acp-2020-607: "Seasonal variation and origins of volatile organic compounds observed during two years at a western Mediterranean remote background site (Ersa, Cape Corsica)"

This manuscript presents an analysis of the VOC concentrations and temporal trends over a 2 years long observation campaign at a remote site located in Corsica and representative of the northwest part of the Mediterranean background atmosphere. The monthly, seasonal and interannual variabilities of 21 NMHCs and 4 OVOCs are reported. Source apportionment using positive matrix factorization in combination with back trajectories analysis was carried out on a selection of 14 NMHC species. Not surprisingly, the five factors solution chosen fails to apportion the selected VOCs into their specific emission sources, as the air masses that reach the remote site are already mixed and processed. Finally, the NMHC temporal concentration trends are compared to those observed in the 17 other European background stations at the same period. Overall, while a significant spatial variability in concentration levels is found, especially in winter, similar seasonal trends are observed.

The work provides valuable scientific information as long term VOCs datasets in back-ground sites are still rather scarce in the Mediterranean region. To my point of view this topic together with the comparison with the 17 other background sites located in Europe is the most interesting feature of the manuscript. On the other hand, I have some concerns regarding the added value brought by the PMF analysis on a limited set of VOCs and the relevance of the solution as meteorology (boundary layer, air mass circulation, temperature) seems to be the main factor driving the temporal trends in a remote background site. The authors should more clearly elaborate on the limits of the PMF with respect to the limited set of VOCs and samples in such a remote site. As a general comment on language and structure, I find the manuscript in its current state unnecessarily long. Topics are repeated saying pretty much the same thing in different sections. For example, many points raised in section 4.1 (Determination of controlling factors) have already been discussed in the section 3.5 (VOC factor analysis) and points raised in section 4.2 (The particular case of winter) have partly been discussed in section 4.1 when fall-winter interannual trends are discussed. Same remark for sections 3.3 (VOC mixing ratios) and 3.5. Some sections lack clarity (see specific comments). Overall, I find it very difficult to extract the main messages of the sections/paragraphs.

A major revision according to these mentioned general comments is consequently required before publication to ACP.

Authors' Responses to Referee #1

We would like to thank the Referee #1 for her/his general feedback and each of her/his useful comments/questions for improving the quality of this manuscript. All comments addressed by both referees have been taken into account in the revised version of the manuscript.

We hope that complementary information provided in the responses and incorporated in the manuscript and the supplement will further convince referee #1 on the relevance of the PMF solution examined in this study.

As suggested by both referees, the revised manuscript was largely rewritten. The introduction was shortened. Complementary information on the VOCs selected in this study and on the PMF analysis are now provided in the Supplement (Sects. S1 and S2, respectively). Sections on results have been reviewed in order to better separate information provided by them and hence removed repetitive ones. Section 3.1 ("Meteorological conditions") was shortened only keeping essential pieces of information to the explanation of seasonal and interannual VOC variations. Descriptive Sects. 3.3 and 3.4 ("VOC mixing ratios" and "VOC variability", respectively) have been limited to the presentation of VOC concentration levels, their abundance and their variations and elements of interpretations linked to factors controlling them were removed or moved in Sect. 4 ("Discussions on the seasonal variability of VOC concentrations"). Sect. 3.4.1-3.4.3 were rewritten grouping results to emphasize similar or different VOC behaviours. Note that a larger number of OVOCs is now considered in the Sect. 3.4.3 ("Oxygenated VOCs") and comparisons with other VOC measurements performed at Ersa were moved in the revised Supplement (Sect. S4). Section 3.5 ("Major NMHC sources") was limited to the presentation of the 5 NMHC factors identified in this study and results on their seasonal and interannual variations were removed or moved in Sect. 4. The other factorial analysis previously realized with the summer 2013 VOC dataset has been better used to support factor identification in this study. As a result, Sect. 3.5.6 ("Towards the best experimental strategy to characterize variation in VOC concentrations observed at a remote background site") has been reviewed to better highlight (i) the relevance of the PMF solution to identify NMHC sources and (ii) its limitation to examine VOC concentration variations observed at Ersa. The Sect. 3.5.6 is supported by commentary results presented in the Supplement (Sects. S5 and S6). Section 4 has been restructured in order to distinguish factors controlling VOC concentration variations in spring and summer (Sect. 4.1) from those in fall and winter (Sect. 4.2) and OVOC concentration variations have also been incorporated. The description of the 17 European sites, whose NMHC concentration variations are discussed in Sect. 5 ("VOC concentration variations in continental Europe"), was moved to the Supplement (Sect. S7). The conclusion has also been rewritten.

In this respect, several figures were notably modified including in the supplement. Please note that figures numbers are now different in this new version. Additional sections have been added to the Supplement to present and discuss the selection of the VOCs in this study and the relevance of the PMF solution.

In the present document, authors' answers to the specific comments addressed by Referee #1 are mentioned in **blue**, while changes made to the revised manuscript are shown in **green**. Note that, the comments are listed in the different order than initial one of referee #1, to make easier the understanding of interconnected responses. The comments on the manuscript are listed as follows:

1/Sect. 1 Introduction

The introduction could be shortened and focused on the scientific context and goals of the study. For example, information given on the various national and international programs is not essential here (Page 3, line 8-13 ; Page 3, line 32 to Page 4, line 4).

As advised by referee #1, the introduction was shortened in the revised manuscript (of 13 lines). We removed precisions on European short-term field campaigns as the development of long-term observations in Europe were sufficient to explain our motivations to conduct Ersa VOC measurements during two-years. We also removed the presentation of international programs (ACTRIS, EMEP and WMO-GAW) as proposed by referee #1. However, we decided to keep the presentation of ChArMEx program within which VOC measurements were conducted at Ersa during two years. Corrections applied in Sect. 1 in the revised manuscript (from Page 2 line 19 to Page 4 line 2):

“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 extensively characterize VOC sources, it is meaningful to examine their chemical composition, in addition to identifying the factors controlling their variations at different time scales.

VOC regional distributions are eminently changing 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 meteorological conditions. Therefore, these elements underline the necessity to carry out long-term VOC measurements. ~~In Europe, studies essentially focus on urban and suburban locations (e.g., Derwent et al., 2014 and von Schneidemesser et al., 2010 in United Kingdom; Salameh et al., 2019 and Waked et al., 2016 in France; Roemer et al., 1999 in the Netherlands; Fanizza et al., 2014 in Italy), reflecting concerns about the role of VOCs in urban air quality control, efficiency assessment of national VOC emission regulation implementations, and population exposure. European VOC observations in the background atmosphere are still dedicated largely to process studies and short-term research missions. However,~~ There are growing efforts now 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 multi-year studies were conducted ensuing the increasing demand for high quality VOC data, and long-term monitoring have led to international programs like the European Research Infrastructure for the observation of Aerosol, Clouds and Trace gases (ACTRIS - https://www.actris.eu/; last access: 03/04/2020), the European Monitoring and Evaluation Program (EMEP - http://www.emep.int/; last access: 03/04/2020 - 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: 03/04/2020). Regarding VOCs,~~ These research studies principally explored the emission regulation efficiency, links between tropospheric ozone production and changes in VOC concentrations, and assessed seasonal variations and regional distributions in VOC concentrations. Nonetheless, investigations on 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 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 through 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 concentrations 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 the lack of extensive in-situ observations. ~~In order to improve our actual comprehension of the complexity of the Mediterranean atmosphere, it is essential to increase the atmospheric pollutant observations, including speciated and reactive VOCs, at representative regional background sites.~~ 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: 03/04/2020), the project ChArMEx (the Chemistry-Aerosol Mediterranean Experiment, http://charmex.lsce.ipsl.fr, last access: 03/04/2020; Dulac, 2014) ~~focused on the development and coordination of regional research actions. More precisely, ChArMEx~~ 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 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 better understand 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.

~~The present study was designed to characterize the seasonal variations in the sources of VOCs affecting the western Mediterranean atmosphere. An extensive chemical composition dataset was collected at a receptor site considered to be representative of the northwestern basin.~~ In this article, we present and discuss ~~ambient levels and~~ factors controlling seasonal and interannual variations of a selection of VOCs observed at the Ersa station ~~of the Corsican Observatory for Research and Studies on Climate and Atmosphere-ocean environment (CORSiCA - https://corsica.obs-mip.fr/, last access: 03/04/2020; Lambert et al., 2011),~~ over more than two years ~~as part of the ChArMEx project~~ (from early June 2012 to late June 2014). ~~Selected species include alkanes, alkenes, alkyne, aromatic compounds and oxygenated VOCs (OVOCs), which were measured using off-line techniques.~~ To this end, this study describes (i) the concentration levels of the targeted VOCs, (ii) ~~specify~~ 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) ~~examine~~ the representativeness of the Ersa station in terms of seasonal variations in VOC concentrations impacting continental Europe."

2/Sect. 2.2.1, Page 6, line 8

"44 C5-C16" Check consistency with Table 1 where 50 VOC are listed to be sampled with the solid adsorbent.

The 44 C_5-C_{16} NMHCs indicated in Sect. 2.2.1 ("VOC measurements") comprise 28 C_5 - C_{16} alkanes/alkenes, 6 monoterpenes and 10 C_6 - C_9 aromatics. The six additional VOCs are the 6 C_6 - C_{11} n-aldehydes that is why 50 VOCs are listed in Table 1 to be sampled with multi-sorbent cartridges. Moreover, as advised by referee #1, we checked the consistency of the number of VOCs measured per instrument in the revised manuscript. Some corrections were also applied to Table 1 in the revised manuscript to make this information clearer:

"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.

Instrument	**Steel canisters**	**DNPH cartridges – Chemical desorption (acetonitrile) – HPLC-UV**	**Multi-adsorbent 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

”

3/Sect. 2.2.1, Page 6, line 1

It is not clear when these additional 150 off-line air samples were taken; over the 2-year period? at which frequency?

To clarify when the VOC samples (from canisters, DNPH cartridges and multi-sorbent cartridges) were collected over the 2-year period, the Fig. S1 was added in the revised Supplement:

“

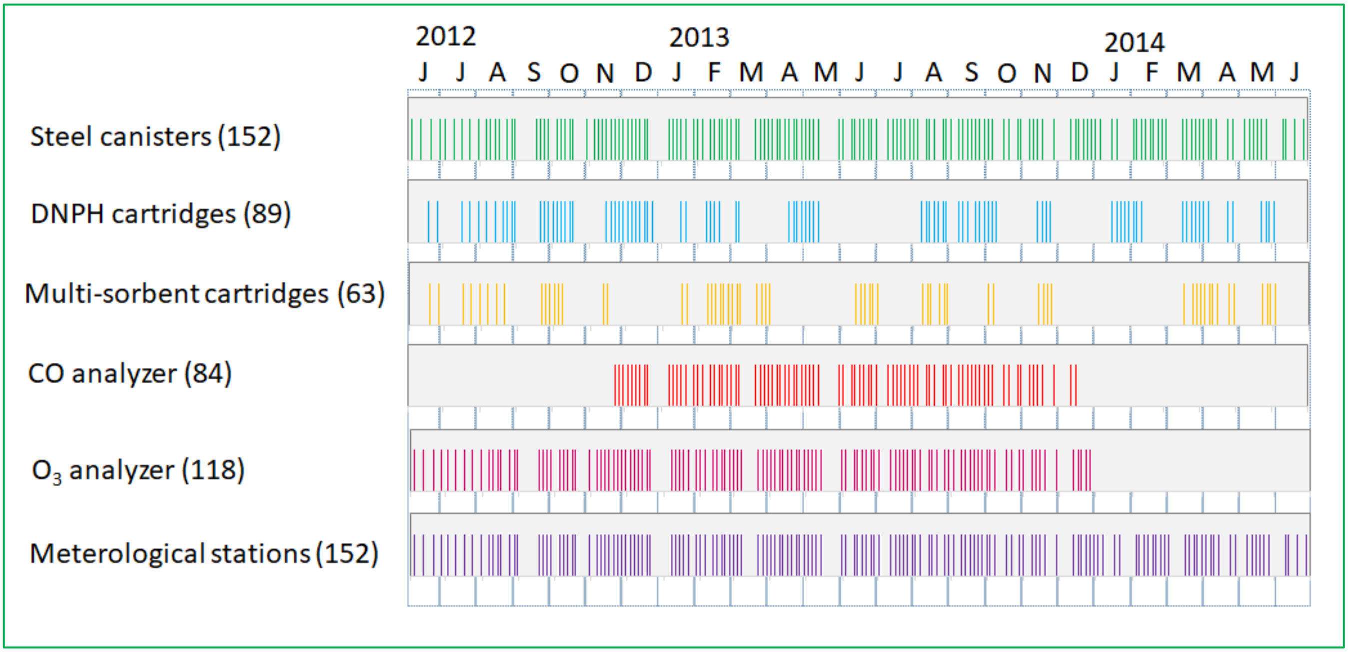


Figure S1: Data collection status indicating when VOC samples were carried out over the two-year period and when concurrent ancillary measurements were realized. The numbers indicated within parentheses correspond to the total number of data observations.”

This figure is indicated in the first paragraph of the revised Sect. 2.2.1 (“VOC measurements”; Page 5 lines 9-13):

“During a 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 housing the analysers. Table 1 describes VOC measurements set up throughout the observation period and Fig. S1 specifies their collection periods."

The same collection days were considered for steel canisters and cartridges (i.e. DNPH and multi-sorbent ones).

4/Sect. 2.2.3, Page 7

Section 2.2.3 ("Additional high frequency VOC measurements performed at Ersa") and 3.4.4: the information provided in this section is already given in Section S3 ("comparison of VOC measurements with other ones performed at Ersa"). I suggest removing this section from the main text and to merge it with S3.

As proposed by referees #1 and #2 (comment 48), we removed the sections 2.2.3 ("Additional high frequency VOC measurements performed at Ersa") and 3.4.4 ("Comparisons with other VOC measurements performed at Ersa") and merged all these results in the revised Sect. S4 ("Comparison of VOC measurements with other ones performed at Ersa"). In the revised manuscript, the Sect. S4 is now introduced in Sect. 3.4. ("VOC variability"). Correction applied in the revised manuscript in Sect. 3.4 (Page 11 lines 13-16):

"In addition, the comparison between the VOC monitoring measurements investigated in this study with concurrent campaign measurements performed during the summers 2012-2014 is investigated in Sect. S4 of the Supplement, in order to examine the representativeness of the 2-yr observation period with regard to summer concentration levels."

5/Sect. 2.3, Page 8, lines 4-11

Page 8, lines 4-11 are duplicates of lines 22-29 from the Section S1 ("Identification and contribution of major sources of VOCs by EPA PMF 5.0 approach").

The authors decided to merge the information concerning inputs' selection and preparation, and the selection and the optimization of the PMF solution in the revised Sect. S2 ("Identification and contribution of major sources of NMHCs by EPA PMF 5.0 approach"). As a result, the Sect. 2.3 ("Identification and contribution of major sources of VOCs") in the revised manuscript has been shortened. Correction applied in the revised manuscript in Sect. 2.3 (Page 7 lines 2-9):

"In order to characterize NMHC concentrations measured at Ersa, 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 a multilinear engine ME-2 (Paatero, 1999), and followed the guidance on the use of PMF (Norris et al., 2014). Using NMHC inputs composed of 152 atmospheric data points of 14 variables (13 single primary HCNMs and another one resulting of 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."

The revised Sect. S2 is presented in the response to referee #1 comment 7.

6/Sect 2.3, Page 8, lines 4-5

It appears that the biweekly samples were collected between 09h00-13h00 UTC for 7 months and between 12h00-16h00 UTC for 15 months. The authors should comment the sampling strategy and tell whether this sampling time shift could impact the PMF analysis and the interannual variations, especially for species with strong diurnal variations such as biogenic VOCs.

The different collection times of the biweekly samples are mainly explained by logistical reasons. The Ersa observation site was created in June 2012 on a windmill farm and involved different measurements carried out by several laboratories (such as IMT Lille-Douai, LSCE, CNRM and Qualitair Corse). Considering the remote location of the study site, laboratories involved in the ChArMEx enhanced observation period at Ersa decided to organize a common routine to manage all instruments. Each instrumental procedure was specified and an intervention was scheduled every two weeks with a turnover of the participants depending on their availability.

To assess the possible effect of this sampling time shift on the PMF analysis, we investigated correlations between reconstructed and observed VOC concentrations in function of the two periods. The results were incorporated in the revised Sect. S2 ("Identification and contribution of major sources of NMHCs by EPA PMF 5.0 approach", the whole revised Sect. S2 is presented in response to referee #1 comment 7):

"S2.4 Optimization of the selected PMF solution
[...]

Moreover, since sampling time of NMHC measurements from canister shifted several times during the two studied years (Sect. 2.2.1 and Table 1), correlations between reconstructed and observed NMHC concentrations as a function of sampling periods were examined (Table S6). Slightly different correlation results were observed for observations resulting from samples collected from 12:00-16:00 UTC (from early June 2012 to late October 2012 and from early January 2013 to late October 2013) compared to those from 09:00-13:00 UTC (from early November 2012 to late December 2012 and from early November 2013 to late June 2014). The PMF model slightly overestimated TVOC concentrations resulting from samples collected from 09:00-13:00 and slightly underestimated those collected from 12:00-16:00, mostly due to the reconstruction of ethane and propane concentrations in both cases. Concerning more reactive NMHCs, ethylene, i-butane, isoprene, toluene and EX concentrations are better reconstructed for samples collected from 12:00-16:00 while propene, i-pentane, n-pentane and n-hexane concentrations are better reconstructed for those from 09:00-13:00. The most impacted species by the sampling time shift was n-pentane, since the PMF model did not identify the sources influencing the high concentrations of n-pentane observed over short periods (see Fig S9) and mostly noticed with samples from 12:00-16:00. More generally, the influence of the sampling time shift on PMF results also depends on the frequency and the amplitude of NMHC concentration variations over short periods for the two cases.

Table S6: Evaluation of reconstructed NMHC concentrations by the PMF model as a function of the sampling time shift.

	All period			Samples collected from 09:00-13:00 UTC			Samples collected from 12:00-16:00 UTC		
	slope	intercept	r^2	slope	intercept	r^2	slope	intercept	r^2
Ethane	0.997	0.006	0.999	0.986	0.029	0.996	1.002	0.001	0.999
Ethylene	0.727	0.064	0.779	0.593	0.111	0.673	0.796	0.044	0.827
Propane	1.000	-0.011	0.968	0.929	0.052	0.949	1.046	-0.035	0.977
Propene	0.534	0.024	0.438	0.632	0.018	0.489	0.497	0.026	0.418
i-Butane	0.832	0.029	0.897	0.761	0.056	0.869	0.893	0.015	0.904
n-Butane	0.967	0.004	0.963	0.954	0.010	0.957	0.975	0.002	0.961
Acetylene	0.952	0.008	0.975	0.991	0.003	0.991	0.941	0.007	0.972
i-Pentane	0.686	0.053	0.644	0.783	0.054	0.765	0.623	0.052	0.600
n-Pentane	0.421	0.081	0.332	0.852	0.032	0.788	0.295	0.085	0.238

Isoprene	0.956	0.005	0.996	0.872	0.005	0.996	0.971	0.006	0.998
n-Hexane	0.510	0.032	0.519	0.668	0.026	0.738	0.419	0.035	0.410
Benzene	0.889	0.022	0.895	0.918	0.027	0.849	0.873	0.018	0.911
Toluene	0.582	0.092	0.599	0.526	0.105	0.501	0.626	0.083	0.669
EX	0.527	0.103	0.515	0.452	0.112	0.431	0.582	0.095	0.578
TVOC	1.004	-0.186	0.992	0.988	-0.083	0.987	1.009	-0.213	0.993

”

Given these results, average concentrations are moderated in the revised Sect. 3.3 (“VOC mixing ratios”) by clarifying them for the two periods in Table S1 of the revised Supplement:

“Table S1: Average concentrations ± standard deviations (µg m^{-3}) of selected VOCs measured at Ersa from June 2012 to June 2014 as a function of the measurement sampling times (see Table 1).

	Species	Samples collected from 09:00-13:00	Samples collected from 12:00-16:00
BVOCs	**Isoprene**	0.08 ± 0.21	0.21 ± 0.35
	α-Pinene	0.13 ± 0.11	0.49 ± 0.71
	Camphene	0.01 ± 0.03	0.03 ± 0.07
	α-Terpinene	0.02 ± 0.03	0.09 ± 0.18
	Limonene	0.08 ± 0.17	0.24 ± 0.34
Anthropogenic NMHCs	**Ethane**	2.43 ± 0.70	1.57 ± 0.80
	Propane	1.28 ± 0.62	0.81 ± 0.62
	i-Butane	0.36 ± 0.25	0.19 ± 0.16
	n-Butane	0.51 ± 0.29	0.31 ± 0.25
	i-Pentane	0.32 ± 0.26	0.26 ± 0.22
	n-Pentane	0.27 ± 0.28	0.23 ± 0.21
	n-Hexane	0.09 ± 0.06	0.08 ± 0.05
	Ethylene	0.38 ± 0.20	0.30 ± 0.18
	Propene	0.07 ± 0.04	0.07 ± 0.04
	Acetylene	0.31 ± 0.20	0.25 ± 0.27
	Benzene	0.35 ± 0.16	0.30 ± 0.22
	Toluene	0.37 ± 0.26	0.30 ± 0.24
	Ethylbenzene	0.06 ± 0.07	0.05 ± 0.07
	m,p-Xylenes	0.14 ± 0.15	0.15 ± 0.14
	o-Xylene	0.07 ± 0.09	0.09 ± 0.09
OVOCs	**Formaldehyde**	0.96 ± 0.48	1.82 ± 1.44
	Acetaldehyde	0.68 ± 0.17	1.11 ± 0.44
	i,n-Butanals	0.13 ± 0.07	0.34 ± 0.69
	n-Hexanal	0.15 ± 0.10	0.26 ± 0.32
	Benzaldehyde	0.15 ± 0.12	0.15 ± 0.12
	n-Octanal	0..07 ± 0.05	0.13 ± 0.24
	n-Nonanal	0.49 ± 0.43	0.18 ± 0.15
	n-Decanal	0.43 ± 0.34	0.14 ± 0.13
	n-Undecanal	0.09 ± 0.06	0.06 ± 0.06
	Glyoxal	0.07 ± 0.04	0.07 ± 0.05
	Methylglyoxal	0.07 ± 0.04	0.21 ± 0.16
	Acetone	3.32 ± 1.77	4.84 ± 2.95
	MEK	0.34 ± 0.11	0.37 ± 0.16

"

Factor contributions are also moderated in the revised Sect. 3.5 ("Major NMHC sources") by clarifying them for the two periods in Table 5 of the revised Supplement:

"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

"

Concerning interannual BVOC variations, some precautions were taken for BVOC results in Sect. 3.4.1 ("Biogenic VOCs"; Page 12 lines 11-14) of the revised manuscript:

"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 be considered cautiously given variable day-to-day and strong diurnal BVOC variations which were observed during the summer 2013 observation period (Kalogridis, 2014)."

Results were also moderated in Sect. 3.5.1 ("Local biogenic source (factor 1)"; Page 15, lines 5-11):

"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 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 the contributions of additional primary BVOCs (the sum of monoterpenes) and some OVOCs (carboxylic acids, methanol and acetone) and the clear diurnal variations of the local primary biogenic source."

Reference

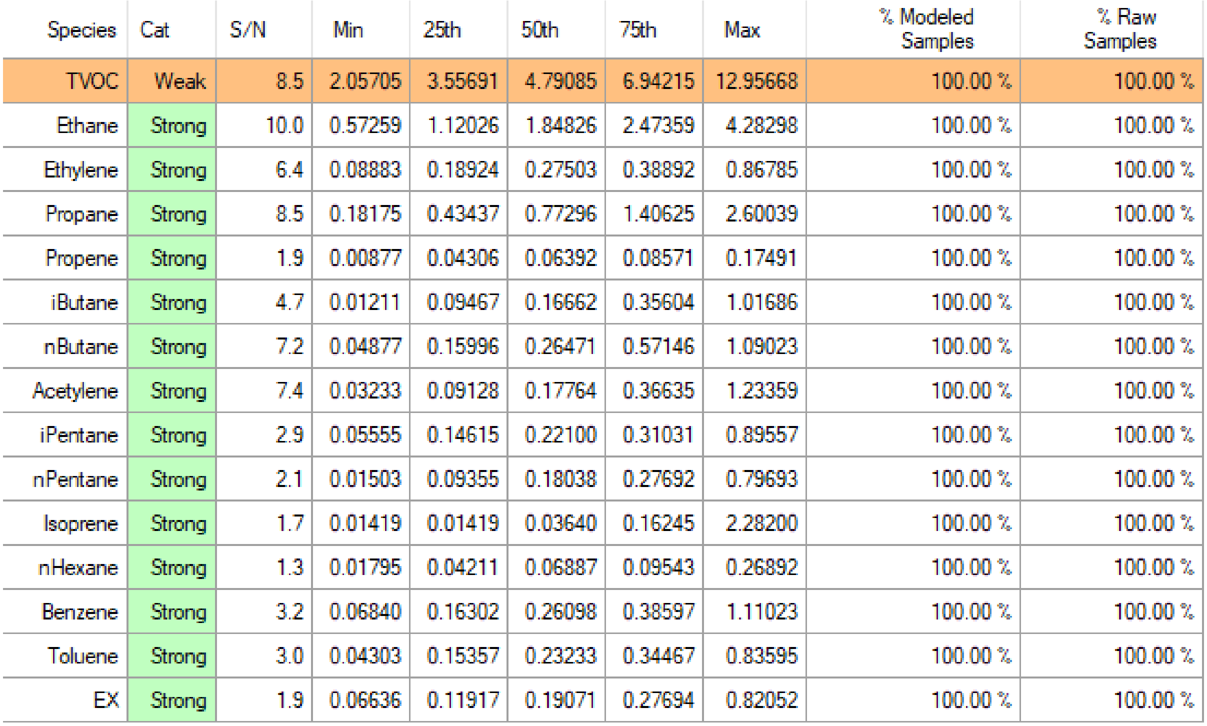
Kalogridis, A.: Caractérisation des composés organiques volatils en région méditerranéenne, Université Paris Sud - Paris XI. [online] Available from: https://tel.archives-ouvertes.fr/tel-01165005, 2014.

7/Sect. 2.3, Page 8, lines 16-20

It is said that the PMF model results reconstructs on average 99% of the total concentration of the 14 selected species, but in the meantime 5 out of the 14 selected are not properly captured by the PMF solution. Also, ethane and propane account for 50% of the VOC mass. In these given circumstances, is the percentage of total reconstructed mass relevant to assess the quality of the PMF solution? It would be helpful to include more information on the PMF preprocessing, and on the diagnostic plots (Q/Q(exp) values vs number of factors, scatter plots of the measured vs. reconstructed concentrations, scaled residuals, if and why outliers were removed from the time series, etc..).

Firstly, the high proportion of long-lived VOCs usually characterizes remote background sites such as Ersa (e.g., Sauvage et al., 2009 and Leuchner et al., 2015) since more reactive species are more prone to react before reaching the receptor sites. Moreover, the reconstruction of measured concentrations by the PMF depends mainly on VOC concentration levels, their variability as well as their uncertainties (related to their signal-to-noise ratio, Debevec et al., 2017 – see Table A below). Lower relative uncertainties are globally related to long-lived VOCs in this study compared to those of more reactive VOCs (see Table 3; see response to referee #1 comment 15). As a consequence, the PMF model will favour in the study the reconstruction of the VOCs with the longest lifetime, the highest concentration levels and the highest S/N ratios (i.e. ethane, propane, i-butane, n-butane and acetylene – see Table A) to maximize the reconstruction of the total variable (TVOC in this study). Given these circumstances, the percentage of the total reconstructed mass is relevant to assess the quality of the PMF solution but is not sufficient alone. As a result, the methodology to identify the optimal factor of the PMF solution for this study is developed in the revised version of Sect. S2 (“Identification and contribution of major sources of NMHCs by PMF 5.0 approach”). Furthermore, note that no outlier was removed from the dataset in order to maximize the number of input data. Sharp increases in VOC concentrations were qualified by higher uncertainties than other input data. The PMF model was hence less sensitive to them, as it takes into account the quality of input data by means of their possible weighing as a function of their uncertainties. Difference between Q_{robust} and Q_{true} of the selected PMF solution in this study was only of 18% (Table S5), indicating some but not heavy impact of outliers on the Q-value (Norris et al, 2014).

Table A: capture of our input data statistics obtained with the EPA PMF 5.0 tool.



