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

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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.

Keywords: formaldehyde, volatile organic compounds, TD-GC/MS, waste treatment, outdoor air quality

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; Nagele 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 was 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). Toluene 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 minutes. 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 >75ºC, 70 mg), Carbopack X (activated graphitized black carbon, medium sorption strength, target analytes: C_3-C_7

(light hydrocarbons, boiling points between 50-150ºC), 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 150ºC), 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 were 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 400ºC, sealed with Swagelock end caps fitted with PTFE ferrules and stored at 4ºC 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).

The methodology is described in the literature (Ribes et al., 2007; Gallego et al., 2009a). Primary thermal desorption of the sampling tubes was carried out at 300ºC with a helium flow rate of 55 ml min^{-1} for 10 minutes. A double split was applied to the TD system (cold trap inlet and outlet splits of 11 ml min^{-1}). The cold trap (U-T15ATA: TO-15/TO-17 Air Toxics trap, Markes) was maintained at -30ºC. After primary desorption, the cold trap was rapidly heated from -30ºC to 300ºC (secondary desorption) and maintained at this temperature for 10 minutes. Analytes were then injected onto the capillary column (DB-624, 60 m x 0.32 mm x 1.8 µm, inert for active compounds) via a transfer line heated at 200˚C. The column oven temperature started at 40˚C for 1 min, increased to 230˚C at a rate of 6˚C min^{-1} and was then maintained at 230˚C for 5 min. Helium (99.999%) carrier gas flow in the analytical column was approximately 1.8 ml min^{-1} (1.4 bar).

The electron impact source was obtained with an electron energy of 70 eV. Mass spectral data were acquired over a mass range of 20-300 amu. Quantification of samples was conducted by the external standard method according to Ribes et al., 2007. Calibration curves of all evaluated VOCs were freshly prepared, clean tubes were spiked and they were injected onto the TD-GC/MS daily.

2.5.1 Quality control

Extreme precautions are required to ensure reproducible quality results. Every day the mass spectrometer was manually tuned at m/z=69, 131, 264 and 502 and air leaks (m/z= 4, 18 and 28) were controlled.

To avoid artifacts generation, both ATD trap and sampling tubes were properly conditioned. A trap heat was done daily before analysis at 330ºC for 20 min. After the trap heating, analytical blank samples, i.e. two clean multi-sorbent bed tubes, were analysed before the injection of the samples and standards. Precision, repeatabilities of 7 standards, were found to be ≤ 11%, reaching the EPA performance criteria (US EPA, 1999). Method detection limits (MDL) were calculated through the analysis of 7 replicates of the lowest concentrated standard, which presented a signal to noise factor between 2.5 and 10. The obtained standard deviation (SD) for the replicates concentrations was multiplied for 3.14 (Student's t value at the 99% confidence interval), according to the U.S. EPA (Part 136-Guidelines establishing test procedures for the analysis of pollutants, Appendix B). MDL were between 0.01-0.2 ng per sample. The linearity range of the multi-point calibration was ≥ 0.99 in for all compounds.

2.6 Data treatment

Formaldehyde and VOCs emission factors were calculated using the concentrations determined in the biogas engines and the process chimneys exhausts, and the emission flows of the mentioned exhausts. The Air Pollution Model (TAPM, CSIRO, Australia) was used to determine the concentrations derived from the waste treatment plants assuming maximum emission conditions, i.e. 3 biogas engines functioning during 24h 365 days a year. TAPM was chosen due to the robustness of the method used to predict meteorology and pollutant concentration, which solves approximations to the fundamental fluid dynamics and scalar transport equations, while other air pollution models that could be used to predict hour by hour pollution concentrations generally employ semi-empirical/analytic approaches based on Gaussian plumes or puffs. These models typically use either a simple surface based meteorological file or a diagnostic wind field model based on available observations. TAPM consists of coupled meteorological prognostic with air pollution concentrations, eliminating the need to have site-specific meteorological observations. Instead, the model predicts the important flows to local-scale air pollution, such as sea breezes and terrain induced flows, against a background of larger-scale meteorology provided by synoptic analyses (Hurley, 2008).

The accuracy of TAPM was checked for two US tracer experiments (Kincaid and Indianapolis) used internationally for model inter-comparison studies, for several annual US dispersion datasets (Bowline, Lovett and Westvaco), for annual meteorology and/or dispersion in various regions throughout Australia (Hurley et al., 2008).

Concentration maps derived from real ambient air concentrations were done using SURFER® 13 (Golden Software, Inc).

3. Sampling locations

3.1 Waste treatment facilities evaluated

WTP 1 is a mechanical-biological waste treatment (MBT) plant located in the metropolitan area of Barcelona, which has been operating for 14 years and has a processing capacity of 245,000 tons year^{-1} of municipal residues, composing both a selected organic fraction (85,000 tons year^{-1}) and a waste fraction (160,000 tons year^{-1}).

WTP 2 is a MBT plant also located in the metropolitan area of Barcelona, which has been operating for 11 years and has a processing capacity of 287,500 tons year^{-1} of municipal residues: selected organic fraction (100,000 tons year^{-1}), waste fraction (160,000 tons year^{-1}) and light packaging (27,500 tons year^{-1}). (Figure 1).

In both WTP the selected organic fraction is anaerobically fermented in a methanation process to obtain biogas. After methanation, the remaining organic matter is composted through an aerobic process. The waste fraction goes through a first stage of mechanical pre-treatment in order to separate the organic matter from the inorganic materials, and recover the recyclable materials (paper, metal, glass, plastic). The separated organic matter from this waste fraction is then composted via an aerobic treatment, together with the remaining organic matter from the methanation.

The obtained biogas from both waste treatment plants is combusted in biogas engines to produce electricity. Additionally, indoor emissions form the different processes developed in the plants are treated passing the air through a biofilter system and eventually emitted outdoors by two and one process chimneys in WTP 1 and WTP 2, respectively.

3.2 Biogas engines sampling

Samples were taken in the exhaust pipes of the biogas engines. Exhaust gases were emitted at high temperatures, between 500 and 600ºC, and formaldehyde measurement could subsequently be difficult (Heikkilä, 2014). A Testo 06008765 probe (700 mm length, maximum temperature: 1000ºC) was used to take the samples, being connected to an SKC Airchek 2000 pump with a PTFE (Polytetrafluorethylene) tube to reduce the gas temperature to the optimum value recommended for the sampling tubes (maximum sampling temperature: 100ºC). Prior to start the sampling, a 5 minutes purge was applied to remove all air from the PTFE tube from the probe to the sampling pump. Formaldehyde active sampling tubes, provided with built-in ozone scrubber, were connected to the sampling pump with PTFE tubes ensuring a minimum dead volume. Samples were taken at 200 ml min^{-1}. Once the samples were taken, tubes were re-caped, taken to laboratory, stored at 4ºC in a clean refrigerator and analysed within the next 3 days. Samples were taken between July and November 2014 in both WTPs evaluated.

3.3 Process chimneys sampling

VOCs and formaldehyde were dynamically sampled by connecting custom packed glass multi-sorbent tubes and formaldehyde active sampling tubes provided with built-in ozone scrubber to AirChek 2000 SKC pumps, and samples were taken at 100 and 200 ml min^{-1}, respectively. Once the samples were collected, both for VOCs and formaldehyde, tubes were re-caped, carried to the laboratory, stored at 4ºC in a clean refrigerator and analysed within the next 3 days. Samples were taken between July and September 2014 in WTP 2 for both formaldehyde and VOCs, and during February 2015 in WTP 1 for formaldehyde only.

3.4 Immission sampling

Ambient air immission sampling in WTP 2 surroundings was done in February 2015 using active sampling tubes: DNPH-coated adsorbent tubes with built-in ozone scrubber and custom packed glass multi-sorbent tubes for formaldehyde and VOCs, respectively. Sampling tubes were connected to air collector pump samplers specially designed in the LCMA-UPC laboratory (Roca et al., 2003). The flow sampling rate was 70 ml min^{-1}. Samples were taken daily during 7-10 days depending on the sampling point. (Figure 1).

