Seasonal variation and origins of volatile organic compounds observed during two years at a western Mediterranean remote background site (Ersa, Cape Corsica)

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Abstract. An original time series of about 300 atmospheric measurements of a wide range of volatile organic compounds (VOCs) has been obtained at a remote Mediterranean station on the northern tip of Corsica Island (Ersa, France) over 25 months from June 2012 to June 2014. This study presents the seasonal variabilities of 35 selected VOCs, and their various associated sources. The VOC abundance was largely dominated by oxygenated VOCs (OVOCs) along with primary anthropogenic VOCs having a long lifetime in the atmosphere. VOC temporal variations were then examined. Primarily of local origin, biogenic VOCs exhibited notable seasonal and interannual variations, related to temperature and solar radiation. Anthropogenic compounds showed increased concentrations in winter (JFM months) followed by a decrease in spring/summer (AMJ/JAS months), and higher winter concentration levels in 2013 than in 2014 by up to 0.3 µg m^{-3} in the cases of propane, acetylene and benzene. OVOC concentrations were generally high in summertime, mainly due to secondary anthropogenic/biogenic and primary biogenic sources, whereas their lower concentrations during fall and winter were potentially more influenced by primary/secondary anthropogenic sources. Moreover, an apportionment factorial analysis was applied to a database comprising a selection of 14 ~~primary~~ individual or grouped VOCs by means of the positive matrix factorization (PMF) technique. A PMF 5-factor solution was taken on. It includes an anthropogenic factor (which contributed 39% to the total concentration~~s~~ of the ~~selected~~ VOCs selected in the PMF analysis) connected to the regional background pollution, three other anthropogenic factors (namely short-lived anthropogenic sources, evaporative sources, and long-lived combustion sources; which together accounted for 57%)~~,~~ originating from either nearby or more distant emission areas (such as Italy and south of France),~~;~~ and a local biogenic source (4%). Variations in these main sources impacting VOC concentrations observed at the Ersa station ~~are~~ were also investigated at seasonal and interannual scales. In spring and summer, VOC concentrations observed at Ersa were the lowest in the 2-yr period, despite higher biogenic source contributions. ~~and since~~ During these seasons, anthropogenic sources advected to Ersa were largely influenced by chemical transformations and

vertical dispersion phenomena and were mainly of regional origins. During fall and winter, anthropogenic sources showed higher ~~accumulated~~ contributions when European air masses were advected to Ersa and could be associated with potential emission areas located in Italy and possibly more distant ones in central Europe. Higher VOC winter concentrations in 2013 than in 2014 could be related to ~~anthropogenic source~~ contribution variations in anthropogenic sources probably governed by their emission strength ~~of the main anthropogenic sources identified in this study together~~ with external parameters, i.e. weaker dispersion phenomena and the pollutant depletion. High frequency observations collected during several intensive field campaigns conducted at Ersa during the three summers 2012-2014 confirmed findings drawn from bi-weekly samples of the 2-yr period in terms of summer concentration levels and source apportionment. However, they also suggested that higher sampling frequency and temporal resolution, in particular to observe VOC concentration variations during the daily cycle, would have been~~are~~ ~~needed~~ necessary to confirm the deconvolution of the different anthropogenic sources identified ~~by~~ following the PMF approach. Finally, comparisons of the 25 months of Ersa observations ~~at Ersa~~ with VOC measurements conducted at 17 other European monitoring stations highlighted the representativeness of the Ersa station for monitoring seasonal variations in VOC regional pollution impacting continental Europe. Nevertheless, ~~winter~~ VOC winter concentration levels can significantly vary between sites, pointing out spatial variations in anthropogenic source contributions. As a result, Ersa concentration variations in winter were more representative of VOC regional pollution impacting central Europe. Moreover, i~~I~~nterannual and spatial variations in VOC winter concentration levels ~~variations in winter~~ were ~~also~~ significantly impacted by synoptic phenomena influencing meteorological conditions observed in continental Europe, suggesting that short observation periods may reflect the variability of the identified parameters under the specific meteorological conditions of the study period.

1 Introduction

The main trace pollutants in the atmosphere encompass a multitude of volatile organic compounds (VOCs), with lifetimes varying from minutes to months (e.g., Atkinson, 2000). Their distribution is principally owing to (i) multiple natural and anthropogenic sources, which release VOCs directly to the atmosphere. At a global scale, natural emissions are quantitatively larger than anthropogenic ones (Guenther et al., 2000) and the largest natural source is considered to be the vegetation (Finlayson-Pitts & Pitts, 2000; Guenther et al., 2000, 2006). In urban areas, numerous anthropogenic sources can abundantly emit various VOCs (Friedrich and Obermeier, 1999). Once in the atmosphere, VOC temporal and spatial variabilities are notably influenced by (ii) mixing processes along with (iii) removal processes or chemical transformations (Atkinson, 2000; Atkinson and Arey, 2003). Accordingly, with a view to thoroughly~~extensively~~ characterize VOC sources, it is meaningful to examine their chemical composition, ~~in addition to identifying~~and identify the factors controlling their variations at different time scales.

VOC regional distributions ~~are eminently changing~~change considerably as a result of various confounding factors, namely the emission strength of numerous potential sources, diverse atmospheric lifetimes and removal mechanisms, transport process and ~~fluctuating~~ fluctuations in meteorological conditions. Therefore, these elements underline the necessity to carry out long-term VOC measurements. ~~There are g~~Growing efforts ~~now~~ are currently being made to conduct European background measurements over several seasons (e.g., Seco et al., 2011), one year (such as Helmig et al., 2008; Legreid et al., 2008) and even several years (Solberg et al., 1996, 2001 and Tørseth et al., 2012 at several European sites; Hakola et al., 2006 and Hellén et al., 2015 in Scandinavia; Dollard et al., 2007; Grant et al., 2011 and Malley et al., 2015 in United Kingdom; Borbon et al., 2004; Sauvage et al., 2009 and Waked et al., 2016 in France; Plass-Dülmer et al., 2002 in Germany; Navazo et al., 2008 in Iberian Peninsula; Lo Vullo et al., 2016 in Italy). These research studies principally explored the effectiveness of emission regulations~~ efficiency~~ and~~,~~ links between tropospheric ozone production and ~~changes in~~ VOC concentration levels. They also~~s,~~ ~~and~~ assessed seasonal variations and regional distributions ~~in~~ of VOC concentrations. Nonetheless, investigations ~~on~~ of principal factors governing temporal and spatial variations in VOC concentration levels in the European background atmosphere remain scarce. However, the consideration of the influence of (i) source emission strength variations (built upon a factorial analysis – e.g., Lanz et al., 2009 and Lo Vullo et al., 2016), (ii) long-range transport of pollution (e.g., by the examination of air mass trajectories combined with ~~measured~~ concentrations measured at a study site; Sauvage et al., 2009) and (iii) fluctuations in meteorological conditions (which are prone to disperse the pollutants ~~on a regional or long-range scale~~ over long distances ~~through~~ by convective and advective transport) can supply relevant information to deal more in depth with the evaluation of seasonal variations and regional distribution of VOC concentrations in the European background atmosphere.

Particulate and gaseous pollutants detrimentally affect the Mediterranean atmosphere. Accordingly, they are prone to increase aerosol and/or ozone concentration levels in the Mediterranean, regularly higher compared to most regions of continental Europe, and primarily during summer (Doche et al., 2014; Nabat et al., 2013; Safieddine et al., 2014). The Mediterranean region is known to be a noteworthy climate change "hot spot", which is expected to go through severe warming and drying in the 21st century (Giorgi, 2006; Kopf, 2010; Lelieveld et al., 2014). As a consequence, this can have serious consequences on the release of VOCs from biogenic and anthropogenic sources along with their fate in the atmosphere, with uncertain predicted impacts (Colette et al., 2012, 2013; Jaidan et al., 2018). Actually, the examination of air composition, concentration levels and trends in the Mediterranean region persist to be challenging, primarily ~~on account of~~due to the lack of extensive in-situ observations. Given this context, as part of the multidisciplinary regional research program MISTRALS (Mediterranean Integrated Studies at Regional and Local Scales; http://mistrals-home.org/, last access: 11/10/2020), the project ChArMEx (the Chemistry-Aerosol Mediterranean Experiment, http://charmex.lsce.ipsl.fr, last access: 11/10/2020; Dulac, 2014) aims at assessing the current and future state of the atmospheric environment in the Mediterranean along with examining its repercussions on the regional climate, air quality and marine biogeochemistry. ~~In~~ Within the framework of ChArMEx, several observation periods were conducted at the Ersa station, a remote site considered to be representative of the northwestern Mediterranean basin, in order to explain variations in VOC concentrations affecting the western Mediterranean atmosphere. Michoud et al. (2017) characterized the variations in VOC concentrations observed at Ersa in summer 2013 (from 15 July to 5 August 2013) by identifying and examining their sources.

In this article, we have presented and discussed the factors controlling seasonal and interannual variations of a selection of VOCs observed at the Ersa station over more than two years (from early June 2012 to late June 2014). To this end, this study describes (i) the concentration levels of the targeted VOCs, (ii) their temporal variations at seasonal and interannual scales, (iii) the identification and characteristics of their main sources by statistical modelling, (iv) the evaluation of their source contributions on seasonal bases, together with (v) the representativeness of the Ersa station in terms of seasonal variations in VOC concentrations impacting continental Europe.

2 Material and Methods

2.1 Study site

Located in the northwestern part of the Mediterranean Sea, Corsica Island is a French territory situated 11 km northerly from Sardinian coasts, 90 km easterly from Tuscany (Italy) and 170 km southerly from the French Riviera (France). Being the 4th largest Mediterranean island, its land corresponds to an area of 8681 km^2 encompassed by around 1000 km of coastline (Encyclopædia Britannica, 2018). Corsica contrasts to other Mediterranean islands due to the importance of its forest cover (about a fifth of the island).

Within the framework of the ChArMEx project, an enhanced observation period has been set-up at a ground-based station in the north of Corsica (Ersa; 42.969°N, 9.380°E) over 25 months, from early June 2012 to late June 2014.~~,~~ ~~with t~~The aim ~~of~~ was to provid~~eing~~e a high quality controlled climatically relevant gas/aerosol database following the recommendations and criteria of international atmospheric chemistry networks, i.e.~~,~~ the Aerosol, Clouds and Trace gases Research Infrastructure (ACTRIS - https://www.actris.eu/; last access: 11/10/2020), the European Monitoring and Evaluation Program (EMEP - http://www.emep.int/; last access: 11/10/2020 - Tørseth et al., 2012), and the Global Atmosphere Watch of the World Meteorological Organization (WMO-GAW - http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html; last access: 11/10/2020). ~~This~~ The Ersa remote site is part of the Corsican Observatory for Research and Studies on Climate and Atmosphere-ocean environment (CORSiCA - https://corsica.obs-mip.fr/, last access: 11/10/2020; Lambert et al., 2011) and is located on the highest point of a ridge equipped with windmills (see the orographic description of the surroundings in Cholakian et al., 2018), at an altitude of 533 m above sea level (a.s.l.). Given its position on the north of the 40-km long Cape Corsican peninsula (Fig. 1), the Mediterranean Sea is clearly visible from the sampling site on west, north, and east sides (2.5-6 km from the sea; see also the figure presented in Michoud et al., 2017). The station was initially set up in order to monitor and examine pollutions advected to ~~the receptor site~~Ersa by air masses transported over the Mediterranean and originating from the Marseille-Fos-Berre region (France; Cachier et al., 2005), the Rhone Valley (France), and the Po Valley (Italy; Royer et al., 2010), namely largely industrialized regions. The Ersa station is about 30 km north of Bastia (Fig. 1), the second largest Corsican city (44121 inhabitants; census 2012) and the main harbour. An international airport (Bastia-Poretta) is located 16 km further south of Bastia city centre. More than two millions of passengers transited in Corsica per Bastia during the tourist season (May-September) in 2013, (ORT Corse, 2013; http://www.corse.developpement-durable.gouv.fr/IMG/pdf/Ete2013.pdf, last access: 11/10/2020). However, as the Cape Corsican peninsula benefits in the south from a mountain range (peaking between 1000 and 1500 m a.s.l.) acting as a natural barrier, the sampling site is therefore not affected by transported pollutions originating from Bastia. Only small rural villages and a small local fishing harbour (Centuri) are found within 5 km of the measurement site. Additionally, the Ersa station is accessible by a dead end road serving only the windmill site, surrounded by vegetation made up of Mediterranean maquis, a shrubland biome characteristically consisting of densely growing evergreen shrubs, and also roamed by a herd of goats from a nearby farm. Some forests (78~~-~~% of holm oaks, with some cork oaks and chestnuts) are also located nearby, thus ensuring that local anthropogenic pollution does not contaminate in-situ observations. As a result, the Ersa station can be characterized as a remote background Mediterranean site.

2.2 Experimental Set-up

2.2.1 VOC measurements

During a study period of two years, non-methane hydrocarbons (NMHCs) and OVOCs (carbonyl compounds) were measured routinely employing complementary off-line methods. Four-hour-integrated (09:00-13:00 or 12:00-16:00 UTC) ambient air samples were collected bi-weekly (every Monday and Thursday) into steel canisters and on sorbent cartridges. The inlets were roughly 1.5 m above the roof of a container mainly housing trace gas analysers. Table 1 describes VOC measurements set up throughout the observation period and Fig. S1 specifies their collection periods.

As generally realized in the EMEP network, 24 C_2-C_9 NMHCs were collected into Silcosteel canisters of a volume of 6 L, conforming to the TO-14 technique, which is considered adequate for the measurement of many non-polar VOCs (US-EPA, 1997). 152 air samples were realized with a homemade device (PRECOV) for sampling air at a steady flow rate regulated to 24 mL min^{-1} by canisters previously placed under vacuum. NMHC analysis was performed by a gas chromatograph coupled with a flame ionization detector (GC-FID) within three weeks following the sampling. Separation was performed by a system of dual capillary columns supplied with a switching device: the first column was a CP Sil5CB (50 m x 0.25 mm x 1 µm), suitable for the elution of VOCs from six to nine carbon atoms and the other one was a Plot Al_2O_3/Na_2SO_4 (50 m x 0.32 mm x 5 µm), in order to effectively elute VOCs from two to five carbon atoms. Four main steps constituted the quality assurance/quality control program: (i) the implementation of standard operating procedures, (ii) canister cleaning and certification (blank levels < 0.02 ppb), (iii) regular intercomparison exercises and (iv) sampling tests carried out in field conditions and concomitant with in-situ measurements (Sauvage et al., 2009).

About 150 air samples were gathered using sorbent cartridges (63 air samples on multi-sorbent cartridges and 89 additional ones on 2,4-dinitrophenylhydrazine - DNPH - cartridges), by means of an automatic clean room sampling system (ACROSS, TERA Environment, Crolles, France). C_1-C_{16} VOCs were collected via a 0.635 cm diameter 3-m long PFA line. They we~~a~~re then trapped into one of the two cartridge types: a multi-sorbent one consisted of carbopack C (200 mg) and carbopack B (200 mg; marketed under the name of carbotrap 202 by Perkin-Elmer, Wellesley, Massachusetts, USA), or~~and~~ a

Sep-Pak DNPH-Silica one (proposed by Waters Corporation, Milford, Massachusetts, USA). These off-line techniques are further characterized in Detournay et al. (2011) and their satisfying use in-situ has already been discussed by Detournay et al. (2013) and Ait-Helal et al. (2014). Succinctly here, the sampling of 44 C_5-C_{16} NMHCs, comprising alkanes, alkenes, aromatic compounds and six monoterpenes, as well as six C_6-C_{11} n-aldehydes, was conducted at a flow rate fixed at 200 mL min^{-1} and using the multi-sorbent cartridges. These latter were preliminary prepared by means of a RTA oven (French acronym for *"régénérateur d'adsorbant thermique"* – manufactured by TERA Environment, Crolles, France) in order to condition them during 24 h with purified air ~~at~~ heated to 250 °C and at flow rate regulated at 10 mL min^{-1}. ~~In parallel~~Concomitantly, 15 additional C_1-C_8 carbonyl compounds were collected at a flow rate fixed at 1.5 L min^{-1} using the DNPH cartridges. During the field campaign, several ozone scrubbers ~~have been~~were successively inserted in the sampling lines in order to limit any eventual ozonolysis of the measured VOCs: a MnO_2 ozone scrubber was retained for the multi-sorbent cartridges while KI ozone scrubber was placed upstream of the DNPH cartridges. Moreover, stainless-steel particle filters of 2 µm diameter porosity (Swagelok) were installed in order to prevent particle sampling. Then, VOC samples were transferred to the laboratory to be analysed within 6 weeks of their collection using a GC-FID (for the multi-adsorbent cartridges) or by high-performance liquid chromatograph connected to an ultraviolet detector (HPLC-UV; for the DNPH cartridges).

The reproducibility of each analytical instrument ~~has been~~was frequently checked, ~~firstly~~ by analysing a standard~~,~~ and examining results by plotting them on a control chart realized for each compound. The VOC detection limit was determined as 3 times the standard deviation of the blank variation. ~~Obtained d~~Detection limits in this study were all below 0.05 µg m^{-3} for the steel canisters and the DNPH cartridges, and of 0.01 µg m^{-3} for the multi-sorbent cartridges. The uncertainties for each species were evaluated respecting the ACTRIS-2 guidelines for the uncertainty evaluation (Reimann et al., 2018), considering precision, detection limit and systematic errors in the measurements. ~~Evaluated r~~Relative uncertainties assessed in this study ranged from 7% to 43% ~~concerning~~ for the steel canisters, between 7% and 73% for the multi-sorbent cartridges and from 6% to 41% ~~concerning~~ for the DNPH cartridges. Finally, the VOC dataset was validated following the ACTRIS protocol (Reimann et al., 2018).

Among the 71 different VOCs monitored at Ersa during the observation period, 35 VOCs were finally selected in this study following the methodology described in Sect. S1 of the Supplement.

2.2.2 Ancillary measurements

Other trace gases (CO and O_3) and meteorological parameters were ancillary monitored at the Ersa site during the observation period. CO was measured from 22 November 2012 to 16 December 2013 by a cavity ring-down spectroscopy analyser (G2401; Picarro, Santa Clara, California, USA) at a time resolution of 5 min. O_3 was measured from 31 May 2012 to 26 December 2013 ~~by means of~~using an ultraviolet absorption analyser (TEI 49i manufactured by Thermo Environmental Instruments Inc., Waltham, Massachusetts, USA) at a time resolution of 5 min. Meteorological parameters (temperature, pressure, relative humidity, wind speed, wind direction and total – direct and diffuse - solar radiation) were measured every minute from 8 June 2012 to 14 August 2012, and every 5 min from 15 August 2012 to 11 July 2014, with a weather station (CR1000 manufactured by Campbell Scientific Europe, Antony, France) placed at approximately 1.5 m above an adjacent container roof to the one which housed trace gas instruments. Note that ancillary trace gas and meteorological parameter results presented in this study are 4-hour averages concurrent to ~~periods when the~~ VOC sampling periods ~~were realized~~ (see Fig. S1).

2.3 Identification and contribution of major sources of VOCs

In order to characterize NMHC concentrations measured at Ersa with steel canisters (the reasons for this VOC selection are presented in Sect. S2 of the Supplement), we apportioned them within their sources in this study using the positive matrix factorization approach (PMF; Paatero, 1997; Paatero and Tapper, 1994)~~ applied to our concentration dataset~~. The PMF mathematical theory has already been presented in Debevec et al. (2017) and is therefore reminded in Sect. S2~~ of the Supplement~~. We used the PMF version 5.0, an enhanced tool developed by the Environmental Protection Agency (EPA) and including the multilinear engine program version 2 (ME-2; Paatero, 1999), and followed the guidance on ~~the~~ its use ~~of PMF~~ (Norris et al., 2014). Using NMHC inputs composed of 152 atmospheric data points of 14 variables (13 single primary ~~HCNMs~~ NMHCs and another one resulting ~~of~~ from the grouping of C_8 aromatic compounds) and following the methodology presented in Sect S2, a five-factor PMF solution has been selected in this study.

2.4 Geographical origins of VOC sources

2.4.1 Classification of air mass origins

In order to identify and classify air-mass origins, we analysed back trajectories calculated by the on-line version of the HYSPLIT Lagrangian model (the Hybrid Single Particle Lagrangian Integrated Trajectory Model developed by the National Oceanic and Atmospheric Administration – NOAA – Air Resources Laboratory; Draxler and Hess, 1998; Stein et al., 2015) using Ersa as the receptor site (arrival altitude~~ at Ersa~~: 600 m a.s.l.)~~ were analysed~~. For each 4h-atmospheric data point of the field campaign used for the factorial analysis, five back-trajectories of 48 h were computed using GDAS one-degree resolution meteorological data, in order to follow the same methodology as Michoud et al. (2017). The first back trajectory of a set corresponds to the hour when the air sampling was initiated (i.e. 09:00 or 12:00 UTC – see Table 1) and the 4 other ones were calculated every following hour. The time step between each point along the back-trajectories was fixed at 1 hour.

Then, ~~the computed~~ back trajectories were visually classified. Having several back trajectories per sample ~~allows~~ allowed us to check ~~if~~ whether air masses transported to~~at~~ the station over 4 hours were ~~globally~~ of the same origin. ~~As a result, s~~Samples associated with air masses showing contrasted trajectories (e. g., due to a transitory state between two different origins) were classified as of mixed origins (9% of the air masses) and discarded from this study~~ (9% of the air masses)~~. Remaining air masses were then manually classified into five trajectory clusters (marine, Corsica-Sardinia, Europe, France and Spain - Fig. 2 and Table 2) ~~in function of~~depending on their pathway when they reached the Ersa station, their residence time over each potential source region and the length of their trajectories. Additionally, air masses of each cluster were sub~~-~~

divided ~~in function of~~depending on their distance travelled during their 48-h course in order to highlight potential more distant sources from local ones. This sub~~-~~division is also given in Table 2 in order to pinpoint differences in transport times.

2.4.2 Identification of potential emission areas

~~Since the initial origin of an air mass cannot be unquestionably assessed using wind measured at a receptor site,~~ PMF source ~~type~~ contributions ~~from the PMF~~ were coupled with back-trajectories in order to investigate potential emission regions contributing to long-distance pollution transport to the Ersa site. To achieve this, the concentration field (CF) statistical method established by Seibert et al (1994) was chosen in the present study. The CF principle has already been presented in Debevec et al. (2017) and is therefore ~~only~~ reminded in Sect. S3 of the Supplement.

~~For each VOC observation,~~ 72~~3~~-h~~day~~ back-trajectories together with meteorological parameters of interest (i.~~–~~e.~~,~~ precipitation)~~,~~ were retrieved from the GDAS meteorological fields with a PC-based version of the HYSPLIT ~~lagrangian~~ Lagrangian model (version 4~~.4~~ revised in ~~February~~ April 2018~~6~~), following the same methodology as that used for the 48-h back-trajectories previously presented. The arrival time of trajectories at the Ersa station corresponds to the hour when half of the sampling was ~~done~~ carried out (i.e. 11:00 or 14:00 UTC – see Table 1). Note that longer back-trajectories were considered for CF analyses than those for air mass origin classification (Sect. 2.4.1), in order to be in the same conditions as Michoud et al. (2017) and hence to have comparative results between the two Ersa VOC studies.