Species	Cat	S/N	Min	25th	50th	75th	Max	% Modeled Samples	% Raw Samples
TVOC	Weak	8.5	2.05705	3.55691	4.79085	6.94215	12.95668	100.00 %	100.00 %
Ethane	Strong	10.0	0.57259	1.12026	1.84826	2.47359	4.28298	100.00 %	100.00 %
Ethylene	Strong	6.4	0.08883	0.18924	0.27503	0.38892	0.86785	100.00 %	100.00 %
Propane	Strong	8.5	0.18175	0.43437	0.77296	1.40625	2.60039	100.00 %	100.00 %
Propene	Strong	1.9	0.00877	0.04306	0.06392	0.08571	0.17491	100.00 %	100.00 %
iButane	Strong	4.7	0.01211	0.09467	0.16662	0.35604	1.01686	100.00 %	100.00 %
nButane	Strong	7.2	0.04877	0.15996	0.26471	0.57146	1.09023	100.00 %	100.00 %
Acetylene	Strong	7.4	0.03233	0.09128	0.17764	0.36635	1.23359	100.00 %	100.00 %
iPentane	Strong	2.9	0.05555	0.14615	0.22100	0.31031	0.89557	100.00 %	100.00 %
nPentane	Strong	2.1	0.01503	0.09355	0.18038	0.27692	0.79693	100.00 %	100.00 %
Isoprene	Strong	1.7	0.01419	0.01419	0.03640	0.16245	2.28200	100.00 %	100.00 %
nHexane	Strong	1.3	0.01795	0.04211	0.06887	0.09543	0.26892	100.00 %	100.00 %
Benzene	Strong	3.2	0.06840	0.16302	0.26098	0.38597	1.11023	100.00 %	100.00 %
Toluene	Strong	3.0	0.04303	0.15357	0.23233	0.34467	0.83595	100.00 %	100.00 %
EX	Strong	1.9	0.06636	0.11917	0.19071	0.27694	0.82052	100.00 %	100.00 %

Correction applied in the revised supplement materials in Sect. S2:

“~~To characterize VOC concentrations measured at Ersa, we apportioned VOC sources in this study using the positive matrix factorization approach (PMF; Paatero, 1997; Paatero and Tapper, 1994) applied to our VOC concentration dataset. We used the PMF version 5.0, an enhanced tool developed by the Environmental Protection Agency (EPA) and including a multilinear engine ME-2 (Paatero, 1999), and followed the guidance on the use of PMF (Norris et al., 2014).~~

S2.1 PMF approach

PMF is a tool elaborated for a multivariate factor analysis and used for the identification and the characterization of the “p” independent sources of "n” species measured “m” times at a given site. Note that the PMF mathematical theory is detailed elsewhere (Paatero, 1997; Paatero and Tapper, 1994). Concisely, the PMF method is based on the decomposition of a matrix of chemically speciated sample data (of dimension n x m) into two matrices of factor profiles (n x p) and factor contributions (p x m), interpreting each factor as a different source type. Species profiles of each source identified represent the repartition of each species into each given factor, and the amount of mass contributed by each factor to each successive individual sample represents the evolution in time of the contribution from each factor to the various species. The principle can be condensed as:

$$x_{ij} = \sum_{k=1}^{p} g_{jk} \times f_{ki} + e_{ij} = c_{ij} + e_{ij} \,, \qquad (1)$$

where x_{ij} is the ith species measured concentration (in µg m^{-3} here) in the jth sample, f_{ki} the ith mass fraction from kth source, g_{jk} the kth source contribution of the jth sample, e_{ij} the residual resulting of the decomposition and c_{ij} the species reconstructed concentration. The Eq. (1) can be solved iteratively by minimizing the residual sum of squares Q following Eq. (2):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{s_{ij}}\right)^2 \,, \qquad (2)$$

with s_{ij}, the extended uncertainty (in µg m^{-3}) related to the measured concentration of the ith species in the jth sample. A user-provided uncertainty following the procedure presented in Polissar et al. (1998) is also required by the PMF tool to weight individual points. Moreover, negative source contributions are not allowed.

S2.2 VOC dataset and data preparation

In order to have sufficient completeness (in terms of observation number), only primary HCNM measurements from bi-weekly ambient air samples collected into steel canisters from 04 June 2012 to 27 June 2014 were retained in this factorial analysis. The NMHC dataset encompassed 152 atmospheric data points having a time resolution of 4 hours. VOC observations resulting from DNPH and multi-sorbent cartridges were not considered in the PMF analysis since they were sampled only 73 and 52 days concurrently to the collection of steel canisters (Fig. S1). Reconstruction of missing data points would significantly affect the dataset quality. Additionally, the restriction of the number of data points to those common to the three datasets (36 data points) would significantly impact the temporal representativeness of the VOC inputs of the study period and hence limit the discussion on interannual and seasonal variations for statistical robustness reasons. Note that no outlier was removed from the dataset.

NMHC inputs were built using the concentrations of the 17 HCNMs selected in this study (see Sect. S1). The final chemical dataset includes 13 single variables and a grouped one. This latter named “EX” grouped the concentrations of C_8 aromatic compounds, in order to maximize its concentration levels.

Moreover, the data preprocessing and quality analysis of the NMHC dataset are presented in the supplement material of Debevec et al. (2017). Since signal-to-noise (S/N) ratios of the 14 variables retained for the factorial analysis are all higher than 1.2, in this study no variable was categorized as “weak”, and hence downweighted (categorize variables in “weak” means to triple their original uncertainties; Norris et al., 2014).

S2.3 Selected PMF Solution

In order to identify the optimal number of factors for the PMF solution selected in this study, the first step consisted in carrying out numerous successive base runs considering an incremented factor number according to the protocol defined by Sauvage et al. (2009). As a result, PMF solutions composed from 2 to 10 factors, considering 100 runs and a random start, were explored.

Firstly, the selection of the solution among PMF solutions of 2 to 10 factors is based on the analysis of diverse exploratory statistical parameters (Table S3 and Fig. S6) which are as follows:

- Variations in Q_{true} and $Q_{\text{theorical}}$ as a function of the factor number of the PMF solution. Q_{true} is provided by the EPA PMF tool (Norris et al., 2014) following the launch of a base model run. $Q_{\text{theorical}}$ is a calculated parameter following the equation (3). Q_{true} and $Q_{theorical}$ tend to decrease when the factor number increases. A PMF user can choose the PMF solution having a lower Q_{true} compared to the associated $Q_{theorical}$.

- Variation in IM and IS (maximum individual standard deviation and maximum individual column mean, respectively) as a function of the factor number of the PMF solution. IM and IS can be defined following equations (4) and (5), respectively. A PMF user can choose the PMF solution corresponding to a significant break in the slope of IM and/or IS (see also the relative differences d(IM) and d(IS) in Table S3) in function of factor number.
- Variations in average determination coefficients between reconstructed concentrations of the total variable (called in this study TVOC, see Norris et al., 2014) and measured ones (R^2(TVOC)). A PMF user can choose the PMF solution of p factors corresponding to a significant increase of R^2(TVOC) compared to the PMF solution of p-1 factors.
- An optimal PMF solution should also present a symmetrical distribution of residual values related to the total variable as well as a large proportion of them ranging between -2 and 2, especially between -0.3 and 0.3.

$$for\ p \in [2, 10], Q_{theorical} = M \times N - p\ \times (M + N), \qquad (3)$$

with M=152 and N=14 in this study (Sect S2.2).

$$IM = \max\left(\frac{1}{M}\sum_{j=1}^{M}\frac{e_{ij}}{s_{ij}}\right),\ among\ i \in [1, N] \qquad (4)$$

$$IS = \max\left(\sqrt{\frac{1}{M-1}\sum_{j=1}^{M}\left[\frac{e_{ij}}{s_{ij}} - \overline{\left(\frac{e_{ij}}{s_{ij}}\right)}\right]^2}\right),\ among\ i \in [1, N] \qquad (5)$$

The visual inspection of statistical indicators was realized following Fig. S6. Significant breaks in slope of variations of IM as a function of the factor number of the PMF solution were noticed for PMF solutions composed from 3 to 5 factors, from 4 to 6 factors and from 7 to 9 factors (Fig. S6c). Moreover, a significant break in slope of variations of IS as a function of the factor number of the PMF solution was only noticed for PMF solutions composed from 5 to 7 factors (Fig. S6d). R^2(TVOC) increases significantly between PMF solutions of 3 and 4 factors and to a lesser extent between PMF solutions from 4 to 7 factors (Fig. S6e). Contrarily, R^2(TVOC) decreases significantly between PMF solutions of 7 and 8 factors. However, Q_{true} is lower than $Q_{theorical}$ from a PMF solution of 8 factors (Fig. S6a). From a PMF solution of 4 factors, the proportion of residual values ranging between -2 and 2 is higher than 90% and from a PMF solution of 5 factors, the proportion of residual values ranging between -0.3 and 0.3 is higher than 40% (Fig. S6b). As a result, we oriented our choice of optimal PMF solution from 4 to 6 factors.

In order to refine this choice, we also examined correlations between reconstructed concentrations and measured ones for individual species of the selected PMF solutions (Figs S7-S9 and Table S4), their distribution of residual values (Fig S10), the physical meaning of their factor profiles (Fig S11), their factor contribution time series (Fig S11) and correlations between their factors. From a PMF solution of 4 factors, the model identified a factor related to a biogenic source (factor 1 depicted in Fig. S11 and related to isoprene concentrations). A better reconstruction of ethane, acetylene and isoprene concentrations was noticed for a PMF solution of 4 factors (Fig S7). We did not observe any correlation between factors composing the 4-factor PMF solution. From a PMF solution of 5 factors, the model distinguished a factor related to the more reactive species (factor 2 profile composed of ethylene, propene, toluene and EX - Fig. S11) from the factor associated with evaporation sources (factor 3 profile composed of propane, i,n-butanes and i,n-pentanes - Fig. S11). These two factors are not correlated (determination coefficient: 0.35). This deconvolution notably improved the reconstruction by the PMF model of concentrations of ethylene, propene, toluene and EX (Figs. S7 and S9 and Table S4) and slightly improved the distribution of residual values for propene and toluene (Fig. S10). Ethane and isoprene concentrations are fully reconstructed with the PMF solution of 5 factors (Fig. S8 and Table S4) and their residual values were more symmetrical and gathered between -1 and 1 (Fig. S10). The additional factor composing the 6-factor PMF solution compared to the 5-factor one results from the split of the factor related to the more reactive species into two factors. The first one (factor 2 – Fig. S11) is mostly composed of ethylene and propene while the second one (factor 3 – Fig. S11) is composed of propene, i,n-pentanes, toluene and EX. These two factors are not correlated (determination coefficient: 0.02 – Fig. S11). This deconvolution notably improved the reconstruction of ethylene concentrations (Fig. S9 and Table S4), slightly improved the reconstruction of i,n-pentanes, toluene and EX concentrations but degraded propene ones. In terms of residual value distribution, the 6-factor PMF solution mostly improved the ethylene one (Fig. S9). However, ethylene, propene, i,n-pentanes, toluene and EX concentrations observed at Ersa in summer 2013 were mainly explained by the same factor according to Michoud et al. (2017), which supported our choice of a 5-factor PMF solution for this study.

Table S3: Exploratory statistical parameters for the identification of the optimal number of factors of the PMF solution.

Factor number	Q theorical	Q robust mod	Q true	IM	IS	Proportion of residuals between [-2 ;2]	Proportion of residuals > abs(0,3)	Determination coefficient PMF results vs Meas. (R^2)	d(IM) = (IM(p) - IM(p-1))/ IM(p-1)	d(IS) = (IS(p) - IS(p-1))/ IS(p-1)
2	1796	6557	7472	0.9249	3.1160	0.7904	0.8008	0.9653	-	-
3	1630	4352	4749	0.8838	2.5538	0.8604	0.7702	0.9746	0.0444	0.1804
4	1464	3057	3169	0.4239	1.9464	0.9037	0.7049	0.9879	0.5204	0.2378
5	1298	2092	2120	0.2659	1.5157	0.9441	0.6109	0.9920	0.3727	0.2213
6	1132	1545	1547	0.2260	1.1361	0.9615	0.5550	0.9939	0.1503	0.2504
7	966	1161	1162	0.2255	1.0810	0.9737	0.5028	0.9952	0.0021	0.0485
8	800	777	777	0.1153	0.9373	0.9864	0.4384	0.9883	0.4885	0.1329
9	634	558	558	0.1133	0.8282	0.9915	0.3435	0.9873	0.0180	0.1164
10	468	380	380	0.0939	0.7596	0.9953	0.2740	0.9836	0.1713	0.0828

Table S4: Evaluation of reconstructed NMHC concentrations of PMF solutions from 4 to 6 factors as a function of measured NMHC concentrations.

	r^2			slope			intercept		
VOC	**4 factors**	**5 factors**	**6 factors**	**4 factors**	**5 factors**	**6 factors**	**4 factors**	**5 factors**	**6 factors**
(0) TVOC	0.988	0.992	0.994	1.003	1.013	1.013	-0.034	-0.072	-0.060
(1) Ethane	0.992	0.998	0.999	0.977	0.994	1.000	0.037	0.009	-0.001
(2) Ethylene	0.666	0.771	0.985	0.618	0.722	0.938	0.086	0.065	0.017
(3) Propane	0.950	0.968	0.969	0.990	1.002	1.007	-0.010	-0.013	-0.016
(4) Propene	0.275	0.454	0.411	0.350	0.534	0.488	0.034	0.024	0.026
(5) i-Butane	0.894	0.909	0.913	0.820	0.833	0.842	0.033	0.030	0.028
(6) n-Butane	0.946	0.969	0.969	0.953	0.969	0.968	0.009	0.005	0.006
(7) Acetylene	0.989	0.993	0.989	0.952	0.971	0.973	0.008	0.006	0.006
(8) i-Pentane	0.657	0.654	0.712	0.692	0.687	0.743	0.053	0.054	0.046
(9) n-Pentane	0.328	0.331	0.378	0.421	0.419	0.470	0.082	0.082	0.077
(10) Isoprene	0.568	0.995	0.995	0.362	0.998	1.009	0.054	-0.0004	-0.002
(11) n-Hexane	0.560	0.537	0.582	0.546	0.546	0.583	0.029	0.029	0.027
(12) Benzene	0.898	0.918	0.908	0.858	0.896	0.867	0.031	0.022	0.029
(13) Toluene	0.539	0.600	0.630	0.467	0.597	0.677	0.113	0.090	0.083
(14) EX	0.342	0.536	0.623	0.332	0.548	0.665	0.134	0.102	0.079

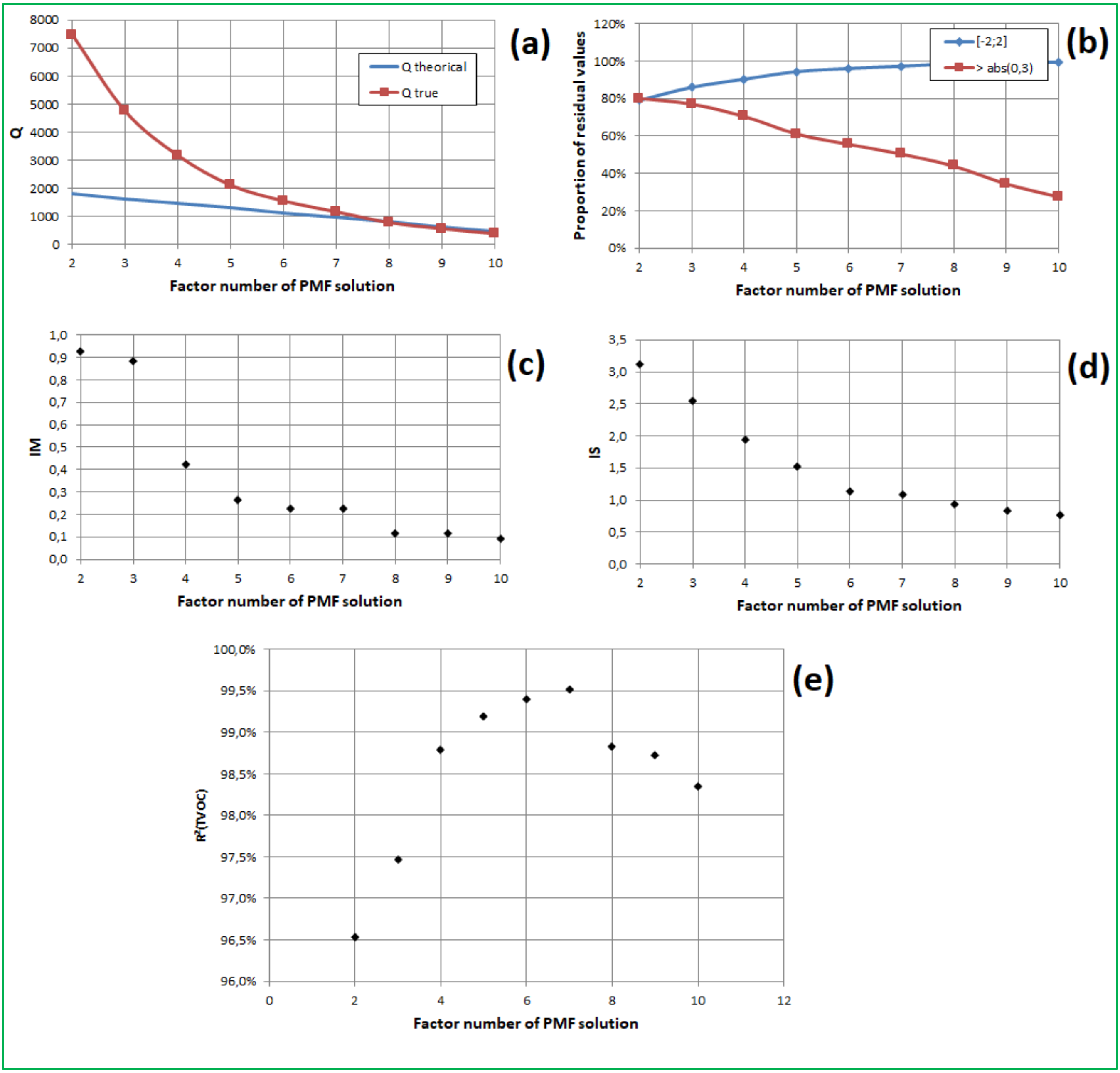


Figure S6: Variations of exploratory statistical parameters as a function of the number of factors of PMF solutions.

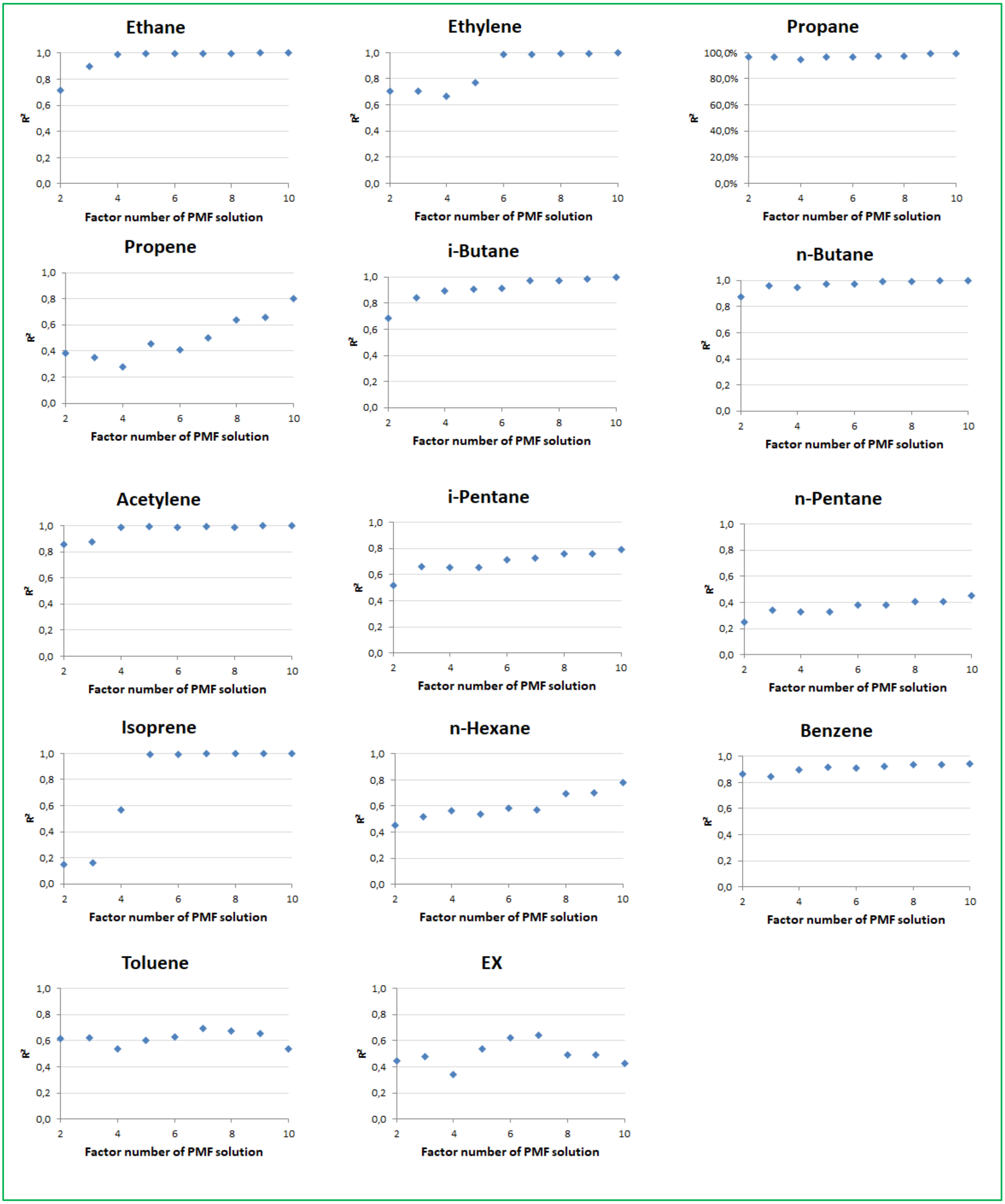
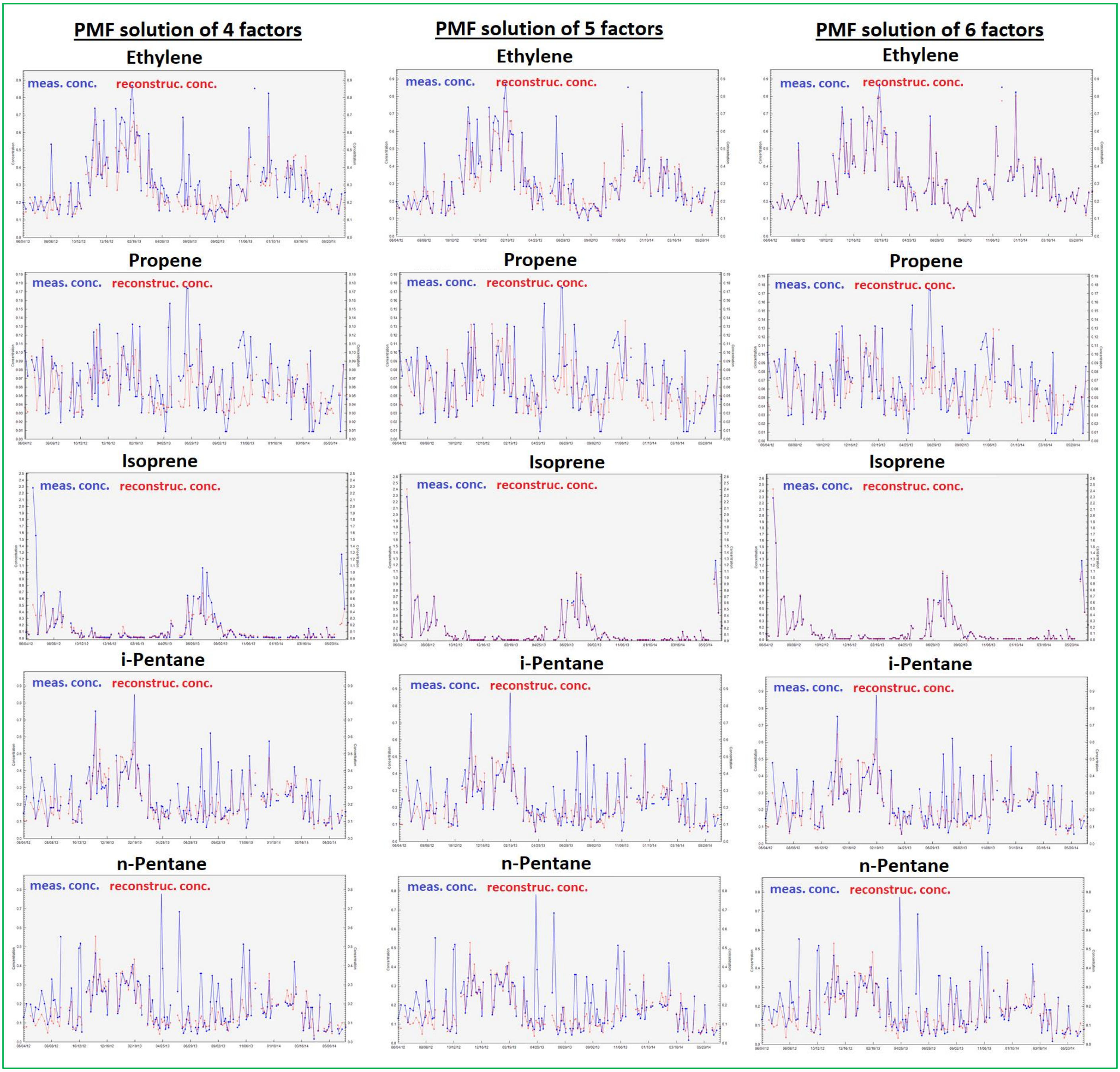


Figure S7: Correlations between reconstructed NMHC concentrations by the PMF model and measured ones as a function of the factor number of PMF solutions.