Formaldehyde ambient air immission sampling in WTP 1 surroundings and in Barcelona city was done in March and April 2015, respectively, using passive DNPH-coated samplers. Samplers were exposed for 7 consecutive days. Two samplers were used for each sampling point, with a total sampling time of 14 days for each sampling point (Figure 1). VOCs were neither determined in WTP 1 surroundings nor in Barcelona city.

4. Results and discussion

4.1 Formaldehyde and VOC emission factors in Waste Treatment Plants

Formaldehyde concentrations obtained from biogas engines' exhausts and process chimneys of the two WTPs are presented in Tables 1 and 2, respectively. Formaldehyde emission factors from biogas engines were higher in WTP 2, even though the highest emission factor was found for engine 1 from WTP 1. During the study, it was observed that higher formaldehyde emissions depended mainly on the engine operational time, being higher when operational hours increased, as could be expected. Regular maintenance has been emphasized to be a very important factor in the diminishing of the exhaust gases emissions and a successful operation of the engine (Naegele et al., 2013; Volker et al., 2010). Formaldehyde emissions from engine 3 in WTP 2 were evaluated at the return from its scheduled maintenance, and the obtained concentrations were lower than the observed from the other WTP 2 engines (Table 1).

Formaldehyde emissions from process chimneys were also higher in WTP 2 than in WTP 1. It must be taken into account that for WTP 2, all emissions were through one single chimney, with an emission flow of 420,000 $m^3 h^{-1}$. On the other hand, WTP 1 emits through two chimneys of 150,000 $m^3 h^{-1}$ each. Even though emission factors from process chimneys are an order of magnitude lower than the ones from biogas engines, as the emission flows are much higher, up to two orders of magnitude, the impact derived from these chimneys can be relevant.

VOC concentrations found in the process chimney of WTP 2 and their emission factors are presented in Table 3. Terpenes (1302-4034 μg Nm^{-3}), and among them limonene (840-2737 μg Nm^{-3}), were the most concentrated compounds, followed by aromatic hydrocarbons (566-5305 μg Nm^{-3}), aldehydes (311-1529 μg Nm^{-3}), acids (145-869 μg Nm^{-3}) and alcohols (191-1202 μg Nm^{-3}). A previous study conducted in this same WTP, that evaluated indoor air in the organic matter pit of the facility, showed that alcohols (21,000-124,000 μg m^{-3}), and among them ethanol (20,000-107,000 μg m^{-3}), were the compounds that contributed in a most important way, followed by terpenoids (16,000-27,000 μg m^{-3}) (Gallego et al., 2014). In another study, conducted in WTP 1, alcohols (38,000-185,000 μg m^{-3}), terpenoids (1800-16,000 μg m^{-3}), esters (2000-15,000 μg m^{-3}) and acids (3600-8200 μg m^{-3}) presented the highest concentrations indoor; with slight variations depending on the evaluated location inside the treatment plant (Gallego et al., 2012). Additionally, indoor total VOC (TVOC) concentrations were in the range of 60-287 mg m^{-3} and 4-118 mg m^{-3} for WTP 1 and 2, respectively. On the other hand, TVOC chimney emission concentrations in WTP 2 were in the range of 4-10 mg m^{-3} (Table 3). As expected, indoor WTP 2 concentrations (Gallego et al., 2014) were much higher than those emitted by the chimney (present study), as the air is cleaned by means of a biofilter before being emitted to outdoor air (Font et al., 2011), showing removal efficiencies by the biofilters up to 85-99% in some cases, i.e. acids, aromatic hydrocarbons, esters and alcohols. Similar removal efficiencies were observed in previous studies using different types of biofilter media such as cork (BTEX: 79% removal, Kown and Cho, 2009), compost (several VOC: between 40-100% removal, Liu et al., 2005), sewage sludge (several VOC: between 52-96% removal, Alfonsín et al., 2013), and activated sludge (benzene and hexane: >70% and >50% removal, Hu and Wang, 2015; several VOC: between 97-99% removal, Ryu et al., 2011).

4.2 Real formaldehyde and VOC ambient air concentrations in Waste Treatment Plants surroundings

Formaldehyde ambient air concentrations in selected locations in the surroundings of the evaluated WTPs are shown in Table 4. Observed concentrations were higher in WTP 2 than in WTP 1 vicinities, yet within the expected formaldehyde concentrations in urban areas, and “normal” under current environmental policies (Salthammer et al., 2013). Previous studies showed similar concentrations in WTP 2 surroundings, with average values between 3.3±1.0-5.5±1.4 μg m^{-3} (Vilavert et al., 2012, 2014). It has to be noted that this area is surrounded by an important number of industrial facilities apart from the studied WTP (Figure 1). On the other hand, WTP 1 surroundings have an important impact of Barcelona harbour, and its nearness to the sea might reduce the impact upon the inhabited area.

VOC ambient air concentrations in WTP 2 surroundings are presented in Table 5. TVOC concentrations (between 91±48 and 242±121 μg m^{-3}) are in line with typical values found in urban areas (Bari et al., 2015; Cometto-Muñiz and Abraham, 2015; Gallego et al., 2103; Geiss et al., 2011), dominated by aromatic hydrocarbons (16-27 % of the TVOC), and much lower than the found in highly polluted/industrialized areas such as Bangladesh (TVOC between 324-970 μg m^{-3}, Do et al., 2015) Yeosu, South Korea (BTX between 1.1-406 μg m^{-3}, Seo et al., 2014) and Salamanca, Mexico (BTX between 94-121 μg m^{-3}, Vega et al., 2011). The value VLA/420 is commonly used to establish maximum concentration limits in urban outdoor air in 24-h periods for non-carcinogenic compounds (Gallego et al., 2011). VLA is the Spanish equivalent for Time Weighted Average (TWA) in working environments, and 420 is an uncertainty factor that takes into account the varied physiological status of people (e.g. children, old and ill people), and widens the exposition to 24 hours instead of the 8 hours established in the TWA (Repetto and Repetto 2009). Neither of the studied compounds is found above these VLA/420 limits. On the other hand, international TVOC guidelines have not been established for outdoor air. However, Mølhave, 1991 established several criteria related to discomfort for indoor TVOC concentrations: comfort range (<0.2 mg m^{-3}), multifactorial exposure range (0.2-3 mg m^{-3}), discomfort range (3-25 mg m^{-3}) and toxic range (>25 mg m^{-3}). Hence, outdoor air TVOC concentrations found in WTP 2 surroundings showed generally good air quality in respect to VOC, with average concentrations mostly in the indoor comfort range (≤200 μg m^{-3}).

However, in WTP 2 surroundings toluene to benzene (T:B) ratios were 7.9±3.5, indicating an important influence of industry in the evaluated locations (Figure 1). T:B ratios can be useful to determine possible emission sources. T:B ratios between 1.5-4.3 are generally related to traffic and mobile sources (Miller et al., 2011; Oiamo et al., 2015; Schnitzhofer et al., 2008; Shaw et al., 2015). On the other hand, higher T:B ratios up to 10 are related to higher toluene emissions coming from industrial and point source emissions (Buczynska et al., 2009; Miller et al., 2011; Morgan et al., 2015). Additionally, toluene and *tert*-butyl methyl ether (TBME) correlate with themselves which indicates a mobile source. On the other hand, they do not correlate when their origin is from industrial emissions (Vega et al., 2011). In Figure 2, two different behaviours can be seen from all recorded samples from all sampling points. A great number of samples showed a correlation between toluene and TBME, indicating a traffic source. Nevertheless, a small number of samples, from 22 January and 11 February, do not show correlation between the mentioned compounds, indicating clearly a source from industrial activities.

Even though TVOC concentrations were found within typical urban values and air quality is good in WTP 2 vicinity, there is an important influence of industry in the area, as it is totally surrounded by industrial parks (Figure 1).