CF analyses applied to VOC source contributions were carried out by means of the ZeFir tool (version 3.7~~5~~0; Petit et al., 2017). Back-trajectories ~~have been~~were shortened (i.e. the ZeFir tool considered shorter back-trajectories than 72 hours) when ~~a~~ precipitation higher than 0.1 mm was encountered along the trajectory (Bressi et al., 2014). As ~~also~~ done by Michoud et al. (2017), back-trajectories have been also shortened when air mass altitudes ~~gone beyond~~exceeded 1500 m a.s.l. in order to discard biases related to the significant dilution impacting air masses reaching the free troposphere. A better statistical significance of the CF results is commonly considered for grid cells with a high~~er~~ number of crossing trajectory points. As a result, some studies applied an empirical weighing function so as to limit the possible influence ~~–~~of ~~high~~ elevated concentrations, which may be observed during occasional episodes ~~with uncommon trajectories~~ (e.g., Bressi et al., 2014; Waked et al., 2014, 2018), on cells having a low number of trajectory points ~~and hence could influence cells having a low number of trajectory points~~. We preliminary tried to apply this weighing function in this study. Exploratory tests revealed that CF results with the empirical weighing function only highlighted local contributions, given the number of air masses ~~considered in~~of this study. The farther a cell ~~is~~ was from the Ersa station, the lower was its corresponding n_{ij} value (number of points of the total number of back-trajectories contained in the ijth grid cell, Sect. S3 of the Supplement), and the more the weighing function tended toward downweighting the ~~low n_{ij} value~~results related to this cell. Therefore, CF results discussed in this study were realized without weighing and these limitations should be taken into account when examining CF analyses, which are hence considered as indicative information.

Finally, the spatial coverage of grid cells ~~is~~ was set from (9° W; 32° N) to (27° E; 54° N), with a grid resolution of 0.3° x 0.3°. Allocated contributions were smoothed following a factor (corresponding to the strength of a Gaussian filter) set to 5 to take into account the uncertainties in the back-trajectory path (Charron et al., 2000).

3 Results

3.1 Meteorological conditions

~~Seasonal variations in pollutant ambient concentrations are commonly recognized to be significantly governed by meteorological parameters (namely temperature, total solar radiation, relative humidity and wind speed). Their m~~Monthly variations in meteorological parameters are depicted in Fig. 3. As the field measurement period covered two years (i.e. from June 2012 to June 2014), their interannual variations are also shown in Fig. 3b.

Air temperatures ~~observed during the observation period~~ showed typical seasonal variations, i.e. the highest ~~temperatures~~ recorded in summer (i.e. ~~from~~ the months of July to September) and the lowest in winter (i.e. ~~from~~ the months of January to March). They were globally in the range of normal values over the period 1981-2010 determined by *Météo-France* (the French national meteorological service; normal values correspond to minimal and maximal mean values determined for Bastia and are available for consultation at http://www.meteofrance.fr/climat-passe-et-futur/climathd, last access: 11/10/2020). Moreover, June~~The range of temperatures recorded in June was rather expanded over the 3 years. In fact, mean~~ temperatures were ~~was~~ ~~lower~~ colder in ~~June~~ 2013 than in ~~June~~ 2012 and 2014 (mean temperature of ~~mean temperature of~~ 24.7 ±5.8 °C, 19.4 ±4.1 °C and 22.5 ±5.4 °C in~~for~~ ~~June~~ 2012, 2013 and 2014, respectively), which could have influenced biogenic emissions. ~~Additionally,~~ Winter temperatures ~~recorded during winter 2013~~ were colder in 2013 than in ~~winter~~ 2014 (mean temperature of 7.0 ±4.1 °C, and 9.7 ±1.5 °C in~~for~~ ~~winter~~ 2013 and 2014, respectively). This finding could be explained by different winter climatic events which ~~have occurred during these two winter periods and have concerned~~ affected a large part of continental Europe in 2013 and 2014. On one hand, European winter was particularly harsh in 2013 caused by changes in air flux orientation originally due to the sudden stratospheric warming of the stratospheric polar vortex (Coy and Pawson, 2015)~~the stratospheric polar vortex underwent a sudden stratospheric warming (SSW; Coy and Pawson, 2015) in early January 2013, having repercussions on the tropospheric polar vortex, which collapsed several times towards Europe. As a result, air flux orientation was modified from north to east, bringing cold air, and hence causing a particularly rigorous European winter 2013~~. On the other hand, most of the western European countries experienced a mild winter in 2014 characterized by its lack of cold outbreaks and nights, and caused by an anomalous atmospheric circulation (Rasmijn et al., 2016; Van Oldenborgh et al., 2015; Watson et al., 2016).

Solar radiation ~~also~~ followed typical seasonal variations, with ~~higher values~~the highest recorded from May to August and ~~lower ones~~the lowest in December and January. ~~Variable solar radiations were observed in spring (i.e. from April to June) and summer. Mean~~ Spring (i.e. the months of April to June) solar radiations ~~was~~ were higher ~~by 29%~~ in ~~spring~~ 2014 ~~compared to spring~~than in 2013 (~~mean solar radiation~~average value of 371 ±157 W m^{-2} and 478 ±153 W m^{-2} in~~for~~ ~~spring~~ 2013 and 2014, respectively). ~~while mean~~Summer solar radiations were~~as~~ higher ~~by 24%~~ in ~~summer~~ 2013 ~~compared to summer~~than in 2012 (~~mean solar radiation~~average value of 332 ±164 W.m^{-2} and 395 ±128 W.m^{-2} in~~for~~ ~~summer~~ 2012 and 2013, respectively). These solar radiation ~~conditions~~ variations ~~could~~ may have ~~have~~ affected~~ed~~ biogenic VOC (BVOC) emissions and photochemical reactions.

~~Globally, r~~Relative humidity followed opposite seasonal variations to temperature and solar radiation. ~~In June 2012, a~~Air in June was dryer ~~compared to~~in 2012 than in ~~June~~ 2013 and 2014 (mean relative humidity of 57 ±15%, 77 ±16% and 67 ±33% in~~for~~ ~~June~~ 2012, 2013 and 2014, respectively). The wind speed did not show a clear seasonal variation over the two years studied. ~~Slightly higher w~~Wind speeds were slightly higher ~~noticed~~ in April and May, which could induce higher dispersion of air pollutants and favour ~~advect air pollutants~~their advection to the Ersa station by~~from~~ ~~more~~ the most distant sources~~ to the Ersa station~~.

3.2 Air mass origins

Occurrences of air mass origins which ~~have~~ influenced Ersa throughout the observation period are indicated in Table 2. The Ersa station was predominantly ~~under the influence of~~influenced by continental air masses coming from Europe (corresponding to cluster 3, 31%), France (cluster 4, 26%), Corsica-Sardinia (cluster 2, 14%) and Spain (cluster 5, 5%) and to a lesser extent by air masses predominantly of ~~predominant~~ marine origin (cluster 1, 15%). Each of these five clusters is mostly associated with a particular trajectory sector (e.g., south for air masses originating from Corsica and/or Sardinia, see Fig. 2) and is defined by a different transit time from continental coasts~~,~~. According to Michoud et al. (2017), transit time can be viewed as an indicator of the last time ~~the potential moment~~ when an air mass could have been enriched ~~by~~ in anthropogenic sources ~~for the last time~~ (Table 2)~~, as observed by Michoud et al. (2017)~~. Continental air masses spent less time over the sea than marine ones. ~~Nonetheless, t~~Transit times of continental air masses over the sea differed depending on ~~in function of~~ how they ~~are~~ were categorized. Air masses originating from Corsica-Sardinia, France and Europe ~~have~~ spent 0-8 hours (median values – Table 2) above the sea before reaching the Ersa station, while the air masses originating from Spain ~~have~~ spent about 36 hours. These contrasting transit times may denote both distinctive atmospheric processing times for ~~the~~ air masses and different oceanic source influences on VOC concentrations observed at the Ersa station.

~~In particular,~~ European and French air masses showed lower transit times over the sea (median value~~s~~ of 6 ~~h~~ and 8 hours, respectively; Table 2) when their trajectories we~~a~~re categorized as long; compared to short ones (23 ~~h~~ and 19 hours, respectively). These findings are based on the fact that an air mass trajectory classified as short has a closer distance between two of its ~~succeeding~~ successive trajectory points compared to another one classified as long. Due to the Ersa location in the Mediterranean Sea, ~~the~~ air masses having trajectories ~~characterized~~ categorized as long ~~have~~ spent ~~more time to~~longer periods above the sea before reaching the Ersa site. Note that European and French air masses were more frequently characterized by long trajectories (accounting for 20% of the air masses observed at Ersa during the studied period, for each) than short ones (11 and 6%, respectively). ~~On the other hand~~Moreover, marine air masses having short and long trajectories ~~have~~ both ~~shown~~

showed long transit times (median values of 40-48 hours – Table 2).~~ and~~ Corsican-Sardinian air masses were only ~~concerned~~ characterized by long trajectories.

3.3 VOC mixing ratios

Statistical results ~~on~~ of concentrations of the 35 VOCs selected in this study (see Sect. S1 in the Supplement) are summarized in Table 3. Their average concentration levels as a function of the measurement sampling time~~s~~ (09:00-13:00 or 12:00-16:00) are also indicated in Table S1. These VOCs were organized into three principal categories: biogenic, anthropogenic, and oxygenated VOCs (5, 16 and 14 targeted species, respectively; Table 3). Isoprene and four monoterpenes were classified into BVOCs, while the other primary hydrocarbons (alkanes, alkenes, alkynes and aromatic compounds) were included into anthropogenic NMHCs, since their emissions are especially in connection with human activities. OVOCs have been presented separately, as these compounds come from both biogenic and anthropogenic (primary and secondary) sources. OVOCs were the most abundant, accounting for 65% of the total concentration of the 35 ~~compounds~~ VOCs selected in this study. They were mainly composed of acetone (contribution of 51% to the OVOC ~~cumulated~~ cumulative concentration). Anthropogenic NMHCs also contributed significantly (26%) to the total VOC concentration ~~of the 35 measured VOCs~~ and principally consisted of ethane and propane (which represented 34 and 17% of the anthropogenic NMHC cumulative concentration~~mass~~, respectively) as well as n-butane (7%). The high contribution of species ~~with~~ which generally have the longest lifetimes in the atmosphere (see Sect. 3.~~4~~5) is consistent with the remote location of the Ersa site and is in agreement with Michoud et al. (2017). BVOCs ~~only~~ contributed little to the total VOC concentration ~~on annual average~~ (~~4~~9% on annual average, 13% in summer)~~, reaching 13% in summer~~. They were mainly composed of isoprene and α-pinene (contribution of 44 and 32% to the BVOC mass, respectively). These compounds are among the major BVOCs in terms of emission intensity for the Mediterranean vegetation (Owen et al., 2001) and accounted for half of isoprenoid concentrations recorded during the intensive field campaign conducted at Ersa in summer 2013 ~~at Ersa~~ (Debevec et al., 2018; Kalogridis, 2014). On the contrary, a larger α-terpinene contribution was noticed during the summer 2013 intensive field campaign than the 2-yr observation period. Note that speciated monoterpenes were measured differently during the summer 2013 field campaign, by means of an automatic analyser (see Sect. S4 in the Supplement).

3.4 VOC variability

Monthly and interannual variations of primary (anthropogenic and biogenic) NMHCs along with OVOCs ~~observed at Ersa~~ selected in this study (Sect. S1) are discussed in this section. Seasonal VOC concentration levels are indicated in Table 4. ~~In addition,~~Note that the results of comparison between the VOC monitoring measurements investigated in this study ~~with~~ and concurrent field campaign measurements performed during the summers 2012-2014 ~~(is~~ presented in Sect. S4 of the Supplement~~), in order to check~~ supported the representativeness of the 2-yr observation period with regard to its summer concentration levels.

3.4.1 Biogenic VOCs

Concentration variations of three selected BVOCs, isoprene, α-pinene and camphene, were analysed at different timescales (monthly/interannual variations; Fig. 4). These BVOCs exhibited high concentrations from June to August, consistently with temperature and solar radiation variations (see Sect. 3.1). Indeed, throughout the summer 2013 ~~SOP~~observation period, Michoud et al.~~,~~ (2017) and Kalogridis (2014) observed that emissions of isoprene and the sum of monoterpenes were ~~merely~~ mainly governed by temperature and solar radiation, ~~considering~~ supported both by the diurnal variations in their concentrations (Geron et al., 2000a; 2000b; Guenther et al., 2000) and their correlations with environmental parameters. Additionally, significant concentrations of α-pinene were noticed from September to November (Fig. 4), while isoprene concentrations were close to the detection limit and temperature and solar radiation were decreasing. However, solar radiation decreased much faster than temperature during these months (Fig. 3), which could suggest additional emissions (Laothawornkitkul et al., 2009), dependent only on temperature contrarily to those prevailing in summer, have influenced α-pinene concentrations during these months. Ozone concentrations, lower in fall (i.e. the months of October to December) than in summer (O_3 concentration variations are depicted in Fig. S2 of the Supplement), also pointed out a weaker degradation of α-pinene in fall.

~~Furthermore, t~~B~~hese b~~iogenic compounds showed significant interannual variations over the ~~two years~~ study period~~ied~~, linked to temperature and solar radiation variations. ~~For instance, h~~Higher ~~mean~~ June concentrations of isoprene and α-pinene were noticed in ~~June~~ 2012 (average concentration of 1.0 ±1.1 and 2.6 ±1.4 µg m^{-3} for isoprene and α-pinene, respectively) and ~~June~~ 2014 (0.7 ±0.5 and 0.2 µg m^{-3}) ~~compared to~~than in ~~June~~ 2013 (0.2 ±0.2 and <0.1 µg m^{-3}). Higher June concentrations of camphene (and α-terpinene; not shown) were also noticed in 2014 than in 2013 (Fig. 4). These concentration levels may be related to the fact that temperature and solar radiation were more favourable to enhance June biogenic emissions ~~in June~~ in 2012 and 2014 ~~compared to~~than in ~~June~~ 2013 ~~meteorological conditions~~ (Sect 3.1). Due to ~~the~~ air relative humidity values observed in June (Sect. 3.1)~~June 2012 and 2014, which were lower than in June 2013~~, we cannot rule out that an increase ~~of~~ in BVOC concentrations may be ~~related~~ linked to a transient ~~drought stress-induced~~ modification of BVOC emissions induced by drought stress (Ferracci et al., 2020, Loreto and Schnitzler, 2010; Niinemets et al., 2004). Moreover, isoprene and α-pinene concentrations in July and August were higher in ~~in July and August~~ 2013 (average concentration of 0.5 ±0.3 and 1.1 ±0.4 µg m^{-3}~~,~~ for isoprene and α-pinene, respectively) than in ~~July and August~~ 2012 (0.3 ±0.2 and 0.6 ±0.3 µg m^{-3}~~, respectively~~). High concentrations of camphene and α-terpinene were also noticed in August 2013 (0.2 ±0.1 and 0.3 ±0.3 µg m^{-3}, respectively; Fig. 4). Solar radiations ~~was~~ were lower in July and August 2012, temperatures ~~was~~ were slightly lower in July 2012 and mean wind speed was slightly higher in July 2012 (Fig. 3~~),~~). These meteorological conditions~~which~~ ~~could~~may have affected biogenic emissions and have favoured their dispersion and their dilution by marine air masses, owing to the position of the Ersa station (Sect. 2.1).

~~Additionally, significant concentrations of α-pinene were noticed from September to November (Fig. 4), while isoprene concentrations were close to the detection limit and temperature and solar radiation were decreasing. However, solar~~

~~radiation decreased much quicker than temperature in fall (Fig. 3), which could suggest additional temperature-dependant emissions (Laothawornkitkul et al., 2009), contrarily to those prevailing in summer, have influenced α-pinene fall concentrations. Moreover, the lower ozone fall concentrations than in summer (O$_3$ concentration variations are depicted in Fig. S2 of the Supplement) also pointed out a weaker degradation of α-pinene in fall.~~ Note that the interpretation of interannual variations in BVOC measurements is based on a limited number of sampling days during the study period and different collection times (Table 1 and Sect. 2.2.1). It should ~~then~~ therefore be considered cautiously, given variable day-to-day and strong diurnal BVOC concentration variations which were observed during the summer 2013 observation period (Kalogridis, 2014).

3.4.2 Anthropogenic VOCs

Variations of a selection of NMHCs~~,~~ are depicted in Fig. 5. These compounds illustrate~~ing~~ contrasted reactivity, ~~(according to~~based on their atmospheric lifetimes (estimated according to ~~considering~~ their photochemical reaction rates~~d~~ with OH radicals defined in Atkinson~~,~~ (1990) and Atkinson and Arey~~,~~ (2003))~~, are depicted in Fig. 5~~. Despite lifetimes in the atmosphere ranging from a few hours to some days, all selected NMHCs were characterized by similar seasonal variations, with an increasing winter trend followed by a decrease in spring/summer (Fig. 5 and Table 4), at the exception of n-hexane, propene and C$_8$ aromatics (which were the most reactive species of the NMHCs selected in this study and ~~which have~~had the lowest concentrations;~~ –~~ Tables 3 and 4). NMHC concentrations were higher in winter than in summer, up to 5 times higher in the case of acetylene (Table 4). Note that ethane concentration levels were ~~still~~ relatively important during summer (mean concentration of 1.0 ±0.2 µg m^{-3}) while other NMHCs showed concentrations below 0.4 µg m^{-3}.

~~Moreover,~~ NMHCs exhibited different concentration levels during the two studied winter periods (Fig. 5). Mean winter NMHC concentrations were higher in 2013 than in 2014 by up to 0.3 µg m^{-3} in the cases of propane, acetylene and benzene (relative differences of 15~~%~~, 42~~%~~ and 42%, respectively). These ~~latter~~ compounds and ethane had the longest lifetimes among those selected in this study. However, ethane concentrations recorded at Ersa did not show any interannual variation over the ~~two years studied~~study period (Fig. 5).

3.4.3 Oxygenated VOCs

Variations of selected OVOCs, illustrating contrasted reactivity (following the ~~according to their atmospheric lifetimes considering their photochemical reaction rates with OH radicals defined in Atkinson, 1990 and Atkinson and Arey, 2003~~same methodology as that applied to NMHCs; Sect. 3.4.2) ~~were~~ are ~~depicted~~ presented in Fig. 6. Formaldehyde, acetaldehyde, glyoxal, methylglyoxal and C$_6$-C$_{11}$ aldehydes have relatively short lifetimes into the atmosphere ~~(photochemical reaction rate with OH radicals of 9-30 10^{-12} cm^3 molecule^{-1}s^{-1})~~ and hence they can result from relatively close sources. On the other hand, acetone and methyl ethyl ketone (MEK) have the longest atmospheric lifetime ~~(0.17-1.22 10^{-12} cm^3 molecule^{-1}s^{-1}) of~~ among the OVOCs selected in this study, and hence they can also result from distant sources and/or be formed within emission-enriched air masses ~~before they reach~~advected to the Ersa station.

Firstly, formaldehyde, methylglyoxal and n-hexanal have shown similar seasonal variations (Fig. 6), with high summer and spring concentrations (Table 4), suggesting an important contribution of primary/secondary biogenic sources to their concentrations. Fu et al. (2008) found that the largest global sources for methylglyoxal were isoprene and to a lesser extent acetone~~, this latter source can contribute to its background concentrations~~. Besides photochemical production, n-hexanal and formaldehyde can be notably emitted by many plant species (Guenther et al., 2000; Kesselmeier and Staudt, 1998; Wild et al, 2003). Interannual variations in formaldehyde, methylglyoxal and n-hexanal summer concentrations confirmed their links with biogenic sources. For instance, the ~~methylglyoxal~~ highest concentrations of methylglyoxal were ~~monitored~~ observed in June 2012 (average concentration of 0.7 µg m^{-3}), similarly to isoprene (Sect. 3.4.1). ~~Concentrations~~ Monthly concentrations of n-hexanal peaked ~~up~~ at 0.7 µg m^{-3} in August 2013, in agreement with monoterpenes, especially camphene and α-terpinene (~~Fig. 4~~Sect. 3.4.1). Formaldehyde showed high concentrations both in June 2012 and August 2013 (2.9 and 3.6 µg m^{-3}, respectively).

Acetaldehyde and acetone have shown ~~similar seasonal variations, with~~ an increase ~~of~~ in their concentrations more marked in summer than in winter (Fig. 6), suggesting they were probably mainly of both secondary (anthropogenic/biogenic) and primary biogenic origins. Acetaldehyde is known to be mainly produced through the chemical transformation of anthropogenic and biogenic VOCs (Rottenberger et al., 2004; Schade and Goldstein, 2001; Seco et al., 2007; Wolfe et al., 2016), particularly in clean and remote areas. Acetaldehyde can also be released by plants (Jardine et al., 2008; Rottenberger et al., 2008; Winters et al., 2009). Acetone emissions are thought to be globally of biogenic rather than anthropogenic origin (Goldstein and Schade, 2000; Schade and Goldstein, 2006). Acetone can also ~~be~~ result~~ed~~ ~~of~~ from the oxidation of various VOCs (Goldstein and Schade, 2000; Jacob et al., 2002; Singh et al., 2004) and roughly half of its concentrations measured at diverse urban or rural sites have been assigned to regional background pollution by several studies (e.g., Debevec et al., 2017; de Gouw et al., 2005; Legreid et al., 2007~~)~~; with regional contributions at a scale of hundreds of kilometres). Additionally, acetaldehyde and acetone concentration variations in winter (e.g., mean February concentration in 2013~~s~~ was 0.5 and 2.4 µg m^{-3} higher ~~0.5 and 2.4 µg m^{-3} in 2013~~ than in 2014, respectively) also pinpointed primary/secondary anthropogenic origins (Sect. 3.4.2).

Glyoxal and MEK showed an increase ~~of~~in their concentrations both in summer and winter (Fig. 6 and Table 4), suggesting they were probably produced by several biogenic and anthropogenic sources. Glyoxal increases ~~Those of glyoxal~~ were in similar proportions (Fig. 6 and Table 4) while the MEK increase in winter was more marked than in summer, which may indicate that primary/secondary anthropogenic sources primarily contributed to MEK concentrations. Fu et al. (2008) found that the largest global sources for glyoxal were isoprene, and to a lesser extent acetylene and direct emissions. MEK can be emitted from both vegetation and numerous anthropogenic sources, and can ~~also be produced as a~~ result ~~of~~ from the oxidation of various VOCs (Yáñez-Serrano et al., 2016 and references therein). Glyoxal and MEK ~~both~~ exhibited different concentration levels during the two studied winter periods since their mean February concentration in ~~February~~ 2013 was 65-75% higher than in ~~February~~ 2014, confirming their links with anthropogenic sources. These two OVOCs also showed different interannual variations in late spring and summer (Fig. 6). The ~~glyoxal~~ highest concentrations of glyoxal were ~~monitored~~

measured in June 2012 (average concentration of 0.2 µg m^{-3}), similarly to isoprene and α-pinene ~~concentration variations~~ (Sect. 3.4.1), when MEK concentrations were among their lowest (0.3 µg m^{-3}).