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
Ethylene
Ethylene
Ethylene
meas. conc.
reconstruc. conc.
Propene
Propene
Propene
Isoprene
Isoprene
Isoprene
i-Pentane
i-Pentane
i-Pentane
n-Pentane
n-Pentane
n-Pentane
Concentration

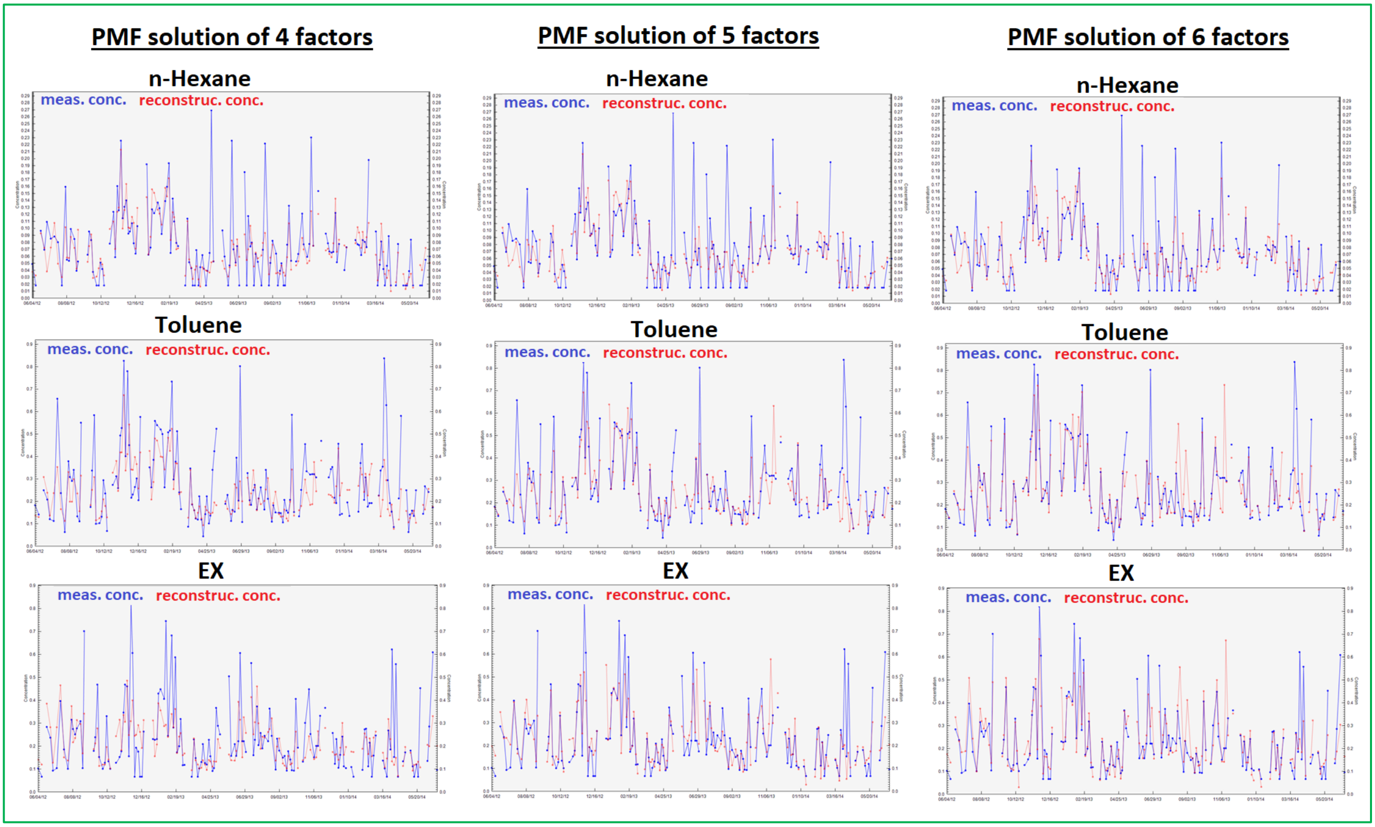
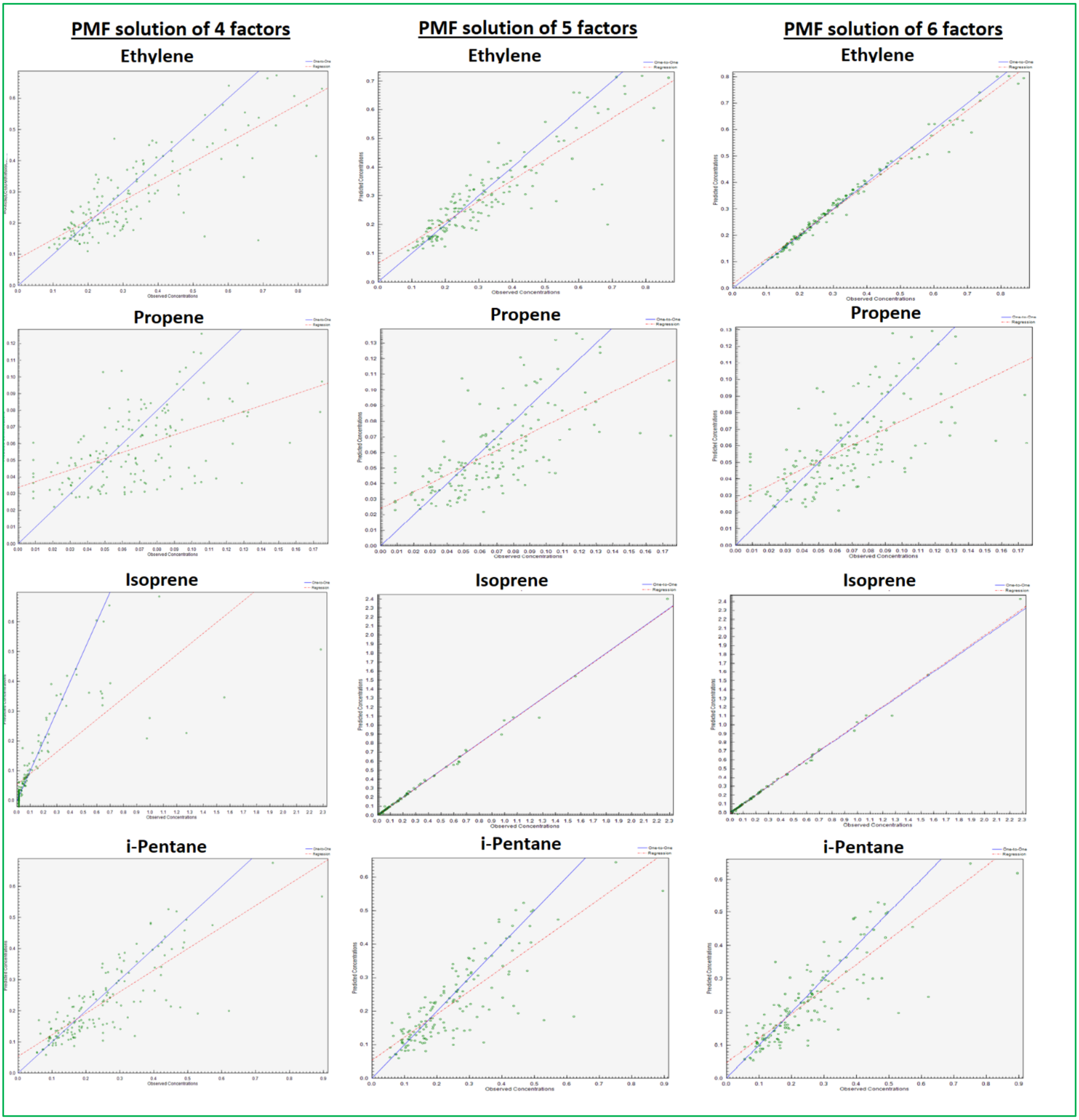
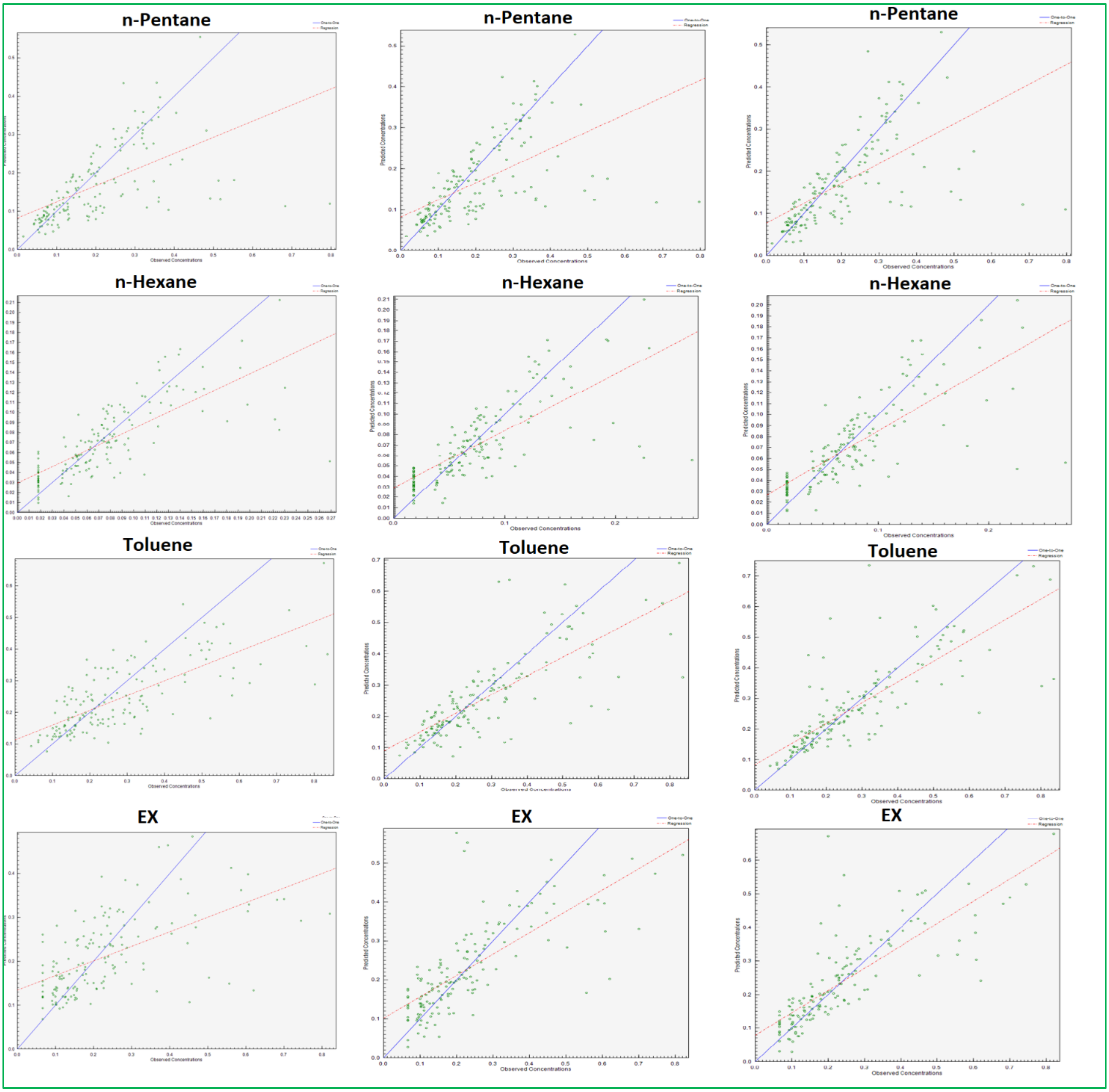


Figure S8: Time series of reconstructed NMHC concentrations for PMF solutions from 4 to 6 factors compared to NMHC measured concentrations. Note that only results of NMHCs not well reconstructed by the PMF model ($r^2 < 0.85$, see Table S4) are presented.


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
Ethylene
Propene
Isoprene
i-Pentane
One-to-One
Regression
Observed Concentrations
Predicted Concentrations



n-Pentane

n-Pentane

n-Pentane

n-Hexane

n-Hexane

n-Hexane

Toluene

Toluene

Toluene

EX

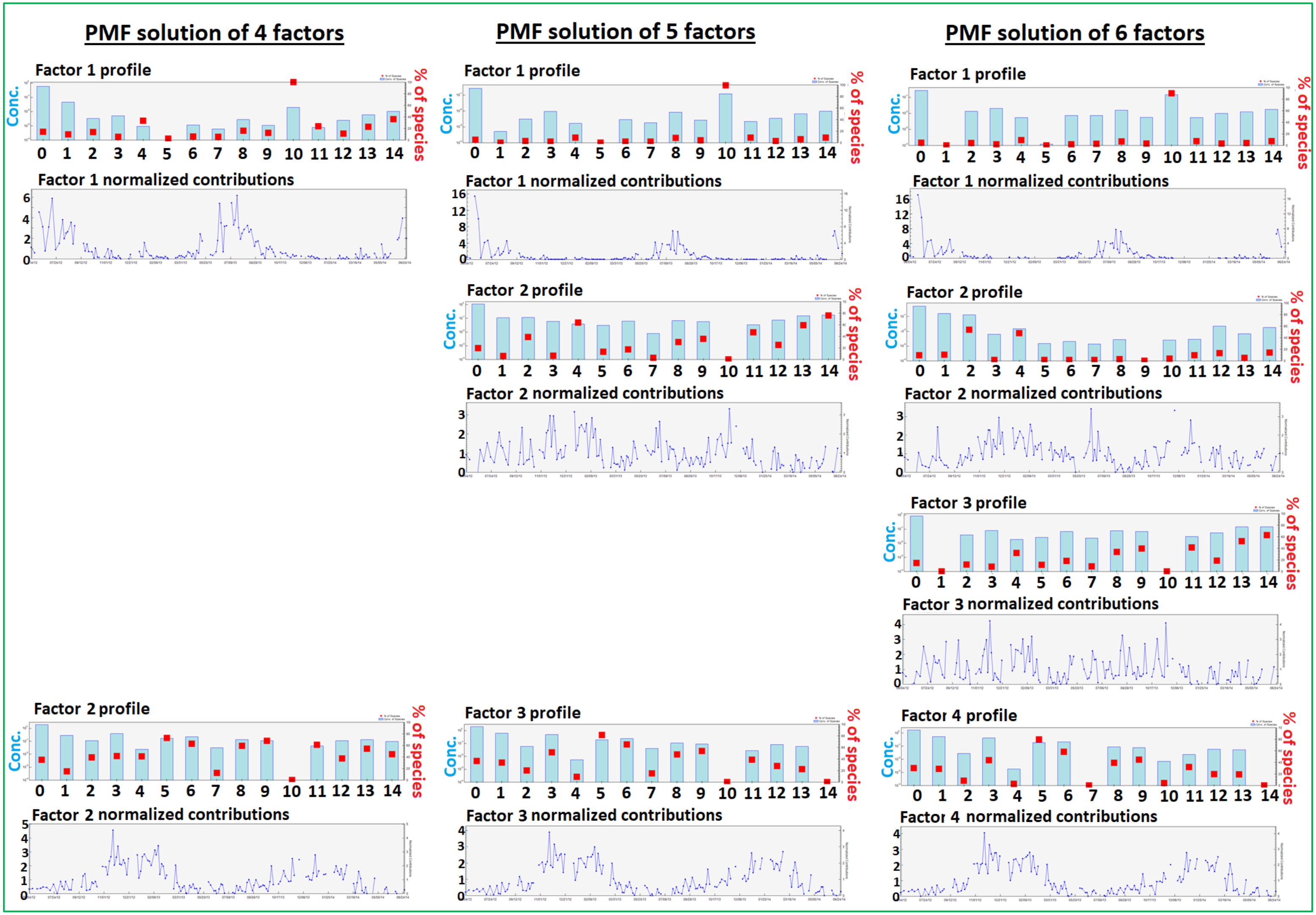
EX

EX

Figure S9: Scatter plots of reconstructed NMHC concentrations for PMF solutions from 4 to 6 factors and NMHC measured concentrations. Note that only results of NMHCs not well reconstructed by the PMF model ($r^2 < 0.85$, see Table S4) are presented.


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
Ethane
-3 -2 -1 0 1 2 3
scaled residuals
Ethylene
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7
-3 -2 -1 0 1 2 3 4 5 6 7
scaled residuals
Propane
-4 -3 -2 -1 0 1 2 3
scaled residuals
Propene
-4 -3 -2 -1 0 1 2 3 4
scaled residuals
i-Butane
-3 -2 -1 0 1 2 3 4 5 6
scaled residuals
n-Butane
-4 -3 -2 -1 0 1 2 3 4 5
scaled residuals
Acetylene
-3 -2 -1 0 1 2 3
scaled residuals

Figure S10: Distributions of scaled residuals as a function of NMHC for PMF solutions composed from 4 to 6 factors.


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
Factor 1 profile
Factor 1 normalized contributions
Factor 2 profile
Factor 2 normalized contributions
Factor 3 profile
Factor 3 normalized contributions
Factor 4 profile
Factor 4 normalized contributions
Conc.
% of species
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

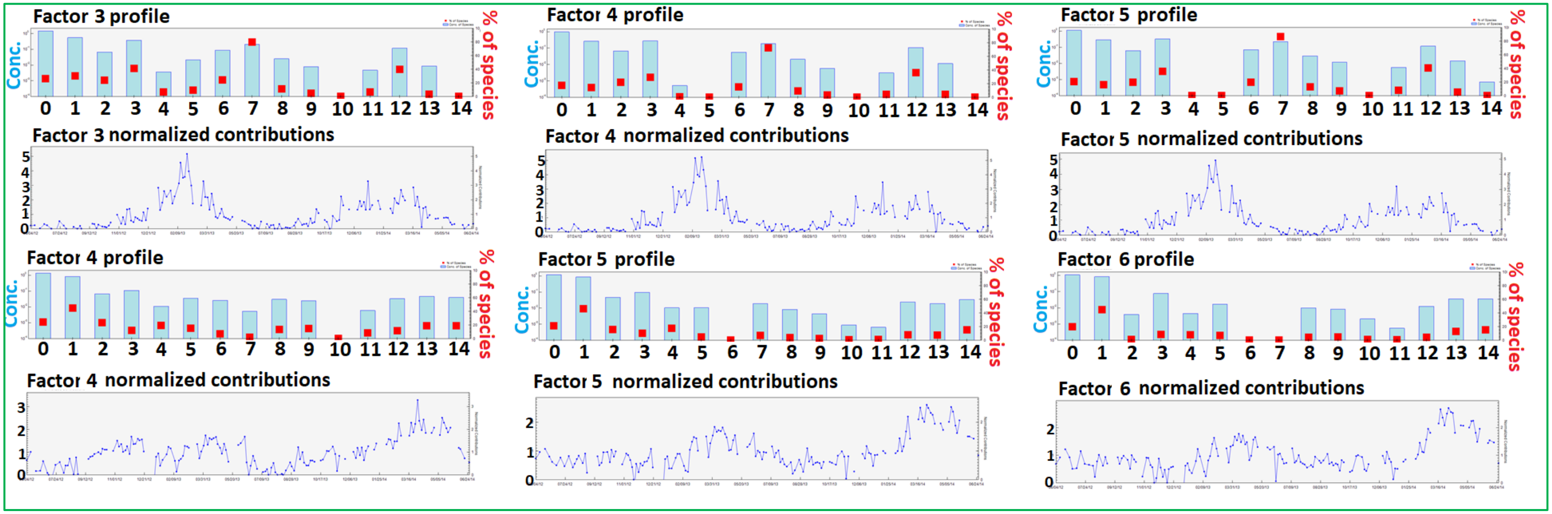

Factor 3 profile
Factor 3 normalized contributions
Factor 4 profile
Factor 4 normalized contributions
Factor 5 profile
Factor 5 normalized contributions
Factor 4 profile
Factor 4 normalized contributions
Factor 5 profile
Factor 5 normalized contributions
Factor 6 profile
Factor 6 normalized contributions

Figure S11: Factor profiles and normalized contribution time series of PMF solutions from 4 to 6 factors. Note that NMHCs 0-14 are listed in Table S4.

S2.4 Optimization of the selected PMF solution

Generally, the non-negativity constraint alone is considered not enough to obtain a unique solution. To reduce the number of solutions, one possible approach is to rotate a given solution and assess the obtained results with the initial solution. Consequently, the optimization of the selected 5-factor PMF solution relies on the exploration of the rotational freedom of the selected PMF solution by acting on the F_{peak} parameter (Paatero et al., 2005; Paatero et al., 2002) following recommendations of Norris et al. (2014) so as to reach an optimized final solution. As a result, a F_{peak} parameter fixed at 0.8 was applied to the selected PMF solution which allowed a finer decomposition of the NMHC dataset following an acceptable change of the Q-value (Norris et al., 2014).

Quality indicators provided by the EPA PMF application have been indicated in Table S5. The PMF model results reconstruct on average 99% of the total concentration of the 14 selected compounds of this study. Individually, almost all chemical species also showed both good determination coefficients and slopes (close to 1 – Table S4) between reconstructed and measured concentrations, apart from propene, n-pentane, n-hexane and EX (see Fig. S9). The PMF model reconstructs well the variations of these species over long periods (Fig. S8) but not over short-periods, explaining their lower determination coefficients and slopes farther from 1 (Table S4). Therefore, PMF model limitations to explain these species should be kept in mind when examining PMF results.

Table S5: Input information and mathematical diagnostic for the results of PMF analysis.

Input information		
Samples	N	152
Species	M	14
Factors	P	5
Runs		100
Nb. Species indicated as weak		0
F_{peak}		0.8
Model quality		
Q robust	Q(r)	2589.7
Q true	Q(t)	2119.9
Maximum individual standard deviation	IM	0.27
Maximum individual column mean	IS	1.52
Mean ratio (modelled vs. measured)	Slope(TVOC)	1.01
$TVOC_{modelled}$ vs. $TVOC_{measured}$	R^2(TVOC)	0.99
Nb. of species with $R^2 > 0.6$		10
Nb. of species with $1.1 > slope > 0.6$		9

The evaluation of rotational ambiguity and random errors in a given PMF solution can be realized with DISP (displacement) and BS (bootstrap) error estimation methods (Brown et al., 2015; Norris et al., 2014; Paatero et al., 2014). As no factor swap occurred in the DISP analysis results, the 5-factor PMF solution is considered adequately robust to be interpreted. Then, bootstrapping was realized by performing 100 runs, and considering a random seed, a block size of 18 samples and a minimum Pearson correlation coefficient of 0.6. Each modeled factor of the selected PMF solution was well mapped over at least 95% of realized runs, assuring their reproducibility.

Moreover, since sampling time of NMHC measurements from canister shifted several times during the two studied years (Table 1), correlations between reconstructed and observed NMHC concentrations as a function of sampling periods are investigated (Table S6). Slightly different correlation results were observed for observations resulting from samples collected from 12:00-16:00 UTC (from early June 2012 to late October 2012 and from early January 2013 to late October 2013) compared to those from 09:00-13:00 UTC (from early November 2012 to late December 2012 and from early November 2013 to late June 2014). The PMF model slightly overestimated TVOC concentrations resulting from samples collected from 09:00-13:00 and slightly underestimated those collected from 12:00-16:00, mostly due to reconstruction of ethane and propane concentrations in both cases. Concerning more reactive NMHCs, ethylene, i-butane, isoprene, toluene and EX concentrations are better reconstructed for samples collected from 12:00-16:00 while propene, i-pentane, n-pentane and n-hexane concentrations are better reconstructed for those from 09:00-13:00. The most impacted species by the sampling time shift was n-pentane, since the PMF model did not identify the sources influencing the high concentrations of n-pentane observed over short periods (see Fig S9) and this was mostly noticeable with the 12:00-16:00 sample set. More generally, the influence of the sampling time shift on PMF results also depends on the frequency and the amplitude of NMHC concentration variations over short periods for the two sample sets.

Table S6: Evaluation of reconstructed VOC concentrations by the PMF model as a function of the sampling time shift.

	All period			Samples collected from 09:00-13:00 UTC			Samples collected from 12:00-16:00 UTC		
	slope	intercept	r^2	slope	intercept	r^2	slope	intercept	r^2
Ethane	0.997	0.006	0.999	0.986	0.029	0.996	1.002	0.001	0.999
Ethylene	0.727	0.064	0.779	0.593	0.111	0.673	0.796	0.044	0.827
Propane	1.000	-0.011	0.968	0.929	0.052	0.949	1.046	-0.035	0.977
Propene	0.534	0.024	0.438	0.632	0.018	0.489	0.497	0.026	0.418
i-Butane	0.832	0.029	0.897	0.761	0.056	0.869	0.893	0.015	0.904
n-Butane	0.967	0.004	0.963	0.954	0.010	0.957	0.975	0.002	0.961
Acetylene	0.952	0.008	0.975	0.991	0.003	0.991	0.941	0.007	0.972
i-Pentane	0.686	0.053	0.644	0.783	0.054	0.765	0.623	0.052	0.600
n-Pentane	0.421	0.081	0.332	0.852	0.032	0.788	0.295	0.085	0.238
Isoprene	0.956	0.005	0.996	0.872	0.005	0.996	0.971	0.006	0.998
n-Hexane	0.510	0.032	0.519	0.668	0.026	0.738	0.419	0.035	0.410
Benzene	0.889	0.022	0.895	0.918	0.027	0.849	0.873	0.018	0.911
Toluene	0.582	0.092	0.599	0.526	0.105	0.501	0.626	0.083	0.669
EX	0.527	0.103	0.515	0.452	0.112	0.431	0.582	0.095	0.578
TVOC	1.004	-0.186	0.992	0.988	-0.083	0.987	1.009	-0.213	0.993

”

References

Brown, S. G., Eberly, S., Paatero, P., and Norris, G. A.: Methods for estimating uncertainty in PMF solutions: Examples with ambient air, and water quality data, and guidance on reporting PMF results, Sci. Total Environ., 518–519, 626–635, doi:10.1016/j.scitotenv.2015.01.022, 2015.

Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., and Locoge, N.: Origin, and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus), Atmos. Chem. Phys., 17, 11355–11388, doi:10.5194/acp-17-11355-2017, 2017.

Leuchner, M., Gubo, S., Schunk, C., Wastl, C., Kirchner, M., Menzel, A., and Plass-Dülmer, C.: Can positive matrix factorization help to understand patterns of organic trace gases at the continental Global Atmosphere Watch site Hohenpeissenberg?, Atmos. Chem. Phys., 15, 1221–1236, doi:10.5194/acp-15-1221-2015, 2015.

Norris, G., Duvall, R., Brown, S., and Bai, S.: EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals, and User Guide Prepared for the US Environmental Protection Agency Office of Research, and Development, Washington, DC. [online] Available from: https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf, 2014.

Paatero, P.: Least squares formulation of robust non-negative factor analysis, Chemom. Intell. Lab. Syst., 37, 23–35, doi:10.1016/S0169-7439(96)00044-5, 1997.

Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111–126, doi:10.1002/env.3170050203, 1994.

Paatero, P., Eberly, S., Brown, S. G., and Norris, G. A.: Methods for estimating uncertainty in factor analytic solutions, Atmos. Meas. Tech., 7, 781–797, doi:10.5194/amt-7-781-2014, 2014.

Paatero, P., Hopke, P. K., Begum, B. A., and Biswas, S. K.: A graphical diagnostic method for assessing the rotation in factor analytical models of atmospheric pollution, Atmos. Environ., 39, 193–201, doi:10.1016/j.atmosenv.2004.08.018, 2005.

Paatero, P., Hopke, P. K., Song, X. H., and Ramadan, Z.: Understanding, and controlling rotations in factor analytic models, Chemom. Intell. Lab. Syst., 60, 253–264, doi:10.1016/S0169-7439(01)00200-3, 2002.

Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., and Sisler, J. F.: Atmospheric aerosol over

Alaska 2. Elemental composition, and sources, J. Geophys. Res. Atmos., 103, 19045–19057, doi:10.1029/98JD01212, 1998.

Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P., and Galloo, J. C.: Long term measurement, and source apportionment of non-methane hydrocarbons in three French rural areas, Atmos. Environ., 43, 2430–2441, doi:10.1016/j.atmosenv.2009.02.001, 2009.

8/Sect. 2.3, Page 8, lines 17-19

I understand that species not properly reconstructed by the PMF model should be categorized as "weak" in the model. This is not the case here, as seen in Table 2, where none of the 14 species are indicated as "weak". Could the author justify this choice?

Firstly, the declaration of a PMF input variable as weak depends on its S/N ratio and not on how the PMF model reconstructs its concentrations. According to Norris et al. (2014), in the EPA PMF 5.0 model, S/N ratios are determined from the equation:

$$\left(\frac{S}{N}\right)_i = \frac{1}{m}\sum_{j=1}^{m} d_{ij} \; with \; d_{ij} = \begin{cases} \left(\frac{x_{ij}-s_{ij}}{s_{ij}}\right), if \; x_{ij} > s_{ij} \\ 0 \quad , if \; x_{ij} < s_{ij} \end{cases},$$

Where d_{ij} is the relative difference between species concentration x_{ij} and the corresponding uncertainty in the considered sample s_{ij}. According to Norris et al. (2014), a S/N ratio of 1 corresponds to species with observations twice higher than uncertainties on average and consequently indicates a species with good signal quality. Moreover, to minimize the weight of contributions of low quality species, the PMF tool allows declaring these species as "weak" (Paatero and Hopke, 2003) and hence tripling their original uncertainties. In this study, we considered a PMF input variable as weak if its S/N ratio is below 1.2. None of the 14 input variables has a S/N ratio below 1.2 (see Table A in response to referee #1 comment 7) that is why no species was declared as "weak" in Table S5 (response to referee #1 comment 7). These elements are now specified in the revised version of Sect. S2 ("Identification and contribution of major sources of NMHCs by PMF 5.0 approach"):

"**S2.2 VOC dataset and data preparation**

[…]

Moreover, the data preprocessing and quality analysis of the VOC dataset are presented in the supplement material of Debevec et al. (2017). Since signal-to-noise (S/N) ratios of the 14 variables retained for the factorial analysis are all higher than 1.2, no variable was categorized as "weak" in this study, and hence downweighted (categorize variables in "weak" means to triple their original uncertainties; Norris et al., 2014). "

Additionally, propene, n-pentane, n-hexane, toluene and EX concentrations are not well reconstructed by the PMF model according to determination coefficients and slopes (Table S4; response to referee #1 comment 7) between their reconstructed and measured concentrations. This piece of information is summarized in Table S5 following two elements ("Nb. of species with $R^2 > 0.6$":10 and "Nb. of species with $1.1 > slope > 0.6$": 9). The limitation of the selected PMF solution to reconstruct the concentrations of these 5 NMHCs is further discussed in response to referee #1 comment 9.

References

Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., and Locoge, N.: Origin, and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus), Atmos. Chem. Phys., 17, 11355–11388, doi:10.5194/acp-17-11355-2017, 2017.

Norris, G., Duvall, R., Brown, S., and Bai, S.: EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals, and User Guide Prepared for the US Environmental Protection Agency Office of

Research, and Development, Washington, DC. [online] Available from: https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf, 2014.