4.3 Formaldehyde immission concentrations in Barcelona city

Formaldehyde ambient air concentrations in Barcelona city are shown in Table 4. Concentrations, ranging between 3.1±0.6 and 4.1±0.2 μg m^{-3}, are of the same order of magnitude of the observed in the evaluated WTPs surroundings. The obtained values are in agreement with the typically found in European, American and Japanese urban areas (Table 6). However, the concentrations were lower than those observed in much more polluted/industrialized Asian cities (Table 6).

4.4 Influence of WTP in formaldehyde and VOC ambient air concentrations

Previous studies were focused in the evaluation of formaldehyde and/or VOC concentrations in the facility surroundings, and the concentrations found were associated with the plant through mathematical models or wind directions and distances to the facility (Vilavert et al., 2011, 2014; Domingo et al., 2015). In the present case, however the exact contributions of the studied WTPs to immission concentrations were calculated.

Formaldehyde concentrations expected in WTP surroundings derived exclusively from the evaluated plants (taking into account the emissions from biogas engines and process chimneys) and calculated for the immission sampling period, are presented in Figures 3 and 4a for WTP 1 and 2, respectively. These data was compared with the real formaldehyde concentrations found in these sampling points during the immission sampling period (Figures 5 and 6a). WTP 1 and 2 formaldehyde emissions contributed with an average value of 2.2±2.9% and 1.9±3.2%, respectively, to formaldehyde ambient air concentrations. The maximum contribution was found in point 8 in WTP 2 surroundings for the 18th February 2015, accounting for a 13.6%. Even though formaldehyde emission concentrations from biogas engines was found to be quite high in some cases (i.e., 0.5±0.2 to 29±6 mg Nm^{-3}, Table 1), as emission flows are relatively low (in the range of 5000 m^3 h^{-1}), their derived concentrations in the surroundings of the WTP are limited. On the other hand, process chimneys present much higher emission flows (in the range of 150,000-420,000 m^3 h^{-1}), however, their emission concentrations were much lower, between 6±1 and 21±10 µg m^{-3}.

In the same way, Figures 4b and 6b present expected TVOC concentrations in WTP 2 surroundings (derived from TVOC chimney emissions) for the immission sampling period, and the contribution of this facility to real immission TVOC concentrations during the same period. In this case, WTP 2 TVOC emissions contributed with 0.3±0.9% to ambient air concentrations. Although WTP 2 contribution to ambient air is quite low, odorous impacts caused by VOC concentrations can be relevant for the compounds that present low odour thresholds, such as several aldehydes (acetaldehyde, benzaldehyde, nonanal, octanal, propanal) or the compounds that are emitted at higher concentrations, such as terpenes (DL-limonene, *p*-cymene, α-pinene) (Table 3).

5. Conclusions

Formaldehyde (biogas engines and process chimneys) and a wide range of VOC (process chimneys) emission factors were determined for two WTPs (MBT plants) in the metropolitan area of Barcelona, Spain. To our knowledge, this is the first time that the contribution of these emissions to real formaldehyde and VOC ambient air concentrations in the surroundings of these facilities has been evaluated in Spain. This contribution was determined to be around 2%, depending on meteorological conditions. As the potential impact of WTPs in urban areas arises important societal concerns, the influence of these facilities upon ambient air quality has to be estimated in the most reliable way, and the determination of real emission factors is a solid mean for that assessment. Additionally, the emission factors provided in the present paper could be useful for the investigation of impacts from similar facilities (already settled or under project) in Spain, or comparable plants where analogous waste compositions are treated in other countries.

WTP surroundings and Barcelona city formaldehyde concentrations are “normal”, within the typical values found in European, American and Japanese urban areas. However, this “normal” does not mean “acceptable” or “safe”; it only focuses on the present circumstances (derived from the diverse supply needs and mobility of 7 billion humans) of formaldehyde concentrations in worldwide ambient air. Hence, formaldehyde emissions to ambient air should be reduced as much as possible, and in the case of WTPs, it is mandatory to focus upon the importance of regular maintenance and engine adjustment of the biogas motors.

Finally, in future studies, diffusive emissions of pollutants from the facilities should also be considered so as to clarify WTP impacts related to VOC and odours, upon their surroundings.

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Table1. Formaldehyde emission concentrations and calculated emission factors for the different biogas engines evaluated.

	Waste Treatment Plant 1				**Waste treatment Plant 2**			
Engine	**1**	**2**	**3**	**5**	**1**	**2**	**3**	**4**
Date	21/7/14	13/11/14	13/11/14	13/11/14	22/7-8/10/14	15/7-3/9/14	8/10/14	21/7/14
Gas temperature (ºC)[1]	554	540	560	600	534-545	519-550	535	555
Number of samples	3	6	4	6	6	6	4	4
Formaldehyde (mg Nm^{-3})	29 ± 6	0.5 ± 0.2	0.7 ± 0.1	1.3 ± 0.2	15 ± 9	22 ± 12	3.5 ± 0.6	18 ± 11
Emission factor (g s^{-1})	**0.04**[2]	**0.001**[2]	**0.001**[2]	**0.002**[2]	**0.02**[3]	**0.03**[3]	**0.01**[3]	**0.03**[3]

[1] Gas temperature at the sampling point
[2] Calculated for an emission flow of 4669.2 m^3 h^{-1}
[3] Calculated for an emission flow of 5000 m^3 h^{-1}

Table 2

Table 2. Formaldehyde emission concentrations and calculated emission factors for the different chimneys evaluated.

	Waste Treatment Plant 1		Waste Treatment Plant 2
Chimney	**1**	**2**	**1**
Date	10-12/2/15	10-12/2/15	15/7/14-8/9/14
Gas temperature (ºC)[1]	11-14	11-14	26-29
Number of samples	3	3	18
Formaldehyde (µg Nm^{-3})	6 ± 2	6 ± 1	21 ± 10
Emission factor (g s^{-1})	**0.0002**[2]	**0.0002**[2]	**0.003**[3]

[1] Gas temperature at the sampling point

[2] Calculated for an emission flow of 150,000 m^3 h^{-1}

[3] Calculated for an emission flow of 420,000 m^3 h^{-1}

Table 3. Range, average ± standard deviation of VOC concentrations (μg Nm^{-3}) and emission factor (mg s^{-1}) found in the process chimney of Waste Treatment Plant 2 (n=12, 21/7/2014, 22/7/2014, 3/9/2014 and 8/9/2014). Concentrations with grey shading exceed the odour threshold of the compound.