Finally, n-nonanal did not show clear seasonal variations. Its March and April concentrations ~~monitored~~ were higher in 2014 than in 2013. An increase in MEK concentrations ~~in March and April 2014~~ was also noticed in March and April 2014 in lower proportion. These findings suggest contributions from different sources in winter/early spring, compared to the rest of the year. Moreover, a slight increase in n-nonanal concentrations was noted in August 2013, which is consistent with a biogenic source contribution (Matsunaga et al., 2003; Wild et al, 2003).

3.5 Major NMHC sources

In the coming section, major ~~NMHC~~ sources which have impacted primary NMHC concentrations measured at Ersa were identified using a PMF 5-factor solution (from simulations presented in Sect. ~~2.3~~S2) ~~and a dataset composed of 14 variables (selected NMHCs measured from steel canisters, see Sect. S2)~~. Figure 7 depicts factor contributions to the species chosen as inputs for the PMF tool along with NMHC contributions to the 5 factors defined by the factorial analysis. Figure 8 and Table 5 show ~~PMF~~ factor contribution time series and their relative contributions to the total concentration~~s~~ of the ~~selected~~ NMHCs selected in this factorial analysis, respectively. Average factor relative contributions as a function of the measurement sampling time~~s~~ are also indicated in Table 5. In the present section, lifetimes were assessed from kinetic rate constants of the reactions of the selected NMHCs with OH (Atkinson and Arey, 2003) given an average OH concentration of 0.5 10^{6} and 2.5 10^{6} molecules cm^{-3} in winter and summer, respectively (Spivakovsky et al., 2000).

As VOC concentrations ~~arised~~ resulted from direct emissions, chemistry, transport and mixing, each individual computed factor cannot be attributed solely to one source category, especially for ~~such~~ a remote receptor site ~~as~~like Ersa. A part of them may not be ~~precisely~~ specifically associated with emission profiles but should rather be ~~explained~~ considered as aged profiles originating from several source regions comprising several source categories (Sauvage et al., 2009). The PMF analysis was hence performed in this study to define co-variation factors of ~~primary VOCs~~NMHCs that were characteristic of aged or local primary emissions along with secondary photochemical transformations taking place during the transport of air masses observed at this remote site (Michoud et al., 2017).

Since the low number of NMHCs considered in the factorial analysis ~~in~~ of this study, PMF result relevance was checked, benefiting from a previous PMF analysis performed with the Ersa VOC summer 2013 dataset (~~42 variables;~~ Michoud et al., 2017; see Sect. 3.5.6). ~~and e~~Experimental strategies to characterize VOC concentration variations at a remote background such as Ersa are also discussed in Sect. 3.5.6.

3.5.1 Local biogenic source (factor 1)

~~The average contribution of factor 1~~Factor 1 contributions to measured concentrations of the NMHCs selected in the factorial analysis ~~is~~ were ~~of~~ 0.2 ±0.4 µg m^{-3} on average ~~during the observation period~~ (corresponding to 4% of the sum of these~~selected~~ NMHCs – Table 5), and peaked~~ing~~ ~~up~~ at 3.1 µg m^{-3} on 20 June 2012. In late spring/summer, it was one of the main factors observed (16% on average and up to 53%; Fig. 8). The chemical profile of factor 1 depicts an elevated contribution of isoprene, ~~recognized~~ known as a chemical marker for biogenic emissions, having its variability fully related to this factor. The isoprene relative contribution to factor 1 is 70%. The estimated tropospheric lifetime of isoprene was quite short (winter: ~~5.~~6 hours and summer: ~1~~.1~~ hour), indicating that this compound was emitted mostly by local vegetation. Consequently, factor 1 is labelled "local biogenic source". Note that factor 1 contribution to selected NMHC concentrations ~~observed at Ersa during the 2-yr period~~ may be slightly influenced by the two different sampling times used during the 2-yr observation period (Table 5) ~~and~~ as well as the number of VOCs and data points considered in the PMF analysis (see Sects. 3.4.1 and S2). However, Michoud et al. (2017) ~~has~~ provided additional information on this local primary biogenic source in summer, ~~such as~~like the contributions of additional primary BVOCs (the sum of monoterpenes) and some OVOCs (carboxylic acids, methanol and acetone), and presented ~~the~~ its clear diurnal variations ~~of the local primary biogenic source~~.

3.5.2 Short-lived anthropogenic sources (factor 2)

Factor 2 contributed 19% ~~of~~ to the sum of the selected ~~measured~~ NMHCs ~~was attributed to factor 2~~ (Table 5; average contribution of 1.0 ±0.5 µg m^{-3}). This factor is mainly consisted of ~~primary anthropogenic compounds, such as~~ toluene (73% of its variability attributed to this factor; Fig. 7), C$_8$ aromatic compounds (93%), ethylene (48%) and propene (83%), typically emitted by combustion processes and with short-to-medium lifetimes (winter: ~~24 h~~1-4~~.1~~ days; summer: 5-20 hours). The cumulative relative contribution of these VOCs to factor 2 is 66%. Besides road traffic, toluene is also a good marker for solvents generated by industrial sources (Buzcu and Fraser, 2006; Leuchner et al., 2015; Zhang et al., 2014), suggesting that this profile could also be imputed to industrial sources. Additionally, a significant proportion of C$_5$-C$_6$ alkanes, i.e. i-pentane (32% explained), n-pentane (37%) and n-hexane (51%), typically emitted by gasoline evaporation and with medium lifetimes (winter: 4-6 days; summer: 21-31 hours ~~1.3 day~~), also contributes 19% to this factor ~~by 19%~~. Factor 2 did not show a good correlation with CO (Pearson correlation coefficient only of 0.2). As a conclusion, f~~F~~actor 2 is hence attributed to the grouping of several short-lived anthropogenic sources, partly related to gasoline combustion and/or evaporation and solvent use. Note that the PMF model did not reconstruct well 5 of the species composing this factor (propene, n-pentane, n-hexane, toluene, and C$_8$ aromatics;~~–~~ Sect. S2 in the Supplement), especially their concentration variations over short periods. As a result, factor 2 contributions over short periods may be underestimated. However, given the objectives of this study, the examination of factor 2 contribution variations will be limited to seasonal and interannual ones (Sect. 4). Factor 2 contribution variations over a short period ~~was~~ were previously investigated in Michoud et al. (2017).

Regarding factor 2 contributions coupled with air mass ~~clusters~~ origins (Fig. 9), more elevated contributions were noticed at Ersa under the influence of continental air masses coming from France and Europe. The distinction of short-trajectories from long ones (see Sect. 3.2) highlighted that factor 2 was potentially influenced by relatively close sources when Ersa received air masses from continental France, whereas other continental European sources were probably more distant (Fig. 9). Furthermore, CF analysis applied to factor 2 contributions (see Fig. S3 of the Supplement) confirmed that this factor was influenced by various potential emission areas, either located in Italy (the Po Valley and Central Italy), France (southeast region) or possibly in central Europe (western Hungary, Croatia and Slovenia). Given the CF results, ship emission contribution cannot be discarded as well, as already suggested in~~by~~ Michoud et al. (2017). Indeed, ship emissions are predominantly composed of light alkenes, aromatic compounds and heavy alkanes (> C_6 compounds; Eyring et al., 2005).

3.5.3 Evaporative sources (factor 3)

~~The average contribution of f~~Factor 3 contributions to ~~the sum of~~ the selected ~~measured~~ NMHC concentrations ~~is approximately estimated at~~were 1.2 ±1.0 µg m^{-3} on average (22% of their sum; Table 5)~~ during the studied period~~. The profile of this anthropogenic factor displays an important contribution from alkanes, principally i-/n-butanes (having lifetimes of 10-11 days in winter, and ~2 days in summer) ~~and~~ with more than 69% of their variabilities explained by factor 3 (Fig. 7), along with i-/n-pentanes~~ (50%), n-pentane (59%)~~, n-hexane ~~(42%)~~ and propane (~~43~~42-59%; lifetimes of 4-21 days in winter, and 21 hours-4 days in summer). The cumulat~~ed~~ive relative contribution of these alkanes to factor 3 is up to 88%. ~~The~~ C_3-C_6 alkanes are identified in the gasoline composition and evaporation sources (storage, extraction and distribution of gasoline or liquid petroleum gas; Sauvage et al., 2009 and references therein). Additionally, propane can be viewed as a relevant profile signature of natural gas transport, storage and use (Leuchner et al., 2015). ~~The cumulated relative contribution of these alkanes to factor 3 is up to 88%. As a result~~Consequently, this factor can be viewed as “evaporative sources”.

Regarding factor contributions as a function of air mass ~~clusters~~ origins (Fig. 9), more elevated contributions were ~~noticed~~ noticed at the Ersa station when aged air masses originated from France and Europe and were probably transported toward Ersa by relatively distant sources. According to the CF analysis applied to factor 3 contributions (Fig. S3 of the Supplement), the Po Valley (especially Emilia-Romagna, an Italian region centre for food and automobile production), central Italy, the southeast of France and the Sardinian region seemed to be identified as main potential emission areas for factor 3, as well as possibly more distant emission areas in central Europe such as western Hungary (i.e. western Transdanubian region specialised in automotive and machinery industries).

3.5.4 Long-lived combustion sources (factor 4)

The average contribution of factor 4 to the ~~total concentration of the~~ selected ~~measured~~ NMHC concentrations~~s~~ is ~~roughly~~ evaluated at 0.9 ±0.7 µg m^{-3} (corresponding to 16% of their sum;~~—~~ Table 5)~~ on average during the observation period~~. Its profile displays an important contribution from acetylene (100% explained; Fig. 7), benzene (49%) and propane (37%), with lifetimes of 19-26 days in winter and ~~of~~ 4-5 days in summer. ~~and with an~~The average ~~cumulated~~ cumulative relative contribution of these VOCs to ~~this factor of~~factor 4 is 80%. Aromatic compounds and acetylene are generally associated with combustion sources, such as vehicle exhaust (e.g., Badol et al., 2008; Pang et al., 2014). However, factor 4 is characterized by a loading of benzene much more superior to toluene one (49 and 3~~-~~%, respectively), suggesting it is more related to a residential heating source than a traffic one (Elbir et al., 2007; Leuchner et al., 2015; Sauvage et al., 2009). Factor 4 profile, mainly composed of long-lived species together with a low contribution of shorter-lived species, may indicate that it is related to partly aged air masses which were advected towards the Ersa station. These suggestions are consistent with the fact that this factor correlated particularly well with CO (Pearson correlation coefficient of 0.8). As a result, this factor can be viewed as "long-lived combustion sources", including residential heating.

~~Furthermore, f~~Factor 4 showed higher contributions when the Ersa station received European air masses (see Fig. 9), ~~especially by those~~particularly those ~~having ~~with a long trajectory, which is consistent with factor 4 profile examination~~ies~~. The CF analysis depicted in Fig. S3 of the Supplement only pointed out western Hungary and to a lesser extent the Po Valley, as main potential emission areas for factor 4.

3.5.5 Regional background (factor 5)

Contributing ~~at ~~39% to the ~~total concentration of the ~~selected ~~measured ~~NMHC concentrations~~s~~ (average contribution of 2.2 ±1.0 µg m^{-3}), factor 5 corresponds to the dominant ~~NMHC ~~source detected at Ersa during the study period. ~~The ~~Its profile ~~of this factor ~~is principally ~~dominated by ~~composed of ethane~~, ~~(having its variability fully explained by factor 5~~; (~~Fig. 7)~~,~~ and ~~is also composed of ~~propane (18% explained; lifetimes of 21-93 days in winter and 4-19 days in summer). Their relative contribution to factor 5 is up to 96% and they ~~These compounds, with lifetimes of 21-93 days in winter and of 4-19 days in summer, ~~typically result from the transport, storage and use of natural gas~~ and their relative contribution to factor 5 was up to 96%~~. Additional anthropogenic NMHCs with shorter lifetimes are attributed to this factor, including ethylene~~ (16% explained)~~ and propene (12-16% explained; lifetimes of 21 hours~~- to ~~3 days in winter and ~~of ~~4-13 hours in summer), despite a low contribution to factor 5 mass (~3%). Given t~~Hence, t~~he high abundance of ~~of ~~long-lived species in its profile~~ may result here from aged air masses advected to the Ersa station. Consequently~~, factor 5 can be viewed as a regional contribution of diverse remote sources of the Mediterranean region, thus indicating the continental regional background (Hellén et al., 2003; Leuchner et al., 2015; Sauvage et al., 2009; regional contributions at a scale of hundreds of kilometres). ~~These sources were advected towards the sampling site by aged air masses, which have not been recently in contact with supplementary anthropogenic sources. Within the time of emission transport from distant sources, atmospheric oxidation depletes a large proportion of the reactive species and the remaining fraction is mainly constituted of the less-reactive VOCs, like ethane and propane. ~~As a ~~result~~conclusion, we associated factor 5 with the "regional background".

Factor 5 showed slightly higher contributions when the Ersa station was under the influence of European air masses, ~~(especially~~particularly those having a long ~~trajectories ~~trajectory ~~and hence(~~potentially connected to distant emission areas; Fig. 9). As expected, the CF analysis applied to factor 5 contributions did not clearly pinpoint a specific potential emission area (Fig. S3 of the Supplement), apart from maybe western Hungary and to a lesser extent the Po Valley~~, which are areas experiencing high anthropogenic emissions~~.

3.5.6 Towards the best experimental strategy to characterize variations in VOC concentrations observed at a remote background site

In this study, we decided ~~The choice ~~to restrain the number of VOCs in the factorial analysis~~,~~ in order to have a better temporal representativeness of factor contributions (see Sect. S2)~~, as well as VOC measurement temporal resolution and collection~~

~~periods and the number of observations, ~~. This choice ~~have ~~has undoubtedly had some consequences on the PMF solution results of this study (in terms of factor number, chemical profiles and variations). ~~As a result~~Consequently, ~~the 2-yr PMF results of this study~~to support our results,~~ have been supported~~ ~~by the consideration of the other VOC source apportionment previously performed with the Ersa summer 2013 dataset (Michoud et al., 2017). These two studies provided complementary results. On one hand, the SOP-1b intensive field campaign occurred in summer 2013 and offered good conditions to (i) monitor at a specific period anthropogenic sources, influenced by several geographic origins, along with local biogenic sources and secondary oxygenated sources and (ii) to assess their diurnal variations. On the other hand, the 2-yr monitoring period had the advantage to examine seasonal and interannual variations of main primary sources impacting VOC concentrations observed at the Ersa station. These two studies also helped to discuss on the best experimental strategy to characterize variations in VOC concentrations measured at a remote background site surrounded by vegetation such as Ersa (Sect. 2.1).~~

~~Firstly, the comparisons of~~we compared ~~the ~~our 5-factor PMF solution modelled with the 2-yr NMHC dataset (14 variables, 152 4-h resolution observations), with the 6-factor PMF solution modelled with the ~~shorter ~~summer 2013 VOC dataset (42 variables, 329 1.5-h resolution observations;~~,~~ Michoud et al., 2017). The comparative study (see Sect. S5 in the Supplement) pointed out a good representativeness of the primary sources identified in this study~~ (Sect. S5 in the Supplement)~~. Overall, ~~primary ~~sources identified in ~~the two~~both factorial analyses as influencing ~~VOC ~~NMHC concentrations at Ersa had similar chemical compositions, regarding NMHCs in common. This finding supports the relevance of the 17 NMHCs selected in the factorial analysis of this study to identify major ~~primary ~~sources which have influenced Ersa ~~VOC~~NMHC concentrations over two years and suggests that ~~these selected NMHCs~~they include~~d~~ ~~dominant ~~key source tracers~~ of these sources~~.

In order t~~T~~o support ~~this ~~these statements, ~~a ~~we computed a summer 2013 PMF solution~~, realized considering ~~only with the ~~17 ~~NMHCs selected in the factorial analysis of this study~~ as inputs~~, and we~~ was~~ ~~examined and ~~compared it with the summer 2013 PMF solution modelled with a higher VOC number ~~of VOCs ~~by Michoud et al. (2017~~; Sect. S6 in the Supplement~~). Results (see Sect. S6 in the Supplement) revealed a global consistency of the two summer 2013 PMF solutions in terms of factor chemical composition, regarding NMHCs in common between the two factorial analyses, and contribution variations, at the exception of those of short-lived anthropogenic sources (which may also depend on additional VOCs; Sect. S6)~~, ~~. ~~at the exception of those of short-lived anthropogenic sources (which may also have depended on additional VOCs – Sect. S6). ~~PMF factorial analyses computed with a limited VOC number~~ have hence~~ therefore show~~n~~ limitations in the investigation of short-lived anthropogenic sources influencing Ersa VOC concentrations g~~, g~~iven the remote location of the Ersa station~~ (Sect. 2.1), the fact that these anthropogenic sources included several source categories of variable emission strength and from different emission areas (Sect. 3.5.2 and Michoud et al., 2017) and the high variabilities over short periods of VOCs mainly attached to these sources (Sect. S2)~~.

The two studies on Ersa VOC measurements also helped to discuss here the best experimental strategy to characterize variations in VOC concentrations measured at a remote background site surrounded by vegetation such as Ersa (Sect. 2.1). Firstly, t~~Furthermore, t~~he consideration of monoterpenes in the 2-yr PMF analysis would significantly increase the contribution of primary biogenic sources (see Sect. 4.1). A better temporal resolution and coverage of the VOC measurements would have been beneficial in this study ~~for a better~~to further assess~~ment of~~ the contribution of local biogenic sources, considering BVOC day-to-day variations (~~,~~ as ~~noticed in~~assessed with the summer 2013 dataset; ~~(~~Sect. 3.4.1). Additional measurements of speciated monoterpenes, sesquiterpenes and BVOC oxidation products would even help identifying different local sources associated with various emitting Mediterranean plants (Owen et al., 2002). This statement is ~~supporting~~ supported by the fact that different interannual ~~BVOC concentration~~ variations in BVOC concentrations were noticed between isoprene and selected speciated monoterpenes in this study (Sect. 3.4.1). Contrarily, c~~C~~oncentrations of non-speciated monoterpenes and isoprene measured in summer 2013 were mainly attributed to the same primary biogenic source ~~as for isoprene concentrations~~ in Michoud et al. (2017). However, concentration v~~But v~~ariations of~~in~~ the sum of monoterpenes may have ~~reflected~~ mirrored those related to abundant biogenic species such as α-pinene, and ~~hence~~ thus masked those characterizing more-reactive species such as α-terpinene (Kalogridis, 2014; Debevec et al., 2018).

The limited number~~range~~ of VOCs included in ~~the~~ our PMF study had the advantage ~~to~~ of a better deconvolution by the PMF model of~~lve~~ primary sources and a better reconstruction ~~by the PMF model~~ of measured VOCs having low concentrations (Sects. S2 and S6), without the need to minimize the weight of species ~~which had~~having elevated background levels (unlike~~ for~~ ethane, methanol and acetone ~~of the summer 2013 VOC dataset~~in~~;~~ Michoud et al., 2017). These low concentrations thus represented a higher proportion ~~on~~ of the total ~~measured~~ VOC concentrations that the model was supposed to explain. The longer time scale of VOC measurements (i.e. the 2-yr period) ~~presented here~~ even helped to deconvolve long-lived combustion sources from regional background (Sect. S5). However, PMF comparison results also raised the importance of ~~the consideration of~~ a finer time resolution and a higher temporal coverage of VOC measurements conducted over a long period at a remote background site such as Ersa to support ~~results from~~ source apportionment results, in terms of ~~deconvolution~~ decorrelation of anthropogenic sources. Indeed, anthropogenic sources identified in this study with ~~the 4-h~~bi-weekly observations ~~in this study~~ have shown some significant correlations between them (Sect. S5), as a ~~consequence~~ result of~~ their~~ similar seasonal variations in concentrations of NMHCs composing them (Sects. 3.4.2 and 4). The consideration of diurnal variations in the 2-yr factorial analysis ~~of diurnal variations~~ would help limiting this potential statistical bias.

The incorporation of 19 OVOCs in the source apportionment of Michoud et al. (2017) had little impact on the ~~identification~~ deconvolution of main ~~primary~~ sources influencing NMHC~~VOC~~ concentrations observed at the Ersa station (Sects. S5 and S6~~),~~). B~~b~~ut, it can modify their relative contributions to the total VOC concentration, emphasizing ~~the contribution~~ those of local biogenic/anthropogenic sources and decreasing ~~the contribution~~those of regional anthropogenic sources (Michoud et al, 2017). ~~The~~ VOCs ~~observed at Ersa~~ were largely dominated at Ersa by OVOCs (Sect. 3.3), especially in summer (Michoud et al., 2017). OVOC abundance observed at Ersa was further increased by the measurement of alcohols and carboxylic acids, carried out only in summer 2013 with~~by~~ automatic analysers (Sect. S4). The incorporation of OVOCs in the 2-yr PMF analysis would have helped to better identify co-variations between these species (Sect. 3.4.3) and their proportion ~~associated with~~resulting from primary sources, but the limited number of samples realized with DNPH cartridges did not ~~favor~~favour it (Fig. S1 and Sect. S2). Formaldehyde has shown in this study high concentration levels (Table 3) and clear seasonal variations (Sect. 3.4.3) ~~in this study~~ and would have been of high interest ~~to be considered~~ in the summer 2013 PMF analysis.

4. Discussions on the seasonal variability of VOC concentrations

In this section, seasonal accumulated concentrations of the 35 VOCs selected in this study (21 NMHCs and 14 OVOCs; Sect. S1) are examined (Fig. 10) so as to identify the prevailing drivers of their variations. Measured concentrations of the 17 NMHCs selected in the factorial analysis (Sect. 3.5) ~~have been~~were distributed among their major sources in Fig. 10. Figure S4 presents separately variations in NMHC factor contributions. ~~As a reminder, anthropogenic sources originated from different locations, including local and more distant ones, and should therefore be considered as more or less aged emissions advected to Ersa.~~ Based on the work of Michoud et al. (2017) and Kalogridis (2014), it has been assumed in this study that the concentrations of the four monoterpenes (Table 1), not included in the PMF analysis, were fully emitted by the local vegetation. Biogenic sources refer here to the grouping of the PMF biogenic source and speciated monoterpenes. The coming discussion has been structured in two steps: on one hand the factors explaining the VOC concentration levels and their variations in spring and summer and on the other hand the factors controlling those in ~~winter~~ fall and ~~fall~~winter.