Paatero, P. and Hopke, P. K.: Discarding or downweighting high-noise variables in factor analytic models,Pap. Present. 8th 15Int. Conf. Chemom. Anal. Chem., 490, 277–289, doi:10.1016/S0003-2670(02)01643-4, 2003.

9/Sect. 2.3, Page 8, line 19

The authors specify that “PMF model limitations to explain these species should be kept in mind when examining PMF results”. A more detailed discussion would be helpful for the reader to appreciate the limits of the proposed PMF solution. A rough estimate based on figure 8 indicates that these species make up approximatively 80% of the concentration of Factor 2 (short-lived species).

Firstly, the high proportion of long-lived VOCs (such as ethane and propane) usually characterized remote background sites such as Ersa (e.g., Sauvage et al., 2009 and Leuchner et al., 2015) since more reactive species are more prone to react before reaching the receptor sites. Reactive species such as propene, n-hexane, toluene, and C_8 aromatics (EX) have shown low concentration levels (Table 3 in the revised version of the manuscript, see response to referee #1 comment 15) and high variability, especially on short periods (Fig. S8 in the revised version of the supplement, see response to referee #1 comment 7), compared to long-lived VOCs.

Moreover, the reconstruction of measured concentrations by the PMF depends on VOC concentration levels, their variability as well as their uncertainties (related to their signal-to-noise ratio, Debevec et al., 2017 – see responses to referee #1 comments 7 and 8). More reactive species are prone to have higher relative uncertainties degrading their S/N ratios (Table A - see response to referee #1 comment 7) and hence have lower S/N ratios compared to VOCs with longer lifetime. As a result, the PMF model favoured in this study the reconstruction of the NMHCs with the longest lifetime, the highest concentration levels and the highest S/N ratios (i.e. ethane, propane, i-butane, n-butane and acetylene – see Table A) to maximize the reconstruction of the total variable (TVOC). The improvement of the capture of more reactive NMHCs may demand to increase the number factor of the PMF solution (as shown with the PMF solution composed of 6 factors in Sect. S2.3 - response to referee #1 comment 7). However, due to the limiting number of VOCs and the temporal coverage and the time resolution of the observations considered in this factorial analysis, a PMF solution with a higher number of factors will statistically improve the reconstruction of the more reactive species, but the additional factors may not have a physical meaning.

As a result, we decided to select and examine a PMF solution composed of 5 factors, to the detriment of the reconstruction of concentrations of more reactive species. The proposed PMF solution did not reconstruct well 5 NMHCs, which were propene, n-pentane, n-hexane, toluene, and EX, following their correlation between reconstructed and observed concentrations (Table S4 and Fig. S9 - see response to referee #1 comment 7), hence the remark “PMF model limitations to explain these species should be kept in mind when examining PMF results”. However, the PMF model reconstructed well the variations of these species over long periods (Fig. S8) but not over short-periods, explaining their lower determination coefficients and slopes farther from 1. The aim of this study is to present and discuss ambient levels and variations of a selection of VOCs observed at the Ersa station over more than two years. We principally investigated seasonal and interannual variations in this study. The good reconstruction by the PMF model of concentration variations of reactive species over long-period was considered sufficiently adapted to the objectives of this study.

Moreover, as pinpointed by referee #1, these species corresponded to a large part of the factor 2 contributions (short-lived anthropogenic sources). Consequently, some precisions were brought into the revised Sect 3.5.2 (“Short-lived anthropogenic sources (factor 2)”) to better introduce the PMF model limitations to the reader. Correction applied in the revised manuscript in Sect. 3.5.2 (Page 15 lines 21-27):

"Factor 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 previously investigated in Michoud et al. (2017)."

Finally, as recommended by both referees, the Sect. 3.5.6 ("Towards the best experimental strategy to characterize variation in VOC concentrations observed at a remote background site") was fully revised to better highlight the relevance of the PMF solution examined in this study as well as its limitations. The revised Sect. 3.5.6 can be found in the response to referee #2 comment 49.

References

Leuchner, M., Gubo, S., Schunk, C., Wastl, C., Kirchner, M., Menzel, A., and Plass-Dülmer, C.: Can positive matrix factorization help to understand patterns of organic trace gases at the continental Global Atmosphere Watch site Hohenpeissenberg?, Atmos. Chem. Phys., 15, 1221–1236, doi:10.5194/acp-15-1221-2015, 2015.

Michoud, V., Sciare, J., Sauvage, S., Dusanter, S., Léonardis, T., Gros, V., Kalogridis, C., Zannoni, N., Féron, A., Petit, J. E., Crenn, V., Baisnée, D., Sarda-Estève, R., Bonnaire, N., Marchand, N., Dewitt, H. L., Pey, J., Colomb, A., Gheusi, F., Szidat, S., Stavroulas, I., Borbon, A., and Locoge, N.: Organic carbon at a remote site of the western Mediterranean Basin: Sources, and chemistry during the ChArMEx SOP2 field experiment, Atmos. Chem. Phys., 17, 8837–8865, doi:10.5194/acp-17-8837-2017, 2017.

Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P., and Galloo, J. C.: Long term measurement, and source apportionment of non-methane hydrocarbons in three French rural areas, Atmos. Environ., 43, 2430–2441, doi:10.1016/j.atmosenv.2009.02.001, 2009.

10/Sect. 2.3, Page 8, line 6

Could the authors elaborate on the choice of the VOCs included in the PMF? This is a rather limited range of VOCs, compared to other studies (see for example Abeleira et al., 2017, 46 VOCs; Yuan et al., 2012, 73 VOCs). Can the authors provide a rough estimate of their contribution to the total VOCs mass concentration?

Our choice of the VOCs included in this study was based on two reasons: (i) we had planned to measure VOCs using off-line techniques since we could not be frequently present at the Ersa station (which would have been necessary to manage on-line measurements). (ii) We chose to include only VOC measurements realized with canisters in the PMF analysis to maximize the number of data observations.

We would like to inform referee #1 that the selection of the 35 VOCs selected in this study is now presented in the revised Supplement in Sect. S1 ("VOCs selected in this study"; see response to referee #2 comment 19). They comprised 17 NMHCs measured by steel canisters, 4 additional NMHCs measured by multi-sorbent cartridges, 4 carbonyl compounds measured using multi-sorbent cartridges and 10 additional carbonyl compounds measured using DNPH cartridges.

Among the 169 days of the 2-yr period when VOCs were measured at least by one of the three measurement techniques (Fig. S1 – response to referee #1 comment 3), DNPH and multi-sorbent cartridges were sampled only 73 and 52 days concurrently to the collection of steel canisters. Sampling days common to the three off-line techniques were only 36 days. As a result, the reconstruction of missing data points of each dataset would be arduous and would significantly affect the final dataset quality. Additionally, the restriction of the number of data points to those common to the three datasets would significantly impact the temporal representativity of the NMHC inputs of the study period and hence limiting the discussion on interannual and seasonal variations for statistical robustness reasons. Given these reasons, we made the choice to limit the factorial analysis to the 17 NMHCs measured by steel canisters in this study. These pieces of information have been incorporated in the revised Sect. S2 (see Sect. S2.2 in the response to referee #1 comment 7).

We are aware that the VOC number (17) considered in the PMF analysis discussed in this study is limited compared to other studies (like those indicated by referee #1). The choice of the VOC range in the PMF analysis and its consequences were better discussed in the revised version (see responses to referee #1 comments 7 and 9 and referee #2 comment 49). Moreover, we stressed that our field campaign has taken place over more than two years whereas those of Yuan et al. (2012) and Abeleira et al. (2017) were much shorter (2 months and 16 weeks, respectively). Given the longer study period of the ChArMEx observation field campaign, we adapted the measurement strategy and only VOC off-line measurements were planned. The automatic analysers have been planned only for the purpose of the ChArMEx intensive field campaign of summer 2013, as reported by Michoud et al. (2017). Factorial analyses covering more than a year of VOC measurements at remote sites remain scarce in Europe (such as Sauvage et al. 2009 and Lo Vullo et al. 2016) and they are of high interest to better understand VOC long-term variations (as introduced in Sect. 1 of the manuscript; response to referee #1 comment 1). In this study, we pointed out PMF-derived factors controlling VOC concentration variations at remote sites may be controlled by the meteorological conditions that have occurred during the study period, when issued from short observation periods (i.e. up to two months). Moreover, from our experience gained with this field campaign, we provided some advises in the revised Sect. 3.5.6 (“Towards the best experimental strategy to characterize variation in VOC concentrations observed at a remote background site” – see response to referee #2 comment 49) and in the conclusion (see response to referee #2 comment 73) on the adapted strategy for long-term VOC observations at remote sites (in terms of the VOC number as well as the time resolution and the temporal coverage of VOC measurements).

Then, to check the relevance of the 17 NMHCs selected as inputs in the PMF analysis presented in this study, we benefited from the PMF analysis conducted with the summer 2013 VOC dataset. The PMF solution selected by Michoud et al. (2017) was obtained considering a larger number of VOCs (42), which is more comparable to VOC datasets of Abeleira et al. (2017) and Yuan et al. (2012). Comparisons in Sect. S5 (“Comparisons of VOC source apportionment with previous one performed at Ersa”) highlighted a consistency between the two VOC source apportionments performed at Ersa. Furthermore, we checked a 4-factor PMF realized with the summer 2013 dataset restricted to the 17 NMHCs considered in this study. We selected a 4-factor PMF solution as 4 primary sources were identified in Michoud et al. (2017). The comparison results have been added in Sect. S6 of the revised Supplement, as following:

“Section S6: Examination of a summer 2013 PMF solution realized considering the 17 NMHCs selected in this study

To check the relevance of the 17 NMHCs selected as inputs in the PMF analysis presented in this study, we benefited from the PMF analysis previously conducted with the larger summer 2013 VOC dataset. The PMF solution selected by Michoud et al. (2017) was realized considering a larger number of VOCs (42). In this section, we selected a summer 2013 PMF solution composed of 4 factors, as 4 primary sources were identified in Michoud et al. (2017), and considering a VOC dataset of 13 variables (those selected for the 2-yr PMF solution, at the exception of propene which was not measured in summer 2013 at a 90-min time resolution). The two PMF solution comparison results are presented in Figs. S16 and S17. The same species dominantly composed the paired factors of the two PMF solutions (Fig. S16) suggesting that the 13 variables selected in this study comprised dominant tracers of the primary sources influencing VOC concentrations observed at Ersa in summer 2013. The primary biogenic source of the PMF solution with the VOC subset (factor 4 – Fig. S16) is composed of a lower proportion of anthropogenic NMHCs and a higher isoprene one. Species composing anthropogenic sources in low proportion tend to have been reduced with the 4-factor PMF solution (factors 1-3 – Fig. S16), suggesting a better deconvolution of the sources, at the exception of ethane proportion in the chemical profile of short-lived anthropogenic sources (factor 3) which increased. Concerning factor contribution variations (Fig. S17), medium-lived anthropogenic sources and the biogenic source showed the same variability in the two PMF solutions (determination coefficients: 0.85-0.89). Similar results were noticed for long-lived anthropogenic sources (determination coefficient: 0.72), at the exception of the last days of the special observation period. However, short-lived anthropogenic sources have shown different inter-diel variations as a function of the PMF solution, even if factor contribution variations globally followed the same pattern (Fig. S17). This factor contribution variability seems to be not only influenced by the variations in concentrations of reactive selected NMHCs composing it (Fig. S16) but can be by other species such as ethane (for the one of the 4-factor PMF solution), C_9 aromatics, 2-methylfuran and OVOCs (carboxylic acids, acetone, isopropanol and n-hexanal; Michoud et al., 2017). Note that formic and acetic acids, and acetone concentrations corresponded to 42% of the total measured concentrations of the VOCs selected for the factorial analysis (Michoud et al., 2017).

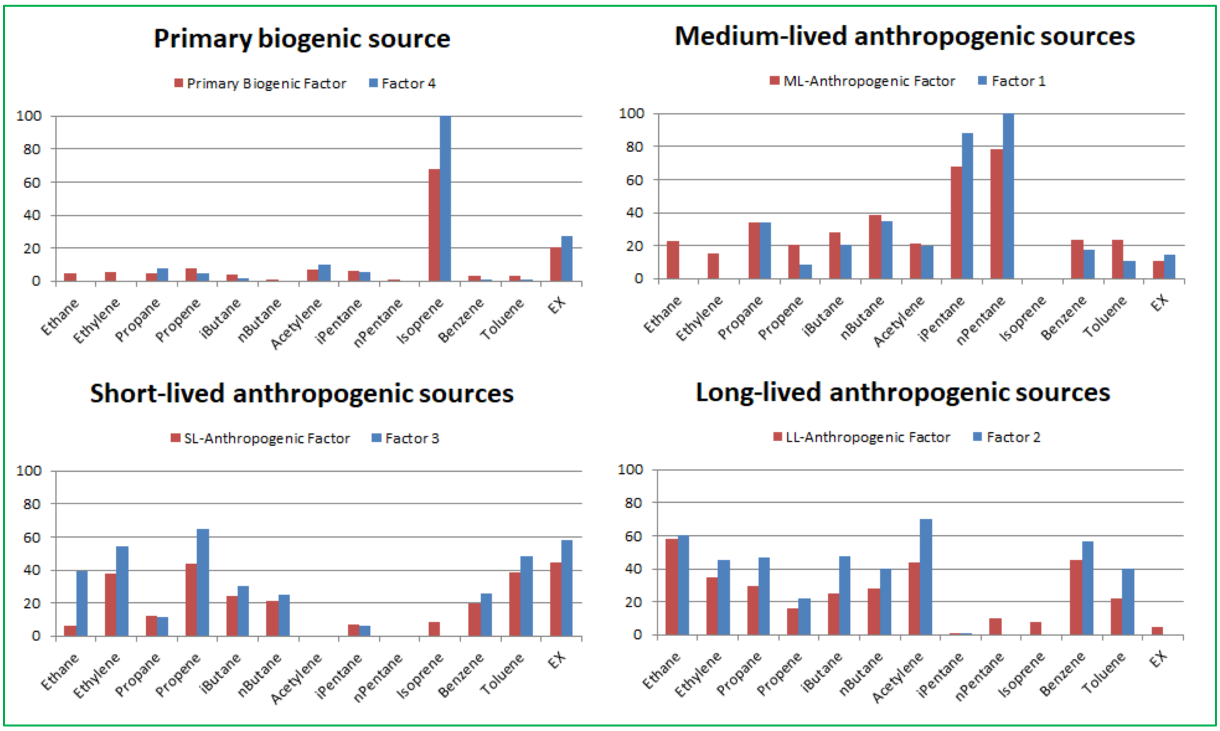


Figure S16: Chemical profiles (percent of each species apportioned to each factor - %) of the 4-factor PMF solution (13 variables; blue bars) compared to a selection of VOCs composing chemical profiles of the 4 primary sources identified in Michoud et al. (2017) owing to a 6-factor PMF solution (42 VOC dataset; red bars).

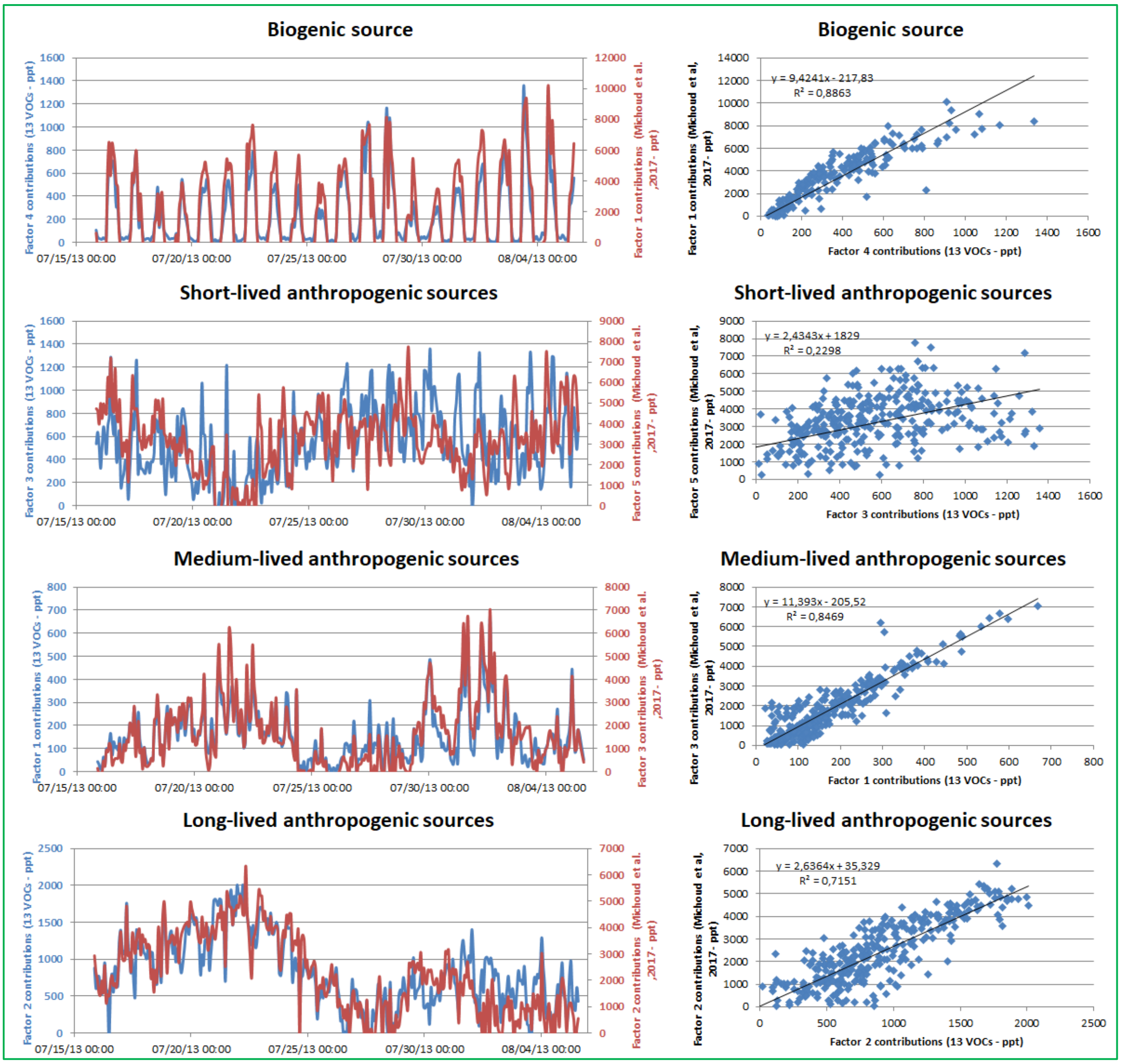
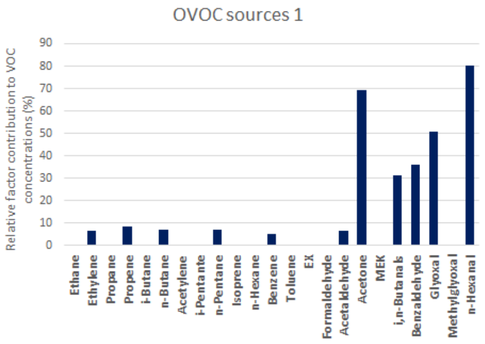
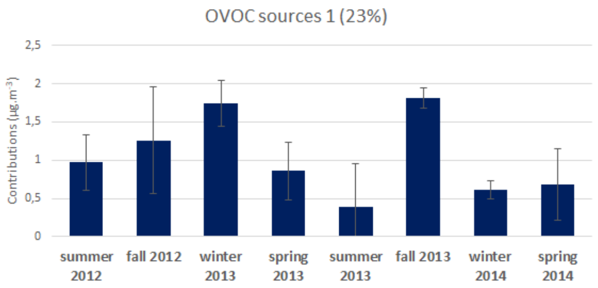
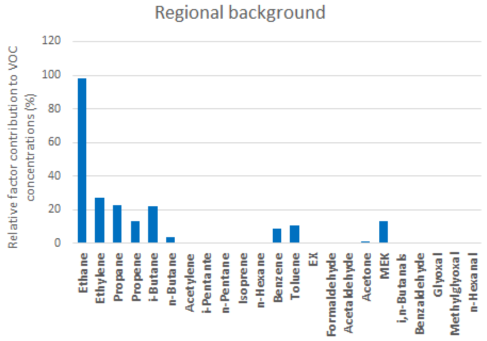


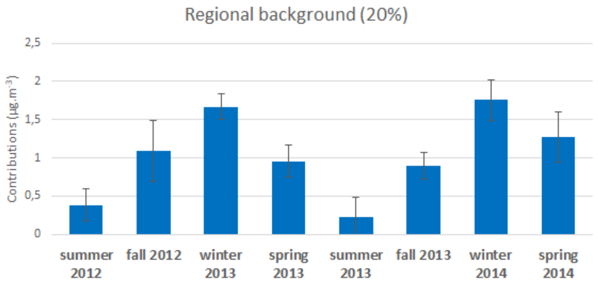
Figure S17: Times series (on the left) and scatter plots (on the right) of contributions (in ppt) of factors composing the 4-factor PMF solution (13 variables; blue lines) compared to the 4 primary sources identified in Michoud et al. (2017) owing to a 6-factor PMF solution (42 VOC dataset; red lines).“

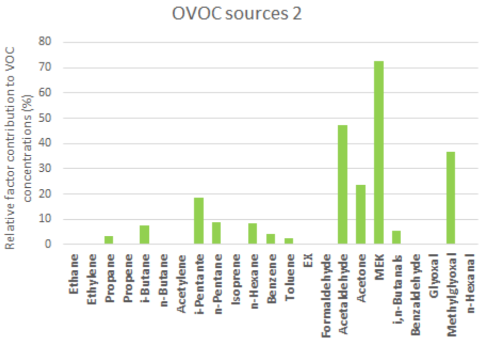
Furthermore, preliminary tests of exploring PMF solutions composed from 2 to 10 factors using an input dataset gathering VOC measurements using steel canisters and DNPH cartridges and composed of 73 observations and 23 variables were realized. The same methodology as presented in Sect. S2 (see response to referee #1 comment 7) was followed. An 8-factor PMF solution considering a Fpeak of 0.5 was further examined (see factor profiles and seasonal contributions in Fig. A). The reconstruction of the 14 variables related to HCNMs (Table B) is quite similar to the one with the steel canister dataset (Sect. S2; response to referee #1 comment 7) and the five same species were not well reconstructed (propene, n-pentane, n-hexane, toluene and EX). The reconstruction of ethylene concentrations by the selected 8-factor PMF solution is better compared to the one with the 5-factor PMF solution of 14 variables (Sect. S2). Two carbonyl compounds were not well reconstructed (glyoxal and benzaldehyde – Table B) by the 8-factor PMF solution of 23 variables. Moreover, the solution is composed of three factors mostly composed of OVOCs (cumulative relative contribution: 50%), 4 factors related to anthropogenic sources (cumulative relative contribution: 44%) and a factor related to the local biogenic source (relative contribution to the total variable of 6%). From a PMF solution of 8 factors, a factor was clearly related to the local biogenic source, notably improving the reconstruction of isoprene concentrations. Despite the different number of data observations, the 8-factor PMF solution identified the same 5 primary sources as those presented in Sect. 3.5 (“Major NMHC sources”). A lower proportion of n-hexane and propene concentrations were attributed to the short-lived anthropogenic factor of the 8-factor PMF solution (Fig. A) compared to the one of the 5-factor PMF solution (see the revised Fig. 7 in response to referee #1 comment 18). OVOC concentrations were mostly apportioned to the three additional factors (named OVOC sources 1-3 which explained 88% of the total OVOC concentrations – Fig. A below) and could be considered mostly of secondary origins. Different interannual and seasonal contributions were observed for these three OVOC sources. The factor named ‘OVOC sources 1’ apportioned the larger part of OVOC concentrations (42%) mostly due to acetone contribution. This factor shows an increasing trend in the cold season as anthropogenic sources. Higher contributions of ‘OVOC sources 1’ and short-lived anthropogenic sources were noticed in fall 2013. Given the fact that the factor entitled ‘OVOC sources 1’ is both composed of short-to-long-lived OVOCs and given their interannual and seasonal variations, the sources related to this factor could be both of local and regional anthropogenic origins. Moreover, higher contributions of the factor ‘OVOC sources 2’ were noticed in summer 2012, consistently with a secondary biogenic origin (mostly related to the local biogenic source). Higher contributions of the factor ‘OVOC sources 3’ were noticed in summer 2013, consistently with secondary biogenic origins (both related to the local biogenic source explaining isoprene concentrations but also monoterpenes such as camphene and a-terpinene, which have shown higher concentrations in summer 2013 – see the revised Fig. 4; response to referee #2 comment 22). Links with anthropogenic sources are not discarded for ‘OVOC sources 2 and 3’ but they cannot be examined in this study. Moreover, concentrations of methylglyoxal, i,n-butanals, acetaldehyde and acetone were partly attributed to the local biogenic source (explained 6-32% of these OVOC concentrations, which represent 7% of the total OVOC concentrations), consistently with their seasonal variations (see response to referee #1 comment 16). Primary anthropogenic origins for MEK and glyoxal were supposed considering their seasonal concentration variations (see response to referee #1 comment 16) and were especially attributed to evaporative sources (explained 0-20% of these OVOC concentrations, which represent 5% of the total OVOC concentrations). A lower proportion of OVOC concentrations were apportioned to primary sources compared to Michoud et al. (2017), which could be linked to the measured OVOCs in the two studies, the study periods and the number and the resolution of the VOC measurements.

