Estimation of unidentified non-methane hydrocarbons in urban air based on highly correlated compound pairs

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HIGHLIGHTS

- An estimation method for NMHCs' mixing ratios was developed, validated, and applied.
- The method may be applied to other standard monitoring site that uses a GC-FID.
- New data may be obtained after processing historical NMHCs databases.
- NMHCs' total reactivity and O_3 forming potential may be calculated more accurately.

ARTICLE INFO

ABSTRACT

Gas Chromatography coupled with Flame Ionization Detector (GC-FID) is used worldwide for non-methane hydrocarbons' (NMHCs) monitoring. Being a non-selective detector, identification and coelution problems may hamper the reliability of data. An estimation method was developed, based on the correlation of easily measured NMHCs with those unknowns. Correlations were calculated from data obtained with a Gas Chromatograph coupled with a Mass Spectrometer Detector (GC-MSD) after gathering more than 1500 hourly mixing ratio data of 67 NMHCs. The method was developed and validated for an urban area but it may be adapted and applied to other locations. Now it is possible to estimate mixing ratios of some important ozone precursors previously not resolved with the GC-FID, such as 2,2,4-trimethylpentane and 1,2,3-trimethylbenzene. As a result, a six year-long database was enlarged by 34% allowing for a more accurate calculation of the total reactivity and NMHCs' ozone forming potential.

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1. Introduction

In the most recent report published about Air Quality in Europe tropospheric ozone (O_3) and particulate matter (PM) were considered Europe's most problematic pollutants in terms of damage to human health and, hence, policies and measurement strategies are now enforced to reduce their levels (EEA, 2012). Such reduction cannot be solely obtained with a decrease in their straight emissions as, among other sources, non-methane hydrocarbons (NMHCs) play a very important role as precursors of O_3 and PM (Parrish et al., 2011). In particular, O_3 is formed from a chain of complex photochemical reactions once their main precursors — NMHCs, nitrogen oxides (NO_x), and carbon monoxide (CO) — are emitted, and secondary organic aerosol (SOA) may be formed from some NMHCs (Derwent et al., 2010).

NMHCs and NO_x, the main O_3 precursors in Europe, showed a decreasing tendency from 2001 to 2010. Regarding O_3, most Airbase stations — monitoring sites that provide Air Quality data to Airbase, the Air Quality database from EEA — reported a slight decrease in its annual mean concentration. Nevertheless, some stations heavily affected by traffic registered an O_3 increase (de Leeuw, 2012). It has also been reported that a decrease in NMHC concentrations do not reduce significantly the one of O_3 due to the complexity of its ozone forming processes (EEA, 2012).

In order to understand the atmospheric O_3 and PM formation processes and their trends, it is essential to have access to long-

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term, continuous, and high-time resolution databases of their main precursors. NO_x and CO concentrations are, in general, well reported (EEA, 2012; US EPA, 2012) but not the ones of individual NMHCs which require more complex analytical procedures (Król et al., 2010). Each individual species may be related to its yield to form O_3 and SOA and are also responsible of other adverse effects, such as toxicity and carcinogenicity (ATSDR, 2011; IARC, 2013), or Global Warming Potential as greenhouse gas (IPCC, 2007). For all these reasons is substantially important to correct, complete, and enlarge the existing long-term databases in order to report reliable mixing ratios of individual NMHCs species.

Gas Chromatography with Flame Ionization Detector (GC-FID) is the most widely used method for the speciated, high-time resolution monitoring of NMHCs in ambient air. The main advantages of the FID are its inexpensiveness, stability, easy maintenance, and versatility (Tanner et al., 2006). FID, however, has low sensitivity for some compounds and, as many other non-selective detectors, coeluting compounds cannot be quantified (Badjagbo et al., 2007; Kato et al., 2011). Those difficulties can be overcome by using a selective and more sensitive detector which allows the positive identification of NMHCs, such as the Mass Spectrometer Detector (MSD) (de Blas et al., 2011). When compared with the FID, the MSD is more expensive, less stable in field conditions, and requires more complex and time-consuming data acquisition and management processes (Christensen et al., 2005; Cuadros-Rodríguez et al., 2007).

To date most NMHCs' mixing ratios estimation methods are based on air quality models, such as the one able to predict mixing ratios of 56 NMHCs in a remote coastal site of southern Taiwan during 2 weeks' period in May 2010 (Liu et al., 2012). Other authors predict speciated NMHCs' mixing ratios, grouped by carbon bond types, by using meteorological and photochemical models, and comparing their results with hourly measured mixing ratios at close-by Photochemical Assessment Monitoring Stations (PAMS) sites within the northeastern US between June and August of 2006 (Doraiswamy et al., 2009). To our knowledge, only few authors have used statistical models to predict NMHCs' mixing ratios. Recent models, based on multiple regression analysis techniques, have been described for the prediction in European urban areas of some aromatic compounds such as benzene (Vlachokostas et al., 2011), toluene (Vlachokostas et al., 2012), and ethylbenzene (Vlachokostas et al., 2013). As a different line of thought, due to the important role of the hydroxyl radical (OH) in the ozone production mechanism, other authors predict the contribution of unidentified species to OH reactivity instead of estimating NMHCs mixing ratios (Kato et al., 2011).