4.1 VOC concentration variations in spring and summer

Firstly, the 21 NMHCs selected in this study have shown low concentrations during ~~summer~~ spring and summer~~pring~~ periods (average seasonal accumulated concentration of 4.6 ±0.1 µg m^{-3}; Fig. 10) while the 14 OVOCs exhibited high concentrations (8.0 ±1.8 µg m^{-3}). PBL height can be high~~er~~ in these seasons (von Engeln and Teixeira, 2013), favouring vertical dispersion. OVOC concentration levels in ~~summer~~ spring and summer~~pring~~ are in agreement with a high~~er~~ photochemical decay of VOCs, which were rapidly depleted. Consequently, the most reactive VOCs composing emission profiles of the anthropogenic sources can have reacted and/or been dispersed before reaching the Ersa station. The clear seasonal cycles of these sources, with a decline in their contributions in spring and summer (Fig. S4), confirmed this finding.

~~Moreover, r~~Regional background ~~explained~~ contributed in spring and summer from 24 to 53% ~~of~~ to ~~the~~ total NMHC ~~Ersa~~ concentration~~s of the NMHCs selected in this study~~. As natural gas sources were attributed to the regional background (Sect. 3.5.5), a decrease in their emissions can presumably occur in the hot season, enhancing the decline in regional background contributions (Fig. S4). These regional background contributions also suggest that aged emissions advected by air masses to the Ersa station significantly influenced VOC concentrations observed during these seasons. This statement is also in agreement with the high acetone concentration levels in ~~summer~~ spring and summer~~pring~~ (4.8 ±1.5 µg m^{-3}; Fig. 10). As a reminder, this carbonyl compound can result from distant sources and/or be formed within polluted air masses before ~~they~~ reaching the Ersa station (Sect. 3.4.3). As ~~pinpointed by~~shown in Fig. 10, biogenic sources contributed to ~~the~~ total NMHC concentrations especially in summer (up to 41%), in connection with temperature and solar radiation variations (Sect. 3.4.1). This finding is also supported by the high summer concentration levels of formaldehyde, methylglyoxal, acetaldehyde and acetone (Fig. 10; Sect. 3.4.3). Short-lived anthropogenic sources explained in spring and summer from 16 to 24% of the NMHC concentrations. Despite the high reactivity of the VOCs composing these anthropogenic sources (Sect. 3.5.2), their contributions were not reduced as sharply as those of other anthropogenic sources (Fig. S4), which ~~can probably~~may be related to high influences of ship transport and relatively close potential emission areas (Sect. 3.5.2). Evaporative and long lived combustion sources only contributed from 6 to 16% in spring and summer, as they likely originated from emission areas relatively distant from the Ersa station (Sects. 3.5.3 and 3.5.4). Low contributions of long-lived combustion sources can also be partly explained by a lower source strength (especially for residential heating source; Sect. 3.5.4).

Looking now at the interannual variations during ~~summer~~ spring and summer~~pring~~ periods, Fig. 10 highlights that ~~the~~ total NMHC concentrations ~~of the selected NMHCs~~ were in the same range during the two summer periods as well as the two spring ones (absolute difference was ~~of~~ 0.2 µg m^{-3} between summers 2012 and 2013 and below 0.1 µg m^{-3} between springs 2013 and 2014). As depicted in Fig. S4, ~~summer~~ spring and summer~~pring~~ contributions of evaporative sources, long-lived combustion sources, and regional background~~,~~ were in the same range over the study~~ied~~ period, as well as MEK concentrations (0.3-0.4 µg m^{-3}; Fig. 10), which have been attributed mostly to anthropogenic (primary/secondary) sources (Sect. 3.4.3). These findings can suggest that these anthropogenic sources, originating from distant emission areas, were largely influenced during these seasons by pollutant depletion and vertical/horizontal dispersion~~ during these seasons~~. ~~Summer~~ Spring and summer~~pring~~ contributions of short-lived anthropogenic sources ~~seemed~~ appear to be more variable over the study period~~as a function of the year~~ (0.7-1.1 µg m^{-3}; Figs 10 and S4). ~~This finding~~This finding suggests that these sources were largely influenced by origins of air masses, which hence advected to Ersa numerous emissions, potentially of variable strength and from various locations relatively close to Ersa. Furthermore, biogenic sources showed slightly higher summer contributions in 2013 than in 2012 (1.9 and 1.4 µg m^{-3}, respectively), especially ~~owing~~ in link to concentrations of monoterpenes~~ during the two summer periods~~ (Fig. 10) and consistent with temperature and solar radiation variations (Sect. 3.4.1). ~~Higher s~~Summer concentrations of formaldehyde and acetone were also ~~noticed~~ higher in 2013 than in 2012 (differences of 1.5-1.6 µg m^{-3}) while acetaldehyde and methylglyoxal ones were in the same range (Fig. 10), in agreement with isoprene. Considering regional background contributions and MEK concentrations in summer periods, interannual variations in acetone summer concentrations seem to ~~rather link~~be related to a change in its biogenic primary/secondary contributions rather than a change in its background levels. These findings suggest~~, in summer 2013,~~ enhanced emissions from the local vegetation in summer 2013, partly related to the release of monoterpenes, and/or higher biogenic secondary contributions. For similar reasons, ~~slightly higher~~ spring contributions of biogenic sources were slightly higher~~observed~~ in 2014 than in 2013 (Fig. 10). Transient drought stress of the vegetation could also have influenced BVOC emissions in spring 2014 (Sect. 3.4.1).

4.2 VOC concentration variations in fall and winter

During fall and winter periods, total NMHC concentrations ~~of the selected NMHCs~~ increased (7.8 ±1.2 µg m^{-3}) while OVOC concentrations declined (7.1 ±0.8 µg m^{-3}). The decline in OVOC concentration levels mainly result from the decrease in acetone and formaldehyde concentrations (3.3 ±0.8 µg m^{-3} and 1.0 ±0.3 µg m^{-3}, contributing 34-52% and 10-16% to ~~the~~ total

OVOC concentrations~~ of 34-52% and 10-16%~~, respectively), partly related to a weaker biogenic activity. Chemical reaction rates also dropped in fall and winter as a consequence of ~~decreased ~~the decrease in OH concentrations ~~owing ~~related to ~~lower~~the decline in available UV light and temperatures (Fig. 3). ~~Hence~~As a result, VOCs were not removed from the atmosphere as quickly as in ~~summer ~~spring and summer~~pring~~,~~. This statement is~~ in agreement with OVOC concentration levels. PBL height also decreased during these seasons, impacting ~~the ~~pollutant vertical dispersion. These conditions, favouring ~~the ~~pollutant advection and accumulation, explained the higher contributions of anthropogenic sources perceived at Ersa in fall and winter, especially those from sources mainly of regional origins (Fig. S4).

The regional background and evaporative sources were identified as the dominant contributors to ~~the ~~total NMHC concentrations ~~of the selected NMHCs measured at Ersa ~~in fall and winter (contributions of 31-45% and ~~of ~~22-29%, respectively). Long-lived combustion sources also contributed ~~significantly ~~particularly ~~to NMHC concentrations specifically~~ in winter (explaining 18-24% of ~~the ~~total NMHC concentrations), since the ~~typical ~~low ~~winter ~~ambient temperatures typical of winter (Fig. 3) may ~~involve ~~lead to an increased use of residential heating (Sect. 3.5.4). In order t~~T~~o better identify regional influences, average ~~winter and fall ~~contributions of the anthropogenic sources in fall and winter were investigated as a function of air mass origin in Fig. 11. During these seasons, the Ersa station was mostly influenced by continental air masses coming from Europe and France (their ~~cumulated ~~cumulative occurrences were from 36~~%~~ to 70%). NMHC anthropogenic sources showed higher accumulated contributions when European air masses were advected to Ersa (Fig 11), and they could be attributed to potential emission areas located in Italy and possibly more distant ~~potential emission areas~~ones in central Europe (Sect. 3.5). To a lesser extent, high ~~anthropogenic source ~~accumulated contributions of anthropogenic sources were also noticed when Ersa received air masses originating from continental France (potential emission areas located in the southeast of France) and Corsica-Sardinia.

Figure 10 highlights notable interannual variations in VOC concentrations in winter (absolute difference of 3.5 µg m^{-3}), while they were in the same range in fall (differences below 0.1 µg m^{-3}). Indeed, ~~winter~~NMHC winter concentrations ~~of the selected NMHCs ~~were higher in 2013 (9.4 µg m^{-3}) than in 2014 by up to 1.9 µg m^{-3}, similarly to OVOC winter concentrations (7.5 and 6.0 µg m^{-3} in 2013 and 2014, respectively). Even though winter contributions of long-lived combustion sources, short-lived anthropogenic sources and evaporative sources were significantly reduced in 2014 compared to in 2013 (absolute differences from 0.3 to 0.9 µg m^{-3}; Fig. 10), the seasonal pattern of their variations were similar in 2013 and 2014, as depicted in Fig. S4. These findings could be an evidence of homogenous regional background pollution distribution at synoptic scale. ~~Mean r~~Regional background winter contributions ~~monitored ~~observed in 2013 and 2014 (absolute difference below 0.1 µg m^{-3}; Fig. 10) are also in agreement with this suggestion. Acetone and MEK winter concentrations were lower in 2014 than in 2013 (Fig. 10), which could be related to variations in their anthropogenic primary/secondary sources rather than in their background levels.

~~Moreover, t~~The interannual variations in VOC winter concentrations could be partly explained by occurrences and origins of air masses advected to the Ersa station, their enrichment in different anthropogenic sources (based on potential emissions areas observed in winters 2013 and 2014; Fig. 12) and ~~hence ~~their respective contributions~~, according to~~ (Fig. 11)~~.~~

~~This statement is also in agreement with results depicted in Fig. 12 which presents potential emissions areas associated with the 4 primary anthropogenic sources in winters 2013 and 2014~~. On one hand, Ersa was more under the influence of European air masses in winter 2013 than in winter 2014 (occurrences of 37 and 18%, respectively). When continental European and French air masses were advected to Ersa, anthropogenic sources showed higher accumulated winter contributions in 2013 (10.8~~-~~ and 9.6 µg m^{-3}, respectively; Fig. 11) than in 2014 (8.2~~-~~ and 7.8 µg m^{-3}). ~~During~~ In winter 2013, the main potential emission areas for the anthropogenic NMHC sources were located in Italy (Tuscan coasts and the Po Valley), central Europe (Slovenia and western Hungary) and to a lesser extent the south of France. Contrariwise, in winter 2014, ~~while~~ Ersa did not seem to be influenced at all by air masses originating from central Europe ~~in winter 2014~~ (especially from Slovenia and Hungary; ~~–~~ Fig. 12)~~. Surprisingly,~~ and potential emission areas located in the Po Valley and the southeast of France ~~, known to experience high anthropogenic emissions,~~ did not ~~seem to have~~ contribute~~d~~ significantly to VOC concentrations ~~in winter 2014~~. On the other hand, the Ersa station ~~more frequently~~ received air masses originating from Corsica-Sardinia, i.e. relatively close potential emission areas, more frequently in winter ~~winter~~ 2014 than in winter ~~winter~~ 2013 (occurrences of 24 and 0%, respectively). ~~Accumulated~~ The cumulative contribution of anthropogenic sources in winter 2014 ~~contribution associated with~~under Corsican-Sardinian air mass influence ~~in winter 2014~~ was only 7.0 µg m^{-3} (Fig. 12). These findings can suggest less aged (but rather low) emissions have influenced Ersa concentrations in winter 2014, ~~and can~~ partly explaining why ~~the lower~~ OVOC winter concentrations observed at Ersa were lower in 2014 than in 2013.

~~The different amplitudes of anthropogenic source contributions observed between the two winter periods may also result in different influences of meteorological conditions. These latter can have affected anthropogenic emission strengths as well as chemical transformations occurring inside air masses all along their transport to the Ersa station. These statements are consistent with interannual variations in OVOC winter concentrations.~~ Moreover, ~~To support these suggestions, we can notice that~~ most countries of western Europe experienced different winters in 2013 and 2014 (see Sect. 3.1 and Fig. S5 of the Supplement). As a reminder, winter 2013 was considered rather rigorous, since e.g., French temperatures were lower up to 1-1.5 °C than average value for 1981-2010 according to Météo France (http://www.meteofrance.fr/climat-passe-et-futur/bilans-climatiques/bilan-2013/bilan-de-lhiver-2012-2013, last access: 11/10/2020). On the other hand, winter 2014 was rather mild and temperatures were the hottest of the 1951-2014 period (mean temperature for Europe was ~2.6 °C higher than the pre-industrial period; EEA, 2015). As a consequence, the interannual variations in VOC winter concentrations may also result from different influences of meteorological conditions. Indeed, m~~M~~eteorological winter conditions were probably more favourable to induce higher OH concentrations in 2014 than in 2013, leading to higher photochemical decay, and so lower NMHC concentrations observed at the Ersa station. Nevertheless, OVOC winter concentrations were higher in 2013 than in 2014, which can therefore highlight they were mainly due to increased contributions from anthropogenic sources of regional origins, offsetting thus the less degradation of VOCs in winter 2013. Moreover, w~~Higher~~ inter 2014 temperatures along with the lack of cold nights ~~in winter 2014 (Van Oldenborgh, 2015)~~(Sect. 3.1) may ~~also~~ have affected the source strength, especially of long-lived combustion sources. ~~Furthermore, r~~Rain event intensities and occurrences in winters 2013 and 2014 could also have impacted enrichment in anthropogenic (primary/secondary) sources of air masses advected to Ersa, and hence have influenced Ersa VOC concentrations. Note that ~~in northern Italy,~~ a very high monthly rainfall was recorded in northern Italy in winter 2014 (300% higher ~~by 300%~~ than the seasonal ~~normal~~ average values for the 1981-2010 period; see Fig. S5 of the Supplement). Abundant rainfalls were also noticed in the southeast of France during winter 2014 (the highest ones recorded over the 1959-2014 period, according to Météo France; http://www.meteofrance.fr/climat-passe-et-futur/bilans-climatiques/bilan-2014/bilan-climatique-de-l-hiver-2013-2014, last access: 11/10/2020). As a consequence, these meteorological conditions ~~should~~ may have reduced anthropogenic source contributions resulting from potential emission areas located in~~from~~ the Po Valley and the southeast of France in winter 2014.

5. VOC concentration variations in continental Europe

From June 2012 to June 2014, NMHC measurements were concurrently conducted at 17 other European background monitoring stations (described in Sect. S7), allowing us (i) to examine the representativeness of the Ersa station in terms of seasonal variations in NMHC concentrations impacting continental Europe and (ii) to provide some insights on dominant drivers for VOC concentration variations in Europe built on what we have learned from Ersa's VOC observations.

Figure 13 depicts monthly concentration time series of a selection of NMHCs measured at the 18 European monitoring stations (including Ersa). Concentrations of

NMHCs with typically medium-to-long lifetimes in the atmosphere, i.e. ethane, propane, n-butane, acetylene and benzene~~ (Sect 3.4.2)~~, were examined here since ~~their concentrations~~they can be significantly influenced by regional contributions, as observed in this study (Sect. 3.5) and elsewhere (Debevec et al., 2017; Michoud et al., 2017; Sauvage et al., 2009). ~~Globally, these selected anthropogenic NMHCs measured at Ersa showed the same seasonal variations as observed at other European stations (Sect 3.4.2), i.e. with an increasing winter trend followed by a decrease in spring/summer, and hence assuring the representativeness of the Ersa station for monitoring regional pollution in Europe.~~ As a reminder, concentrations observed at Ersa were mainly explained in this study by regional background for ethane, ~~by~~ long-lived combustion sources for propane, acetylene and benzene, and ~~by~~ evaporative sources for n-butane (see Sect. 3.5 and Fig. 7). The study of concentration variations of these source tracers can thus help to highlight temporal and spatial variations in source contributions to NMHC concentrations observed in most of continental Europe. ~~As a result, the study of concentration variations of these source tracers may help to highlight temporal and spatial variations in source contributions to NMHC concentrations observed in most of continental Europe.~~ In addition, despite its shorter lifetime compared to other NMHCs of the selection, Fig. 13 also presents ethylene concentration variations ~~were also examined in this study~~in order to investigate short-lived anthropogenic source importance and variability in continental Europe. ~~As a result, the study of concentration variations of these source tracers may help to highlight temporal and spatial variations in source contributions to NMHC concentrations observed in most of continental Europe.~~

Globally, concentrations of these selected NMHCs measured at the 17 European stations showed the same seasonal variations as observed at Ersa (Fig. 13 and Sect 3.4.2), hence assuring the representativeness of the Ersa station for monitoring regional pollution in continental Europe. On the one hand, ~~Monthly~~ NMHC monthly concentration levels~~s~~ in summer were European wide low~~er~~ and relatively homogeneous ~~from June to August~~ whatever the location and the typology of the station. T~~(t~~he highest absolute differences between ~~anthropogenic~~ NMHC summer concentrations measured at two stations ~~in summer~~ was ~~of~~ 0.4-0.7 µg m^{-3} for ethane, 0.1-0.2 µg m^{-3} for acetylene, 0.1-0.7 µg m^{-3} for propane and benzene, 0.2-0.6 µg m^{-3} for n-butane and 0.3-1.2 µg m^{-3} for ethylene~~)~~. ~~It~~ They suggest~~s~~ that the temperature was the main driver in regulating summer concentration levels, linked to photochemistry processes and the vertical dispersion (Sect. 4.1). Ethane concentration levels were still relatively important during summer (~~mean concentrations >~~above 1.0 µg m^{-3}) suggesting long-range transport (up to intercontinental pollution transport) was among the main parameters governing VOC summer concentrations in continental Europe. On the other hand, anthropogenic NMHC monthly concentration levels in winter appear to be more spatially variable in continental Europe~~ in winter~~. ~~Indeed, t~~The highest absolute differences between ~~VOC~~NMHC winter concentrations measured at two stations were ~~of~~ 1.3-2.6 µg m^{-3} for ethane, 0.6-1.6 µg m^{-3} for propane, acetylene and benzene, 0.6-1.4 µg m^{-3} for n-butane, and 1.2-4.1µg m^{-3} for ethylene. ~~These concentration level differences~~They may probably highlight spatial variations in anthropogenic source contributions to NMHC winter concentrations observed in continental Europe~~ in winter~~. The l~~L~~owest~~er~~ NMHC winter concentrations ~~of the selected NMHCs~~ were observed at stations located in southern and western Europe, including Ersa, other French sites and high-altitude ones (see Fig 13 and Sect. S7). Note that high-altitude sites may have the particularity~~, compared to the other European sites,~~ of being frequently in free-tropospheric conditions, compared to the other European sites. Additionally, southwestern France and Po valley experienced a wet winter both in 2013 and 2014 (see Sect. 4.2 and Fig. S5 of the Supplement) that may have had a significant impact on the enrichment in NMHC anthropogenic sources of air masses advected to these regions, and hence can have participated in the decrease in NMHC winter concentrations monitored at nearby stations. ~~At stations located in central Europe (i.e. stations located in Switzerland, Germany and Czech Republic - see Sect. S7),~~ NMHC winter concentrations tended to be more elevated a~~A~~t stations located in central Europe (i.e. ~~stations~~those located in Switzerland, Germany and Czech Republic - see Sect. S7), than those in~~in winter compared to~~ southern and western Europe.~~an observations~~ This was~~,~~ especially noticed for NMHCs ~~species potentially~~ mainly explained by long-lived combustion sources, evaporative sources and short-lived anthropogenic sources, which could suggest that these ~~these~~ central European stations were under different influences. These findings are consistent with Ersa NMHC ~~primary~~ source contribution variations as a function of air mass origin~~s~~ ~~observed at Ersa~~ and CF analyses examined in this study (Sect. 4.2 and Figs. ~~11~~ 9 and S3 of the Supplement). Furthermore, precipitation~~s~~ in central Europe ~~were~~ was less frequent and/or less intense in winter ~~both in winters 2013 and 2014~~ than ~~compared to~~ average~~normal~~ values for the 1981-2010 period (~~average values calculated by the NOAA –~~ see Fig. S5 of the Supplement) both in 2013 and 2014, which may have favoured VOC source contribution accumulation and transport and hence can have induced higher VOC winter concentrations measured at nearby monitoring stations. Additionally, high NMHC winter concentrations were also observed in northern Europe, especially for NMHCs mainly explained by evaporative sources and long-lived combustion sources.

To go further, Fig. 14 depicts accumulated winter concentrations of ~~a selection of~~ 15 selected NMHCs measured in 2013 and 2014 at 14 European monitoring stations (including Ersa)~~ in winters 2013 and 2014~~, in order to investigate dominant drivers for VOC winter concentration variations in Europe ~~build ~~built on what we have learned from Ersa's VOC observations discussed in Sect. 4.2. These selected NMHCs are those taken into account in the PMF analysis ~~applied to Ersa 2-yr NMHC measurements~~of this study (at the exception of ethylbenzene and o-xylene; Sect. S2~~). ~~). Firstly, s~~S~~tations located in southwestern France and Po Valley showed ~~relatively ~~similar NMHC winter concentrations in ~~winters ~~2013 and 2014 (total differences ranged from -0.1 to 0.4 µg m^{-3}). At these sites, winter concentrations of NMHCs potentially explained by long-lived combustion sources have slightly decreased in 2014 compared to in 2013 (reduction of 0.1-0.4 µg m^{-3}, i.e. of 7-24%), which is consistent with synoptic phenomena (Sect. 3.1) inducing warmer temperatures in winter 2014 ~~compared to~~than ~~normal~~ average values for the 1981-2010 period (Fig. S5 of the Supplement). However, NMHC winter concentration levels~~s~~ observed at Ersa and northwestern French stations, ~~and ~~along with their interannual variations, ~~observed at Ersa and in northwestern France ~~were more similar to those in central Europe~~an ones~~ than those in southwestern ~~French ~~France and southern ~~European ones~~Europe (Fig. 14). Indeed, NMHC winter concentrations measured in central Europe were generally significantly higher in 2013 than in 2014 (total differences of 2.6-3.2 µg m^{-3}), with the exception of stations located in northeastern Germany (i.e. WAL, NGL and ZGT stations – Sect. S7; total differences of -2.8-0.7 µg m^{-3}). ~~As observed at Ersa ~~These interannual variations ~~again, in central Europe, NMHC winter concentrations potentially related to anthropogenic sources that have influenced Ersa winter concentrations were higher~~seem to be particularly linked to contribution variations of~~ in 2013 than in 2014, especially for those influenced by~~ long-lived combustion sources (reduction ~~of ~~of 0.7-1.1 µg m^{-3},~~,~~ ~~corresponding to~~i.e. 21-44%~~ of winter 2013 concentrations~~) and short-lived anthropogenic sources ~~contributions ~~(reduction of 0.6-1.3 µg m^{-3}, i.e. of 21-43%). NMHC winter concentrations related to evaporative sources also decreased in 2014 but to a lesser extent (reduction of 0.3-0.5 µg m^{-3}, i.e. of 13-24%). These findings are consistent with winter variations in anthropogenic source contributions impacting VOC concentrations at Ersa (Sect. 4.2), especially when the stations received air masses originating ~~were advected to the site ~~from central Europe (~~Sect. 4.2~~Fig. 11). They also highlight that interannual variations ~~in local contributions to ~~in NMHC winter concentrations observed in central Europe were influenced by both regional and local contributions. Furthermore, d~~Furthermore, ~~ue to synoptic phenomena that have occurred in winters 2013 and 2014~~, as discussed in ~~ (Sect. 3.1~~), have impacted meteorological conditions in central Europe~~, ~~i.e. ~~temperatures in central Europe were respectively colder and warmer compared to average~~normal~~ values for the 1981-2010 period (Fig. S5 of the Supplement)~~). That could partly explain NMHC winter concentration variations in central Europe in 2013 and 2014~~. Interannual variations in w~~W~~inter ~~meteorological differences compared to normal values for the 1981-2010 period in 2013 and 2014~~temperatures were more marked in central Europe ~~compared to~~than in southern France and southern Europe (Fig. S5 of the Supplement), which could partly explain their respective interannual variations. Moreover, NMHC winter concentrations monitored in Scandinavia (represented by PAL station results on Fig. 14) were higher in 2014 than in 2013 (total difference of 0.7 µg m^{-3}), as well as those measured at stations located in northeastern Germany (especially NGL and ZGT stations;~~ –~~ differences of 1.7-2.8 µg m^{-3}). These increases in winter 2014 in these regions concerned ~~especially ~~in particular NMHCs related to long-lived combustion (~~increases of ~~0.2-0.5 µg m^{-3}, i.e. 9-25%) and evaporative sources (0.3-0.4 µg m^{-3}, i.e. 11-18%). Even though these regions experienced a cold winter in 2013 (Fig. S5 of the Supplement), early winter 2014 in northern Europe was also colder than average~~normal~~ values for the

1981-2010 period, ~~since an~~due to an intense cold wave ~~occurred in January 2014 and was associated with~~resulting from a strong anticyclone centred on western Russia and extending from Finland to Crimea. Additionally, winter precipitation~~s~~ in these regions ~~were~~ was less frequent and/or intense than average~~normal~~ values for the 1981-2010 period (Fig. S5 of the Supplement) in 2014 than in 2013 which may have favoured accumulation and transport and hence induced higher NMHC concentrations measured at nearby monitoring stations.