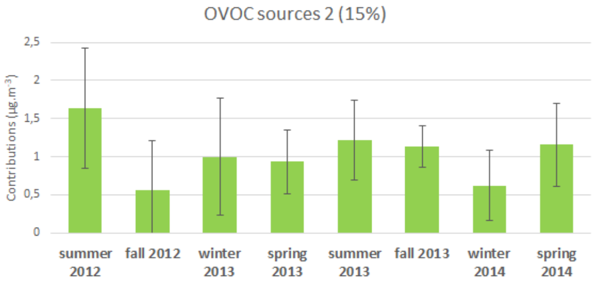

OVOC sources 1
Relative factor contribution to VOC concentrations (%)
90
80
70
60
50
40
30
20
10
0
Ethane
Ethylene
Propane
Propene
i-Butane
n-Butane
Acetylene
i-Pentante
n-Pentane
Isoprene
n-Hexane
Benzene
Toluene
EX
Formaldehyde
Acetaldehyde
Acetone
MEK
i,n-Butanals
Benzaldehyde
Glyoxal
Methylglyoxal
n-Hexanal

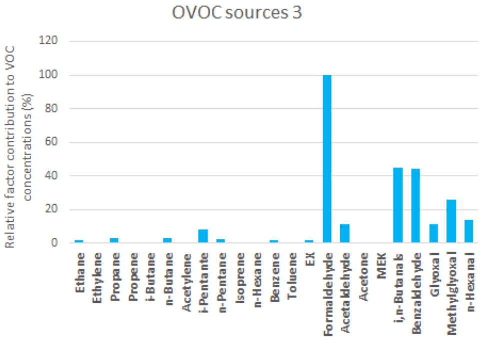

OVOC sources 1 (23%)
Contributions (µg.m-3)
2,5
2
1,5
1
0,5
0
summer 2012
fall 2012
winter 2013
spring 2013
summer 2013
fall 2013
winter 2014
spring 2014

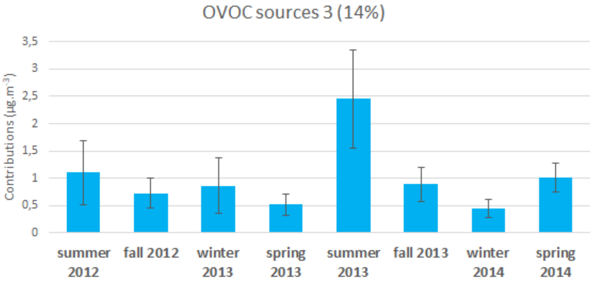

Regional background
Relative factor contribution to VOC concentrations (%)
120
100
80
60
40
20
0
Ethane
Ethylene
Propane
Propene
i-Butane
n-Butane
Acetylene
i-Pentante
n-Pentane
Isoprene
n-Hexane
Benzene
Toluene
EX
Formaldehyde
Acetaldehyde
Acetone
MEK
i,n-Butanals
Benzaldehyde
Methylglyoxal
n-Hexanal

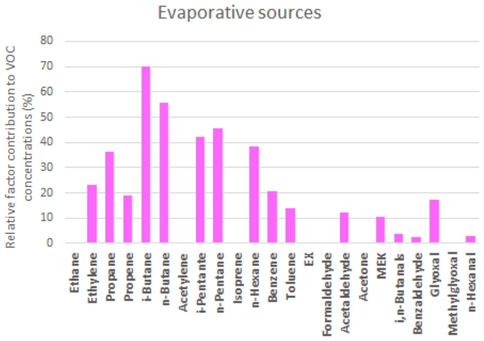

Regional background (20%)
Contributions (µg.m-3)
2,5
2
1,5
1
0,5
0
summer 2012
fall 2012
winter 2013
spring 2013
summer 2013
fall 2013
winter 2014
spring 2014

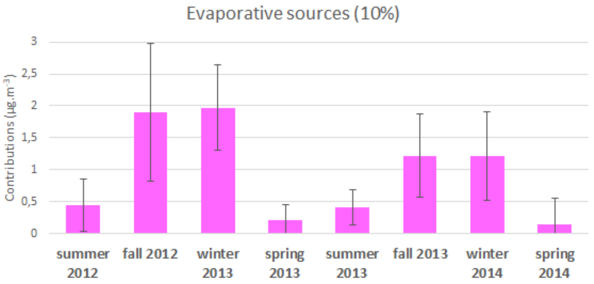

OVOC sources 2
Relative factor contribution to VOC concentrations (%)
80
70
60
50
40
30
20
10
0
Ethane
Ethylene
Propane
Propene
i-Butane
n-Butane
Acetylene
i-Pentante
n-Pentane
Isoprene
n-Hexane
Benzene
Toluene
EX
Formaldehyde
Acetaldehyde
Acetone
MEK
i,n-Butanals
Benzaldehyde
Glyoxal
Methylglyoxal
n-Hexanal


OVOC sources 2 (15%)
Contributions (µg.m-3)
2,5
2
1,5
1
0,5
0
summer 2012
fall 2012
winter 2013
spring 2013
summer 2013
fall 2013
winter 2014
spring 2014


OVOC sources 3
Relative factor contribution to VOC concentrations (%)
120
100
80
60
40
20
0
Ethane
Ethylene
Propane
Propene
i-Butane
n-Butane
Acetylene
i-Pentante
n-Pentane
Isoprene
n-Hexane
Benzene
Toluene
EX
Formaldehyde
Acetaldehyde
Acetone
MEK
i,n-Butanals
Benzaldehyde
Glyoxal
Methylglyoxal
n-Hexanal


OVOC sources 3 (14%)
Contributions (µg.m-3)
3,5
3
2,5
2
1,5
1
0,5
0
summer 2012
fall 2012
winter 2013
spring 2013
summer 2013
fall 2013
winter 2014
spring 2014


Evaporative sources
Relative factor contribution to VOC concentrations (%)
80
70
60
50
40
30
20
10
0
Ethane
Ethylene
Propane
Propene
i-Butane
n-Butane
Acetylene
i-Pentante
n-Pentane
Isoprene
n-Hexane
Benzene
Toluene
EX
Formaldehyde
Acetaldehyde
Acetone
MEK
i,n-Butanals
Benzaldehyde
Glyoxal
Methylglyoxal
n-Hexanal


Evaporative sources (10%)
Contributions (µg.m-3)
3
2,5
2
1,5
1
0,5
0
summer 2012
fall 2012
winter 2013
spring 2013
summer 2013
fall 2013
winter 2014
spring 2014

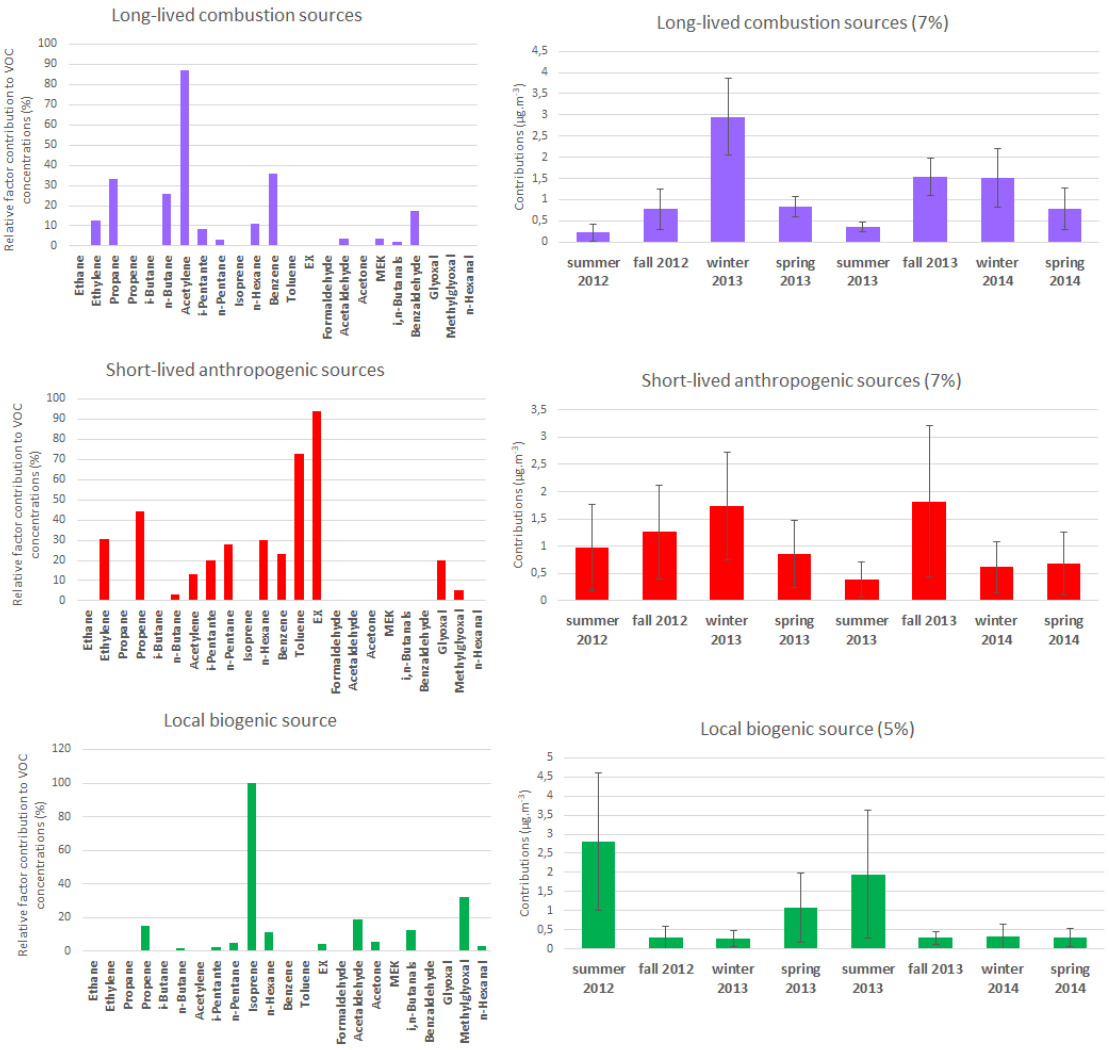


Figure A: Factor chemical profiles (percent of each species apportioned to each factor - %; left) and seasonal contributions (µg.m^{-3}; right) of the 8-factor PMF solution (23 variables). Factors are ordered as a function of their relative contribution to the total VOC mass (percentages into parentheses).

Table B: Evaluation of reconstructed VOC concentrations of the 8-factor PMF solution as a function of measured VOCs.

VOC	R²	Slope (µg.m^{-3})	Intercept (µg.m^{-3})
(0) TVOC	0.993	1.003	-0.013
(1) Ethane	0.996	1.002	-0.005
(2) Ethylene	0.833	0.776	0.050
(3) Propane	0.967	0.974	0.011
(4) Propene	0.514	0.570	0.020
(5) i-Butane	0.929	0.847	0.031
(6) n-Butane	0.966	0.980	0.002
(7) Acetylene	0.995	0.979	0.004
(8) i-Pentane	0.764	0.723	0.058
(9) n-Pentane	0.294	0.416	0.101
(10) Isoprene	0.972	0.869	0.009
(11) n-Hexane	0.568	0.553	0.030
(12) Benzene	0.920	0.869	0.030
(13) Toluene	0.653	0.662	0.0
(14) EX	0.590	0.649	0.081
(15) Formaldehyde	0.999	1.007	-0.009
(16) Acetaldehyde	0.778	0.872	0.084

(17) Acetone	0.995	0.973	0.092
(18) MEK	0.985	0.984	0.005
(19) i,n-Butanals	0.667	0.470	0.078
(20) Benzaldehyde	0.260	0.268	0.080
(21) Glyoxal	0.542	0.515	0.022
(22) Methylglyoxal	0.686	0.683	0.042
(23) n-Hexanal	0.752	0.471	0.052

References

Abeleira, A., Pollack, I. B., Sive, B., Zhou, Y., Fischer, E. V., and Farmer, D. K.: Source characterization of volatile organic compounds in the Colorado Northern Front Range Metropolitan Area during spring and summer 2015, J. Geophys. Res.-Atmos., 122, 3595–3613, https://doi.org/10.1002/2016jd026227, 2017.

Lo Vullo, E., Furlani, F., Arduini, J., Giostra, U., Graziosi, F., Cristofanelli, P., Williams, M. L., and Maione, M.: Anthropogenic non-methane volatile hydrocarbons at Mt. Cimone (2165 m a.s.l., Italy): Impact of sources and transport on atmospheric composition, Atmos. Env., 140, 395-403, doi:10.1016/j.atmosenv.2016.05.060, 2016.

Michoud, V., Sciare, J., Sauvage, S., Dusanter, S., Léonardis, T., Gros, V., Kalogridis, C., Zannoni, N., Féron, A., Petit, J. E., Crenn, V., Baisnée, D., Sarda-Estève, R., Bonnaire, N., Marchand, N., Dewitt, H. L., Pey, J., Colomb, A., Gheusi, F., Szidat, S., Stavroulas, I., Borbon, A., and Locoge, N.: Organic carbon at a remote site of the western Mediterranean Basin: Sources, and chemistry during the ChArMEx SOP2 field experiment, Atmos. Chem. Phys., 17, 8837–8865, doi:10.5194/acp-17-8837-2017, 2017.

Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P., and Galloo, J. C.: Long term measurement, and source apportionment of non-methane hydrocarbons in three French rural areas, Atmos. Environ., 43, 2430–2441, doi:10.1016/j.atmosenv.2009.02.001, 2009.

Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, J. Geophys. Res.-Atmos., 117, 117, D24302, https://doi.org/10.1029/2012jd018236, 2012.

11/Sect. 2.4.2, from Page 9, line 32 to Page 10, line 3

It is unclear what you mean here: "tests that revealed that results only highlighted local contributions…" is it related to exploratory tests with empirical weighting function? Was it finally decided to apply such a weighting function?

The higher the number of trajectory points in a grid cell, the better the statistical significance of the CF model. The ZeFir user can decide to downweight grid cells having a low number of trajectory points by applying the weighing function in order to focus the discussion on potential emission areas on the most frequently observed situations at the receptor site (Waked et al., 2018). Our exploratory tests using the empirical weighing function only highlighted local contributions compared with the unweighted CF results (see Fig. B). This is because the grid cells having the higher number of trajectory points are concentrated close to the Ersa station (see trajectory density in Fig. B).

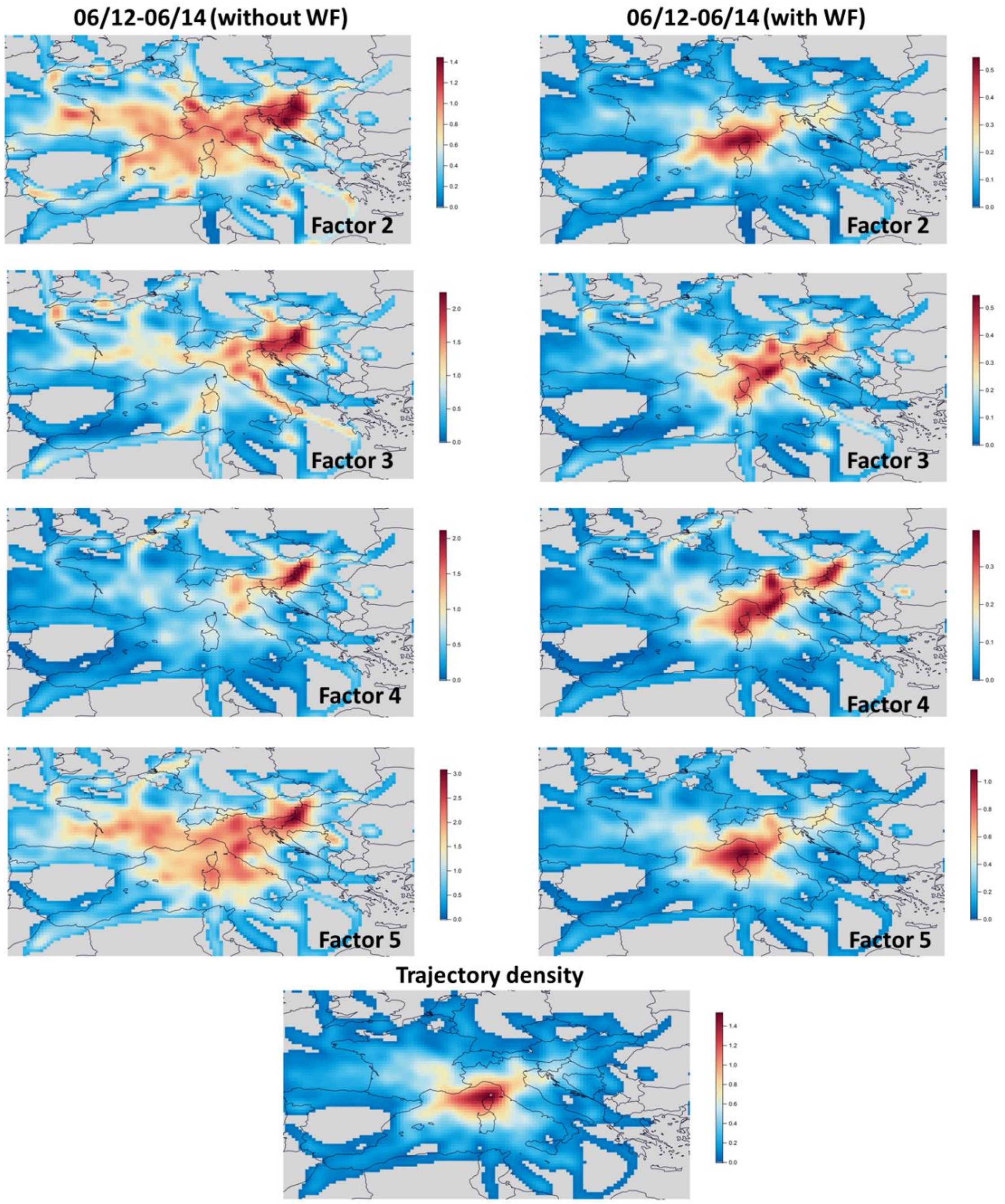


Figure B: Potential source area contributions (in µg m^{-3}) to PMF factors 2-5 using the CF model with (left) and without (right) the weighing function (WF), and trajectory density (bottom). VOC factors: factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background.

Some corrections were applied to the revised Sect. 2.4.2 (“Identification of potential emission areas”; Page 8, lines 15-25) to better introduce the weighing function use and its non-consideration in the CF analyses discussed in this study:

“A better statistical significance of the CF results is commonly considered for grid cells with a higher number of crossing trajectory points. As a result, some studies applied an empirical weighing function so as to limit the possible influence of high concentrations which may be observed during occasional episodes with uncommon trajectories (e.g., Bressi et al., 2014; Waked et al., 2014, 2018) 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 this study. The farther a cell is from the Ersa station, the lower 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 more the weighing function tended toward downweighting the low n_{ij} value. 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."

Reference

Waked, A., Bourin, A., Michoud, V., Perdrix, E., Alleman, L. Y., Sauvage, S., Delaunay, T., Vermeesch, S., Petit, J.-E., and Riffault, V.: Investigation of the geographical origins of PM10 based on long, medium and short-range air mass back-trajectories impacting Northern France during the period 2009–2013, Atmos. Environ., 193, 143-152, doi :10.1016/j.atmosenv.2018.08.015, 2018.

12/Sect. 2.4.2, Page 9, line 28

Can the author explain the meaning of shortening the back-trajectories?

According to Petit et al. (2017), precipitation values at each trajectory endpoint can be used to cut the trajectory where rain occurred, thus avoiding to take the rest of the back-trajectory into account, because the associated air parcel has been washed out. Similarly, an altitude threshold can be used, assuming that above a certain value, the emissions in the air parcel could not reach this trajectory. For example, let us consider an air mass observed at Ersa at a time t after 72 h of transport. It is represented by a 72-h back-trajectory starting at t-0h from Ersa. If the back trajectory reaches an altitude over 1500 m a.s.l. (the altitude threshold used in this study) at time t-50h, the ZeFir tool cuts this air mass back-trajectory and only considers the first 50 h. Moreover, if precipitation occurred at time t-45h, the back-trajectory of the considered air mass may also be shortened by the ZeFir tool to 45 h.

This was clarified in the revised manuscript in Sect. 2.4.2 ("Identification of potential emission areas"; Page 8, lines 12-14):

"Back-trajectories have been shortened (i.e. the ZeFir tool considered shorter back-trajectories than 72 h) 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 1500 m a.s.l. […]."

Reference

Petit, J. E., Favez, O., Albinet, A., and Canonaco, F.: A user-friendly tool for comprehensive evaluation of the geographical origins of atmospheric pollution: Wind, and trajectory analyses, Environ. Model. Softw., 88, 183–187, doi:10.1016/j.envsoft.2016.11.022, 2017.

13/Sect. 2.4.2, Page 9, lines 24-25

Please rephrase this sentence as we understand that longer 3-day back trajectories were considered in order to be in the same conditions as Michoud et al.

It was not rephrased in the revised manuscript since we indeed considered in this case longer, 3-day back trajectories to be in the same conditions as Michoud et al. (2017). More precisely, these 3-day back trajectories were shortened to 2 days for the air mass clustering to be in the same conditions as Michoud et al. (2017). We wanted to have comparative results, in terms of air mass clustering and transit times of each cluster, with the previous study dedicated to summer 2013 Ersa VOC observations, that is why we considered different lengths (namely 2 or 3 days) of back-trajectories in this study. The consideration of shorter back-trajectories does not affect air mass trajectory classification since between t-48h and t-72h, the air mass trajectories continued their pathway without significant change of direction. Air masses which have met recirculation situations were previously discarded as indicated in the original manuscript. However, this sentence was nuanced in the revised manuscript to insist on the interest to respect the same conditions as Michoud et al. (2017) (Page 8, lines 8-10):

"Note that longer back-trajectories were considered for CF analyses than those for air mass origin classification, 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."

Reference

Michoud, V., Sciare, J., Sauvage, S., Dusanter, S., Léonardis, T., Gros, V., Kalogridis, C., Zannoni, N., Féron, A., Petit, J. E., Crenn, V., Baisnée, D., Sarda-Estève, R., Bonnaire, N., Marchand, N., Dewitt, H. L., Pey, J., Colomb, A., Gheusi, F., Szidat, S., Stavroulas, I., Borbon, A., and Locoge, N.: Organic carbon at a remote site of the western Mediterranean Basin: Sources, and chemistry during the ChArMEx SOP2 field experiment, Atmos. Chem. Phys., 17, 8837–8865, doi:10.5194/acp-17-8837-2017, 2017.

14/Sect. 3.2, Page 11

Sect. 3.2 ("Air mass origins") and table 3: it is not clear why trajectories categorized as long have median transit time always shorter than the trajectories categorized as short.

An air mass trajectory classified as short has closer distance between two of its succeeding points compared to another one classified as long (see examples in Fig. C). Due to the location of Ersa in the Mediterranean Sea, the air mass with the shorter trajectory has spent more time to reach the Ersa site from French coastlines compared to an air mass trajectory classified as long (11h and 6h, respectively). This is illustrated by Figure C below.

Figure C: Comparison of transit times between a short and long air mass trajectories both classified into cluster 2 (France).

This was clarified in the revised Sect. 3.2 (“Air mass origins”; Page 10, lines 14-18):

“In particular, European and French air masses showed lower transit times over the sea (median values of 6 h and 8 h, respectively; Table 2) when their trajectories are categorized as long; compared to short ones (23 h and 19 h, respectively). These findings are based on the fact that an air mass trajectory classified as short has closer distance between two succeeding trajectory points compared to another one classified as long. Due to the Ersa location in the Mediterranean Sea, the air masses having trajectories characterized as long have spent more time to reach the Ersa site.”

15/Sect. 3.3 and 3.4.3

Some of the VOCs listed (6 C6 - C11 n-aldehydes) are not discussed at all afterwards, why?

Considering referee #1’s remark on the 6 n-aldehydes collected on multi-sorbent cartridges, they were incorporated to the revised Table 3, as well as additional carbonyl compounds sampled with DNPH cartridges, since OVOC measurements remain rather scarce. They were not discussed in the original manuscript since they were not incorporated in the PMF analysis, and we thought this would limit our examination of OVOC sources and origins.

We would like to inform referee #1 that the Sect. S1 (“VOCs selected in this study”) was added in the revised Supplement in response to referee #2 comment 19. As a consequence, four additional carbonyl compounds sampled with multi-sorbent cartridges (n-octanal, n-nonanal, n-decanal, n-undecanal) and six ones sampled using DNPH cartridges (i,n-butanals, n-hexanal, benzaldehyde, glyoxal and methylglyoxal) were added to the 25 initial VOCs investigated in this study. Corrections applied to Table 3:

“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

"

Some corrections were consequently applied to Sect. 3.3 ("VOC mixing ratios"; from Page 10, Line 23 to Page 11 Line 10):

"Statistical results on concentrations of 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 times (09:00-13:00 or 12:00-16:00) are 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 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 selected in this study. They were mainly composed of acetone (contribution of 51% to the OVOC cumulated concentration). Anthropogenic NMHCs also contributed significantly (26%) to the total concentration of the 35 measured VOCs and principally consisted of ethane and propane (which represented 34 and 17% of the anthropogenic NMHC mass, respectively) as well as n-butane (7%). The high contribution of species with generally the longest lifetime in the atmosphere (see Sect. 3.4) is consistent with the remote location of the Ersa site and in agreement with Michoud et al. (2017). BVOCs only contributed little to the total VOC concentration on annual average (4%), 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 in summer 2013 at Ersa (Debevec et al., 2018; Kalogridis, 2014). On the contrary, a larger α-terpinene contribution was noticed during the summer intensive campaign than the 2-yr observation period. Note that speciated monoterpenes were measured differently during the summer 2013 campaign, by means of an automatic analyser (see Sect. S4 in the Supplement)."

We added an additional table in the Sect. 3.4 ("VOC variability") of the revised manuscript which also includes seasonal average OVOC concentrations:

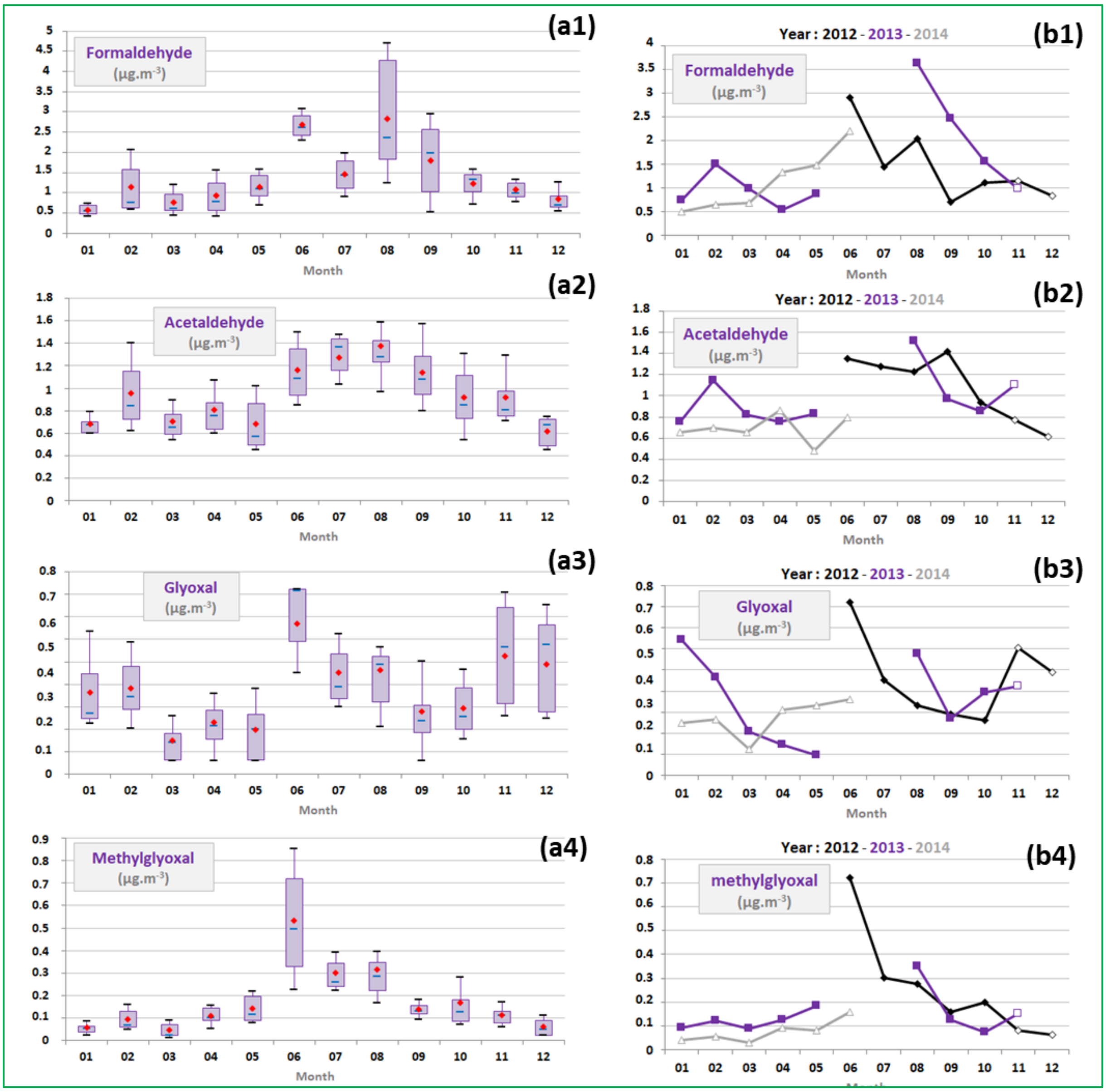
"**Table 4: Seasonal average VOC concentrations (± 1 σ; µg m^{-3})**

	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

"

Some of these additional OVOCs have also been added in the revised Fig. 6:



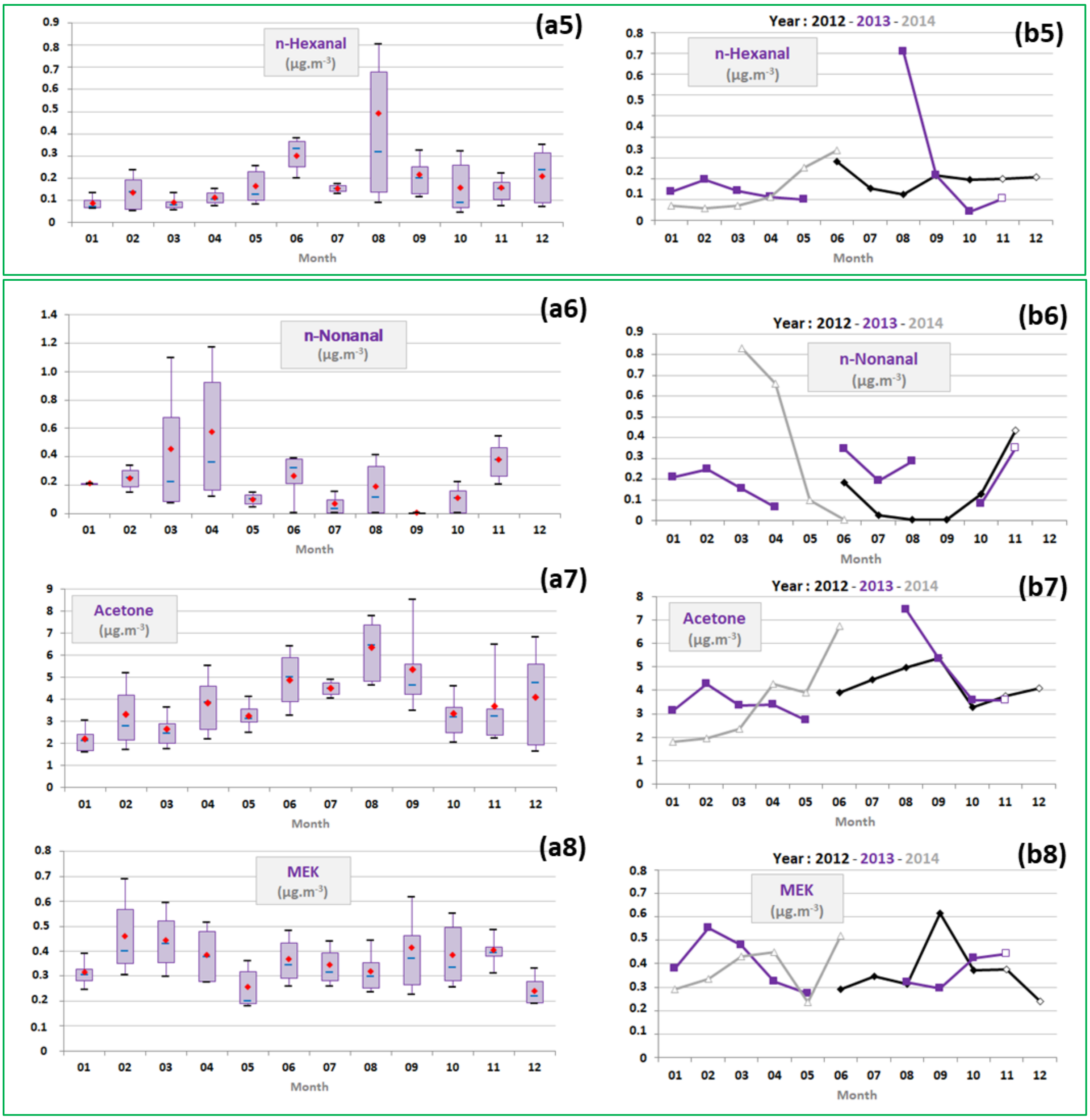


Figure 6: (a) Monthly variations in a selection of oxygenated VOC concentrations (expressed in µg m^{-3}) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict 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.”