The applicability of the method described in this work goes beyond as it allows the estimation of mixing ratios of a number of NMHCs that frequently cannot be neither separated nor detected with GC-FID systems. In other cases they are site-specific and cannot be identified because they are not included on the typical standard mixtures used for calibration. The method was developed in an urban site where long term, hourly NMHC measurements had been carried out with a GC-FID and started with a measurement campaign with a GC-MSD system, followed by a search for correlations between compounds' pairs, where one of them, used as reference, was known to be easily detected by GC-FID. Then both GC-FID and GC-MSD systems were run in parallel for the validation. The correlations found may serve as an example of an enhanced speciation on sites running standard GC-FID systems for NMHC characterization, especially for those of high interest such as some ozone precursors included now on the list recommended for measurement by European Directive 2008/50/CE on ambient air quality, i.e. 2,2,4-trimethylpentane and 1,2,3-trimethylbenzene, which are also included in the measurement protocol of the Photochemical Assessment Monitoring Stations (PAMS) of the US Environmental Protection Agency (US EPA, 2013). As the number

of the species identified and quantified increases, so is the accuracy of the calculation of total NMHCs (TNMHC) and their ozone formation potential (OFP), which leads to a more complex and precise NMHC fingerprint. Moreover, as some compounds are indicative of certain processes, both source apportionment process and the characterization of multipollutant air samples could be simplified (Barzyk et al., 2012).

2. Materials and methods

2.1. Measurement site

NMHC measurements were performed in Bilbao, a medium-size city located in an estuary of complex orography. Bilbao is the main municipality of a metropolitan area which totally accounts for more than one million inhabitants. Ambient air samples were taken from the outside of the Air Quality Laboratory, located at the top floor of the building of the School of Engineering in Bilbao (ETSI-Bilbao), between one of the major road entrances to the city and the main bus station.

The atmospheric dynamics in the area is characterized by winds channeled along the valley, being the ETSI-Bilbao located 400 m southwest of the river. More details about this site and a map are given elsewhere (Durana et al., 2006; de Blas et al., 2011). Local NMHC sources from surrounding industry and road traffic combined with adverse dispersive conditions have caused in the past well documented pollution episodes (Durana et al., 2006).

2.2. Automated GC-FID and GC-MSD

From 1997 to 2001 years and during 2004 urban ambient air NMHC measurements were performed on an hourly, continuously, and on-line basis using an automated GC-FID chromatographic system. Sampling was performed every hour using a Thermal Desorber —TD— (TurboMatrix 150 ATD, Perkin Elmer Waltham, MA, USA). Samples were dried using a Nafion drier (Nafion®, Permapure Inc, Toms Rivers, NJ, USA), which also retained highly-polar NMHCs and, then, concentrated in an electrically cooled trap. In order to carry samples to the chromatographic system, they were desorbed by heating the trap and using helium as a carrier gas. The chromatographic system (VOC Ozone Precursor Analyzer System, PerkinElmer, Waltham, MA, USA) was fitted with two chromatographic columns (PLOT and BP1) and twin FIDs for the identification and quantification of 27 C_2–C_5 and 35 C_6–C_{10} non-polar NMHCs, respectively. A certified gas standard (prepared by UK National Physical Laboratory, NPL) was used for the quantification of the 27 NMHCs included in such gas. The remaining 35 NMHCs were identified using individual standards and were quantified by means of response factors (Durana et al., 2006). Analytical parameters were found: linearity (coefficients of determination, $R^2 > 0.99$), precision (coefficients of variation, CV < 25%) and detection limits, which were below 0.10 ppbv for most compounds. More details about sampling and analysis, such as flow rates, temperatures or features of the chromatographic columns are given elsewhere (Durana et al., 2002, 2006). Collected NMHCs' hourly urban mixing ratio data allowed the creation of one of the most comprehensive databases in Europe at that time (Durana et al., 2006; Navazo et al., 2003).

Being the FID non-selective and not sensitive enough for some compounds, during 1997–2001 and 2004 campaigns it was not possible to quantify some coeluting compounds and other compounds present in very low mixing ratios, particularly 6 anthropogenic C_7–C_{10} NMHCs of great interest in urban areas (1-heptene, 2,2,4-trimethylpentane, i-propylbenzene, o-ethyltoluene, 1,2,3-trimethylbenzene, and p-diethylbenzene). To solve these