6. Conclusions

Within the framework of the ChArMEx project, a monitoring station has been set up and operated from June 2012 to June 2014 at a remote background site of Corsica Island (Ersa) in the northwestern part of the Mediterranean in order to examine seasonal variabilities of 35 selected VOCs (21 NMHCs and 14 carbonyl compounds).

Biogenic VOCs were principally imputed to the local vegetation and exhibited high concentrations and interannual variations in late spring and summer, related to temperature and solar radiation variations. Anthropogenic NMHCs, having atmospheric lifetimes ranging from a few hours to some days, have shown low concentrations in spring and summer since the Ersa station was mostly influenced by aged advected air masses. A~~Primary a~~nthropogenic sources identified in this study were hence largely influenced by the pollutant depletion ~~(in relation to the oxidizing capacity of the environment)~~ and vertical dispersion before reaching the Ersa station, especially those originating from distant emission areas. As a result, the regional background and short-lived anthropogenic sources (from various locations relatively close to Ersa) mainly contributed to NMHC concentrations in ~~summer~~spring and s~~pring~~ummer. ~~The selected a~~Anthropogenic NMHCs were also characterized by high concentration levels in fall and winter and winter concentrations higher in 2013 than in 2014. The weaker pollutant depletion and vertical dispersion in ~~winter~~fall and winter~~fall~~ have favoured the advection to~~at~~ Ersa of air masses enriched ~~by~~in primary anthropogenic sources originating from more distant emission areas (located in France, ~~in~~ Italy and to a lesser extent ~~in~~ Central Europe) than in ~~summer~~ spring and summer~~pring~~. As a result, the regional background, evaporative sources and long-lived combustion sources were identified as the dominant contributors to NMHC ~~the total~~ fall and winter concentrations ~~of the selected NMHCs~~. Interannual variations in their winter contributions were mainly governed by occurrences and origins of air masses advected to the Ersa station as well as by meteorological conditions (temperature and precipitation~~s~~) occurring before they reached the Ersa station.

~~The~~ OVOCs ~~selected in this study~~ largely prevailed in the VOC abundance during the 2-yr monitoring period. They have also shown different seasonal and interannual variations, suggesting several source contributions. OVOC concentrations measured at Ersa were generally higher in summer, which could be the result of a high contribution of secondary anthropogenic and primary/secondary biogenic sources, whereas their concentrations during fall and winter declined and were potentially more influenced by primary/secondary anthropogenic sources, more specifically for MEK and glyoxal. OVOCs have shown higher winter concentrations in 2013 than in 2014, as a result of the enrichment of air masses advected to Ersa ~~by~~ in primary anthropogenic sources of~~from~~ regional origins.

Selected NMHC variabilities in continental Europe supported that Ersa can be considered as a good regional representative station. However, NMHC winter concentration levels can significantly vary temporally and spatially, pointing out spatial variations in anthropogenic source contributions to NMHC concentrations observed in continental Europe, in relation to meteorological conditions. Ersa winter concentration variations were found more representative of central Europe than southern/western or northern Europe. These findings point out the interest in conducting multi-site and multi-year measurements to be sufficiently representative of interannual and spatial variations in regional pollution impacting continental Europe in winter. They also pointed out that the PMF-derived factors controlling VOC concentration variations at remote sites may be mainly controlled by the meteorological conditions that occurred during the study period when issued from short observation periods (i.e. up to two months).

Concurrent datasets of VOC concentrations from 3 summer campaigns performed at Ersa helped to support the representativeness of the 2-yr monitoring period in terms of summer concentration levels, variations, and source apportionment. They also highlight limitations of this study ~~investigating~~ on the investigation of seasonal variations in Ersa VOC concentrations, ~~related to~~in connection with the VOC range and the temporal resolution of their measurements considered in the PMF analysis. After this work, some questions remain ~~in terms of~~regarding the ~~identification and characterization of OVOC sources and origins and of the~~ contribution of local BVOC and OVOC sources at seasonal and interannual scales. It would be interesting to conduct additional long-term VOC measurements at Ersa, including OVOCs and tracers of various primary sources, at a finer time resolution and a higher temporal coverage. This would help to complet~~eing~~ the understanding of determinants governing VOC concentration variations initiated both by Michoud et al. (2017) and this study.

Data availability

Access to ~~EOP~~ the 2-yr and summer 2013 ~~SOP-1b~~ VOC datasets used for this publication is open to registered users following the data and publication policy of the ChArMEx program (http://mistrals.sedoo.fr/ChArMEx/Data-Policy/ChArMEx_DataPolicy.pdf, last access: 11/10/2020). VOC datasets from Ersa summer field campaigns of 2012 and 2014 are available upon request. Please contact Stéphane Sauvage (stephane.sauvage@imt-lille-douai.fr) for further information.

Author contributions

SS, NL, JS and FD designed the research and were involved in the logistics and the collection of VOC samples on the field. TS calculated uncertainties related to VOC measurements conducted with DNPH cartridges and steel canisters and validated them following the ACTRIS protocol. CD, SS, VG and NL ~~analyzed~~ analysed VOC data, conducted and interpreted the VOC PMF analysis and examined dominant factors controlling VOC concentrations. CD wrote the manuscript. All co-authors were involved in data discussion and edited the paper.

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Table 1: Technical details of the set-up for VOC measurements during the field campaign from June 2012 to June 2014. Air samples were collected bi-weekly (every Monday and Thursday) at Ersa from 09:00-13:00 UTC (from early November 2012 to late December 2012 and from early November 2013 to late June 2014) or 12:00-16:00 UTC (from early June 2012 to late October 2012 and from early January 2013 to late October 2013). VOCs are explicitly listed in Sect. S1 of the Supplement.

5

Instrument	**Steel canisters – GC-FID**	**DNPH cartridges – Chemical desorption (acetonitrile) – HPLC-UV**	**Multi-sorbent cartridges – Adsorption/thermal desorption – GC-FID**
Time Resolution (min)	240	240	240
Number of samples	152	91	63
Detection limit (µg m^{-3})	0.01-0.05	0.02-0.05	0.01
Uncertainties $\frac{U(X)}{X}$ Mean [min - max] (%)	25 [7-43]	23 [6-41]	26 [7-73]
Species	24 C_2 - C_5 NMHCs	15 C_1 - C_6 carbonyl compounds	44 C_5 - C_{16} NMHCs 6 C_6 - C_{11} carbonyl compounds
References	Sauvage et al., 2009	Detournay, 2011; Detournay et al., 2013	Ait-Helal et al., 2014; Detournay, 2011; Detournay et al., 2011

Table 2: Back-trajectory clusters for air masses observed at Ersa from June 2012 to June 2014. The transit time (expressed in h) corresponds to the time spent since the last anthropogenic contamination, i.e. since air masses left continental coasts.

Clusters	**Source regions (wind sectors)**	**Transit time (h) Median [min-max]**	**Occurrence (%)**
C1	**Marine**	**48 [18-48]**	**15**
	Marine (SW)		
	Short trajectories	48 [39-48]	7
	Long trajectories	40 [18-48]	5
	Marine (SE)		
	Long trajectories	42 [25-48]	3
C2	**Corsica-Sardinia (S)**	**0 [0-38]**	**14**
	Short trajectories	2 [0-38]	9
	Long trajectories	0 [0-15]	5
C3	**Europe (NE-E)**	**6 [2-44]**	**31**
	Short trajectories	23 [4-44]	11
	Long trajectories	6 [2-16]	20
C4	**France (NW-N)**	**8 [3-48]**	**26**
	Short trajectories	19 [10-48]	6
	Long trajectories	8 [3-19]	20
C5	**Spain (W)**		
	Long trajectories	36 [20-45]	5

Table 3: Statistics (µg m^{-3}), standard deviations (σ - µg m^{-3}), detection limits (DL - µg m^{-3}) and relative uncertainties ~~U(X)/X~~ (Unc. - %) of selected VOC concentrations measured at the site from June 2012 to June 2014.

	Species	Min	25 %	50 %	Mean	75 %	Max	σ	DL	Unc.
BVOCs	**Isoprene**	0.01	0.01	0.04	0.16	0.16	2.28	0.31	0.03	32
	α-Pinene	<0.01	0.03	0.10	0.38	0.57	3.61	0.61	0.01	40
	Camphene	<0.01	0.01	0.05	0.12	0.13	0.78	0.17	0.01	73
	α-Terpinene	<0.01	<0.01	<0.01	0.06	0.05	0.88	0.15	0.01	47
	Limonene	<0.01	<0.01	0.03	0.19	0.36	1.73	0.30	0.01	45
Anthropogenic NMHCs	**Ethane**	0.57	1.13	1.85	1.86	2.46	4.28	0.81	0.01	7
	Propane	0.18	0.44	0.77	0.94	1.41	2.60	0.61	0.02	11
	i-Butane	0.01	0.09	0.17	0.24	0.35	1.02	0.19	0.02	22
	n-Butane	0.05	0.16	0.26	0.37	0.57	1.09	0.26	0.02	13
	i-Pentane	0.06	0.15	0.22	0.25	0.31	0.90	0.14	0.03	25
	n-Pentane	0.02	0.09	0.18	0.20	0.27	0.80	0.13	0.03	33
	n-Hexane	0.02	0.04	0.07	0.08	0.10	0.27	0.05	0.04	43
	Ethylene	0.09	0.19	0.28	0.32	0.39	0.87	0.17	0.01	14
	Propene	0.01	0.04	0.06	0.07	0.09	0.17	0.03	0.02	40
	Acetylene	0.03	0.09	0.18	0.26	0.36	1.23	0.23	0.01	12
	Benzene	0.07	0.16	0.26	0.31	0.39	1.11	0.19	0.03	25
	Toluene	0.04	0.15	0.23	0.28	0.34	0.84	0.17	0.04	26
	Ethylbenzene	0.02	0.02	0.02	0.04	0.05	0.15	0.03	0.04	50
	m,p-Xylenes	0.02	0.07	0.10	0.12	0.14	0.41	0.08	0.04	45
	o-Xylene	0.02	0.02	0.06	0.07	0.10	0.32	0.06	0.04	44
OVOCs	**Formaldehyde**	0.28	0.68	1.17	1.53	1.89	6.30	1.24	0.03	7
	Acetaldehyde	0.40	0.67	0.83	0.96	1.23	2.87	0.41	0.03	22
	i,n-Butanals	<0.01	0.10	0.15	0.26	0.23	5.15	0.56	0.03	20
	n-Hexanal	<0.01	0.08	0.13	0.22	0.24	1.83	0.27	0.03	12
	Benzaldehyde	<0.01	0.06	0.13	0.15	0.22	0.60	0.12	0.04	21
	n-Octanal	<0.01	0.01	0.05	0.05	0.11	1.25	0.20	0.01	39
	n-Nonanal	<0.01	0.07	0.21	0.21	0.37	1.42	0.31	0.01	33
	n-Decanal	<0.01	0.04	0.16	0.16	0.31	1.19	0.26	0.01	33
	n-Undecanal	<0.01	0.04	0.05	0.05	0.08	0.33	0.06	0.01	39
	Glyoxal	<0.01	0.04	0.06	0.07	0.11	0.25	0.05	0.02	27
	Methylglyoxal	<0.01	0.07	0.11	0.16	0.19	0.95	0.15	0.04	23
	Acetone	1.50	2.46	3.57	4.31	4.98	16.49	2.64	0.03	6
	MEK	0.18	0.27	0.33	0.36	0.45	0.90	0.14	0.03	10

Table 4: Average ~~Seasonal average~~ VOC seasonal concentrations (± 1 σ; μg m^{-3}).

	Species	Winter	Spring	Summer	Fall
BVOCs	**Isoprene**	0.1 ± 0.1	0.2 ± 0.5	0.3 ± 0.3	0.1 ± 0.1
	α-Pinene	0.1 ± 0.1	0.3 ± 0.9	0.7 ± 0.5	0.5 ± 0.5
	Camphene	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
	α-Terpinene	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.3	0.1 ± 0.1
	Limonene	0.1 ± 0.1	0.1 ± 0.4	0.4 ± 0.2	0.3 ± 0.3
Anthropogenic NMHCs	**Ethane**	2.9 ± 0.5	1.8 ± 0.6	1.0 ± 0.2	1.9 ± 0.5
	Propane	1.7 ± 0.4	0.6 ± 0.2	0.4 ± 0.2	1.2 ± 0.5
	i-Butane	0.4 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.4 ± 0.2
	n-Butane	0.7 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	0.5 ± 0.2
	i-Pentane	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.3 ± 0.1
	n-Pentane	0.2 ± 0.1	0.2 ± 0.2	0.2 ± 0.1	0.3 ± 0.1
	n-Hexane	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
	Ethylene	0.5 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	0.4 ± 0.5
	Propene	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
	Acetylene	0.5 ± 0.3	0.2 ± 0.1	0.1 ± 0.1	0.3 ± 0.1
	Benzene	0.5 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	0.4 ± 0.1
	Toluene	0.3 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	0.3 ± 0.2
	C8-aromatics	0.2 ± 0.2	0.2 ± 0.2	0.2 ± 0.1	0.2 ± 0.2
OVOCs	**Formaldehyde**	0.8 ± 0.5	1.3 ± 0.8	2.3 ± 1.3	1.1 ± 0.4
	Acetaldehyde	0.8 ± 0.3	0.8 ± 0.3	1.3 ± 0.4	0.8 ± 0.3
	i,n-Butanals	0.1 ± 0.1	0.1 ± 0.1	0.5 ± 1.0	0.1 ± 0.1
	n-Hexanal	0.1 ± 0.1	0.2 ± 0.1	0.4 ± 0.4	0.2 ± 0.1
	Benzaldehyde	0.2 ± 0.1	0.1 ± 0.2	0.2 ± 0.1	0.1 ± 0.1
	n-Octanal	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.4	0.1 ± 0.1
	n-Nonanal	0.3 ± 0.4	0.4 ± 0.4	0.1 ± 0.2	0.3 ± 0.2
	n-Decanal	0.3 ± 0.3	0.3 ± 0.3	0.1 ± 0.1	0.3 ± 0.2
	n-Undecanal	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
	Glyoxal	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
	Methylglyoxal	0.1 ± 0.1	0.2 ± 0.2	0.3 ± 0.2	0.1 ± 0.1
	Acetone	2.7 ± 1.2	3.8 ± 1.4	5.8 ± 1.8	3.7 ± 1.8
	MEK	0.4 ± 0.1	0.3 ± 0.1	0.4 ± 0.2	0.4 ± 0.1

Table 5: Average relative factor contributions ± standard deviations (%) for the whole period and as a function of the measurement sampling times (see Table 1).

Factor	2-yr period	Samples collected from 09:00-13:00	Samples collected from 12:00-16:00
Regional background	39 ± 10	44 ± 10	38 ± 9
Evaporative sources	22 ± 10	23 ± 11	17± 9
Short-lived anthropogenic sources	19 ± 10	16 ± 7	23 ± 10
Long-lived combustion sources	16 ± 7	15 ± 5	14 ± 7
Local biogenic source	4 ± 10	2 ± 7	8 ± 11

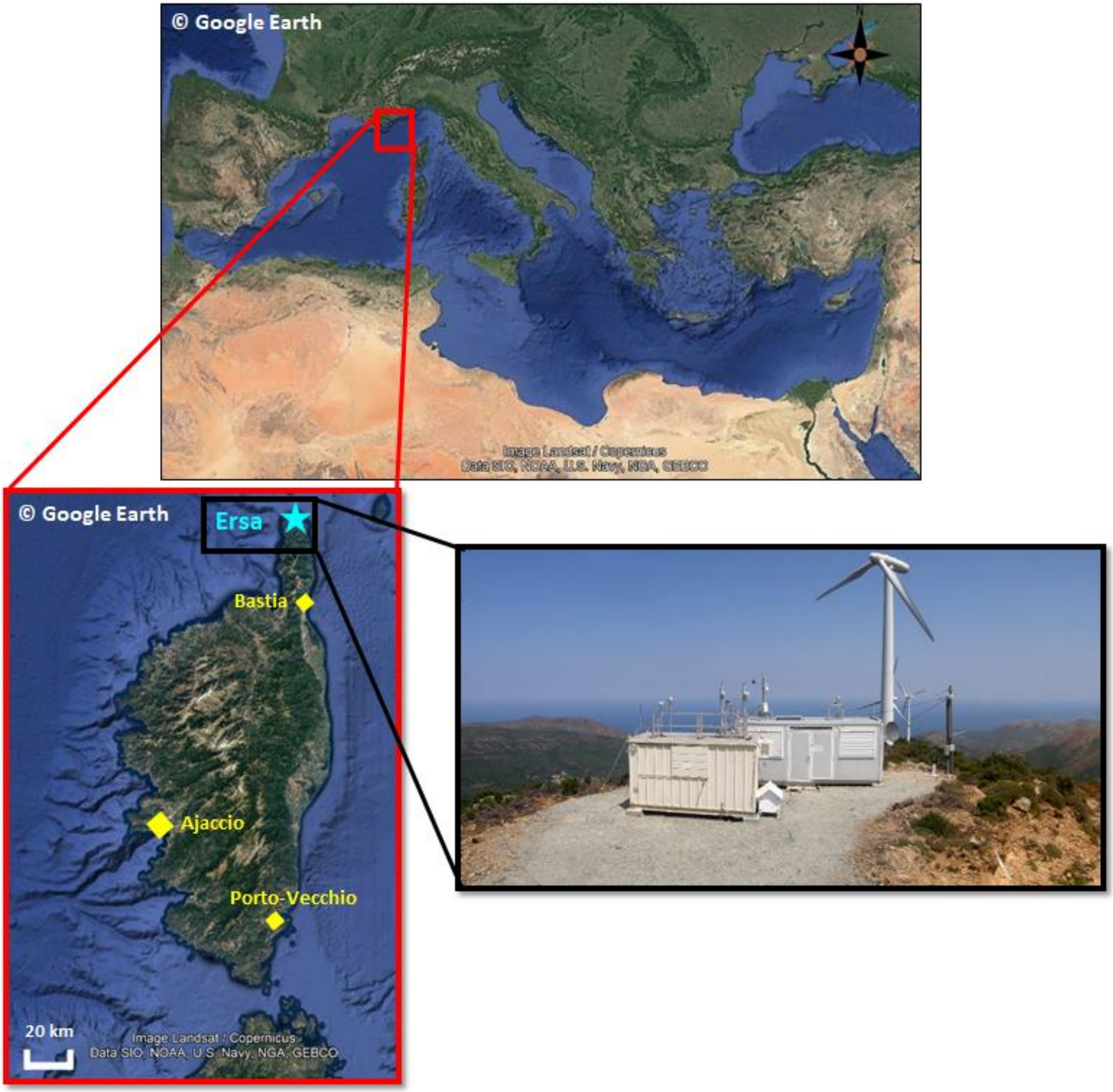


Figure 1: Maps of the Mediterranean region and Corsica (source Google earth) and view of the sampling station. (a) Position of Corsican island in the Mediterranean region. (b) The sampling site and major Corsican agglomerations are displayed as a blue star and yellow diamonds, respectively. (c) Picture of the sampling site, during the 2-yr observation period. Maps provided by Google Earth Pro software (v.7.3.3; image Landsat/Copernicus; data SIO, NO~~O~~AA, U.S, Navy, NGA, GEBCO; © Google Earth).