As a consequence, interpretations of OVOC concentration variations have been developed in the revised manuscript (in Sect. 3.4.3) following referee #1 suggestions (see response to referee #1 comment 16).

16/Sect. 3.4.3, Page 14

This section is hard to follow, line 14-26 are only general considerations with no direct link to the observations. Why not starting with the trends observed (end of line 26, “Formaldehyde and acetaldehyde concentrations...” and use some of the general information to support the discussion. Same comment for acetone and MEK.

We thank referee #1 for this feedback. As a consequence, the Sect. 3.4.3 ("Oxygenated VOCs") has been fully rewritten in the revised manuscript. More OVOCs were now considered in the revised Sect. 3.4.3 (in response to referee #1 comment 15) and OVOCs having similar variations were now presented together (in response to referee #2 general comment). Their seasonal variations were firstly presented and then selected indications concerning their potential sources are used to support the discussion. Interannual variations are used to confirm some statements or highlight additional contributions. Corrections applied in the revised manuscript in Sect. 3.4.3 (from Page 12 line 30 to Page 14 Line 8):

"Variations of selected OVOCs, illustrating contrasted reactivity (according to their atmospheric lifetimes considering their photochemical reaction rates with OH radicals defined in Atkinson, 1990 and Atkinson and Arey, 2003) were depicted in Fig. 6. Formaldehyde, acetaldehyde, glyoxal, methylglyoxal and C_6-C_{11} aldehydes have relatively short lifetime 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 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 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 were monitored in June 2012 (0.7 µg m^{-3}), similarly to isoprene (Sect. 3.4.1). 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). 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 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 resulted of 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 concentrations higher by 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 their concentrations both in summer and winter (Fig. 6 and Table 4), suggesting they were probably produced by several biogenic and anthropogenic sources. 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 the vegetation and numerous anthropogenic sources, and can also be produced as a result of 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 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 were monitored in June 2012 (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 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)."

17/Sect. 3.4.3, Page 15, line 20

The term "regional" is rather vague, can you indicate which geographical areas are included?

Some precisions were brought in this sentence (Page 13, lines 21-24 in the revised manuscript):

"Acetone can also be resulted of 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."

18/Sect. 3.5.1, Page 17, line 1

Biogenic source: "Local biogenic source" instead?

This factor was renamed in Figs. 7, 8, 10 and S3 in the revised manuscript and supplement as proposed by referee #1.

Note that following referee #2 general remark, we decided to move discussions on factor contribution variations into Sect. 4 ("Discussions on the seasonal variability of VOC concentrations") in the revised manuscript, inducing a change in figure numbers and a move of some figures to the Supplement (Fig. S3). Moreover, we decided to incorporate OVOC seasonal concentration levels in Fig. 10 following referee #1 remark 20. Revised Figs. 7, 8, 10 and S3:

“

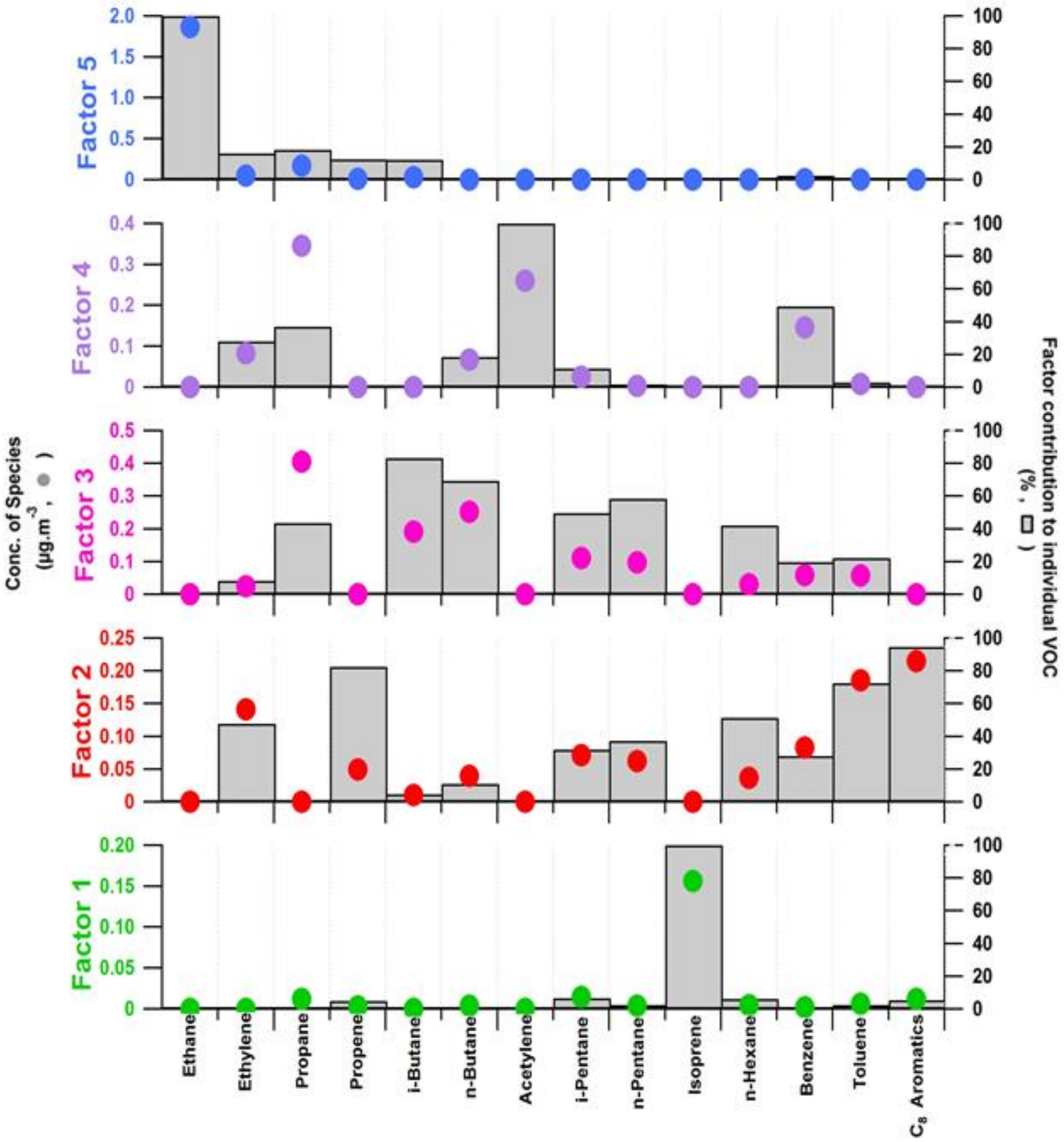


Figure 7: Chemical profiles of the 5-factor PMF solution (14 variables). Factor contributions to each species (µg m^{-3}) and the percent of each species apportioned to the factor are displayed as a grey bar and a color circle, respectively. Factor 1 - local biogenic source; factor 2 - short-lived anthropogenic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

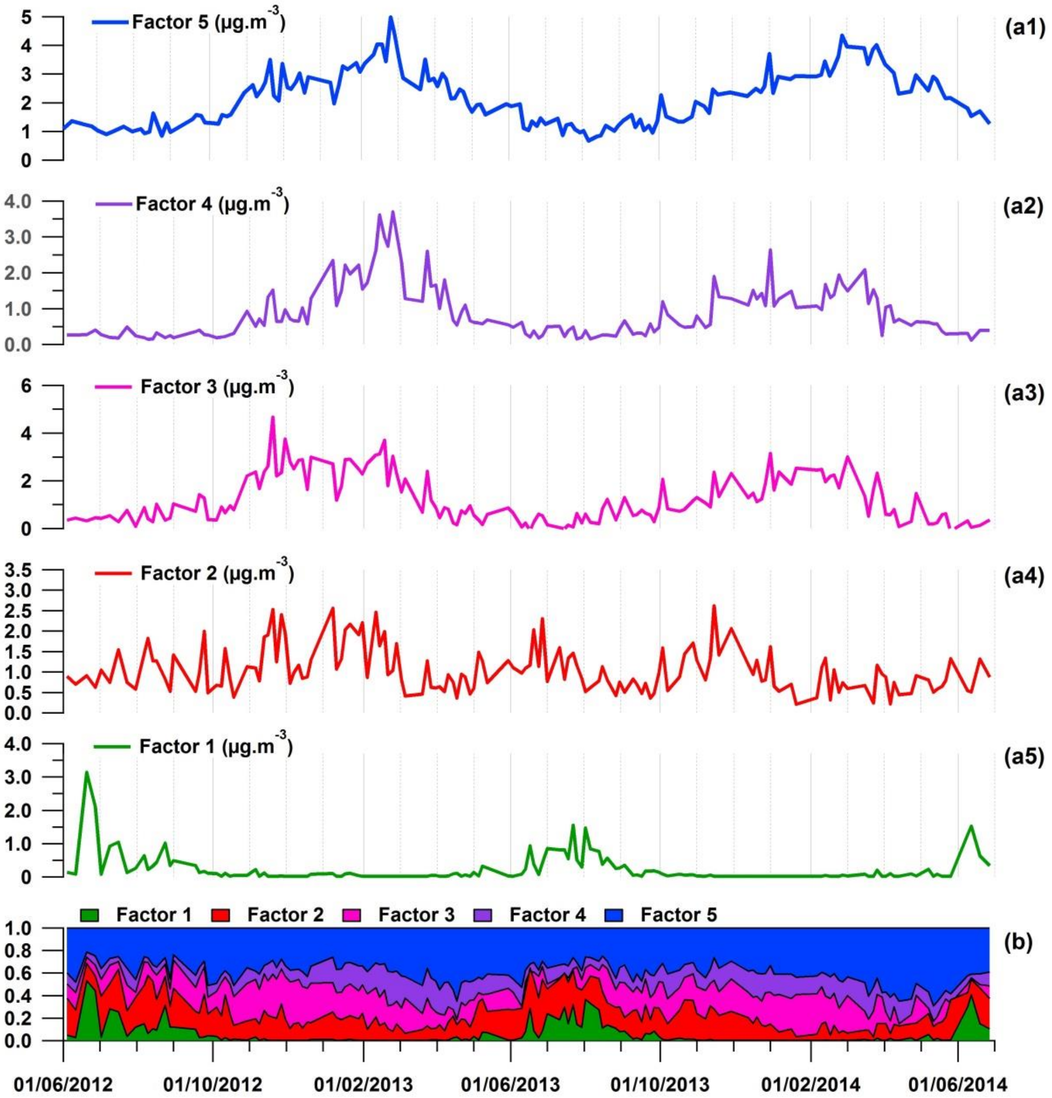


Figure 8: (a) Time series of NHMC factor contributions (µg m^{-3}) and (b) accumulated relative NMHC contributions. Factor 1 - local biogenic source; factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background. 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).

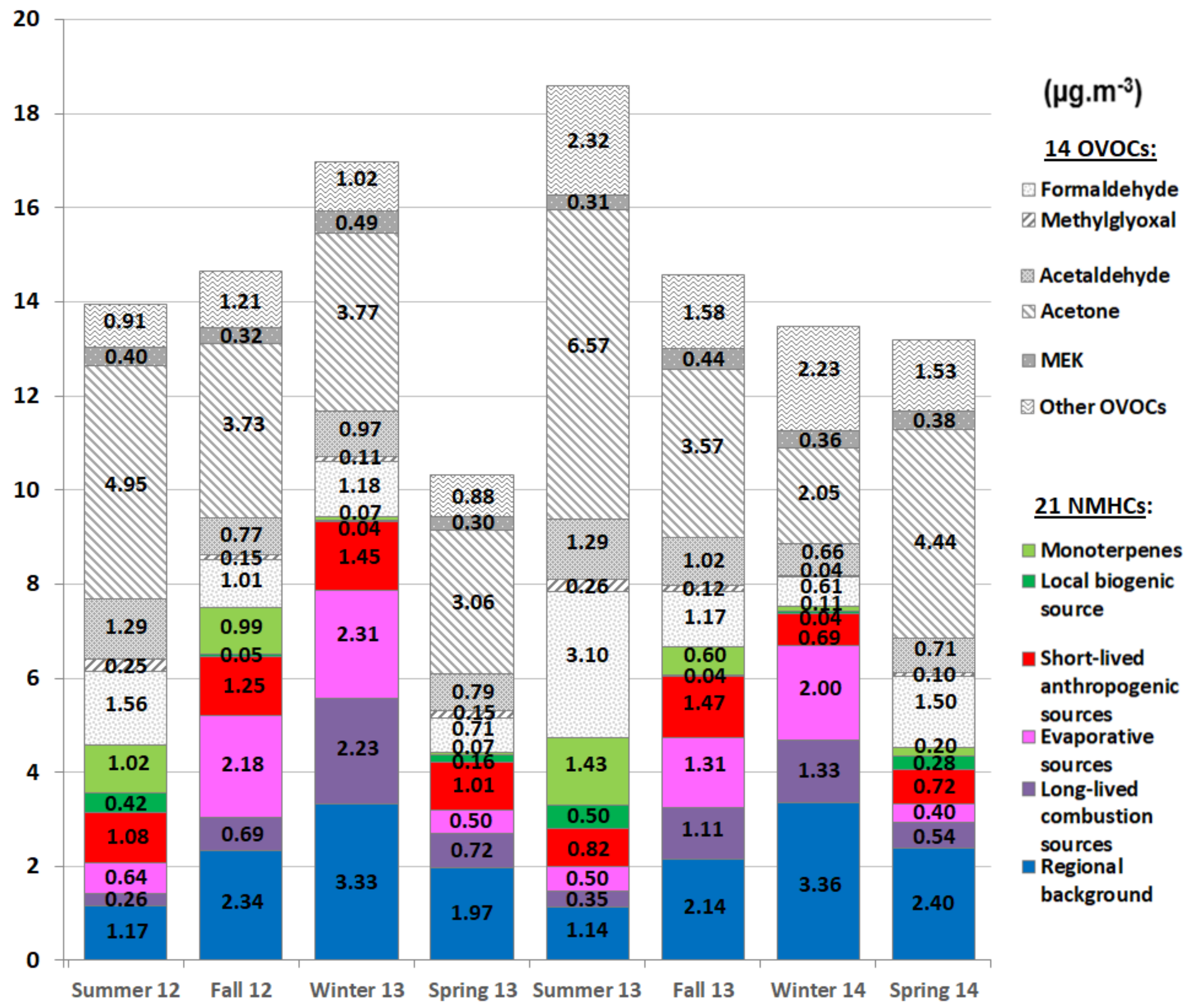


Figure 10: Variations in seasonal averaged accumulated concentrations (expressed in µg m^{-3}) of the 35 VOCs selected in this study. The 17 NHMCs selected for the factorial analysis were apportioned to the five modelled NMHC sources. NMHC seasonal measured concentrations which were not modelled by the 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). 5

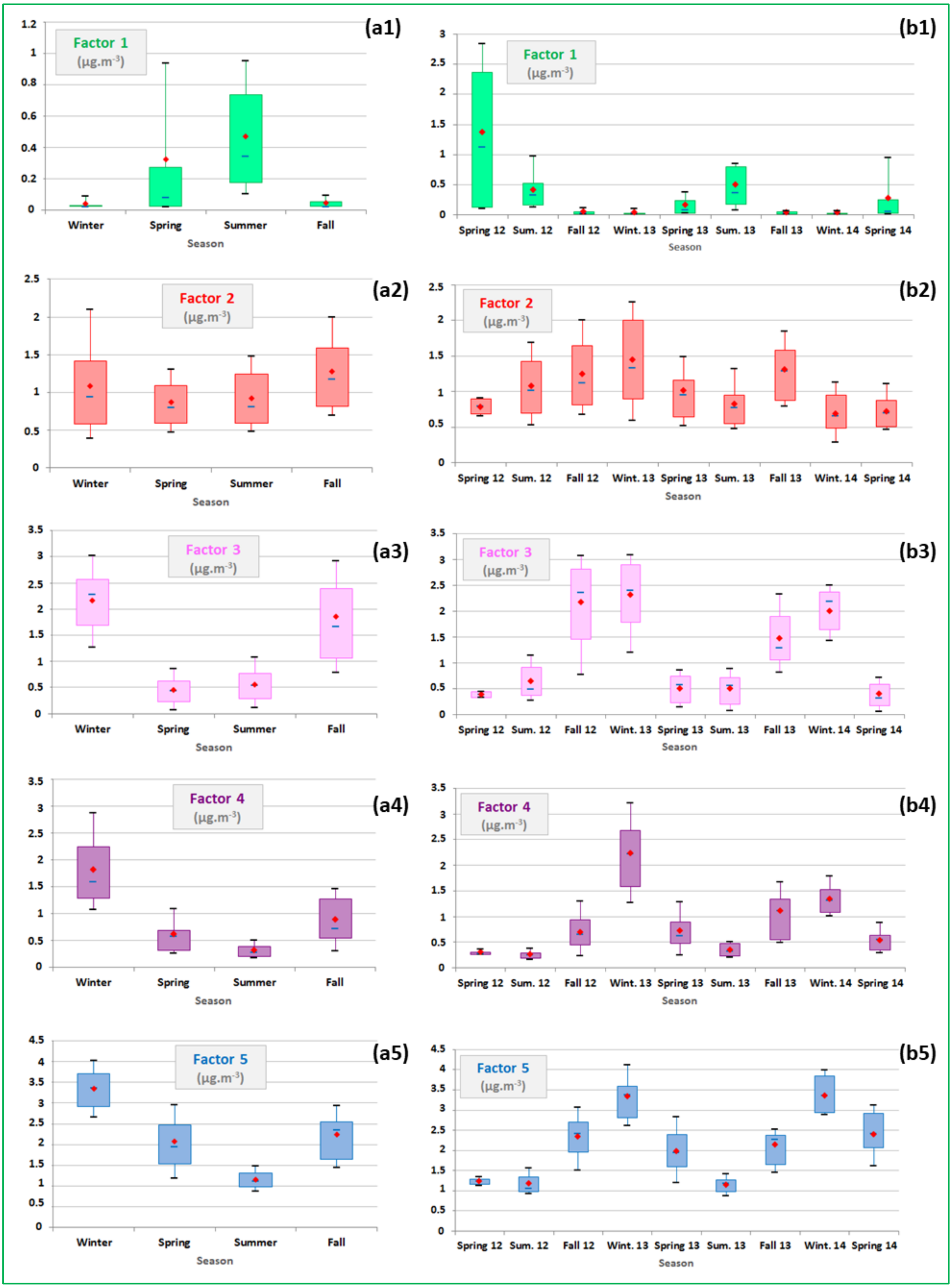


Figure S3: Seasonal (a) and interannual (b) variations in NMHC factor contributions (expressed in µg m^{-3}) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict the first and the third quartiles (i.e. Q1 and Q3) and the ends of the whiskers correspond to the first and the ninth deciles (i.e. D1 and D9). NMHC factors: 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. 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 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).”

19/Sect. 3.5.1, Page 17, line 6

“troposphere is” instead of “troposphere was”?

Past tense is used as we have reported lifetimes of isoprene measured during the 2-yr period, even if isoprene lifetime is generally low. We modified the sentence to avoid any confusion (Page 15, lines 3-5 of the revised manuscript):

“The estimated tropospheric lifetime of isoprene was quite short (winter: 5.6 h and summer: 1.1 h), indicating that this compound was emitted mostly by local vegetation.”

20/Sect. 3.5.1, Page 17, line 1

“to the sum of measured VOC concentrations”: do you include OVOC in this calculation? Anyway, because the list of the VOCs included in the PMF is not exhaustive, the average individual contribution of each factors to the sum of the measured VOCs should be considered with care.

We did not include OVOCs in the calculation as the revised Sect. 3.5 (“Major NMHC sources”) presented NMHC sources only. However, we insisted more in the revised manuscript on the fact that the relative factor contributions are relative to the selected NMHCs for the PMF analysis.

As a consequence some corrections were applied to the revised Sect. 3.5 (Page 14, lines 10-15):

“In the coming section, major NMHC primary 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) and a dataset composed of 14 variables (selected NMHCs measured by steel canister, 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 concentrations of the selected NMHCs in this factorial analysis, respectively.”

Precisions were brought to the revised Sects. 3.5.1-3.5.5 to better specify concerned VOCs in the calculation. For instance “the sum of measured VOCs” was replaced by “the sum of selected measured NMHCs” or “the selected measured NMHCs” in the revised manuscript.

21/Sect. 3.6, Page 20, line 27

Page 20 “Towards the best experimental strategy to characterize variation in VOC concentrations” Larges parts of this section are copy/paste of the section S4 of the SI (page 20, line 28to page 21, line 2; similar to page 10 of the supporting information, lines 1-6 ; page 21,lines 8-19 similar to page 12 of the SI, lines 22-34).

Following referee #1’s remark, information in the revised Sect. 3.5.6 (“Towards the best experimental strategy to characterize variation in VOC concentrations observed at a remote background site“) have been clearly distinguished from those indicated in the Sect. S5 (“Comparisons of VOC source apportionment with previous one performed at Ersa”). The Sect. 3.5.6 now focuses on the relevance of the PMF solution considering the limited range of VOCs examined in this study (see response to referee #2 comment 49). The Sect. S5 has been limited to comparative results. As a result, the information initially repeated in the Sect. S5 was removed in the revised Supplement.

22/Sect. 4.1 Page 21, line 25

“are” instead of “were”.

As proposed by referee #1, the tense was changed in the sentence (Page 20, lines 4-5):

"Firstly, the 21 NMHCs have shown low concentrations during summer and spring periods (average seasonal accumulated concentration of 4.6 ±0.1 µg m^{-3}; Fig. 10) […]."

23/ Sect. 4.1, Page 21, line 25

Page 21 line 25 starting at "Note that.." to line 28 : I suggest to remove this information, it is not essential and distracts the reader from the topic of the section.

The precision on the non-taken into account of VOC concentrations during spring 2012 in Fig. 10 was removed in the revised manuscript.

24/Sect. 4.1, Page 22, lines 6-8

The authors attribute the high contribution of factor 2 (related to short lived species) in spring and summer to relatively nearby sources. Have the authors checked if the correlation with CO was improved in these specific conditions?

The correlation of factor 2 contributions with CO concentrations was not improved considering only spring and summer observations (Pearson coefficients: -0.05 during spring and summer and 0.22 during the 2-yr period). Note that CO measurements were only performed in spring and summer 2013 (see Fig. S1; response to referee #1 comment 3).

25/Sect. 4.2, Page 24, line 24

I don't understand the meaning of the last sentence. Please rephrase "As a consequence, this finding...may be reflected..."

The sentence was removed in the revised Sect. 4.2 ("VOC concentration variations in fall and winter"). However, this information was rewritten in the conclusion for clarity (from Page 26 line 33 to Page 27 line 3) as followed:

"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)."

26/Sect. 5 and Sect. 2.2.4

Page 7, section 2.2.4 ("Concurrent VOC measurements performed at other..") I would suggest shortening this section merge it with section 5. Both sections start with the same 4 lines.

As proposed by referee #1, we removed in the revised manuscript the section 2.2.4 and merged it in Sect. S7 ("Concurrent NMHC measurements performed at other European background stations"). As a consequence, the Fig. 2 of the initial version of the manuscript was also moved in Sect. S7 (as Fig. S18) and Sect. 5 ("VOC concentration variations in continental Europe") was modified. Correction applied in the revised manuscript in Sect. 5 (Page 23, lines 18-23):

"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 considered European monitoring stations (including Ersa). "

Section S7 in the Supplement is the following:

“Section S7: Concurrent NMC measurements performed at other European background monitoring stations

From June 2012 to June 2014, NMHC measurements were concurrently conducted at 17 other European background monitoring stations. These European stations are part of EMEP and GAW networks. Figure S18 shows their geographical distribution. They cover a large part of western and central Europe from Corsica Island in the south to northern Scandinavia in the north, are located at different altitudes (up to 3580 m a.s.l.) and most of them are categorized as GAW ‘regional stations for Europe’. More information on these stations can be found on EMEP (https://www.nilu.no/projects/ccc/sitedescriptions/index.html, last access: 03/04/2020) or GAW station information system (https://gawsis.meteoswiss.ch/GAWSIS//index.html#/, last access: 03/04/2020) sites. NMHC measurements were realized by different on-line (GC or proton-transfer-reaction mass spectrometer - PTR-MS) or off-line techniques (VOCs collected by steel canisters) and were reported in the EMEP EBAS database (http://ebas.nilu.no/Default.aspx, last access: 03/04/2020).