Compound	**Range (μg Nm^{-3})**	**Average ± SD (μg Nm^{-3})**	**Emission factor[1] (mg s^{-1})**	**Odour Threshold[2] (μg m^{-3})**
Alkanes				
cyclohexane	5-88	34±28	4.0±3.3	35,600
n-decane	10-97	44±31	5.1±3.6	11,300
n-hexane	0.7-5	3±2	0.3±0.2	107,000
Total alkanes	**28-190**	**81±58**	**9.4±6.8**	
Aromatic hydrocarbons				
1,2,3-trimethylbenzene	4-24	14±6	1.6±0.7	-[3]
1,2,4-trimethylbenzene	10-109	53±36	6.1±4.2	140
1,3,5-trimethylbenzene	8-40	21±11	2.5±1.3	10,700
1-methylnaphthalene	0.1-1	0.2±0.1	0.02±0.01	-
2-methylnaphthalene	0.1-1	0.3±0.2	0.04±0.03	4
benzene	0.4-10	3±3	0.4±0.4	1,500
ethylbenzene	40-648	193±225	23±26	400
m+*p*-xylene	133-1239	480±424	56±50	770
m+*p*-ethyltoluene	24-132	69±36	8.1±4.2	42
naphthalene	0.2-2	1±1	0.1±0.1	7
n-propylbenzene	8-33	18±8	2.1±1.0	14,400
o-ethyltoluene	9-49	25±13	2.9±1.5	370
o-xylene	55-458	164±148	19±17	770
phenol	3-28	9±7	1.1±0.8	39
styrene	6-40	18±14	2.1±1.6	12
toluene	92-2,635	817±928	95±108	3,800
Total Aromatic hydrocarbons	**566-5,305**	**1,885±1,798**	**220±210**	
Alcohols				
1-butanol	5-32	17±7	2.0±0.9	480
1-propanol	9-75	32±23	3.8±1.7	2,000
ethanol	114-1,078	347±329	41±38	2,000
ethylhexanol	2-28	12±11	1.4±1.3	400
isopropanol	6-50	21±16	2.5±1.8	8,000
Total Alcohols	**191-1,202**	**429±344**	**50±40**	
Ketones				
acetone	11-146	57±51	6.7±6.0	8,600
biacetyl	1-19	9±6	1.1±0.7	5.2
cyclohexanone	25-177	71±57	8.3±6.6	880
methylethylketone	3-101	45±30	5.3±3.5	5,700
methylisobutylketone	5-72	24±23	2.8±2.7	140
Total Ketones	**70-301**	**206±68**	**24.1±7.9**	
Halocarbons				
1,1,1-trichloroethane	0.1-3	1±1	0.1±0.1	5,300
carbon tetrachloride	1-6	3±1	0.4±0.2	1,260,000
chloroform	1-6	3±1	0.3±0.2	500
dichloromethane	3-62	22±22	2.6±2.6	4,100
p-dichlorobenzene	1-9	4±2	0.5±0.3	730
tetrachloroethylene	4-225	68±74	8.0±8.7	8,300

trichloroethylene	2-6	3±1	0.4±0.1	3,900
Total Halocarbons	**24-301**	**105±94**	**12.2±11.0**	
Aldehydes				
2-butenal	3-14	8±3	0.9±0.3	420
acetaldehyde	47-1,389	400±447	47±52	2.7
benzaldehyde	3-23	10±7	1.1±0.8	10
decanal	6-31	14±8	1.6±0.9	51
hexanal	2-21	7±6	0.8±0.7	25
heptanal	4-40	14±12	1.6±1.4	61
nonanal	9-43	22±11	2.5±1.3	20
octanal	74-439	173±135	20±16	10
pentanal	1-21	7±6	0.8±0.7	30
propanal	0.4-15	5±5	0.6±0.6	3.6
Total Aldehydes	**311-1,529**	**659±369**	**77±43**	
Esters				
butyl acetate	1-14	3±4	0.3±0.5	7,700
ethyl acetate	0.3-26	10±9	1.1±1.0	4,600
methyl acetate	0.04-0.3	0.1±0.1	0.01±0.01	22,000
Total Esters	**1-27**	**12±10**	**1.5±1.1**	
Acids				
acetic acid	145-869	436±246	54±29	90
Total Acids	**145-869**	**436±246**	**54±29**	
Terpenes				
camphor	2-5	3±1	0.4±0.1	52
D-limonene	840-2,737	1,480±609	173±71	1,700
p-cymene	203-580	372±137	43±16	200
α-pinene	132-456	255±107	30±13	230
β-pinene	87-317	184±73	21±9	8,900
Total Terpenoids	**1,302-4,034**	**2,294±852**	**268±99**	
Ethers				
tert-butyl ethyl ether	3-18	9±5	1.0±0.5	-
tert-butyl methyl ether	0.03-0.2	0.1±0.1	0.01±0.01	-
Total Ethers	**3-18**	**9±5**	**1.0±0.5**	
Organonitrogenates				
acetonitrile	1-85	19±26	2.2±3.1	285,000
benzothiazole	14-84	33±22	3.9±2.6	442
cyclohexane isocyanato	29-102	48±24	5.6±2.8	-
Total Organonitrogenates	**51-167**	**101±38**	**11.7±4.4**	
Others				
1,3-butadiene	2-14	7±4	0.8±0.5	220
2-butoxyethanol	1-202	51±65	6.0±7.5	37,000
carbon disulfide	0.1-3	1±1	0.1±0.1	110
tetrahydrofuran	1-44	10±13	1.2±1.5	90,000
Total Others	**5-255**	**69±79**	**8.0±9.2**	
Total VOC Concentrations (mg m^{-3})	**4-10**	**6±2**		
Total emission factor (g s^{-1})			**0.9±0.3**	

[1] Emission factor calculated for an emission flow of 420,000 m^3 h^{-1}

[2] Source: “Compilations of odour threshold values in air and water”, L.J.van Gemert (TNO Nutrition and Food Research Institute). Boelens Aroma Chemicals Information Service (BACIS). The Netherlands (2003); “Odor Thresholds for Chemicals with Established Occupational Health Standards” American Industrial Hygiene Association. USA (2009); “Reference Guide to Odor Thresholds for Hazardous Air Pollutants Listed in the Clean Air Act Amendments of 1990”. EPA/600/R-92/047 (2009); Ruth, 1986 and “Measurement of odor threshold by triangle odor bag method”, Y. Nagata. Odor Measurement Review, 118-127, Japan Ministry of Environment (2003).

[3] Value not determined

Table 4. Formaldehyde immission concentrations in the evaluated waste treatment plant surroundings and in Barcelona city.

	Waste Treatment Plant 1 surroundings				
Sampling Point	**1**	**2**	**3**	**4**	**5**
Dates	17-31/3/15	17-31/3/15	17-31/3/15	17-31/3/15	17-31/3/15
Environmental T (ºC)	13-14	13-14	13-14	13-14	13-14
Number of samples*	2	2	2	2	2
Formaldehyde (µg m^{-3})	**2.8 ± 0.3**	**6.0 ± 0.2**	**2.5 ± 0.4**	**2.7 ± 0.3**	**2.5 ± 0.7**
	Waste Treatment Plant 2 surroundings				
Sampling Point	**6**	**7**	**8**	**9**	**10**
Dates	9-23/2/15	9-23/2/15	9-23/2/15	9-23/2/15	9-23/2/15
Environmental T (ºC)	7-11	6-11	6-11	6-11	7-11
Number of samples	8	9	9	9	10
Formaldehyde (µg Nm^{-3})	**5.9 ± 1.0**	**3.9 ± 2.0**	**5.1 ± 1.4**	**6.0 ± 1.3**	**2.9 ± 0.7**
	Barcelona city				
Sampling Point	**11**	**12**	**13**	**14**	
Dates	13-27/4/15	13-27/4/15	13-27/4/15	15-29/4/15	
Environmental T (ºC)	15-16	16-17	16-17	15-17	
Number of samples*	2	2	2	2	
Formaldehyde (µg m^{-3})	**3.1 ± 0.6**	**4.1 ± 0.2**	**3.5 ± 0.5**	**3.6 ± 0.6**	

*Passive samplers (7 days+7 days)

Ecoparc perimeter 1; Ecoparc perimeter next to biogas engines 2; El Prat 3; L'Hospitalet 4; BCN 5
La Llagosta 6; Montcada i Reixac 7; Ripollet Pinetons 8; Ripollet Can Mas 9; Cerdanyola 10
BCN-ETSEIB 11; BCN-Ronda Litoral 12; BCN-Fra Juniper 13; BCN-Balmes 14

Table 5

Table 5. Average ± standard deviation of VOC concentrations (µg Nm^{-3}) found in the different sampling points surrounding Waste Treatment Plant 2.