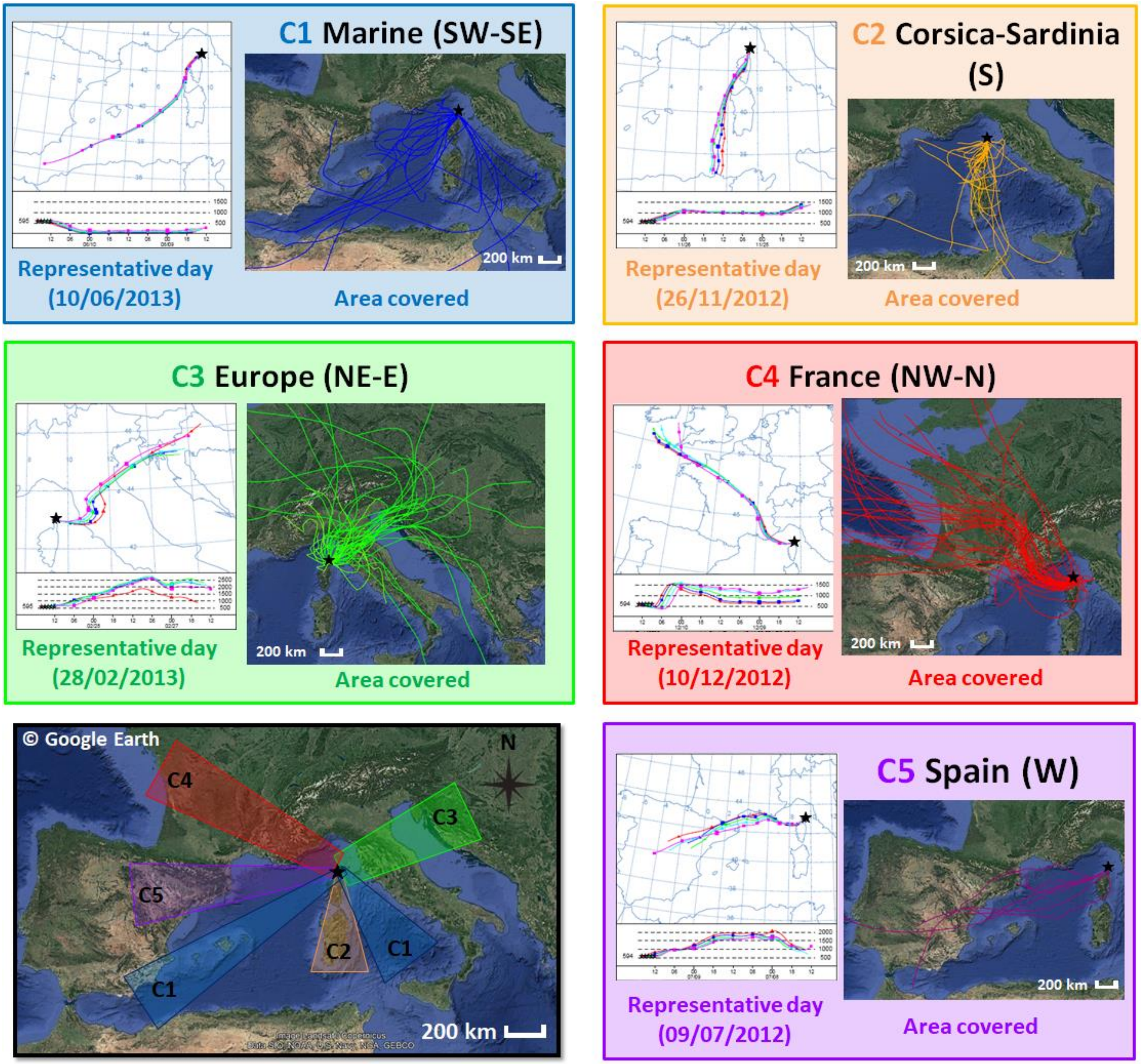


Figure 2: Classification of air masses which impacted the Ersa site during the ~~observation field campaign~~2-yr observation period as a function of their trajectory. Back trajectories simulated with the HYSPLIT Lagrangian model ~~(NOAA-ARL)~~ were classified into five clusters: Marine (cluster 1 – wind sectors SW & SE), Corsica-Sardinia (cluster 2 – S), Europe (cluster 3 – NE-E), France (cluster 4 – NW-N) and Spain (cluster 5 – W). These five clusters were illustrated by example maps with five-trajectories (interval of 1h between each, time of arrival indicated by different ~~colors~~colours of trajectory, the Ersa station represented by a black star) for five ~~single~~ days that are representative of an isolated cluster. ~~To complete~~Finally, areas covered by back-trajectories of each cluster are also indicated. Maps provided by Google Earth Pro software (v.7.3.3; image Landsat/Copernicus; data SIO, NOA~~O~~A, U.S, Navy, NGA, GEBCO; © Google Earth).

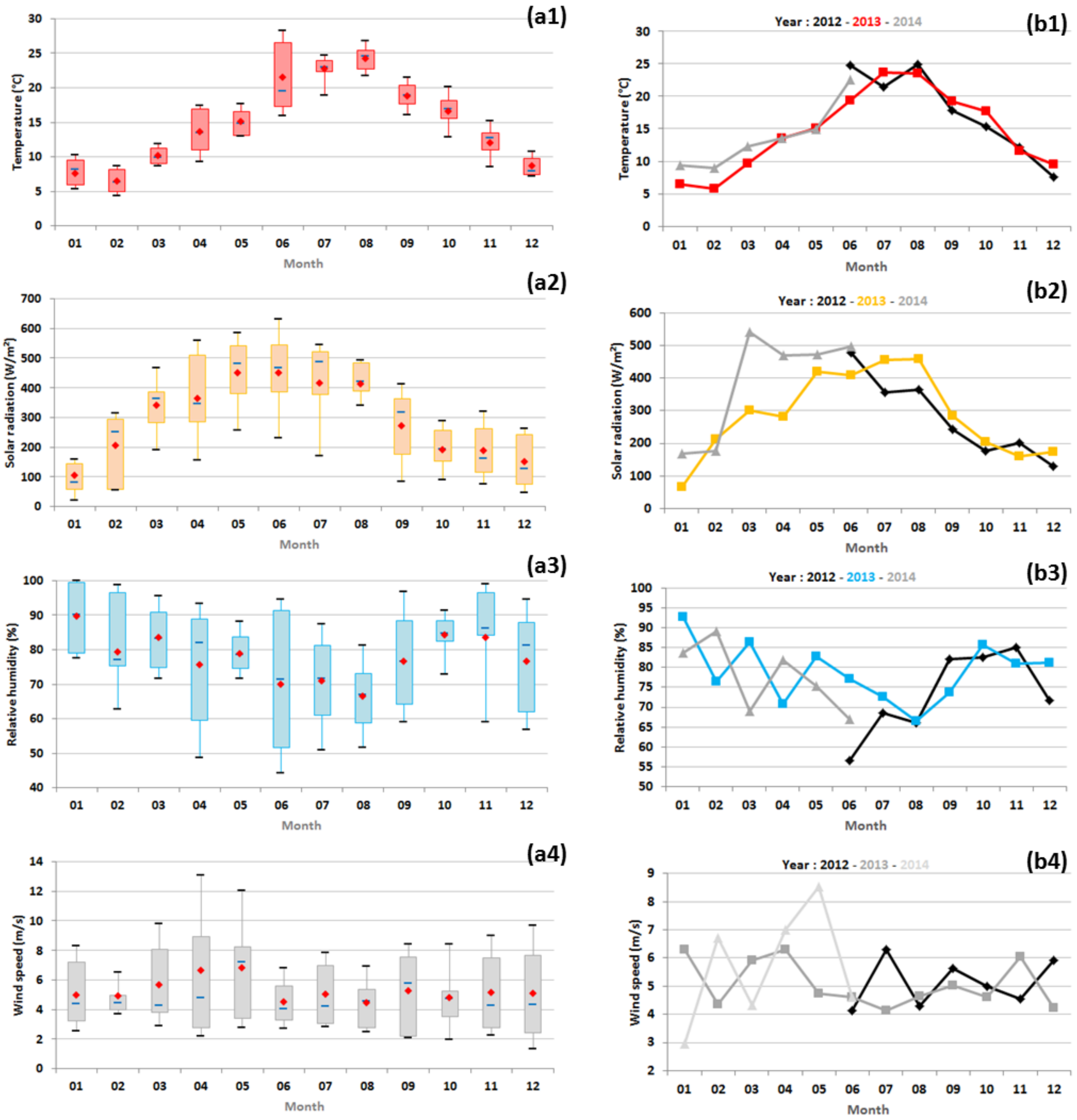


Figure 3: (a) Monthly variations in meteorological parameters (temperature expressed in °C, global solar radiation in W m^{-2}, relative humidity in % and wind speed in m s^{-1}) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict the first and third quartiles ~~(i.e. Q1 and Q3)~~ and the ends of the whiskers correspond to the first and ninth deciles ~~(i.e. D1 and D9)~~. (b) Their monthly average concentrations as a function of the year. Note that meteorological parameter data used in this study were restricted to periods when VOC measurements were realized.

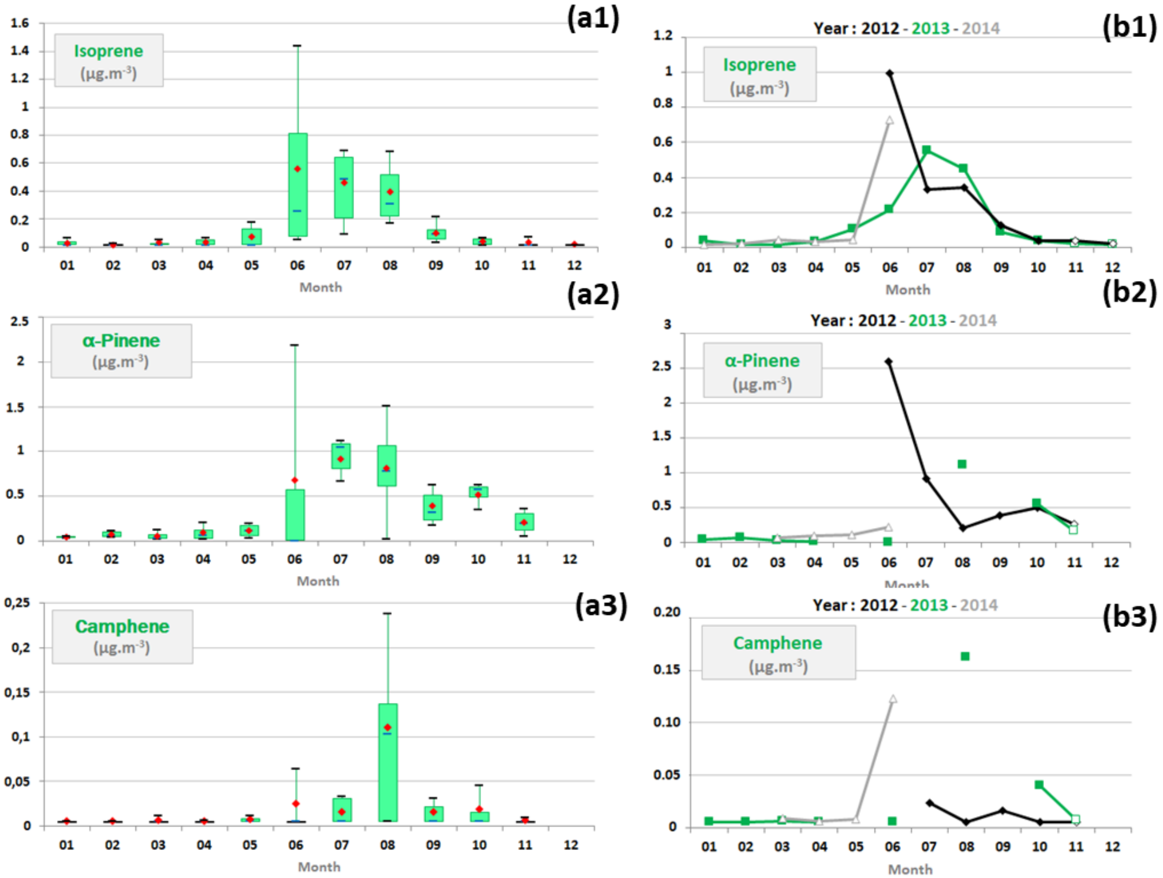
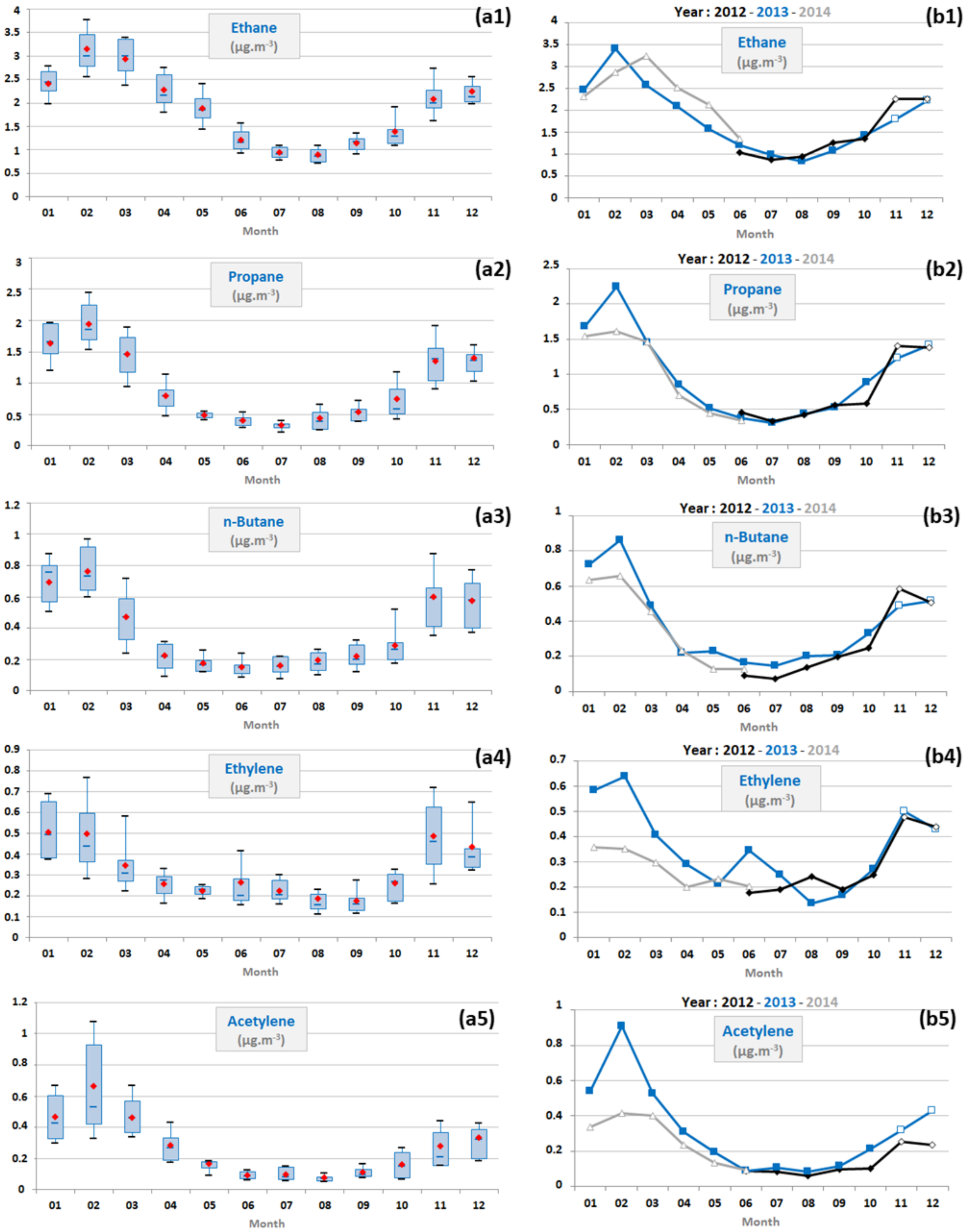


Figure 4: (a) Monthly variations in a selection of biogenic VOC concentrations (expressed in µg m^{-3}) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict the first and third quartiles ~~(i.e. Q1 and Q3)~~ and the ends of the whiskers correspond to the first and ninth deciles ~~(i.e. D1 and D9)~~. (b) Their monthly average concentrations as a function of the year; full markers indicate months when VOC samples were collected from 12:00-16:00 and empty markers those when VOC samples were collected from 09:00-13:00.


(a1)
Ethane
(µg.m-3)
0
0.5
1
1.5
2
2.5
3
3.5
4
01
02
03
04
05
06
07
08
09
10
11
12
Month
(b1)
Year : 2012 - 2013 - 2014
Ethane
(µg.m-3)
0
0.5
1
1.5
2
2.5
3
3.5
4
01
02
03
04
05
06
07
08
09
10
11
12
Month
(a2)
Propane
(µg.m-3)
0
0.5
1
1.5
2
2.5
3
Month
(b2)
Year : 2012 - 2013 - 2014
Propane
(µg.m-3)
0
0.5
1
1.5
2
2.5
Month
(a3)
n-Butane
(µg.m-3)
0
0.2
0.4
0.6
0.8
1
1.2
Month
(b3)
Year : 2012 - 2013 - 2014
n-Butane
(µg.m-3)
0
0.2
0.4
0.6
0.8
1
Month
(a4)
Ethylene
(µg.m-3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Month
(b4)
Year : 2012 - 2013 - 2014
Ethylene
(µg.m-3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Month
(a5)
Acetylene
(µg.m-3)
0
0.2
0.4
0.6
0.8
1
1.2
Month
(b5)
Year : 2012 - 2013 - 2014
Acetylene
(µg.m-3)
0
0.2
0.4
0.6
0.8
1
Month

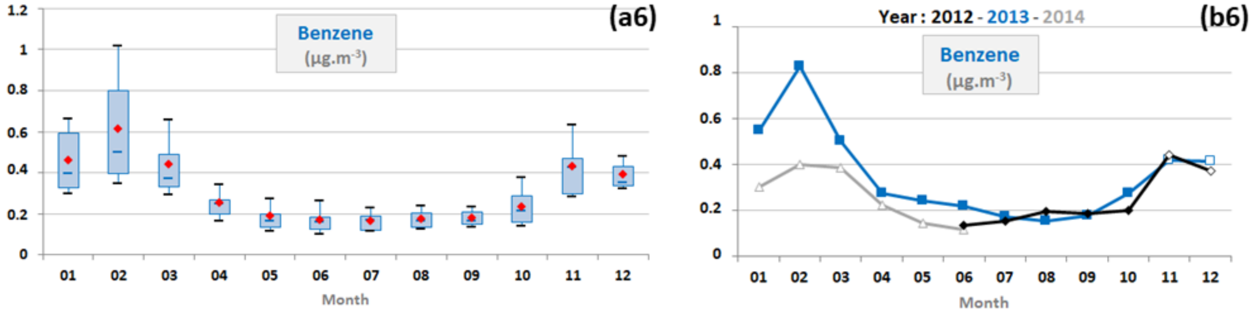
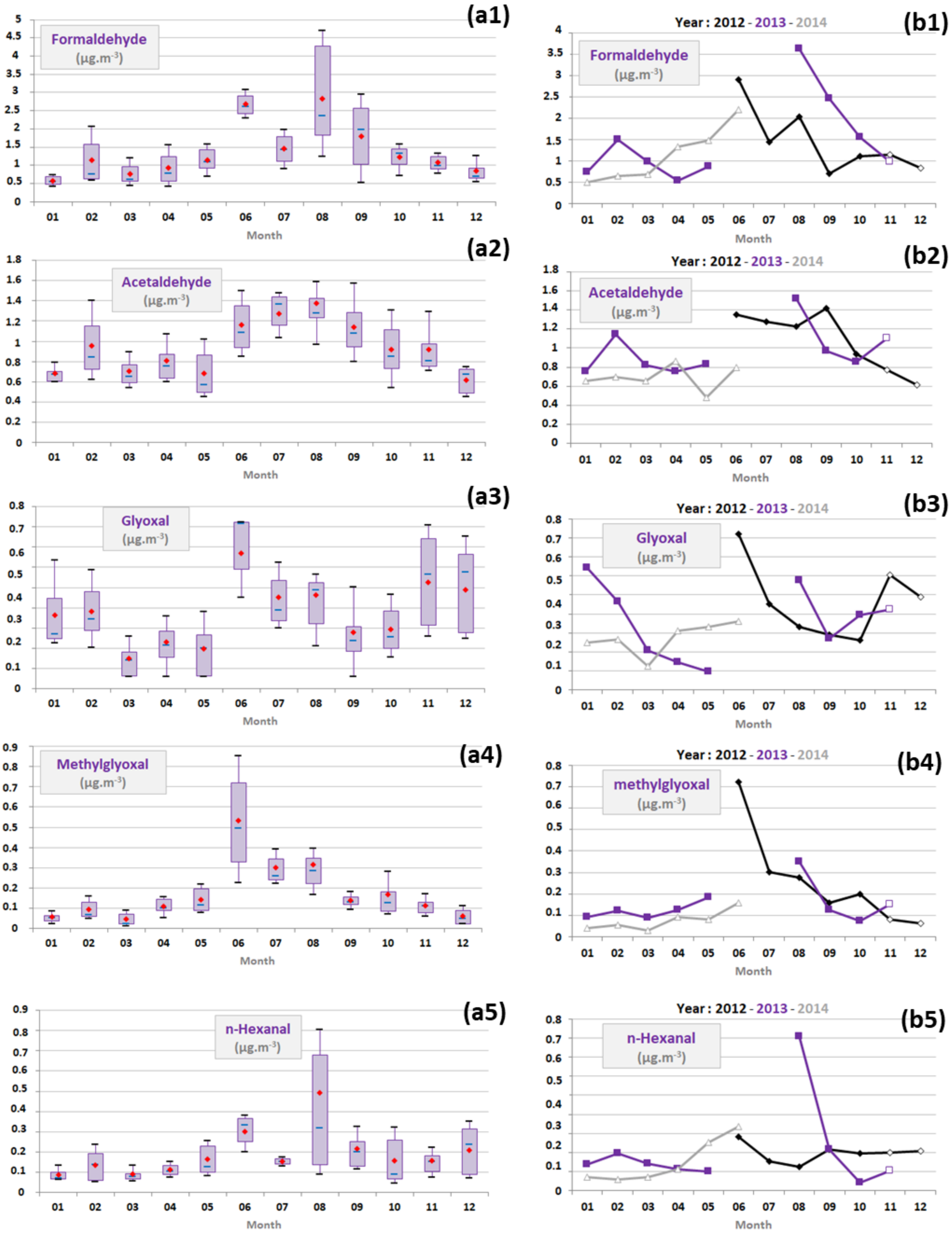


Figure 5: (a) Monthly variations in a selection of anthropogenic VOC concentrations (expressed in µg m^{-3}) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict the first and third quartiles ~~(i.e. Q1 and Q3)~~ and the ends of the whiskers correspond to the first and ninth deciles ~~(i.e. D1 and D9)~~. (b) Their monthly average concentrations as a function of the year; full markers indicate months when VOC samples were collected from 12:00-16:00 and empty markers those when VOC samples were collected from 09:00-13:00.