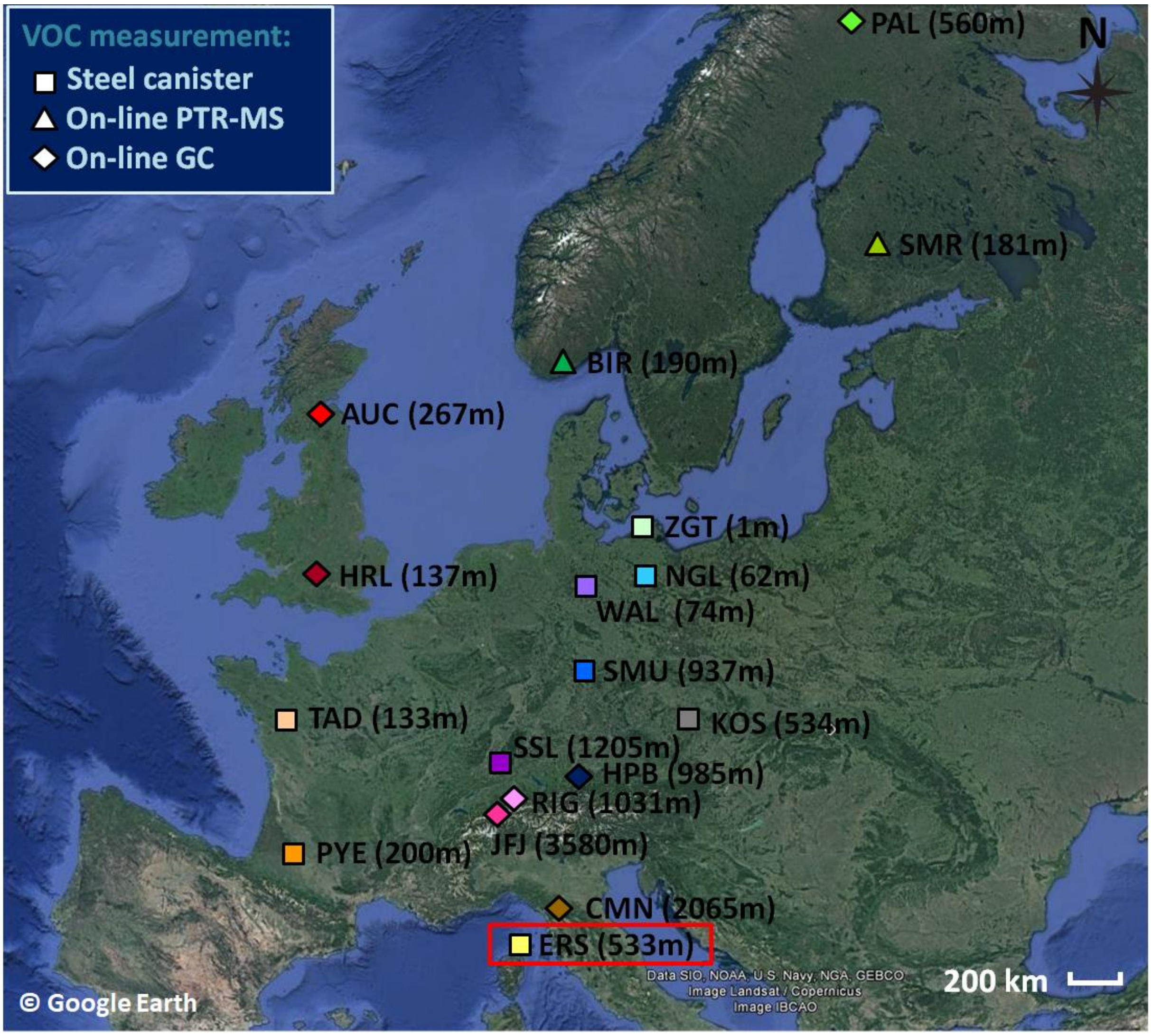


Figure S18: Locations of 18 European monitoring stations that included NMHC measurements conducted from June 2012 to June 2014. These stations are part of EMEP/GAW networks. They are characterized by their GAW identification and their altitudes are given within brackets in reference to the standard sea level. AUC, BIR, ERS, KOS, NGL, PYE, RIG, SMR, SSL and TAD are categorized as GAW ‘regional stations for Europe’. CMN, HPB, JFJ and PAL are categorized as GAW ‘global stations’. AHRL, SMU, WAL and ZGT are considered as GAW ‘other elements stations in Europe’. More precisely, ZGT is a ‘coastal station’ while HRL, SMU and WAL are ‘rural stations’. Note that high-altitude stations such as CMN and HPB could be frequently in free-tropospheric conditions. More information on these stations can be found on EMEP (https://www.nilu.no/projects/ccc/sitedescriptions/index.html, last access: 03/04/2020) or GAW station information system (https://gawsis.meteoswiss.ch/GAWSIS//index.html#/, last access: 03/04/2020) sites.

The Ersa site is underlined in red. Square markers indicate that VOCs were collected by steel canisters and analysed thereafter at laboratories (i.e. off-line measurements). Triangle and diamond markers indicate that VOC measurements were conducted in-situ using PTR-MS or GC systems, respectively. NMap provided by Google Earth Pro software (v.7.3.3 image Landsat/Copernicus – IBCAO; data SIO, NOOA, U.S, Navy, NGA, GEBCO; © Google Earth).”

27/Sect. 5, Page 25, line 18

Page 25 line 18 Please rephrase “were also be taken”.

As recommended by referee #1, this sentence was modified in the revised manuscript (Page 24, lines 1-3):

“In addition, despite its shorter lifetime compared to other NMHCs of the selection, ethylene concentration variations were also examined in this study to investigate short-lived anthropogenic source importance and variability in continental Europe.”

acp-2020-607: “Seasonal variation and origins of volatile organic compounds observed during two years at a western Mediterranean remote background site (Ersa, Cape Corsica)”

The manuscript presents observations of VOCs at the Ersa site in Cape Corsica over a two-year period and provides a comprehensive description and analysis of their behaviour during this time. PMF analysis of the data is presented along with comparison to other station across Europe. The plots are clear and generally well presented. The length of the manuscript, however, is something of a problem with lots of repetition throughout. I am sure there is an interesting story here, but it is difficult to assess what that is from the current article. Careful consideration of each section, it’s findings and their relevance is required in order to make the manuscript worthy of publication. I therefore recommend a major revision of the manuscript. I do however, urge the authors to continue to work on this as I feel it can be a very nice piece. The authors should consider writing the manuscript in terms of the features observed at the site and then use the data and plots to explain that behaviour. In its current format, each compound or group is considered separately and methodically (which leads to a comprehensive, but repetitive narrative) whereas, the behaviour of these different compounds can often be explained by the same phenomena (e.g. a changing boundary layer or temperature difference). I have included suggested changes to individual sections, but these may not be relevant to the newly written article.

Authors’ responses to Referee #2

We would like to thank the Referee #2 for her/his general feedback and each of her/his useful comments/questions for improving the quality of this manuscript. All comments addressed by both referees have been taken into account in the revised version of the manuscript.

As suggested by both referees, the revised manuscript was largely rewritten. The introduction was shortened. Complementary information on the VOCs selected in this study and on the PMF analysis are now provided in the Supplement (Sects. S1 and S2, respectively). Sections on results have been reviewed in order to better separate information provided by them and hence removed repetitive ones. Section 3.1 (“Meteorological conditions”) was shortened only keeping essential pieces of information to the explanation of seasonal and interannual VOC variations. Descriptive Sects. 3.3 and 3.4 (“VOC mixing ratios” and “VOC variability”, respectively) have been limited to the presentation of VOC concentration levels, their abundance and their variations and elements of interpretations linked to factors controlling them were removed or moved in Sect. 4 (“Discussions on the seasonal variability of VOC concentrations”). Sect. 3.4.1-3.4.3 were rewritten grouping results to emphasize similar or different VOC behaviours. Note that a larger number of OVOCs is now considered in the Sect. 3.4.3 (“Oxygenated VOCs”) and comparisons with other VOC measurements performed at Ersa were moved in the revised Supplement (Sect. S4). Section 3.5 (“Major NMHC sources”) was limited to the presentation of the 5 NMHC factors identified in this study and results on their seasonal and interannual variations were removed or moved in Sect. 4. The other factorial analysis previously realized with the summer 2013 VOC dataset has been better used to support factor identification in this study. As a result, Sect. 3.5.6 (“Towards the best experimental strategy to characterize variation in VOC concentrations observed at a remote background site”) has been reviewed to better highlight (i) the relevance of the PMF solution to identify NMHC sources and (ii) its limitation to examine VOC concentration variations observed at Ersa. The Sect. 3.5.6 is supported by commentary results presented in the Supplement (Sects. S5 and S6). Section 4 has been restructured in order to distinguish factors controlling VOC concentration variations in spring and summer (Sect. 4.1) from those in fall and winter (Sect. 4.2) and OVOC concentration variations have also been incorporated. The description of the 17 European sites, whose NMHC concentration variations are discussed in Sect. 5 (“VOC concentration variations in continental Europe”), was moved to the Supplement (Sect. S7). The conclusion has also been rewritten.

In this respect, several figures were notably modified, including in the supplement. Please note that figures numbers are now different in this new version. Additional sections have been added to the Supplement to present and discuss the selection of the VOCs in this study and the relevance of the PMF solution.

In the present document, authors' answers to the specific comments addressed by Referee #2 are mentioned in **blue**, while changes made to the revised manuscript are shown in **green**. The comments on the manuscript are listed as follows:

1/Abstract, Page 1, line 17:

"… The VOC speciation was largely dominated by oxygenated VOCs …"
Should this be the VOC abundance or mass? I'm not sure how speciation can be dominated.

The sentence was modified in the revised manuscript as (page 1, lines 17-18 in the revised manuscript):

"The VOC abundance was largely dominated by oxygenated VOCs (OVOCs) along with primary anthropogenic VOCs having a long lifetime in the atmosphere."

2/Abstract, Page 1, line 18:

"VOC temporal variations are then examined…"
Past tense, should be "were examined"

The sentence was modified in the revised manuscript as (page 1, line 18 in the revised manuscript):

"VOC temporal variations were then examined."

3/Abstract, Page 1, line 19:

"… and solar radiation ones."
Delete "ones"

We deleted "ones" in the revised manuscript (page 1, lines 18-19 in the revised manuscript):

"Primarily of local origin, biogenic VOCs exhibited notable seasonal and interannual variations, related to temperature and solar radiation."

4/Abstract, Page 1, line 20:

"Anthropogenic compounds have shown an increasing concentration trend in winter (JFM months) followed…"
This reads as though the concentrations increase between these months – ie March is bigger than February which is bigger than January – this doesn't appear to be the case from figure 6
"Anthropogenic compounds showed increased concentrations in winter (JFM months) followed…"

The sentence was modified in the revised manuscript as (page 1, lines 20-21 in the revised manuscript):

"Anthropogenic compounds showed increased concentrations in winter (JFM months) followed by a decrease in spring/summer (AMJ/JAS months), […]."

5/Abstract, Page 1, line 21:

"… and different concentration levels in winter periods of 2013 and 2014."
These are inevitably different, but the question is by how much are they different?
Suggest including "by up to ***XX%*** in the case of ***compoundY***"

As suggested by referee #2, the different concentration levels between the two winter periods were clarified. However, we indicated absolute differences instead of relative ones. These latter can be influenced by low concentrations inducing the highest relative differences. The sentence was modified in the revised manuscript as (page 1, lines 21-22 in the revised manuscript):

"[...], and higher concentration levels in winter 2013 than in winter 2014 by up to 0.3 µg m^{-3} in the cases of propane, acetylene and benzene."

6/Abstract, Page 1, line 21:

"OVOC concentrations were generally higher in summertime, mainly due to secondary and biogenic sources, whereas their concentrations during fall and winter were potentially more influenced by anthropogenic primary/secondary sources."

This sentence seems a little confusing to me. I agree that the secondary sources of OVOCs will be increased during summertime and that the contribution from biogenic sources will also be greater during summer. As it is written though, it sounds like the anthropogenic secondary sources only contribute to the OVOC concentrations during the winter months.

Thanks to this referee #2 remark, the sentence was modified in the revised manuscript in order not to discard anthropogenic secondary source contributions to summer OVOC concentrations (page 1, lines 22-24 in the revised manuscript):

"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."

7/Abstract, Page 1, line 26:

When listing the PMF factors, I suggest that these be listed in order of significance in terms of relative contribution.

As proposed by referee #2, PMF factors are listed in the revised abstract in order of their relative contributions to total concentrations of the 17 selected VOCs for the factorial analysis (page 1, lines 26-30 in the revised manuscript):

"A PMF 5-factor solution was taken on. It includes an anthropogenic factor (which contributed 39% to the total concentrations of the selected VOCs 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%)."

8/Abstract, Page 1, line 30:

at the receptor site are also

Suggest changing "receptor site" to ERSA station or observatory

As proposed by referee #2, "receptor site" was replaced by "the Ersa station" in the following sentence (page 1, lines 30-31 in the revised manuscript):

"Variations in these main sources impacting VOC concentrations observed at the Ersa station are also investigated at seasonal and interannual scales."

9/Abstract, Page 2, line 2:

"... winter 2014 ones could ..."

Delete "ones"

As proposed by referee #2, "ones" was removed in the following sentence (page 2, lines 3-5 in the revised manuscript):

"Higher VOC concentrations during winter 2013 compared to winter 2014 ~~ones~~ could be related to anthropogenic source contribution variations probably governed by the emission strength of the main anthropogenic sources identified in this study together with external parameters, i.e. weaker dispersion phenomena and the pollutant depletion."

10/Sect. 2.2.1. VOC measurements:

Where there any compounds measured by the multiple measurement techniques used in the study? If so, were there any comparison exercises performed to ensure consistency?

They were some VOCs measured by different measurement techniques. In Sect. S1 ("VOCs selected in this study"; see response to referee #2 comment 19), it was specified that:

"17 NMHCs were measured both by steel canisters and multi-sorbent cartridges (underlined species in Table S2) and n-hexanal was measured both by DNPH cartridges and multi-sorbent cartridges. Consistency between recovery species was checked during the intensive field campaign of summer 2013 (see Michoud et al., 2017) and was not checked a second time due to the low temporal recovery of the instruments in terms of data points. In this study, the concentrations of 17 NMHCs measured from steel canisters were retained given their higher number of observations and lower uncertainties compared to those measured with multi-sorbent cartridges. Concentrations of n-hexanal measured using DNPH cartridges were retained in this study for the same reason."

11/Sect. 3.1, Page 10, line 14:

"… and the lowest ones in winter …"
Delete "ones"

As proposed by referee #2, "ones" was removed in the following sentence (Page 9, lines 7-8 in the revised manuscript):

"Air temperature observed during the observation period showed typical seasonal variations, i.e. the highest temperatures recorded in summer (i.e. from July to September) and the lowest ~~ones~~ in winter (i.e. from January to March)."

12/Sect. 3.1, Page 10, line 22:

Paragraph beginning "On one hand, western European …" and ending "…across the north Atlantic toward the British Isles (Kendon and McCarthy, 2015)." on P11, L7 seems excessively long. Of key relevance here (to VOC observations) is that the temperatures were different (lower in 2013) and a short statement/sentence to say the lower temperatures were observed across Europe, with relevant citations, would suffice.

As recommended by referee #2, Sect. 3.1 ("Meteorological conditions") has been shortened in the revised manuscript as follows (page 9, lines 15-21 in the revised manuscript):

"This finding could be explained by different climatic events which have occurred during these two winter periods and have concerned a large part of continental Europe. On one hand, ~~western European winter 2013 was considered rigorous and may be caused by a destabilization phenomenon of~~ the stratospheric polar vortex~~. In early January 2013, the established stratospheric polar vortex~~ underwent a sudden stratospheric warming (SSW; Coy and Pawson, 2015) in early January 2013, ~~inducing air warming inside the vortex and a weakening of the cyclonic air circulation around the vortex. Consequently, the polar vortex was moved out of its polar position towards Europe and the SSW ended up splitting the vortex into two lobes, including one setting on western Europe and the Atlantic. These events had~~ having repercussions on the tropospheric polar vortex which ~~also broke, has~~ collapsed several times towards Europe. ~~All these elements modified~~ 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 2014 characterized by its lack of cold outbreaks and nights, caused by an anomalous atmospheric circulation (Rasmijn et al., 2016; Van Oldenborgh et al., 2015; Watson et al., 2016). ~~In fact, the north Atlantic jet stream took a rather zonal orientation and with it the usual storm tracks shifted~~

~~south. On the other side of the Atlantic Ocean, the eastern part of the USA and Canada were struck by cold polar air being advected southward due to the anomalously persistent deflection of the jet stream over the USA. The contrast between cold air advection south across the USA, and the warm tropical Atlantic was likely to have been partly responsible for the persistence and unusual strength of the north Atlantic jet stream. This situation created ideal conditions for active cyclogenesis leading to the generation of successive strong extratropical storms being carried downstream across the north Atlantic toward the British Isles (Kendon and McCarthy, 2015).~~"

13/Sect. 3.1, Page 11, line 15:

"Relative humidity globally followed opposite seasonal variations than temperature and solar radiation ones."
Should read:
"Globally, relative humidity followed opposite seasonal variation to temperature and solar radiation."

As proposed by referee #2, the sentence was modified in the revised manuscript as follows (page 9, line 28 in the revised manuscript):

"Globally, relative humidity followed opposite seasonal variations to temperature and solar radiation ~~ones~~."

14/Sect. 3.1, Page 11, line 15:

"In June 2012, air was dryer compared to June 2013 and 2014 mean relative humidity values …"
Delete:
"mean relative humidity values …" they're not need ed here since these are described in the parentheses.

As proposed by referee #2, the sentence was modified in the revised manuscript as follows (page 9, lines 28-30 in the revised manuscript):

"In June 2012, air was dryer compared to in June 2013 and 2014 ~~mean relative humidity values~~ (mean relative humidity of 57 ±15%, 77 ±16% and 67 ±33% for June 2012, 2013 and 2014, respectively)."

15/Sect. 3.1, Page 11, line 17:

"The wind speed did not show a clear seasonal variation over the two years studied, except maybe higher wind speeds in April and May that could induce higher dispersion of air pollutants and could advect air pollutants from more distant sources to the receptor site."
Suggest changing to "The wind speed did not show a clear seasonal variation over the two years studied. Slightly higher wind speeds in April and May 2014 which could induce higher dispersion of air pollutants and advect air pollutants from more distant sources to the receptor site."

As proposed by referee #2, the sentence was split into two sentences in the revised manuscript as (page 9, lines 30-32 in the revised manuscript):

"The wind speed did not show a clear seasonal variation over the two years studied. Slightly higher wind speeds were noticed in April and May, which could induce higher dispersion of air pollutants and advect air pollutants from more distant sources to the Ersa station."

16/Sect. 3.1, Page 11, line 19:

"May 2014 encountered particularly windy conditions."
I don't think this sentence is warranted (only 1.5 m/s higher than April) and would suggest removing it this sentence, it is not needed

As proposed by referee #2, the sentence was removed in the revised manuscript.

17/Sect. 3.2, Page 11, line 31:

Air masses spending longer periods over the ocean will indeed have undergone more atmospheric processing, but they may also have more influence from oceanic sources of VOCs. While these are likely insignificant compared to the anthropogenic inputs from Continental Europe, I feel they should be mentioned here.

As proposed by referee #2, this piece of information was specified in the revised manuscript (page 10, lines 11-13 in the revised manuscript):

"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."

18/Sect. 3.2, Page 12, line 4:

"showed relatively close transport times"
Change to "... short transport times ..."

As proposed by referee #2, the sentence was modified in the revised manuscript. However, "short" was not used in order not to create confusion regarding transit times associated with marine air masses which were long (up to 40 h). The sentence (page 10, lines 20-21 in the revised manuscript) was modified as follows:

"On the other hand, marine air masses having short and long trajectories have both shown long transit times (40-48 h – Table 2) and Corsican-Sardinian air masses only concerned long trajectories."

19/Sect. 3.3 VOC mixing rations, P12, L8:

The statement "Descriptive statistical results for a selection of 25 VOCs, which showed significant concentration levels during the 2-yr studied period, are summarized in Table 4" implies that more VOCs were measured during the period, but are not reported here because they were below some threshold value decided upon by the authors. If this is the case, there should be a statement describing the selection criteria used to define the "significant concentration levels".

Given referee #2 feedback, the selection of VOCs retained in this study is now described in the revised supplement in Sect. S1, as follows:

"Section S1: VOCs selected in this study

In this section, the selection of the VOCs retained for this study among those measured (see Table S2) is presented. Co-eluted VOCs, i.e. n-pentanal+o-tolualdehyde measured from DNPH cartridges and 2,3-dimethylbutane+cyclopentane measured from multi-sorbent cartridges, were not considered in this study. Concentrations of b-pinene resulting from multi-sorbent cartridges were also not considered in this study for analytical reasons.

17 NMHCs were measured from both steel canisters and multi-sorbent cartridges (underlined species in Table S2) and n-hexanal was measured from both DNPH cartridges and multi-sorbent cartridges. Consistency between recovery species was checked during the intensive field campaign of summer 2013 (see Michoud et al., 2017) and was not checked a second time due to the low temporal recovery of the instruments in terms of data points. In this study, the concentrations of 17 NMHCs measured from steel canisters were retained given their higher number of observations and lower uncertainties compared to those measured with multi-sorbent cartridges. Concentrations of n-hexanal measured using DNPH cartridges were retained in this study for the same reason.

Then, to select the VOCs examined in this study, their percentages of values below their detection limit (DL) were examined and VOCs having more than 50% of their concentrations below their DL were discarded. This criteria has concerned four NMHCs measured from steel canisters (2,2-dimethylbutane, i-octane, n-octane and 1,2,4-trimethylbenzene), one carbonyl compound from DNPH cartridges (acrolein) and seven VOCs measured from multi-sorbent cartridges (2-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, 2,3,4-trimethylpentane and 1,3,5-trimethylbenzene). Furthermore, VOC average signal-to-noise (S/N) ratios were examined. This parameter determines the average relative difference between concentrations and their corresponding uncertainties, thus pondering the results in function of their quality (Norris et al, 2014). Species having a S/N ratio below 1.2 were discarded (see Debevec et al, 2017). This criteria has concerned three additional NMHCs measured from canisters (2-methylpentane, 3-methylpentane and n-heptane), two additional carbonyl compounds measured from DNPH cartridges (propanal and methacrolein) and 14 additional VOCs measured from multi-sorbent cartridges (cyclohexane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexanedecane, 1-hexene, cyclopentene, g-terpinene, styrene and n-heptanal).

Table S2: Listed VOCs as a function of family compounds and instruments. Underlined VOCs were measured by several instruments. Retained VOCs in this study are indicated in bold.

Family compounds	Steel canisters	DNPH cartridges – Chemical desorption (acetonitrile) – HPLC-UV	Solid adsorbent – Adsorption/thermal desorption – GC-FID
ALKANES	**Ethane, propane, i-butane, n-butane, i-pentane, n-pentane,** 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, **n-hexane,** n-heptane, i-octane, n-octane		i-Pentane, n-pentane, 2,2-dimethylbutane, 2,3-dimethylbutane+cyclopentane, 2-methylpentane, 3-methylpentane, n-hexane, cyclohexane, 2-methylhexane, 2,2,3-trimethylbutane, 2,2dimethylpentane, 2,4-dimethylpentane, 2,3-dimethylpentane, n-heptane, 2,3,4-trimethylpentane, i-octane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentandecane, n-hexadecane
ALKENES	**Ethylene, propene**		Cyclopentene, 1-hexene
ALKYNE	**Acetylene**		
DIENE	**Isoprene**		Isoprene
TERPENES			**a-pinene,** b-pinene, **camphene, limonene, a-terpinene,** g-terpinene
AROMATICS	**Benzene, toluene, ethylbenzene, m,p-xylenes, o-xylene,** 1,2,4-trimethylbenzene		Benzene, toluene, ethylbenzene, m,p-xylenes, o-xylene, styrene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene
CARBONYL COMPOUNDS		**Formaldehyde, acetaldehyde,** propanal, **i,n-butanals,** n-pentanal+o-tolualdehyde, **hexanal, benzaldehyde, acetone, MEK,** acrolein, methacrolein, **glyoxal, methylglyoxal**	Hexanal, n-heptanal, **n-octanal, n-nonanal, n-decanal, n-undecanal**

”

The Section S1 is introduced at the end of the revised Sect. 2.2.1 (“VOC measurements”, Page 6, lines 20-21):

“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.”

We would like to inform the referee #2 that the VOC number has increased from 25 to 35 since more carbonyl compound concentration levels and variations are discussed in the revised manuscript, following reviewer #1 suggestion (see referee #1 comment 15). Moreover, following the incorporation of Sect. S1, Table 1 was revised (see response to referee #1 comment 2).

References

Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., and Locoge, N.: Origin, and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus), Atmos. Chem. Phys., 17, 11355–11388, doi:10.5194/acp-17-11355-2017, 2017.

Michoud, V., Sciare, J., Sauvage, S., Dusanter, S., Léonardis, T., Gros, V., Kalogridis, C., Zannoni, N., Féron, A., Petit, J. E., Crenn, V., Baisnée, D., Sarda-Estève, R., Bonnaire, N., Marchand, N., Dewitt, H. L., Pey, J., Colomb, A., Gheusi, F., Szidat, S., Stavroulas, I., Borbon, A., and Locoge, N.: Organic carbon at a remote site of the western Mediterranean Basin: Sources, and chemistry during the ChArMEx SOP2 field experiment, Atmos. Chem. Phys., 17, 8837–8865, doi:10.5194/acp-17-8837-2017, 2017.

Norris, G., Duvall, R., Brown, S., and Bai, S.: EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals, and User Guide Prepared for the US Environmental Protection Agency Office of Research, and Development, Washington, DC. [online] Available from: https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf, 2014.

20/Sect. 3.3, P12, L24:

"On the contrary, larger α-terpinene contribution was noticed during the summer intensive campaign than the 2-yr observation period."
Were these observations made using the same technique or could there be some instrument bias associated with this result? It is important to clarify and state that in the text here.

This observation was made using different measurement techniques (multi-sorbent cartridges concerning the 2-yr period and online GC-FID-MS concerning the summer 2013 period). As recommended by referee #2, this precision was specified in the revised manuscript (Page 11, lines 8-10):

"Note that speciated monoterpenes were measured differently during the summer 2013 campaign, by means of an automatic analyser (see Sect. S4 in the Supplement)."

21/Sect. 3.4, P12, L28:

"… dispersion, dilution processes …"
are these the same thing?

They are not the same thing and are partly linked. Horizontal dispersion processes are mostly driven by wind while vertical dilution processes are more related to variations in PBL height. However, due to the Ersa position at the northern tip of Corsica Island, air masses observed at the receptor site can be diluted with marine ones. Moreover, given referees #1 and #2 general feedbacks, the Sect. 3.4 ("VOC variability") has been refocused in the revised manuscript to the descriptive analysis of VOC variations and factors controlling their source variations are now only discussed in the revised Sect. 4 ("Discussions on the seasonal variability of VOC concentrations"), at the exception of environmental parameters influencing BVOC emission variations. As a result, the sentence was removed. Sect 3.4 was revised as follows (Page 11, Lines 12-16):

~~“The variability in VOC concentration levels is governed by an association of factors involving source strength (e.g., emissions), dispersion, dilution processes and transformation processes (photochemical reaction rates with atmospheric oxidants; Filella and Peñuelas, 2006). At this type of remote site, it is also important to consider the origin of air masses impacting the site as distant sources can play a significant role comparatively to local sources (see Sect. 3.5).~~ Monthly and interannual variations of ~~selected~~ primary (anthropogenic and biogenic) NMHCs along with OVOCs observed at Ersa selected in this study (Sect. S1) are ~~hence~~ discussed in this section. Seasonal VOC concentration levels are indicated in Table 4. In addition, the comparison between the VOC monitoring measurements investigated in this study with concurrent campaign measurements performed during the summers of 2012, 2013 and 2014 is presented in Sect. S4 of the Supplement, in order to check the representativeness of the 2-yr observation period with regard to summer concentration levels.”

22/Sect. 3.4.1, Page 13, lines 2-18:

The authors state “Surprisingly, isoprene and α-pinene concentrations were drastically lower in July 2012…” and then go on to state that the temperature and solar radiation during July were lower, therefore, I fail to see the surprise here.

The bigger surprise here seems to be that the July 2013 isoprene falls below the July 2012 level despite the temperature and solar radiation being higher (increasing emissions) and the wind speed being lower (increasing dispersion) during that period. Perhaps including the wind direction in figure 4 may help to explain this?

Considering referee #2 remark, “Surprisingly” was removed in the sentence in revised manuscript and the sentence was rewritten to examine July and August variations in 2012 and 2013.

We do not understand referee #2 remark on isoprene concentrations in July 2012 and 2013 since isoprene concentrations in July 2012 (black line in Fig. 4) were lower than in July 2013 (green line in Fig. 4), consistently with temperature and light variations (Fig. 3).

Dispersion is rather favoured by high wind speeds while low wind speeds can enhance BVOC accumulation and degradation considering their short lifetimes. However, high wind speeds also increased dilution by air masses owing to the Ersa position on the northern tip of Corsica Island. The Ersa station is also surrounded by vegetation (maquis) and oak forests, that’s why we did not consider 4h-average wind directions to explain BVOC variations. Corrections applied in Sect 3.4.1 (“Biogenic VOCs”; from Page 11 line 32 to Page 12 line 5 in the revised manuscript):

“Moreover ~~Surprisingly~~, isoprene and α-pinene concentrations were ~~drastically~~ higher in July and August 2013 (0.5 ±0.3 and 1.1 ±0.4 µg m^{-3}, 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 radiation was lower in July and August 2012, temperature was slightly lower in July 2012 and mean wind speed was slightly higher in July 2012 (Fig. 3), which could affect biogenic emissions and favour their dispersion and their dilution by marine air masses owing to the position of the Ersa station (Sect. 2.1).”

