. Baker (Deventer, The Netherlands). Perkin Elmer glass tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanized wool, and Carbotrap (20/40 mesh), Carbopack X (40/60 mesh) and Carboxen 569 (20/45 mesh) adsorbents were purchased from Supelco (Bellefonte, PA, USA). Formaldehyde-2,4-dinitrophenylhidrazone analytical standard was obtained from Aldrich (Steinheim, Germany).

2.2. Formaldehyde samplers

Formaldehyde samplers, both active and passive, were based on the 2,4-dinitrophenylhydrazine (DNPH) methodology (Szulejko and Kim, 2015). For passive formaldehyde samples, Radiello chemiadsorbing cartridge code 165 tubes (Fondazione Salvatore Maugeri, Pavia, Italy) and UME^{x} 100 passive samplers were obtained from Supelco (Bellefonte, PA, USA) and SKC (Eighty Four, PA, USA), respectively. For active formaldehyde sampling, Supleco BPE-DNPH cartridges (54278-U) and DNPH-coated adsorbent tubes (226–120) with built-in ozone scrubber were obtained from Supelco (Bellefonte, PA, USA) and SKC (Eighty Four, PA, USA), respectively.

2.3. Formaldehyde analytical instrumentation

Active and passive formaldehyde samples, based on the 2,4-dinitrophenylhydrazine (DNPH) methodology, were treated equal, extracting formaldehyde-2,4-dinitrophenylhydrazone with 2–3 ml of acetonitrile, stirring occasionally during 30 min. The extracts were analysed with HPLC, using a Waters 1525 binary pump, 717 plus autosampler and a 2998 Photo Diode Array Detector at 365 nm. The isocratic elution was done using methanol/water at 65/35 (v/v) at 1 ml min^{-1}. The column used was a Phenomenex C18, 150 mm length, 4.6 mm diameter and 5 μm particle size. The limit of detection was established at <0.1 μg/sample.

2.4. VOC sampling tubes

The multi-sorbent bed tubes were custom packed and composed of Carbotrap (activated graphitized black carbon, weak sorption strength, target analytes: C_5-C_{14} (alcohols, aldehydes, ketones, aromatic hydrocarbons), boiling points > 75 °C, 70 mg), Carbopack X (activated graphitized black carbon, medium sorption strength, target analytes: C_3-C_7 (light hydrocarbons, boiling points between 50–150 °C), 100 mg) and Carboxen 569 (spherical carbon molecular sieve, high sorption strength, target analytes: C_2-C_8 (ultra-volatile hydrocarbons, boiling points between −30 and 150 °C), 90 mg). They were developed in an earlier study and found to be highly versatile regarding polarity and volatility of the target VOCs (Ribes et al., 2007). They have been successfully used for the determination of a wide range of VOC families in different applications (Gallego et al., 2009a, 2012). Moisture content in the chimney emissions during sampling was between 36–67%, an aspect that might complicate the collection and analysis of samples; however, the sorbents are highly hydrophobic and suitable for use in samplings of gases with high humidities (Ribes et al., 2007). Sampling tubes were conditioned before use at 400 °C, sealed with Swagelock end caps fitted with PTFE ferrules and stored at 4 °C for 1 week at most before use.

2.5. VOC analytical instrumentation

VOCs analysis was performed by TD-GC/MS using a Markes Unity Series 2 (Markes International Ltd., Lantrisant, UK) via Thermo Scientific Focus GC fitted with a Thermo Scientific DSQII MSD (Thermo Fisher Scientific, Austin, Texas, USA).