(a1)
Formaldehyde
(µg.m-3)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
01
02
03
04
05
06
07
08
09
10
11
12
Month
(b1)
Year : 2012 - 2013 - 2014
Formaldehyde
(µg.m-3)
4
3.5
3
2.5
2
1.5
1
0.5
0
Month
(a2)
Acetaldehyde
(µg.m-3)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Month
(b2)
Year : 2012 - 2013 - 2014
Acetaldehyde
(µg.m-3)
Month
(a3)
Glyoxal
(µg.m-3)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Month
(b3)
Year : 2012 - 2013 - 2014
Glyoxal
(µg.m-3)
Month
(a4)
Methylglyoxal
(µg.m-3)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Month
(b4)
Year : 2012 - 2013 - 2014
methylglyoxal
(µg.m-3)
Month
(a5)
n-Hexanal
(µg.m-3)
Month
(b5)
Year : 2012 - 2013 - 2014
n-Hexanal
(µg.m-3)
Month

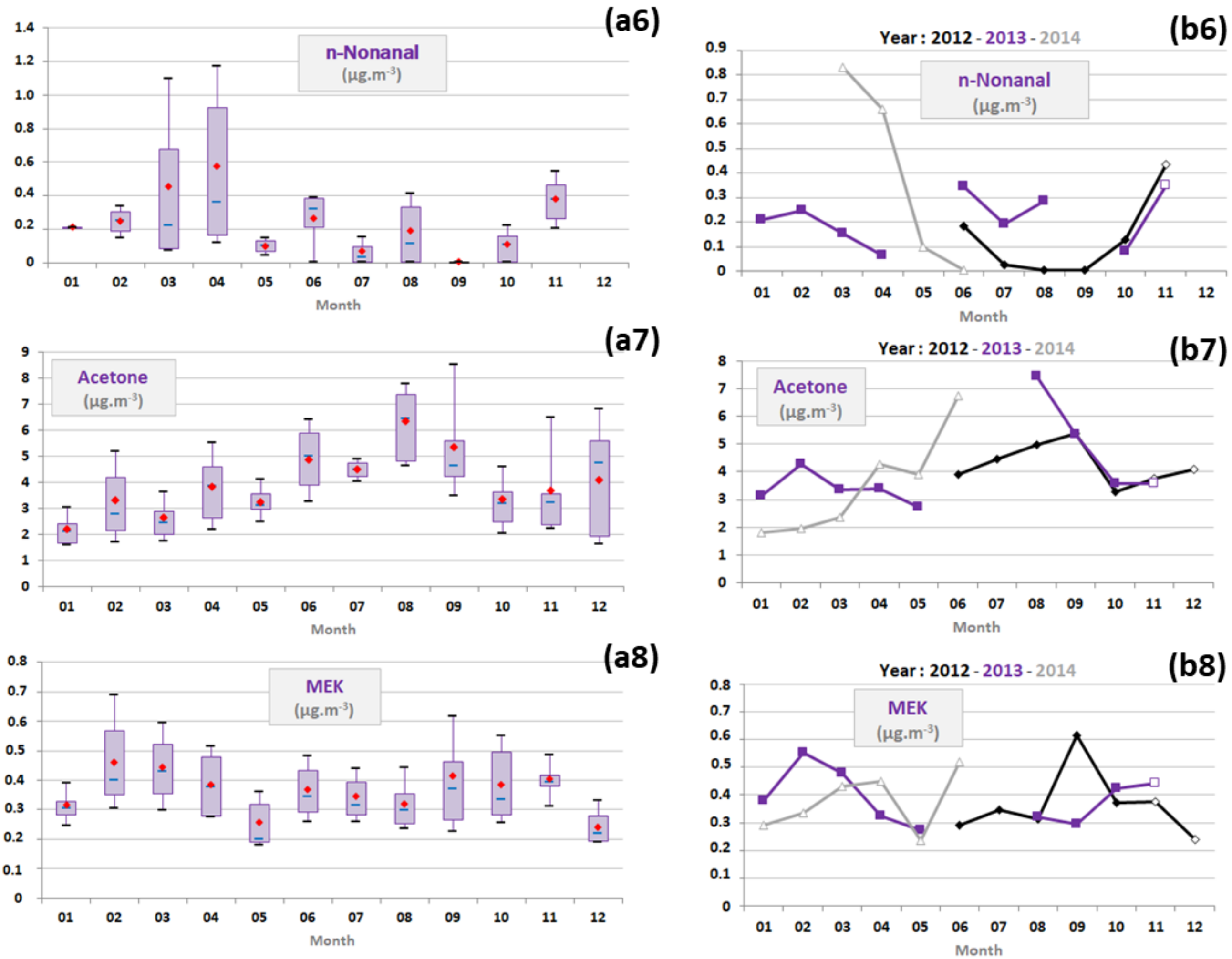


Figure 6: (a) Monthly variations in a selection of oxygenated VOC concentrations (expressed in µg m^{-3}) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict the first and third quartiles ~~(i.e. Q1 and Q3)~~ and the ends of the whiskers correspond to the first and ninth deciles ~~(i.e. D1 and D9)~~. (b) Their monthly average concentrations as a function of the year; full markers indicate months when VOC samples were collected from 12:00-16:00 and empty markers those when VOC samples were collected from 09:00-13:00.

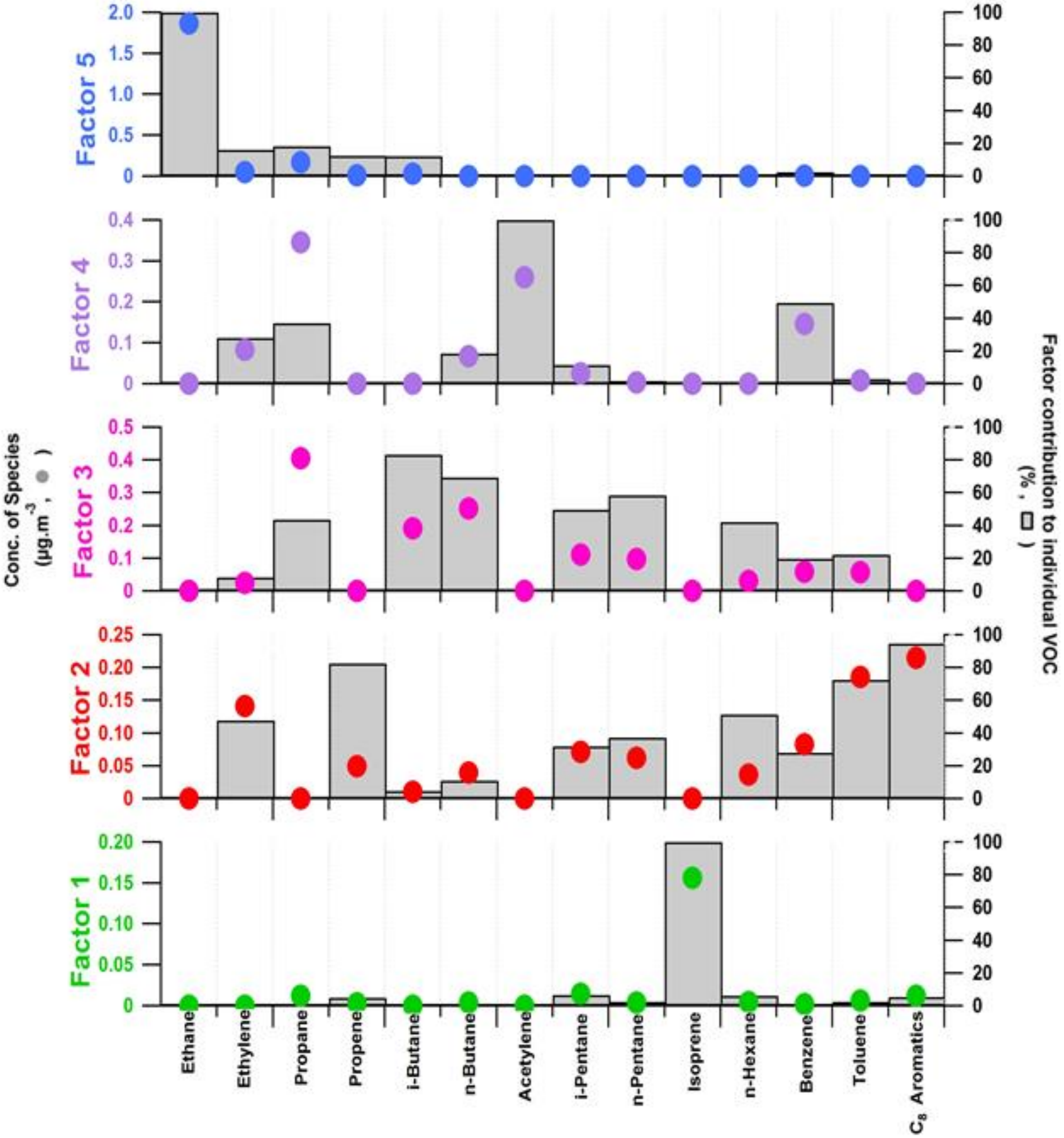


Figure 7: Chemical profiles of the 5-factor PMF solution (14 variables). Factor contributions to each species (µg m^{-3}) and the percent of each species apportioned to the factor are displayed as a grey bar and a ~~color~~coloured circle, respectively. Factor 1 – local biogenic source; factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background.

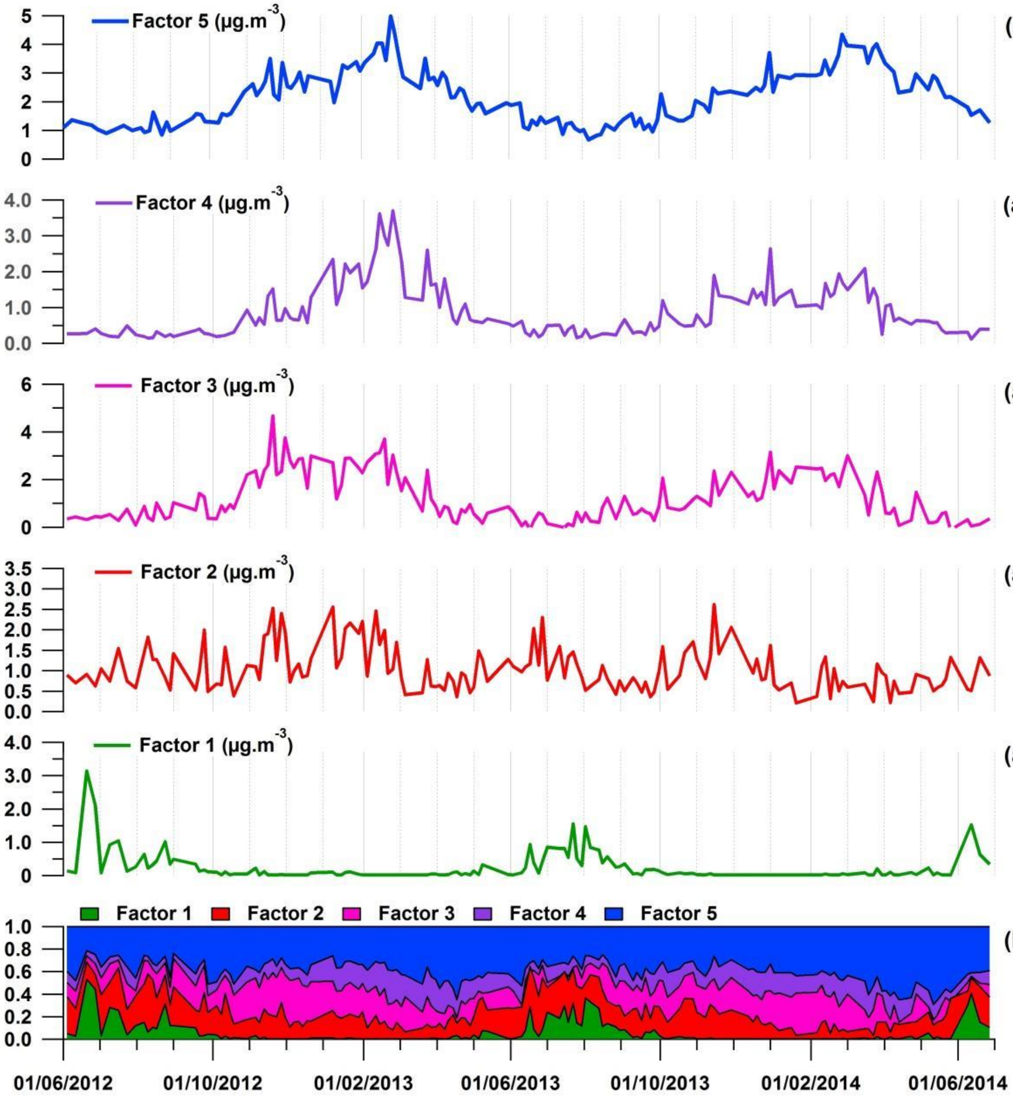


Figure 8: (a) Time series of ~~NMHC~~ factor contributions (µg m^{-3}) and (b) accumulated relative NMHC contributions. Factor 1 - local biogenic source; factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background. Note that the NMHC dataset used for the PMF analysis included different sampling time hours (09:00-13:00 or 12:00-16:00) following shifts during the two-year period (see Table 1).

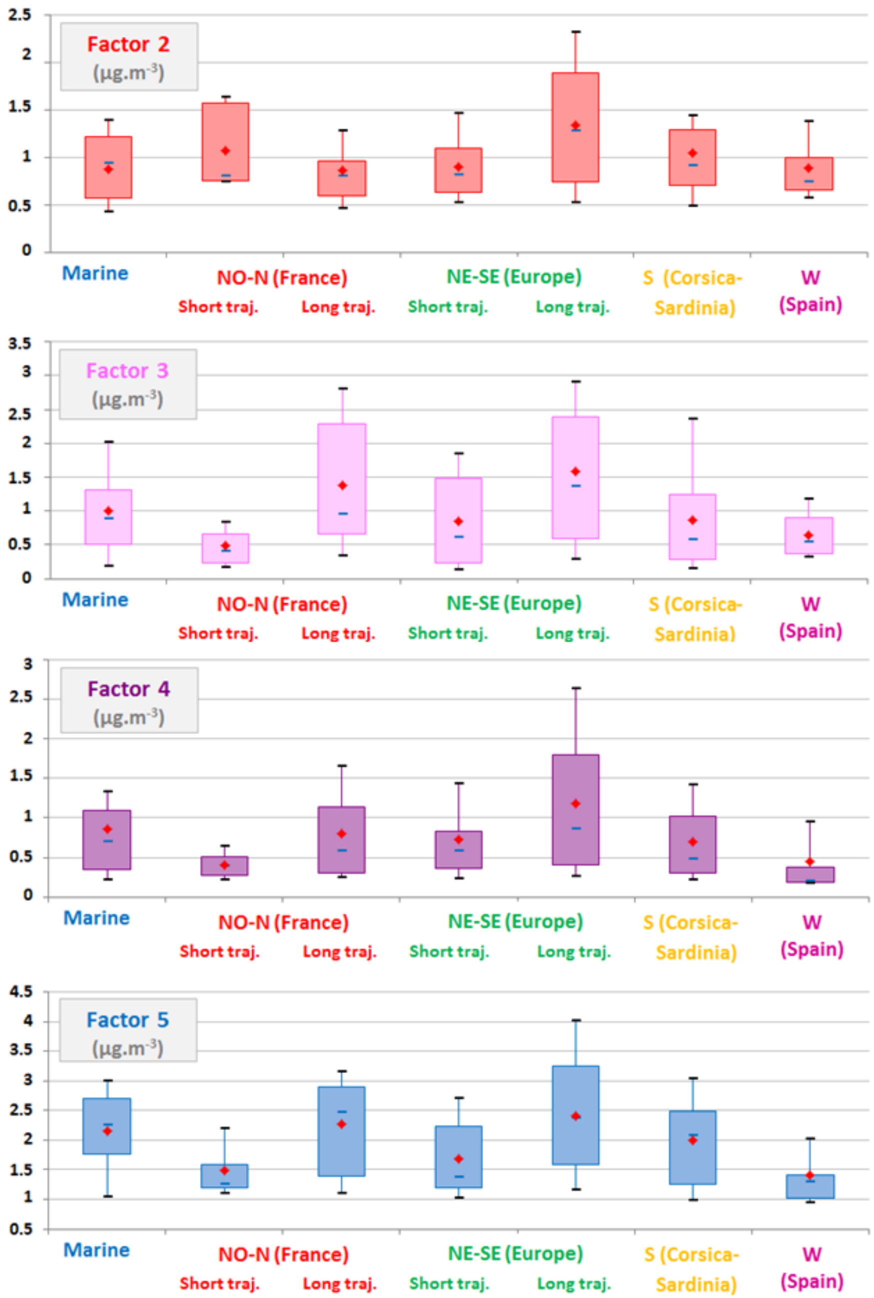


Figure 9: NMHC factor contributions (µg m^{-3}) as a function of air mass origin~~s~~ represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict the first and third quartiles ~~(i.e. Q1 and Q3)~~ and the ends of the whiskers correspond to the first and ninth deciles ~~(i.e. D1 and D9)~~. ~~PMF factors: f~~Factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background. Air masses originating from France and Europe are subdivided into short and long trajectories to highlight local and more distant contributions (see Sect. 3.2). Note that the NMHC dataset used for the PMF analysis included different sampling time hours (09:00-13:00 or 12:00-16:00) following shifts during the two-year period (see Table 1).

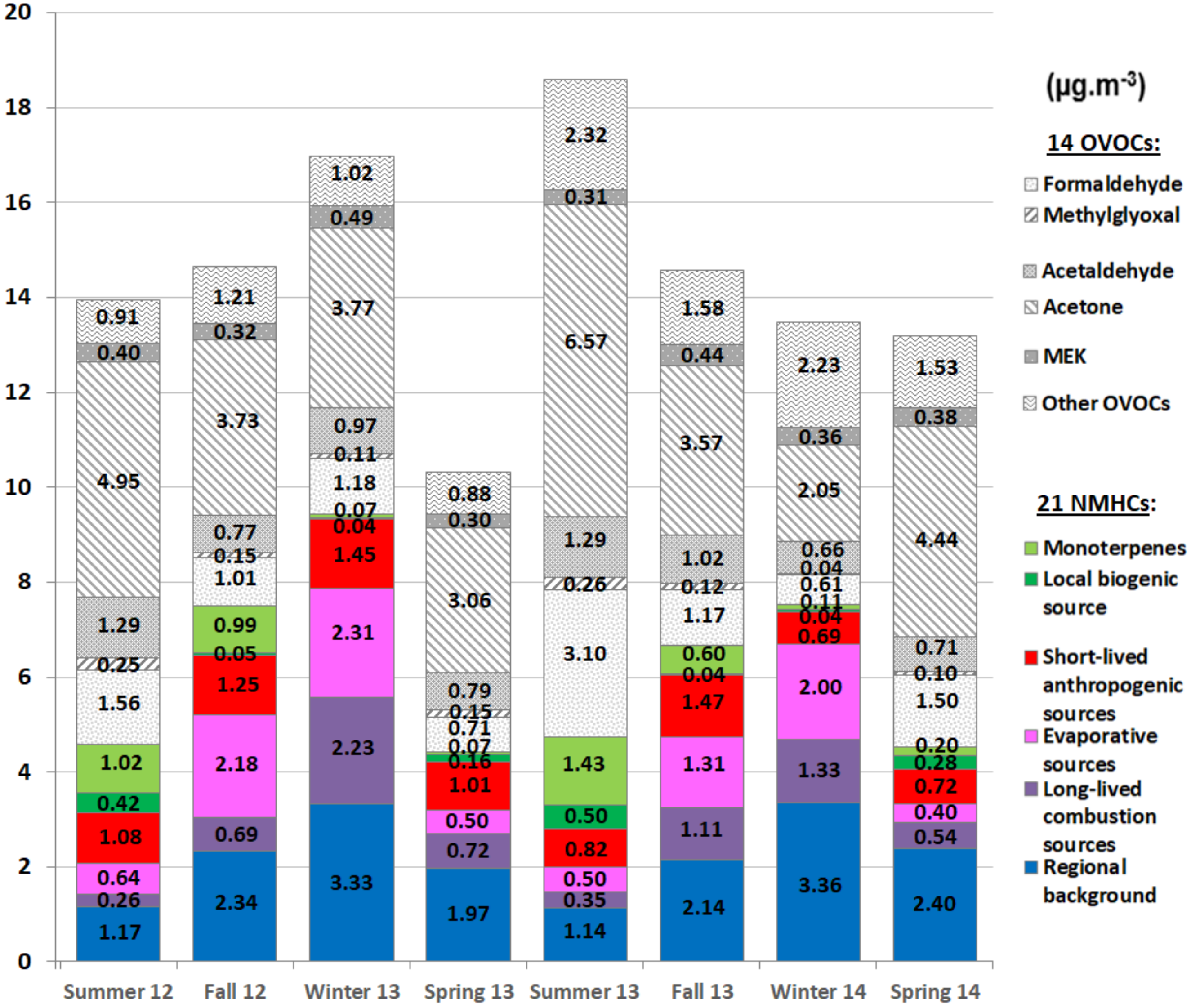


Figure 10: Variations in seasonal averaged accumulated concentrations (expressed in µg m^{-3}) of the 35 VOCs selected in this study. The 17 NHMCs selected in~~for~~ the factorial analysis were apportioned to the five modelled NMHC sources. NMHC seasonal measured concentrations which were not modelled by the PMF tool were lower than 0.09 µg m^{-3} and are not reported here. Winter: 01/01-31/03 periods – spring: 01/04-30/06 periods – summer: 01/07-30/09 periods – fall: 01/10-31/12 periods. Note that the VOC dataset included different sampling time hours (09:00-13:00 or 12:00-16:00) following shifts during the two-year period (see Table 1).

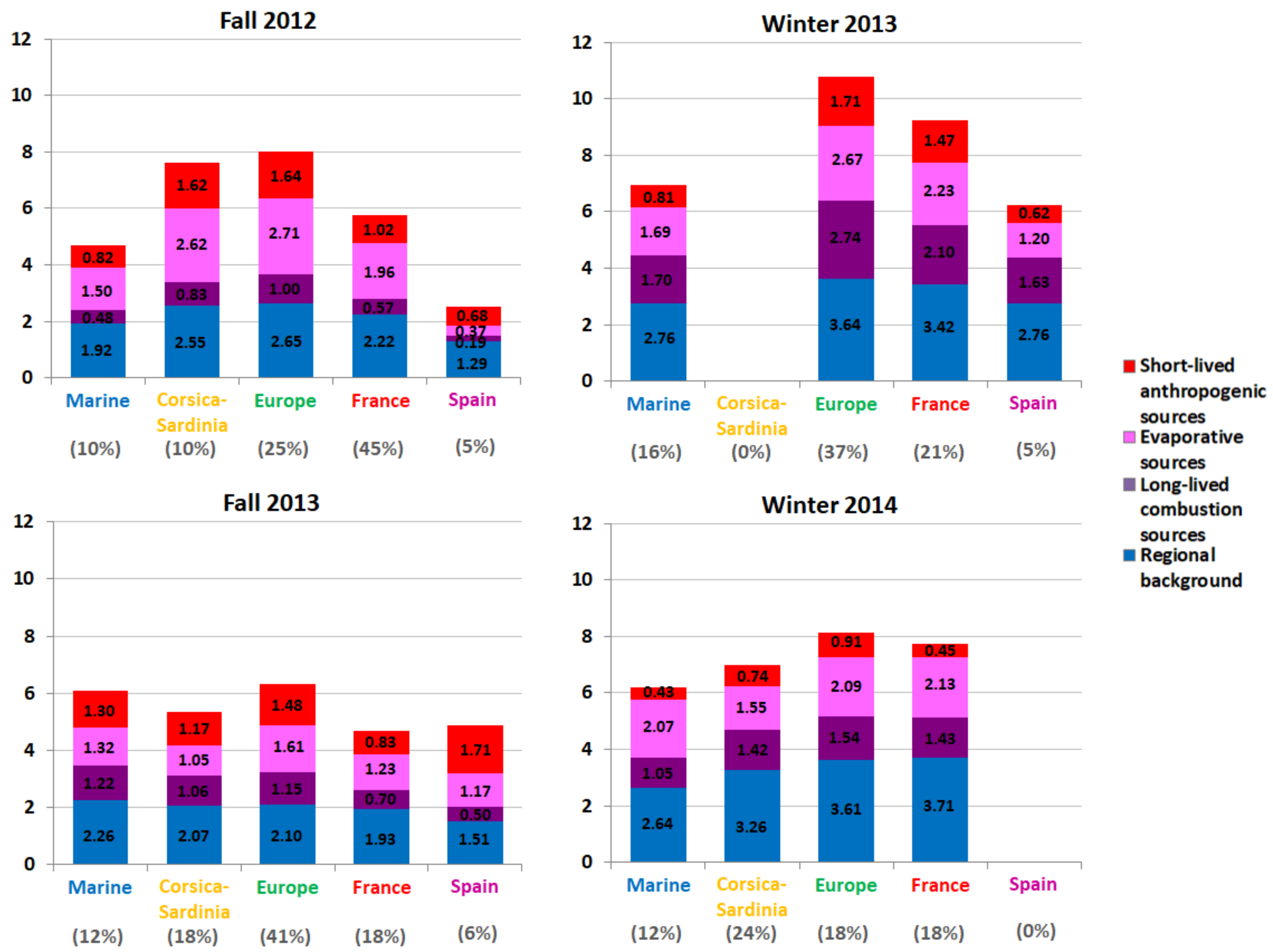


Figure 11: Average a~~A~~ccumulated ~~average~~ contributions (expressed in µg m^{-3}) of the NMHC anthropogenic sources (~~factors 2-5 which explained measured concentrations of the 16 selected NMHCs in the PMF analysis –~~ Sect. 3.5) ~~per season~~in fall and winter as a function of air mass origin~~s~~ (Sect. 3.2). Winter: 01/01-31/03 periods – fall: 01/10-31/12 periods.