Sampling point	**6 (µg Nm^{-3})**	**7 (µg Nm^{-3})**	**8 (µg Nm^{-3})**	**9 (µg Nm^{-3})**	**10 (µg Nm^{-3})**	**VLA/420^{1} (µg m^{-3})**
Number of samples	*n*=7	*n*=8	*n*=9	*n*=9	*n*=8	
Dates	**20-1/6-2/2015**	**20-1/6-2/2015**	**20-1/11-2/2015**	**20-1/11-2/2015**	**20-1/6-2/2015**	
Alkanes						
cyclohexane	2.6±1.5	2.0±1.5	1.6±1.8	1.9±1.8	0.5±0.3	1667
n-decane	1.3±0.7	1.3±1.1	1.2±0.8	1.3±0.5	0.3±0.2	-
n-hexane	1.3±0.6	0.8±0.5	0.9±0.9	1.1±0.8	0.4±0.3	171
Total alkanes	**5.2±2.5**	**4.2±2.9**	**3.7±3.4**	**4.2±2.8**	**1.1±0.6**	
Aromatic hydrocarbons						
1,2,3-trimethylbenzene	0.9±0.7	0.4±0.3	0.5±0.3	0.5±0.3	0.2±0.1	238
1,2,4-trimethylbenzene	2.6±1.6	1.9±1.0	1.9±0.9	2.0±0.8	0.7±0.3	238
1,3,5-trimethylbenzene	0.6±0.4	0.4±0.3	0.5±0.2	0.5±0.2	0.2±0.1	238
1-methylnaphthalene	0.07±0.04	0.05±0.04	0.05±0.04	0.09±0.04	0.04±0.03	-
2-methylnaphthalene	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	-
benzene	3.0±1.4	2.3±1.2	2.1±1.0	2.5±1.0	1.3±0.9	5^{2}
ethylbenzene	4.9±3.2	3.6±2.1	3.0±1.8	3.2±1.4	0.9±0.5	1050
m+*p*-xylene	17±12	11.3±6.4	10.4±6.7	10.7±5.2	3.1±1.7	526
m+*p*-ethyltoluene	2.1±1.2	1.6±0.8	1.7±0.9	1.8±0.6	0.7±0.3	-
naphthalene	0.4±0.2	0.3±0.2	0.3±0.2	0.4±0.2	0.3±0.2	126
n-propylbenzene	0.4±0.2	0.3±0.1	0.3±0.2	0.3±0.1	0.1±0.1	-
o-ethyltoluene	0.5±0.3	0.4±0.2	0.4±0.2	0.4±0.2	0.2±0.1	-
o-xylene	4.3±2.5	3.0±1.6	2.8±1.5	2.9±1.2	1.1±0.5	526
styrene	2.5±1.5	1.9±1.4	1.4±1.0	1.8±1.1	0.4±0.2	205
toluene	27±19	19±12	20±14	21±12	5.3±3.1	457
Total Aromatic hydrocarbons	**66±42**	**46±26**	**46±28**	**48±21**	**14.6±7.4**	
Alcohols						
1-butanol	7.6±4.3	4.3±2.0	1.3±0.8	1.7±1.0	0.6±0.6	145

1-propanol	2.1±0.9	1.4±0.9	1.3±1.3	1.1±0.9	0.3±0.2	1191
ethanol	5.6±3.1	4.1±2.2	7.2±5.9	6.8±5.9	38±37	4548[3]
ethylhexanol	1.0±0.4	0.4±0.2	0.4±0.2	5.9±4.0	0.1±0.1	-
isopropanol	15.3±8.0	9.5±6.6	10.0±6.9	8.4±3.6	2.9±2.3	1191
Total Alcohols	**32±14**	**20±10**	**20±14**	**23.9±8.2**	**42±39**	
Ketones						
acetone	24±14	17.1±9.4	14.3±8.8	18.5±8.6	6.6±4.6	2881
biacetyl	0.3±0.4	0.2±0.3	0.2±0.2	0.3±0.3	0.03±0.02	-
cyclohexanone	2.1±1.4	1.6±1.0	1.4±0.8	2.8±1.6	0.4±0.2	98
methylethylketone	8.0±4.3	6.0±4.5	4.9±3.5	5.9±2.5	1.2±0.7	1429
methylisobutylketone	1.4±0.8	1.1±0.6	0.9±0.7	0.9±0.7	0.2±0.1	198
Total Ketones	**36±20**	**26±14**	**22±13**	**29±12**	**8.3±5.2**	
Halocarbons						
1,1,1-trichloroethane	0.03±0.01	0.03±0.02	0.04±0.02	0.04±0.02	0.02±0.01	1321
carbon tetrachloride	1.0±0.3	1.0±0.4	1.0±0.5	1.1±0.7	0.6±0.5	76
chloroform	0.8±0.5	0.5±0.3	0.4±0.3	0.5±0.2	0.3±0.1	24
dichloromethane	4.6±4.6	3.4±4.6	4.0±3.3	3.1±1.7	0.7±0.5	421
p-dichlorobenzene	0.02±0.01	0.01±0.01	0.01±0.01	0.02±0.01	0.01±0.01	291
tetrachloroethylene	2.8±1.4	3.1±1.7	4.6±2.2	4.3±3.9	0.7±0.4	410
trichloroethylene	0.6±0.4	0.6±0.5	7.3±13.8	1.2±1.8	0.2±0.1	131
Total Halocarbons	**9.8±5.9**	**8.6±6.0**	**17±16**	**10.2±5.2**	**2.3±1.1**	
Aldehydes						
acetaldehyde	1.1±0.6	1.1±0.3	1.3±0.6	1.3±0.7	4.2±2.4	110[3]
benzaldehyde	2.4±1.3	1.7±0.9	2.2±1.0	2.0±0.8	0.7±0.3	-
hexanal	2.0±0.9	1.1±0.5	2.0±0.9	1.5±0.7	0.4±0.3	-
heptanal	0.6±0.1	0.3±0.1	2.8±1.1	0.7±0.3	0.2±0.1	-
nonanal	2.4±1.4	1.8±1.0	2.8±2.0	2.4±2.0	0.7±0.6	-
octanal	1.5±0.8	0.6±0.4	2.6±1.4	1.4±0.8	0.4±0.2	-
pentanal	0.4±0.2	0.2±0.1	0.6±0.4	0.3±0.2	0.1±0.1	426

propanal	0.4±0.2	0.4±0.2	0.5±0.3	0.4±0.2	0.3±0.2	110
Total Aldehydes	**10.8±4.8**	**7.1±3.2**	**14.9±5.9**	**10.0±4.9**	**6.8±2.7**	
Esters						
butyl acetate	7.9±5.0	7.7±4.5	7.6±6.5	6.9±3.6	1.2±1.2	1724
ethyl acetate	24±16	22±17	27±23	26±18	2.4±2.0	3476
methyl acetate	1.9±0.9	1.9±1.2	2.0±1.3	2.0±0.8	0.5±0.3	1467
Total Esters	**34±21**	**31±21**	**37±29**	**35±21**	**3.7±2.7**	
Terpenoids						
D-limonene	3.4±1.5	2.5±2.0	1.6±1.3	2.3±1.4	0.5±0.3	262
p-cymene	0.6±0.3	0.6±0.4	0.4±0.4	0.9±0.7	0.2±0.1	-
α-pinene	2.7±1.5	2.3±1.6	2.2±1.7	2.8±1.9	0.9±0.6	269
β-pinene	0.4±0.2	0.3±0.2	0.2±0.2	0.4±0.2	0.1±0.1	269
Total Terpenoids	**7.1±3.5**	**5.6±4.1**	**4.5±3.1**	**6.4±3.9**	**1.7±0.9**	
Ethers						
tert-butyl ethyl ether	2.0±1.0	1.4±0.7	1.6±0.8	1.7±0.6	0.7±0.3	50
tert-butyl methyl ether	0.3±0.3	0.2±0.2	0.6±1.2	0.3±0.3	0.04±0.03	437
Total Ethers	**2.3±1.2**	**1.6±0.8**	**2.2±1.8**	**1.9±0.8**	**0.6±0.4**	
Organonitrogenates						
acetonitrile	0.2±0.1	0.1±0.1	0.1±0.1	0.2±0.2	0.1±0.1	162
benzothiazole	3.2±1.6	4.1±2.2	0.4±0.7	9.2±5.0	0.4±0.7	-
cyclohexane isocyanato	2.1±0.8	2.0±1.1	1.4±0.7	1.2±0.4	0.4±0.4	-
cyclohexane isothiocyanato	0.2±0.1	0.2±0.1	0.06±0.03	0.08±0.04	0.015±0.003	-
Total Organonitrogenates	**5.6±2.5**	**6.4±3.0**	**2.0±1.2**	**10.6±5.0**	**0.9±0.9**	
Glycols						
1-methoxy-2-propanol	8.6±4.2	3.2±2.2	2.4±1.9	2.6±1.5	0.5±0.5	893
2-butoxyethanol	7.3±2.0	4.4±1.9	4.5±2.0	4.9±2.6	3.5±1.8	233
Total Glycols	**15.9±6.1**	**7.6±3.4**	**6.9±3.2**	**7.5±3.1**	**3.9±1.6**	
Others						
1,3-butadiene	1.1±0.7	0.8±0.4	0.8±0.5	0.8±0.4	0.7±0.3	11