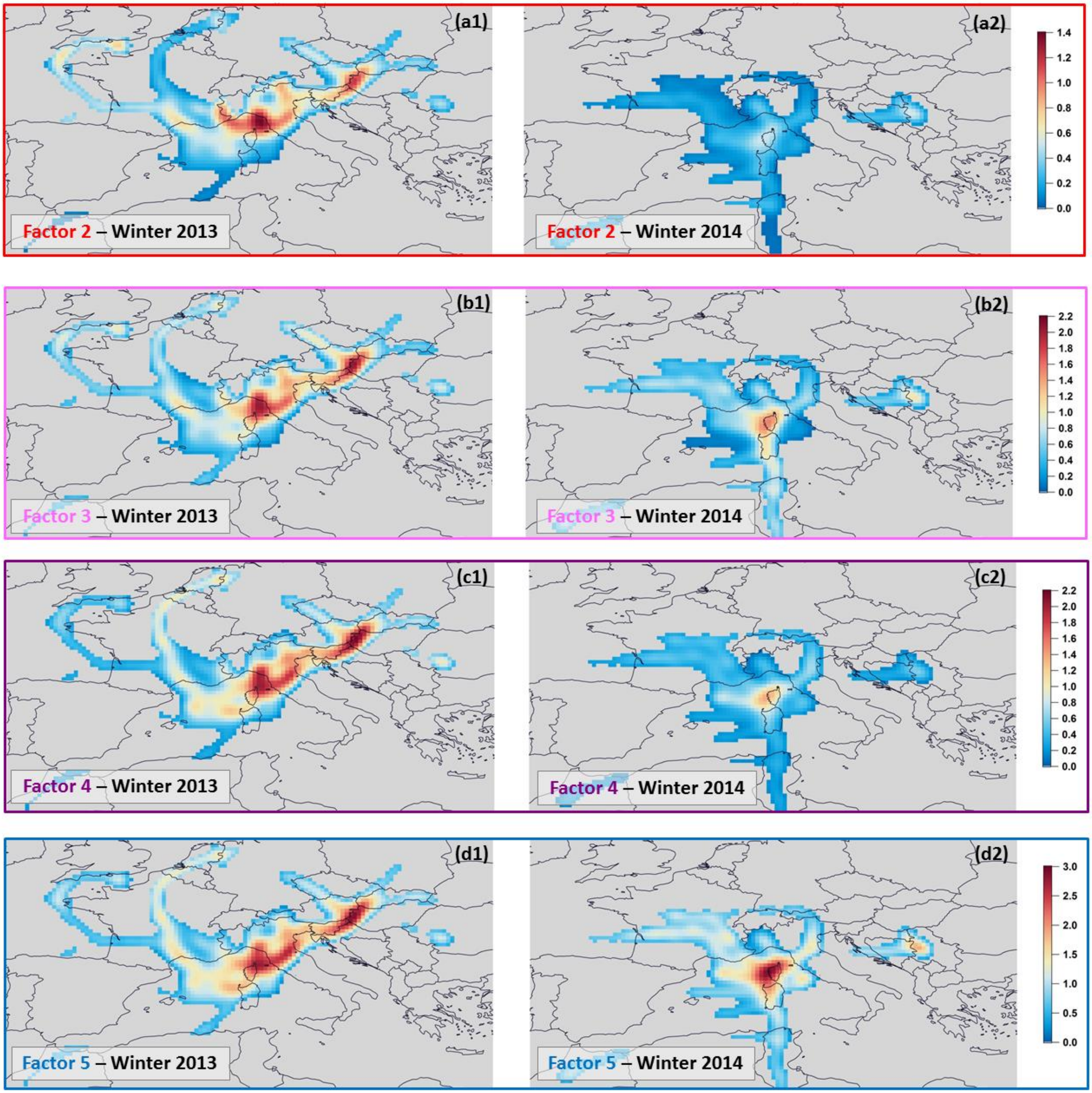
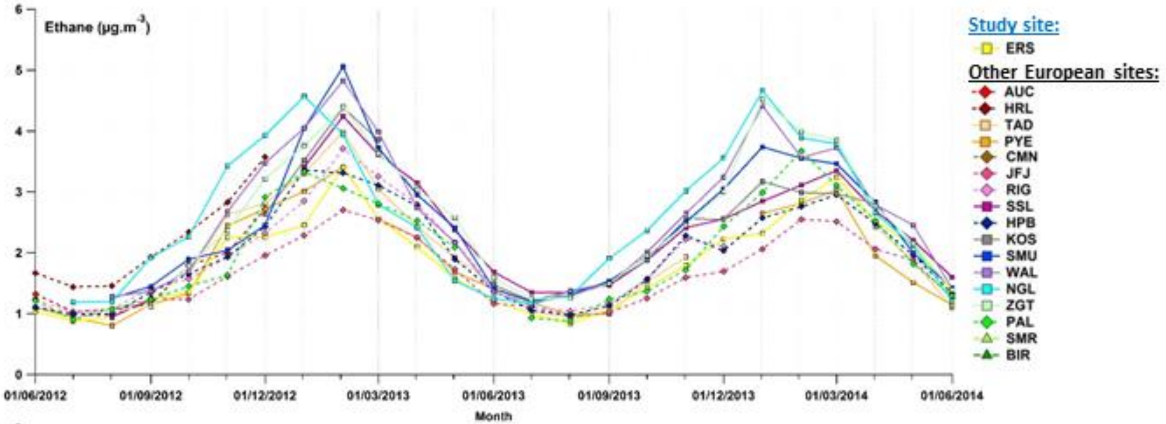
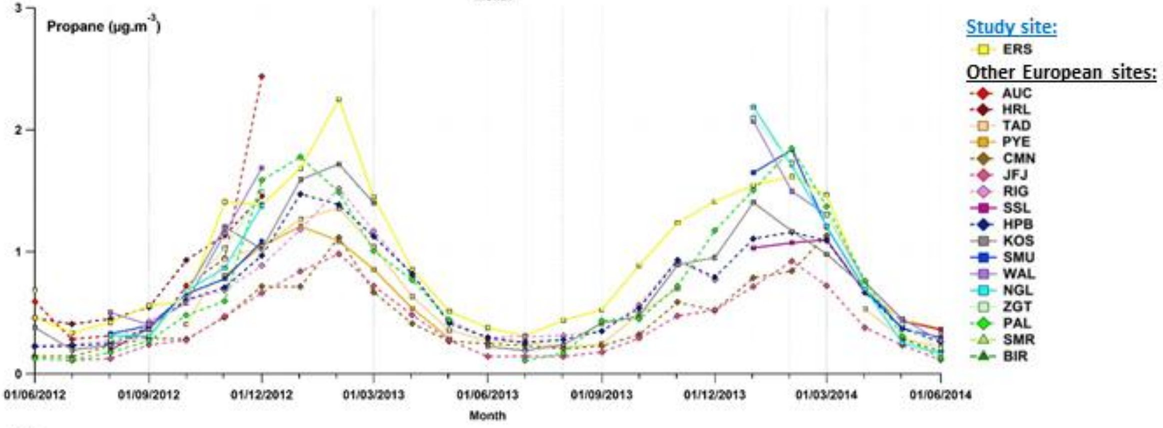
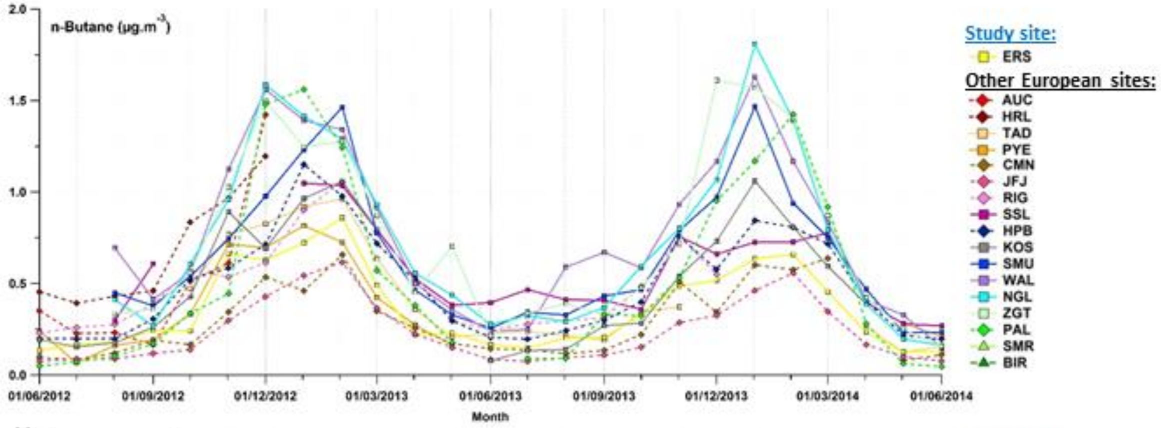
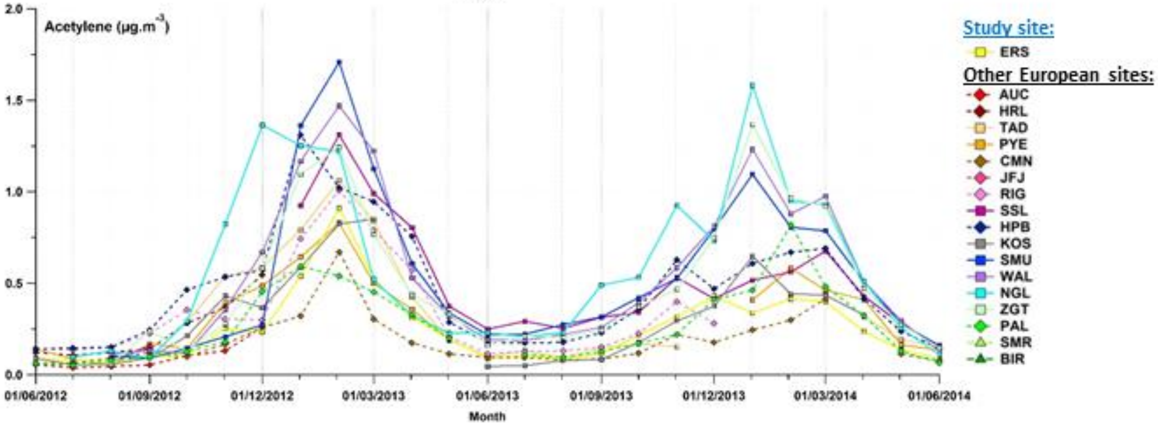


Figure 12: Potential source areas contributions to ~~factors 2-5~~NMHC anthropogenic sources during winters 20~~0~~13 and 2014. Contributions are expressed in µg m^{-3}. Factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background. Winter: 01/01-31/03 periods~~ – fall: 01/10-31/12 periods~~.


Ethane (µg.m⁻³)
0
1
2
3
4
5
6
01/06/2012
01/09/2012
01/12/2012
01/03/2013
01/06/2013
01/09/2013
01/12/2013
01/03/2014
01/06/2014
Month
Study site:
ERS
Other European sites:
AUC
HRL
TAD
PYE
CMN
JFJ
RIG
SSL
HPB
KOS
SMU
WAL
NGL
ZGT
PAL
SMR
BIR


Propane (µg.m⁻³)
0
1
2
3
01/06/2012
01/09/2012
01/12/2012
01/03/2013
01/06/2013
01/09/2013
01/12/2013
01/03/2014
01/06/2014
Month
Study site:
ERS
Other European sites:
AUC
HRL
TAD
PYE
CMN
JFJ
RIG
SSL
HPB
KOS
SMU
WAL
NGL
ZGT
PAL
SMR
BIR


n-Butane (µg.m⁻³)
0.0
0.5
1.0
1.5
2.0
01/06/2012
01/09/2012
01/12/2012
01/03/2013
01/06/2013
01/09/2013
01/12/2013
01/03/2014
01/06/2014
Month
Study site:
ERS
Other European sites:
AUC
HRL
TAD
PYE
CMN
JFJ
RIG
SSL
HPB
KOS
SMU
WAL
NGL
ZGT
PAL
SMR
BIR


Acetylene (µg.m⁻³)
0.0
0.5
1.0
1.5
2.0
01/06/2012
01/09/2012
01/12/2012
01/03/2013
01/06/2013
01/09/2013
01/12/2013
01/03/2014
01/06/2014
Month
Study site:
ERS
Other European sites:
AUC
HRL
TAD
PYE
CMN
JFJ
RIG
SSL
HPB
KOS
SMU
WAL
NGL
ZGT
PAL
SMR
BIR

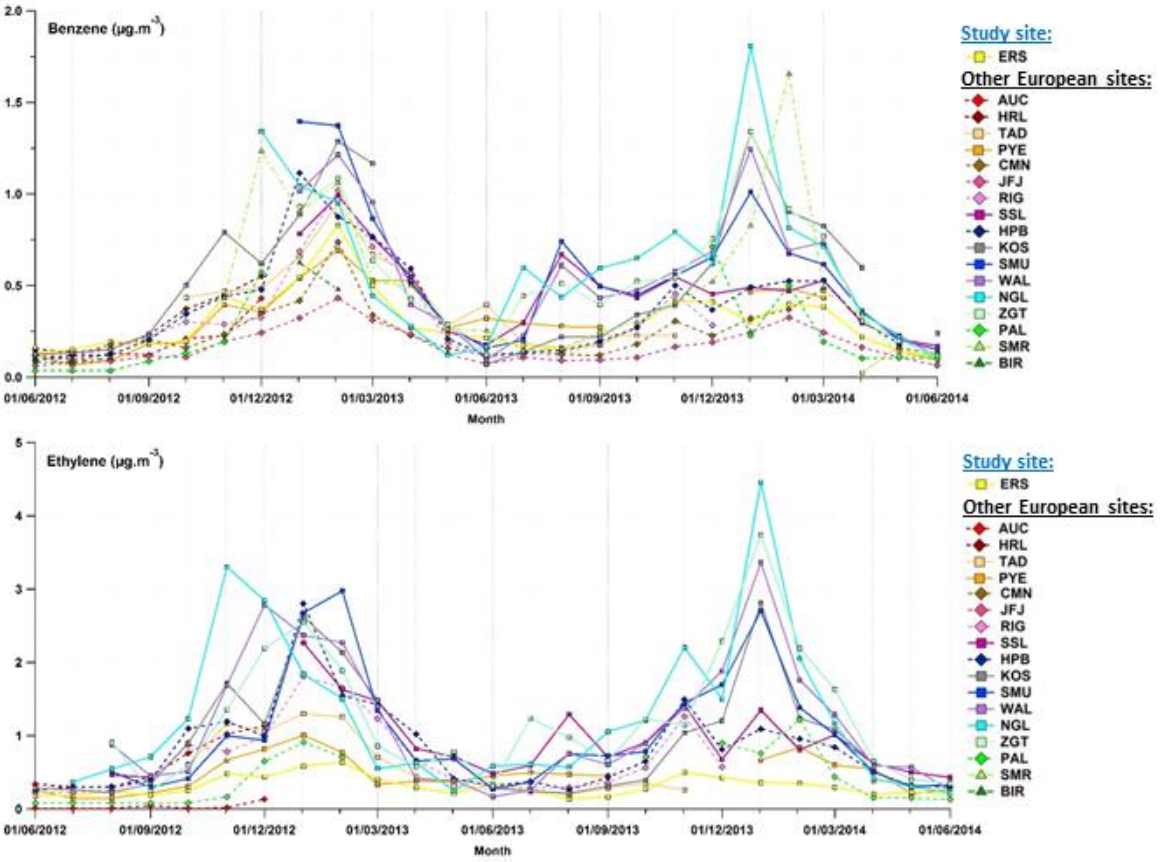


Figure 13: Monthly concentration time series of a selection of NMHCs (expressed in µg m^{-3}) measured at Ersa and 17 other European monitoring stations. Stations are indicated according to their GAW identification (see Sect. S7). "ERS" refers to the study site.

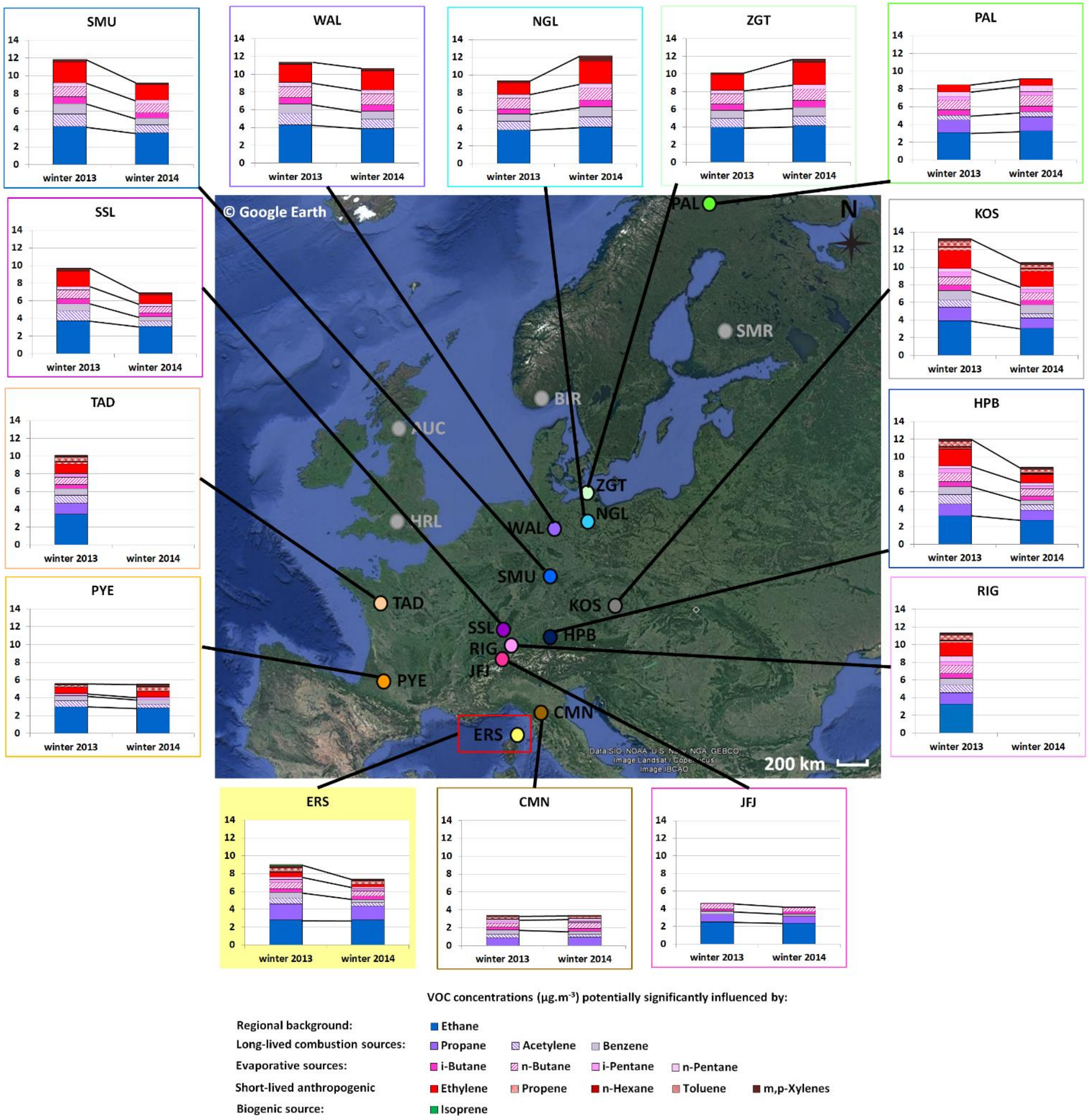


Figure 14: Average a~~A~~ccumulated ~~average~~ concentrations of a selection of 15 VOCs (expressed in µg m^{-3}) measured at Ersa and 13 other European monitoring stations in winters 2013 and 2014. Stations are indicated according to their GAW identification (see Sect. S7). "ERS" refers to the study site and its location and results are highlighted. Selected VOCs ~~in this study~~ are those taken into account in the factorial analysis ~~applied to the Ersa two-year NMHC dataset~~of this study. Note that ~~for some stations, accumulated concentrations are incomplete since only VOC measured at a station at both winter periods were taking into in this comparison~~

~~analysis, at the exception of TAD and RIG stations. For these latter, ~~NMHC measurements did not cover the winter 2014 period at TAG and RIG stations~~, that’s why accumulated concentrations were only indicated for winter 2013 period~~. For AUC, HRL, BIR and SMR stations, represented by grey markers, NMHC measurements were not realized both during winters 2013 and 2014, or were conducted with a PTR-MS and hence we considered accumulated concentrations only of aromatic compounds are not sufficiently representative for interannual variations in NMHC winter concentrations. Map provided by Google Earth Pro software (v.7.3.3 image Landsat/Copernicus – IBCAO; data SIO, NOA~~O~~A, U.S, Navy, NGA, GEBCO; © Google Earth).