carbon disulfide	0.2±0.1	0.2±0.1	0.3±0.2	0.4±0.2	0.1±0.1	36
tetrahydrofuran	0.5±0.3	0.4±0.2	0.3±0.2	0.3±0.2	0.3±0.2	357
Total Others	**1.8±1.0**	**1.4±0.7**	**1.4±0.7**	**1.5±0.6**	**1.0±0.5**	
rf. toluene	15.5±8.7	10.6±5.7	10.8±5.5	11.8±5.0	3.8±1.8	
Total VOC concentrations (µg m^{-3})	**242±121**	**177±94**	**188±113**	**200±74**	**91±48**	

Sampling point: La Llagosta 6; Montcada i Reixac 7; Ripollet Pinetons 8; Ripollet Can Mas 9; Cerdanyola 10

[1] VLA: Valor Límite Ambiental-Exposición Diaria: the Spanish correspondence for threshold Limit Value-Time Weighted Average (TLV-TWA). 420 is an uncertainty factor that takes into account the varied physiological status of people (Repetto and Repetto, 2009)

[2] European Directive 2008/50/EC

[3] As VLA-EC: Valor Límite Ambiental-Exposición de corta duración (maximum of 15 minutes during the daily exposure).

Table 6. Formaldehyde concentrations (µg m^{-3}) in worldwide urban areas.

Location	**Formaldehyde (µg m^{-3})**	**Citation**
WTP 1 surroundings (Spain)	2.5±0.4 - 6.0±0.2	Present study
WTP 2 surroundings (Spain)	2.9±0.7 - 6.0±1.3	Present study
Barcelona (Spain)	3.1±0.6 - 4.1±0.2	Present study
Torino (Italy)	1.6±0.7	Bono et al., 2010
Rome (Italy)	2.8±1.1	Santarsiero and Fuselli, 2008
Hagfors (Sweden)	3.7	Gustafson et al., 2007
Zajecar (Serbia)	5.1	Jovanović et al., 2014
European cities	2.6 (0.3 - 7.3)	Geiss et al., 2011
European urban areas	0.4±0.2 - 4.9±1.4	Bruinen de Bruin et al. 2008
USA urban areas	6.4	Liu et al., 2006
Japanese cities	1.7 - 4.3	Uchiyama et al., 2015
Saõ Paulo (Brazil)	1.4 - 8.0	Coelho et al., 2010
Beijing (China)	15.4	Liu et al., 2014
Hong Kong (China)	2.0 - 15.4	Cheng et al., 2014
Kaohsiung (Taiwan, ROC)	7.3 - 39.4	Wang et al., 2010
Yeosu (South Korea)	n.d. - 31	Seo et al., 2014
Gwangyang (South Korea)	2 - 29	Seo et al., 2014

Figure 1. Sampling locations. Blue polygons indicate industrial areas.

Figure 2. Correlation between toluene and *tert*-buthyl methyl ether (TBME) concentrations in WTP 2 surroundings.

Figure 3. Calculated average formaldehyde concentrations (µg m^{-3}) derived from emissions from WTP 1 during the immission sampling periods: a) WTP 1 surroundings: 17-31/03/2015 and b) Barcelona city: 13-29/4/2015.

Figure 4. Calculated average formaldehyde and VOC concentrations (µg m^{-3}) derived from emissions from WTP 2 during the immission sampling period (9-23/2/2015). a) Formaldedhyde and b) VOCs.

Figure 5. Experimental average formaldehyde concentrations (µg m^{-3}) in WTP 1 surroundings vs. calculated concentrations derived from the WTP during immission sampling (WTP 1 surroundings, points 1-5, 17-31/3/2015; Barcelona city, points 11-14, 13-29/4/2015).

Figure 6. Experimental average a) formaldehyde and b) TVOC concentrations (µg m^{-3}) in WTP 2 surroundings vs. calculated concentrations derived from the WTP during immission sampling (9-23/2/2015).

Figure 1

Click here to download Figure: Figure 1.pptx

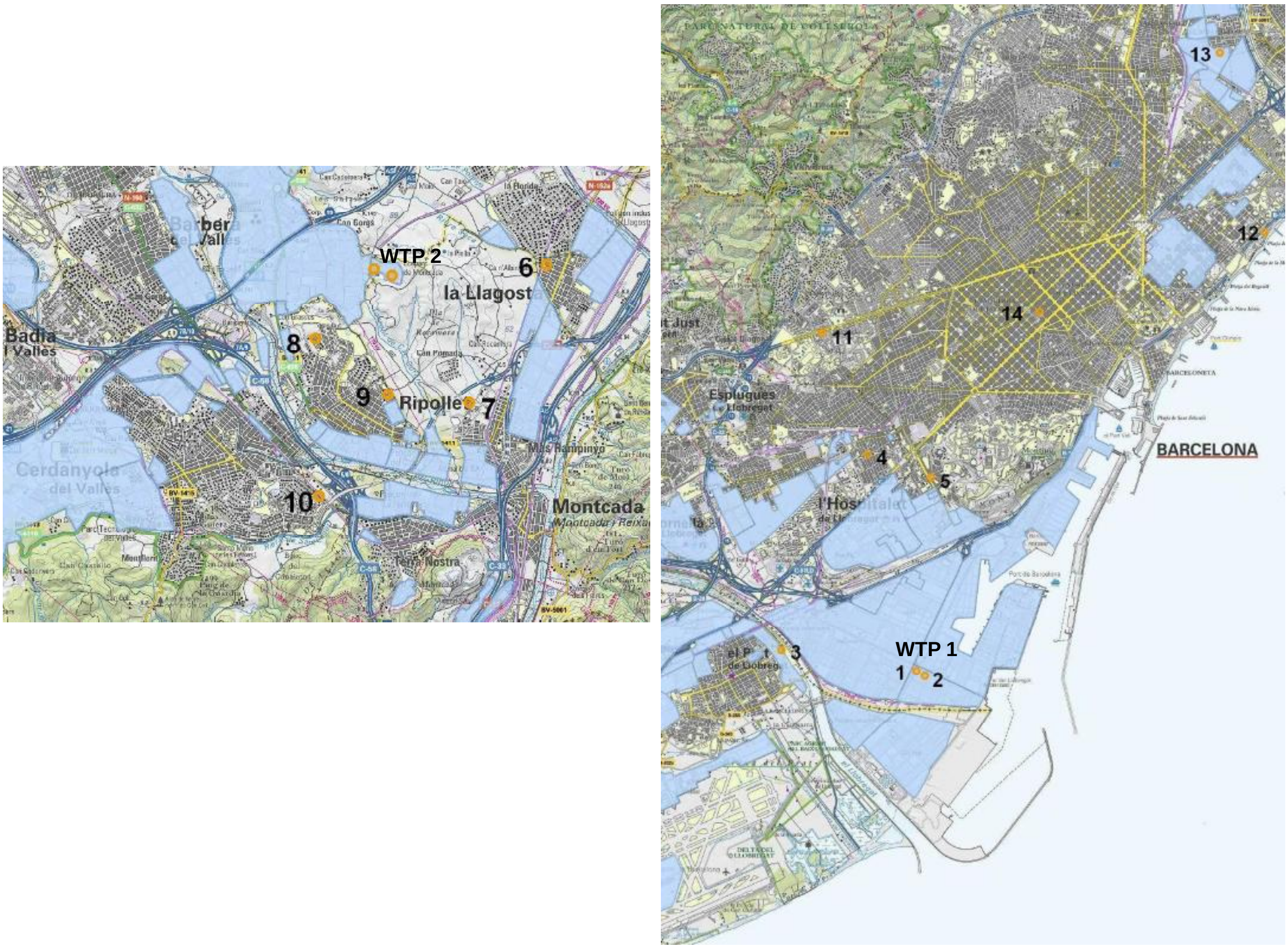


Figure 2

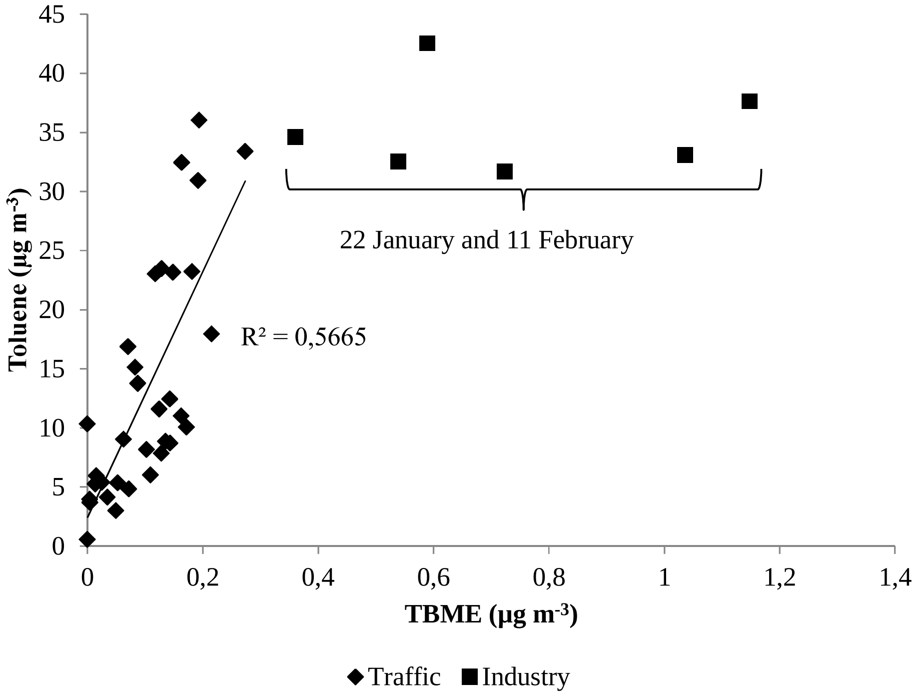

45
40
35
30
25
20
15
10
5
0
Toluene (µg m⁻³)
0
0,2
0,4
0,6
0,8
1
1,2
1,4
TBME (µg m⁻³)
R² = 0,5665
22 January and 11 February
◆ Traffic
■ Industry

Figure 3

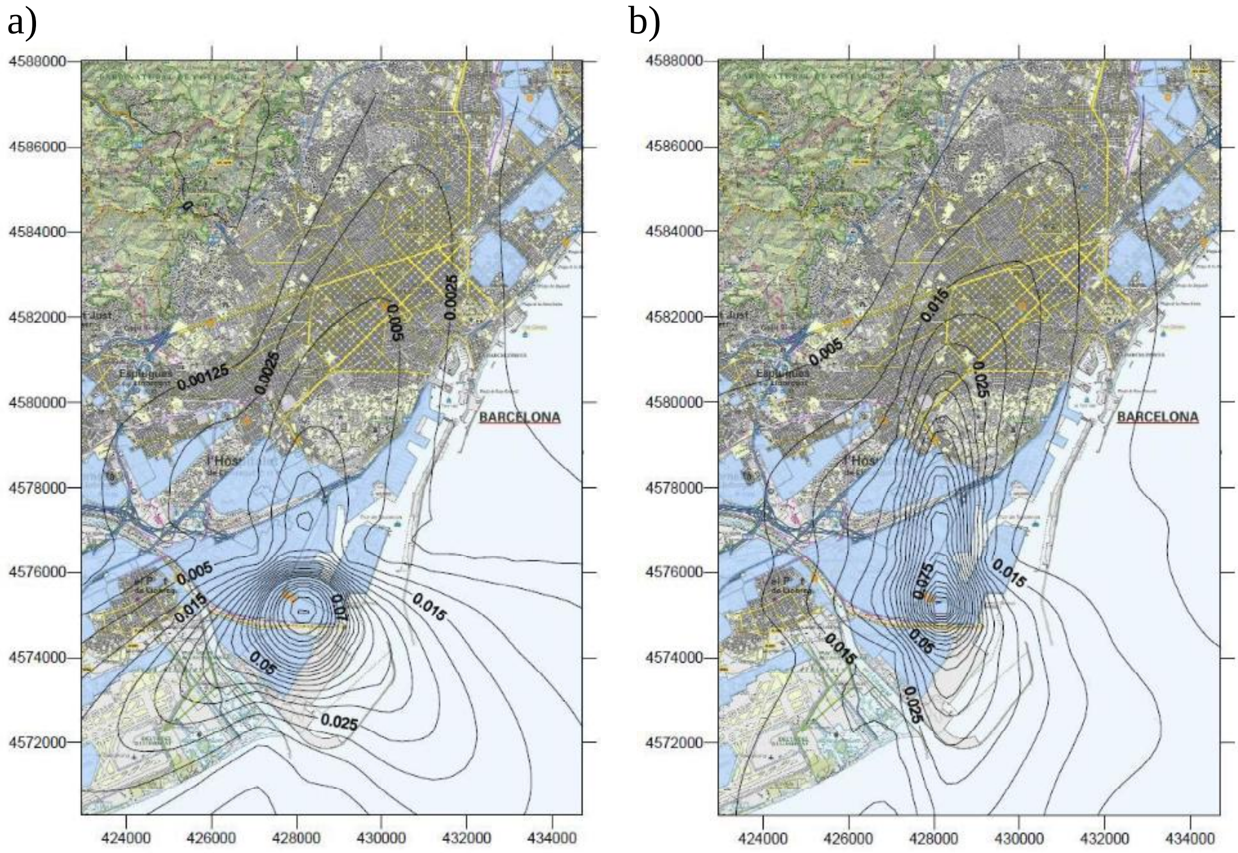

a)
b)
4588000
4586000
4584000
4582000
4580000
4578000
4576000
4574000
4572000
424000
426000
428000
430000
432000
434000
BARCELONA
0.00125
0.0025
0.005
0.0025
0.005
0.015
0.05
0.07
0.015
0.025
0.005
0.015
0.025
0.075
0.05
0.015
0.015
0.025

Figure 4

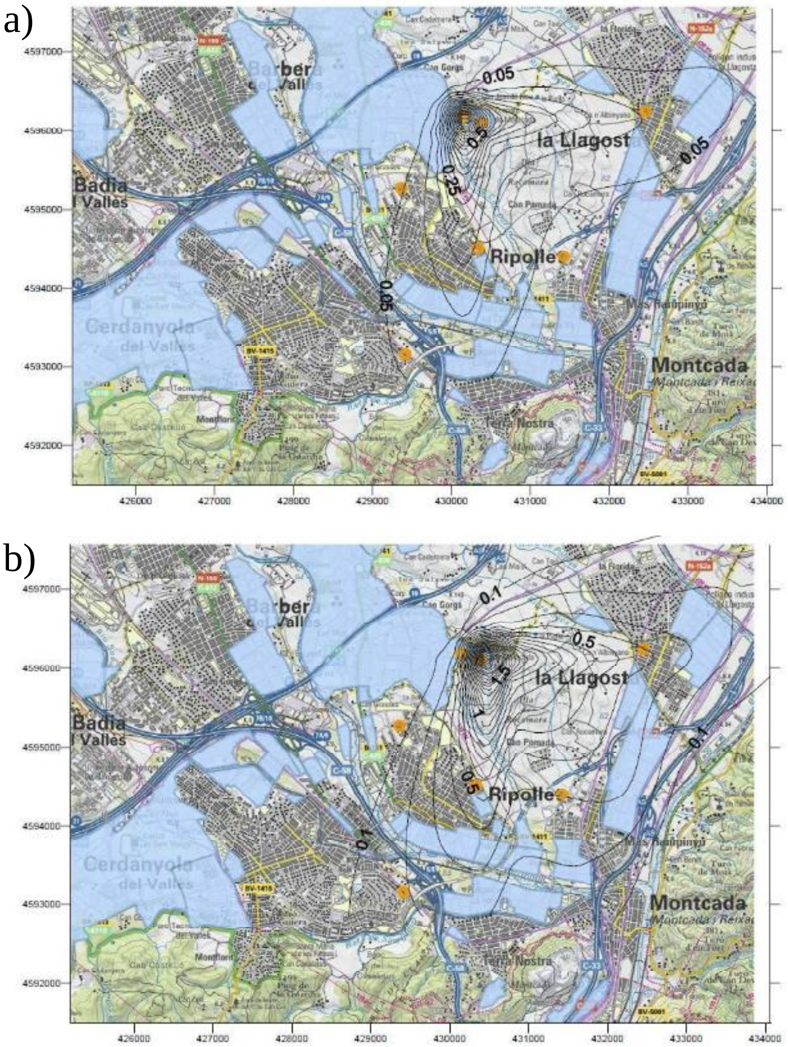

a)
0.05
0.5
0.25
0.05
0.05
la Llagost
Ripollet
Barberà del Vallès
Badia del Vallès
Cerdanyola del Vallès
Montcada
Montcada i Reixac
Mas Rampinyo
Terra Nostra
Can Gorgs
Can Pamada
4597000
4596000
4595000
4594000
4593000
4592000
426000
427000
428000
429000
430000
431000
432000
433000
434000
b)
0.1
0.5
1.5
1
0.5
0.1
0.1
la Llagost
Ripollet
Barberà del Vallès
Badia del Vallès
Cerdanyola del Vallès
Montcada
Montcada i Reixac
Mas Rampinyo
Terra Nostra
Can Gorgs
Can Pamada
4597000
4596000
4595000
4594000
4593000
4592000
426000
427000
428000
429000
430000
431000
432000
433000
434000

Figure 5

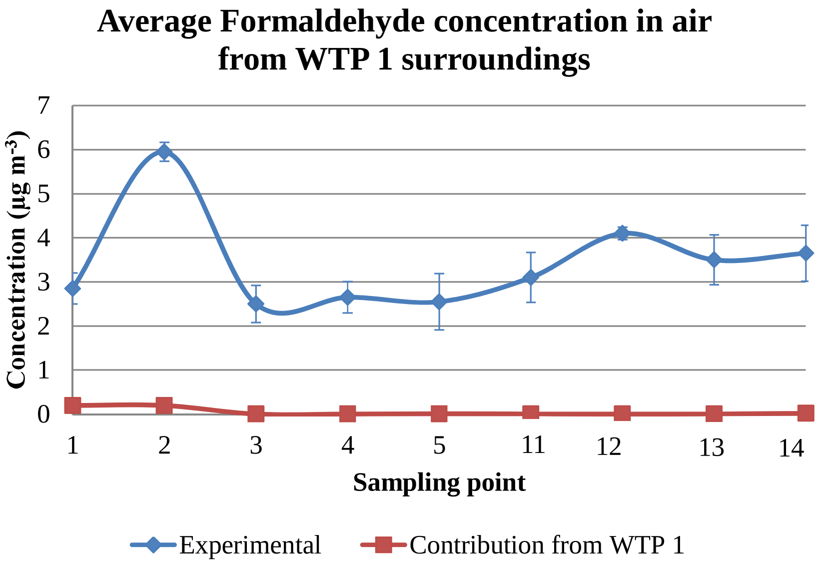
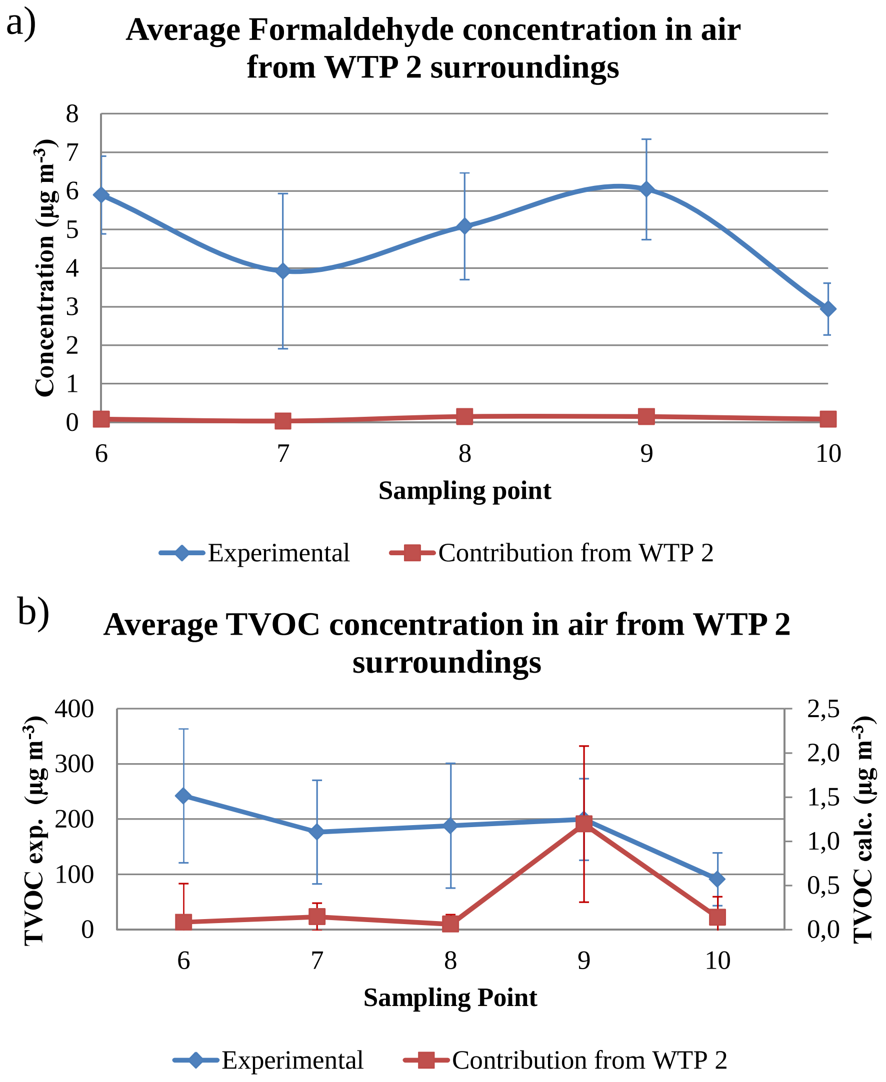

Average Formaldehyde concentration in air
from WTP 1 surroundings
Concentration (µg m-3)
0
1
2
3
4
5
6
7
1
2
3
4
5
11
12
13
14
Sampling point
Experimental
Contribution from WTP 1

Figure 6


a)
Average Formaldehyde concentration in air from WTP 2 surroundings
Concentration (µg m-3)
0
1
2
3
4
5
6
7
8
6
7
8
9
10
Sampling point
Experimental
Contribution from WTP 2
b)
Average TVOC concentration in air from WTP 2 surroundings
TVOC exp. (µg m-3)
0
100
200
300
400
TVOC calc. (µg m-3)
0,0
0,5
1,0
1,5
2,0
2,5
6
7
8
9
10
Sampling Point
Experimental
Contribution from WTP 2