We would like to inform referee #2 that Fig. 4 was modified in the revised manuscript, following the incorporation of additional BVOCs into the discussion of their variabilities in Sect. 3.4.1 ‘”Biogenic VOCs”):

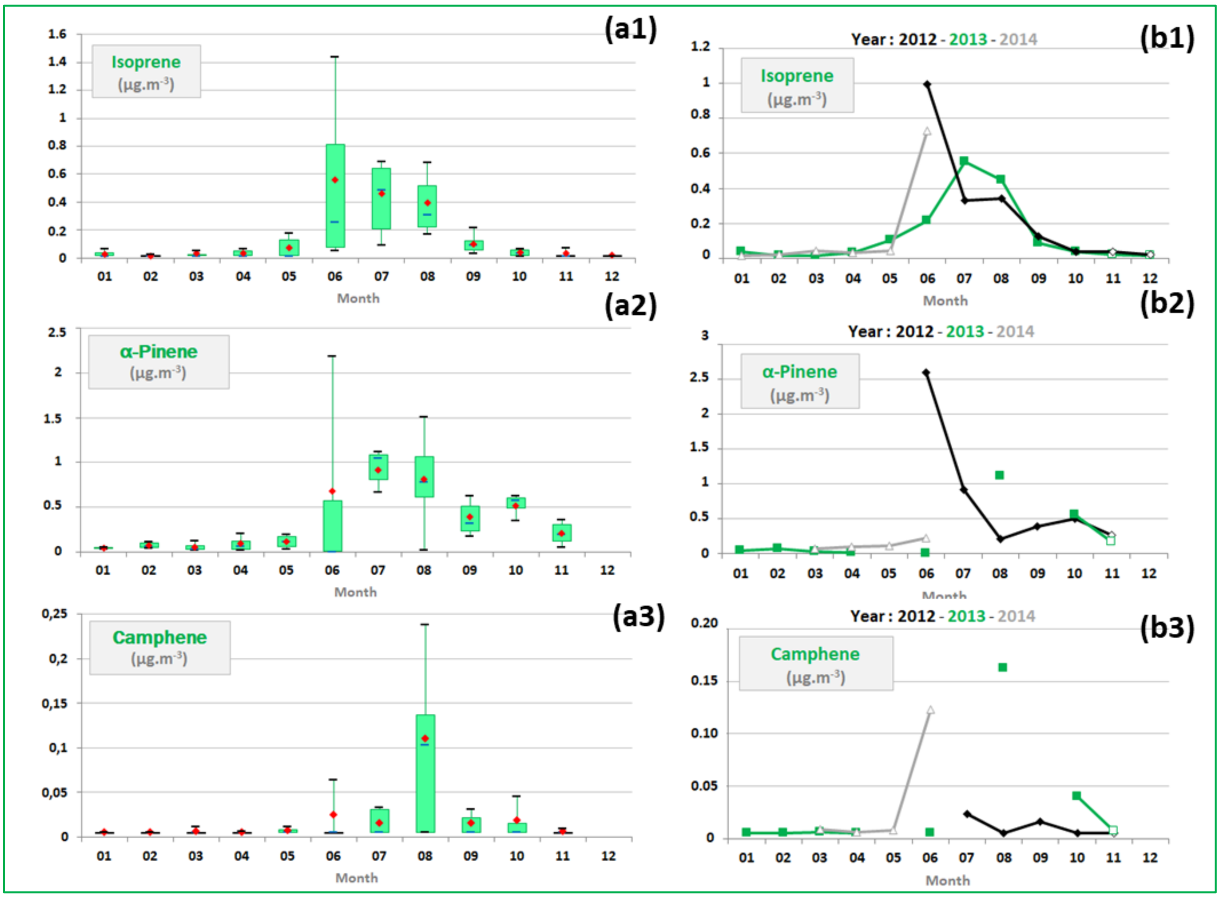


Figure 4: (a) Monthly variations in a selection of biogenic VOC concentrations (expressed in µg m⁻³) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict 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."

23/Sect. 3.4.1, Page 13, line 10:

"… which may be related to the fact that temperature and solar radiation were more favourable to enhance biogenic emissions in June 2012 compared to June 2013 and 2014 meteorological conditions …"

There is also the effect of relative humidity to consider here. Figure 4 shows the relative humidity was lower in June 2012 and 2014 compared to 2013, see the work of Ferraci et al. for the effect of drought conditions on the emissions of isoprene. Links to this research would be useful here.

We thank referee #2 for the indication of this interesting recent work (Ferracci et al., 2020) on controlling parameters of isoprene emissions. As proposed by referee #2, this research was integrated in the revised manuscript to support drought impact on BVOC emissions (Page 11, lines 24-32 in the revised manuscript):

"For instance, higher mean concentrations of isoprene and α-pinene were noticed in June 2012 (1.0 ±1.1 and 2.6 ±1.4 µg m⁻³ for isoprene and α-pinene, respectively) and June 2014 ones (0.7 ±0.5 and 0.2 µg m⁻³) compared to 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 biogenic emissions in June 2012 and 2014 compared to in June 2013 meteorological conditions (Sect 3.1). Due to relative humidity values observed in June 2012 and 2014, which were lower than in June 2013, we cannot rule out that an increase of BVOC concentrations may be related to a transient drought stress-induced modification of BVOC emissions (Ferracci et al., 2020; Loreto and Schnitzler, 2010; Niinemets et al., 2004)."

References

Ferracci, V., Bolas, C. G., Freshwater, R. A., Staniaszek, Z., King, T., Jaars, K., Otu-Larbi, F., Beale, J, Malhi, Y., William Waine, T., Jones, R. L., Ashworth, K. and Harris, N. R. P.: Continuous isoprene measurements in a UK temperate forest for a whole growing season: Effects of drought stress during the 2018 heatwave, Geophysical Research Letters,47, e2020GL088885, https://doi.org/10.1029/2020GL088885, 2020.

Loreto, F. and Schnitzler, J.-P.: Abiotic stresses and induced BVOCs,Trends Plant Sci.,15,154–166,https://doi.org/10.1016/j.tplants.2009.12.006, 2010.

Niinemets, Ü., Loreto, F., and Reichstein, M.: Physiological and physicochemical controls on foliar volatile organic compound emissions, Trends Plant Sci., 9, 180–186, https://doi.org/10.1016/j.tplants.2004.02.006, 2004.

24/Sect. 3.4.1, Page 13, line 16:

"This finding could be the result of a weaker degradation of α-pinene due to lower ozone concentrations observed from October to December compared to summer …"
Emissions of isoprene are light and temperature dependant while monoterpenes are thought to be solely temperature dependant. I'd suggest that the difference in seasonal cycles of isoprene and alpha-pinene is due to the difference between the solar radiation and temperature profiles: solar radiation falls much quicker than temperature which may have the effect of "switching off" the isoprene emissions before the alpha-pinene emissions.

Monoterpenes emissions dependency is related to the emitting vegetation type (e.g., Owen et al., 2002). Emissions of monoterpenes are solely dependent on temperature when they are produced by plants disposing of a storage capability (Laothawornkitkul et al., 2009). Otherwise, their emissions are dependent on both temperature and solar radiation. During the intensive summer observation period, diel concentration variations of monoterpenes were examined (Kalogridis, 2014). They showed similar diel variations to isoprene. Hourly concentration variations of monoterpenes and isoprene were also well correlated, suggesting a common predominant source and similar dependence on the environmental parameters governing their emissions. Concentrations of monoterpenes were also correlated with both temperature and light (Kalogridis, 2014) as isoprene, confirming environmental parameters controlling their emissions in summer. As a result, monoterpenes measured at the Ersa station are not thought to be solely temperature dependent over the entire observation period.

However, the specific seasonal behavior of monoterpenes in fall could highlight additional sources from different emitting plants than those predominantly observed in summer. As indicated by referee #2, solar radiation fell much quicker than temperature in fall which may have the effect of "switching off" the biogenic emissions from plants not having storage capacity. Persistent concentration levels of monoterpenes in fall could be resulted from biogenic emissions, solely dependent on temperature, from plants having storage capability. Nevertheless, hourly BVOC measurements would have been helpful to confirm this statement.

Following this discussion, we slightly modified interpretations of fall BVOC concentration levels as follows (Page 12, lines 5-11):

"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 (see Fig. S2 of the Supplement) also pointed out a weaker degradation of α-pinene in fall."

References

Kalogridis, A.: Caractérisation des composés organiques volatils en région méditerranéenne, Université Paris Sud - Paris XI. [online] Available from: https://tel.archives-ouvertes.fr/tel-01165005, 2014.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D., and Hewitt, C.N.: Biogenic volatile organic compounds in the Earth sys-tem, New Phytol., 183, 27–51, https://doi.org/10.1111/j.1469-8137.2009.02859.x, 2009.

Owen, S. M., Harley, P., Guenther, A., and Hewitt, C. N.: Light dependency of VOC emissions from selected Mediterranean plant species, Atmos. Env., 36, 3147-3159, 2002.

25/Sect. 3.4.2, Page 13, line 16:

"… characterized by almost the same seasonal variation …"
Replace with "similar": "… characterized by similar seasonal variation …"

As proposed by referee #2, "almost the same seasonal" was replaced in the following sentence (page 12, lines 18-19 in the revised manuscript):

"Despite lifetimes in the atmosphere ranging from a few hours to some days, all selected NMHCs were characterized by similar seasonal variation, […]."

26/Sect. 3.4.2, Page 13, line 27:

"… considering its low photochemical reaction rate with OH radicals …"
"… due to its low photochemical reaction rate with OH radicals …"

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

27/Sect. 3.4.2, Page 13, line 27:

"… with the highest atmospheric lifetime …"
Replace with "Longest": "… with the longest atmospheric lifetime …"

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

28/Sect. 3.4.2, Page 13, line 28:

"… It is typically emitted by natural gas use and can be also considered as a tracer of the most distant sources."
Transport and storage of natural gas are also important sources here.

We thank the referee #2 for this proposition but this sentence was removed in the revised manuscript, as the Sect. 3.4.2 was refocused on the description of NMHC concentration variations and hence source information was removed. However, this precision was considered in Sect. 3.5.3 ("Evaporative sources (factor 3)") in the following sentence (Page 16, lines 11-12 in the revised manuscript):

"Additionally, propane can be viewed as a relevant profile signature of natural gas transport, storage and use (Leuchner et al., 2015)."

It was also considered in Sect. 3.5.5 ("Regional background (factor 5)") in the following sentence (page 17, lines 7-9 in the revised manuscript):

"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 […]"

29/Sect. 3.4.2, Page 14, line 2:

"… four to ten times higher than ethane one (Atkinson, 1990; Atkinson and Arey, 2003)"
Remove "one", it's not required here.

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

30/Sect. 3.4.2, Page 14, line 4:

"… e.g., Leuncher et al., 2015)."
Should be "Leuchner"

We thank the referee #2 for this remark, but the sentence was removed in the revised manuscript since the Sect. 3.4.2 ("Anthropogenic VOCs") has been refocused on the description of NMHC concentration variations. However, this typo was corrected elsewhere in the revised manuscript (e.g., see response to referee #2 comment 28).

31/Sect. 3.4.2, Page 14, line 6:

"… winter 2014 ones."
Remove "ones", it's not required here.

We thank the referee #2 for this remark, but the sentence was removed in the revised manuscript and was replaced by the following sentence (page 12, lines 24-26 in the revised manuscript):

"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)."

32/Sect. 3.4.2, Page 14, line 11:

As a result, winter variations of concentration levels concerned at a time close sources and more distant ones and will be more investigated thereafter (Sect. 4.2)."
I don't think this sentence makes sense. Just a statement that the winter period will be investigated later in the manuscript would suffice.

We thank the referee #2 for this remark, but the sentence was removed in the revised manuscript since the Sect. 3.4.2 ("Anthropogenic VOCs") has been refocused on the description of NMHC concentration variations.

33/Sect. 3.4.3, Page 14, line 21:

"Nevertheless, acetaldehyde is only produced as a second or higher-generation oxidation product of isoprene for all its reaction pathways with atmospheric oxidants (Millet et al., 2010)."
I don't know what this means – further clarity in the text is needed here.

It means that acetaldehyde is produced by the oxidation of first-generation oxidation products of isoprene (those directly produced from the oxidation of isoprene). However, this sentence was removed in the revised manuscript as we did not precise acetaldehyde secondary sources in the revised Sect. 3.4.3 ("Oxygenated VOCs", following referee #2 general comment and referee #1 comment 16.

34/Sect. 3.4.3, Page 14, line 30:

"… with air temperature one,"
Remove "one", it's not required here.

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

35/Sect. 3.4.3, Page 14, line 31:

"… which can denotes that"
Replace with "denote": "… which can denote that"

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

36/Sect. 3.4.3, Page 14, line 32:

"These findings are in agreement with a large result on BVOC oxidation on the local photochemistry."
Remove this sentence, not required.

As suggested by referee #2, this sentence was removed in the revised manuscript.

37/Sect. 3.4.3, Page 14, line 32:

"… remained relatively significant during fall …"
significant to what?

We used "significant" in the sense of "high". However, in the revised manuscript, we only present their more important variations (those in summer). Information on minor contributions were hence removed, including this sentence.

38/Sect. 3.4.3, Page 15, line 9:

"and since meteorological conditions in August 2013 were more favorable to photochemical processes"
What "meteorological conditions" do the authors refer to here? If it is just the higher solar radiation, then state this in the text.

In the revised manuscript, meteorological conditions in August 2012 and 2013 are now discussed in the Sect. 3.4.1 ("Biogenic VOCs", see response to referee #2 comment 22). As a result, these meteorological conditions are not discussed a second time in Sect. 3.4.3 ("Oxygenated VOCs") and the sentence was removed and replaced in the revised manuscript by (Page 13, lines 11-14):

"For instance, the methylglyoxal highest concentrations were monitored in June 2012 (0.7 µg m^{-3}), similarly to isoprene (Sect. 3.4.1). 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). Formaldehyde showed high concentrations both in June 2012 and August 2013 (2.9 and 3.6 µg m^{-3}, respectively)."

39/Sect. 3.4.3, Page 15, line 17:

"Acetone is the OVOC of the selection with generally the highest atmospheric lifetime, considering its photochemical reaction rate …"
Unclear, suggest changing to: "Of the measured OVOCs, acetone has the longest atmospheric lifetime, considering its photochemical reaction rate …"

As proposed by referee #2, the sentence was modified in the revised manuscript (from Page 12 line 32 to Page 13 line 4):

"Formaldehyde, acetaldehyde, glyoxal, methylglyoxal and C$_6$-C$_{11}$ aldehydes have relatively short lifetime 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 the OVOCs selected in this study, and hence they can also result from distant sources and/or be formed within polluted air masses before they reach the Ersa station."

40/Sect. 3.4.3, Page 15, line 22:

"Acetone showed similar seasonal variations than formaldehyde and acetaldehyde, …"
Replace with "to": "Acetone showed similar seasonal variations to formaldehyde and acetaldehyde, …"

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript. It was replaced by (page 13 lines 15-16 in the revised manuscript):

"Acetaldehyde and acetone have shown similar seasonal variations, with an increase of their concentrations more marked in summer than in winter (Fig. 6), […]."

41/Sect. 3.4.3, Page 15, line 25:

"… remained significantly high during winter …"
Significant to what? Either include a parameter or remove "significantly" from the sentence.

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

42/Sect. 3.4.3, Page 15, line 28:

"… than summer 2013 one, …"
Remove "one", it's not required here.

We thank the referee #2 for this proposition but this sentence was removed in the revised manuscript.

43/Sect. 3.4.3, Page 15, line 30:

"… than winter 2014 one, …"
Remove "one", it's not required here.

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript. It was replaced by (page 13 lines 24-26 in the revised manuscript):

"Additionally, acetaldehyde and acetone concentration variations in winter (e.g., mean February concentrations higher by 0.5 and 2.4 $\mu g\,m^{-3}$ in 2013 than in 2014, respectively) also pinpointed primary/secondary anthropogenic origins (Sect. 3.4.2)."

44/Sect. 3.4.3, Page 15, line 30:

"… but admitted low enough to allow advection to the receptor site …"
Delete admitted", not needed here.

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

45/Sect. 3.4.3, Page 16, line 2:

"… from other OVOC ones …"
Remove "ones", it's not required here.

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

46/Sect. 3.4.3, Page 16, line 2:

"Indeed, MEK concentrations did not show seasonal variations except an increasing winter trend …"

Increased concentrations in winter sounds very much like a seasonal variation. From figure 7, it appears that there is a weak seasonal cycle droning 2013, but this is not replicated (or at least not so clear) in the other years.

MEK seasonal variations were presented differently in the revised manuscript (Page 13, lines 27-30):

"Glyoxal and MEK showed an increase of their concentrations both in summer and winter (Fig. 6 and Table 4), suggesting they were probably produced by several biogenic and anthropogenic sources. Those of glyoxal were in similar proportions (Fig. 6 and Table 4) while MEK increase in winter was more marked than in summer, which may indicate that primary/secondary anthropogenic sources primarily contributed to MEK concentrations."

In 2013, MEK showed an increase of its concentrations in winter, but it was not measured in summer 2013. As a result, potential biogenic contributions could have occurred in summer 2013 and could change MEK seasonal variations interpretations in 2013.

47/Sect. 3.4.3, Page 16, line 6:

"… in February 2013 was by 0.2 µg m-3 higher than …"
Remove "by", it's not required here.

As proposed by referee #2, the sentence was modified in the revised manuscript as follows (from Page 13, line 33 to Page 14 line 1):

"Glyoxal and MEK both exhibited different concentration levels during the two studied winter periods since their mean concentration in February 2013 was 65-75% higher than in February 2014, confirming their links with anthropogenic sources"

48/Sect. 3.4.4, Comparisons with other VOC measurements performed at Ersa

I don't think this section is needed as it doesn't say a lot. Perhaps the link to the supplementary material could be included in one of the earlier discussion sections.

As recommended by both referees #2 and #1 (comment 4), we removed Sects. 2.2.3 ("Additional high frequency VOC measurements performed at Ersa") and 3.4.4 ("Comparisons with other VOC measurements performed at Ersa") and merged all these results in the revised Sect. S4 ("Comparison of VOC measurements with other ones performed at Ersa"). In the revised manuscript, the Sect. S4 is now introduced in Sect. 3.4. ("VOC variability"). Correction applied in the revised manuscript in Sect. 3.4 (Page 11 lines 13-16):

"In addition, the comparison between the VOC monitoring measurements investigated in this study with concurrent campaign measurements performed during the summers 2012-2014 is investigated in Sect. S4 of the Supplement, in order to check the representativeness of the 2-yr observation period with regard to summer concentration levels."

49/Sect. 3.5 VOC factorial analysis

Perhaps some further explanation of the reasoning behind choosing a subset of the measured compounds is required here? Along with a discussion of whether limiting the number of species that are included in the PMF analyses may well affect the result and the number of factors. Perhaps a discussion of how the results here compare to the shorter, intensive campaign results published earlier would help here?

Firstly, as suggested by referee #2, the selection of the 35 VOCs retained in this study is now presented in the revised Supplement in Sect. S1 ("VOCs selected in this study"; response to referee #2 comment 19). Additionally, the methodology of the selection of the PMF solution is now presented in Sect. S2

("Identification and contribution of major sources of NMHCs by PMF 5.0 approach"; in response to referee #1 comment 7). It is specified that (in S2.2 "VOC dataset and data preparation"):

"In order to have sufficient completeness (in terms of observation number), only primary HCNM measurements from bi-weekly ambient air samples collected into steel canisters from 04 June 2012 to 27 June 2014 were retained in this factorial analysis. The NMHC dataset encompassed 152 atmospheric data points having a time resolution of 4 hours. VOC observations resulting from DNPH and multi-sorbent cartridges were not considered in the PMF analysis since they were sampled only 73 and 52 days concurrently to the collection of steel canisters (Fig. S1). Reconstruction of missing data points would significantly affect the dataset quality. Additionally, the restriction of the number of data points to those common to the three datasets (36 data points) would significantly impact the temporal representativeness of the VOC inputs of the study period and hence limiting the discussion on interannual and seasonal variations for statistical robustness reasons. Note that no outlier was removed from the dataset."

Note that, a developed discussion on the limited number of VOCs retained for the PMF analysis is proposed in response to referee #1 comment 10. Moreover, the consideration of the PMF solution of the shorter campaign to consolidate our results has been specified in the revised Sect. 3.5 ("Major NMHC sources", page 14 lines 26-29):

"Since the low number of NMHCs considered in the factorial analysis in this study, PMF result relevance was checked, benefiting from previous PMF analysis performed with the Ersa VOC summer 2013 dataset (42 variables; Michoud et al., 2017) and experimental strategies to characterize VOC concentration variations are discussed in Sect. 3.5.6."

We referred to the summer 2013 PMF solution when we encountered limitations with the 2-yr PMF solution (in Sect. 3.5.1 "Local biogenic source (factor 1)" and Sect. 3.5.2 "Short-lived anthropogenic sources (factor 2)"; see responses to referee #1 comments 6 and 9).

Finally, a discussion on the limited number of species to PMF results has been incorporated in the Sect. 3.5.6 ("Towards the best experimental strategy to characterize variation in VOC concentrations observed at a remote background site") and supported by comparisons of PMF results presented in Sect. S5 ("Comparisons of VOC source apportionment with previous one performed at Ersa") and Sect. S6 ("Examination of a summer 2013 PMF solution realized considering the 17 NMHCs selected in this study", see response to referee #1 comment 10). Section 3.5.6 has hence been reviewed to better highlight the relevance of the PMF solution to identify primary NMHC sources and its limitation to examine VOC concentration variations observed at Ersa. Corrections applied to Sect. 3.5.6 (from Page 17, line 26 to Page 19, line 23 in the revised manuscript):

"The choice to restrain the number of VOCs in the factorial analysis, to have a better temporal representativeness of factor contributions (Sect. S2), as well as VOC measurement temporal resolution and collection periods and the number of observations, have undoubtedly had some consequences on the PMF solution results of this study (in terms of factor number, chemical profiles and variations). As a result, the 2-yr PMF results of this study 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 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 the 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) 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 factorial analyses as influencing VOC concentrations at Ersa had similar chemical compositions, regarding NMHCs in common. This finding supported the relevance of the 17 NMHCs selected in the factorial analysis of this study to identify major primary sources which have influenced Ersa VOC concentrations over two years and suggested that these selected NMHCs included dominant tracers of these sources.

To support this statement, a summer 2013 PMF solution, realized considering only the 17 NMHCs selected in the factorial analysis of this study as inputs, was examined and compared with the summer 2013 PMF solution modelled with a higher number of VOCs by Michoud et al. (2017; Sect. S6 in the Supplement). Results 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 have depended on additional VOCs – Sect. S6). PMF factorial analyses have hence shown limitations in the investigation of short-lived anthropogenic sources influencing Ersa VOC concentrations, given 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).

Furthermore, the 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 for a better assessment of the contribution of local biogenic sources, considering BVOC day-to-day variations, as noticed in summer 2013 (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 by the fact that different interannual BVOC concentration variations were noticed between isoprene and selected speciated monoterpenes in Sect. 3.4.1. Concentrations of non-speciated monoterpenes measured in summer 2013 were mainly attributed to the same primary biogenic source as for isoprene concentrations in Michoud et al. (2017). But variations in the sum of monoterpenes may have reflected those related to abundant biogenic species such as α-pinene, and masked those characterizing more-reactive species such as α-terpinene (Kalogridis, 2014; Debevec et al., 2018).

The limited range of VOCs included in the PMF study had the advantage to better deconvolve 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 elevated background levels (like for ethane, methanol and acetone of the summer 2013 VOC dataset; Michoud et al., 2017). These low concentrations thus represented a higher proportion 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 at a remote background site such as Ersa to support results from source apportionment, in terms of deconvolution of anthropogenic sources. Indeed, anthropogenic sources identified with the 4-h observations in this study have shown some significant correlations between them (Sect. S5), as a consequence of their similar seasonal variations (Sects. 3.4.2 and 4). The consideration 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 of main primary sources influencing VOC concentrations observed at the Ersa station (Sects. S5 and S6), but can modify their relative contributions, emphasizing the contribution of local biogenic/anthropogenic sources and decreasing the contribution of regional anthropogenic sources (Michoud et al, 2017). The VOCs observed at Ersa were largely dominated 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 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 primary sources, but the limited number of samples realized with DNPH cartridges did not favor it (Fig. S1 and Sect. S2). Formaldehyde has shown high concentration levels (Table 1) and clear seasonal variation (Sect. 3.4.3) in this study and would have been of high interest to be considered in the summer 2013 PMF analysis."

50/Sect. 3.5, Page 16, line 27:

"… should rather be explained as aged profiles originating from several sources assimilating to several source categories …"

Should this be: "… should rather be explained as aged profiles originating from several source regions comprising several source categories …"?

We thank the referee #2 for this proposition. The sentence was modified in the revised manuscript (page 14, lines 20-22 in the revised manuscript):

"A part of them may not be precisely associated with emission profiles but should rather be explained as aged profiles originating from several source regions comprising several source categories (Sauvage et al., 2009)."

51/Sect. 3.5.1, Page 17, line 6:

"The relative load of this VOC for the factor 1 is 70%."
Clarify what is meant by this statement.

It means that isoprene concentrations corresponded to 70% of the factor 1 mass. The sentence was modified in the revised manuscript (Page 15, line 3) as follows:

"The isoprene relative contribution to the factor 1 is 70%."

52/Sect. 3.5.2 Short-lived anthropogenic sources (factor 2)

The description of Factor 2 and its influences is rather vague and contains a number of potential contributing sources. This is a result of this type of analysis, but the authors need to be wary of making contradicting statements, for example describing "slightly higher contributions during fall" (P17, L27), then "factor 2 contributions were also significant in spring and summer" (P17, L32) and then "mean monthly factor 2 contributions (Fig. 10b2) pointed out no clear seasonal variation over the study period" I think this is due to the differences observed between different years and so care should be taken not to generalise here.

Given the location and the site typology of the Ersa station, we think that factor 2 encompasses different source categories (combustion processes, solvent use and gasoline evaporation) of various origins. Following the referee #2 remark, we insisted on this statement and the following sentence was modified (Page 15, lines 21-23):

"Factor 2 is hence attributed to the grouping of several short-lived anthropogenic sources, partly related to gasoline combustion and/or evaporation and solvent use."

We would like to inform referee #2 that factor 2 contribution variations were no longer presented in Sect. 3.5.2 ("short-lived anthropogenic sources (factor 2)"), since Sects. 3.5.1-3.5.5 have been refocused on the identified primary sources associated with the 5 factors of the selected PMF solution. Seasonal and interannual variations in factor contributions are now used only in Sect. 4 ("Discussions on the seasonal variability of VOC concentrations") to explain VOC concentration variations observed at the Ersa station during the 2-yr period.

In Sect. 4, we checked our statements on factor 2 contribution variations. Given the fact that factor 2 regrouped several anthropogenic sources of various origins and limitations of the PMF model to reconstruct some VOCs composing factor 2 (see responses to referee #1 comment 9 and referee #2 comment 49), we decided to limit the discussion on factor 2 contribution variation in the revised manuscript.

53/Sect. 3.5.2, Page 17, line 16:

"This latter is mainly consisted of primary anthropogenic …"
What is meant by "This latter"?

"This latter" referred to factor 2. It was used to avoid the repetition. Given referee #2 remark, it was modified in the revised manuscript (Page 15, lines 13-14):

"This factor is mainly consisted of primary anthropogenic compounds, […]"

54/Sect. 3.5.2, Page 17, line 19:

"… with an average contribution to the sum of measured VOC concentrations from this factor of 66%."
Is this correct? Looking at figure 9(b), factor 2 does not appear to ever be 66% of the total.

Here, we wanted to say that concentrations of toluene, EX, ethylene and propene contributed to factor 2 by 66%, on average (i.e. the factor 2 explained 66% on average of their concentrations). Factor 2 contribution to the total measured concentrations of the 17 NMHCs selected for the PMF analysis was 19%. Given referee #2 remark, this statement was modified in the revised manuscript (Page 15, line 16) as follows:

"The relative contribution of these VOCs to factor 2 is 66%."

55/Sect. 3.5.2, Page 17, line 31:

"… winter, conducting to less dilution of emissions, …"
suggest changing to "leading to"

We thank the referee #2 for this proposition but the sentence was removed in the revised manuscript.

56/Sect. 3.5.2, Page 17, line 32:

"However, factor 2 contributions were also significant in spring and summer …"
This only appears to be the case in 2013.

We thank the referee #2 for this proposition this sentence was removed in the revised manuscript, since Sects. 3.5.1-3.5.5 have been refocused on the identified sources associated with the 5 factors of the selected PMF solution. Seasonal and interannual variations in factor contributions are now used only in Sect. 4 ("Discussions on the seasonal variability of VOC concentrations") to explain VOC concentration variations observed at the Ersa station during the 2-yr period. To explain VOC concentration variations in spring and summer, it is indicated that (page 21, lines 1-4):

"Summer and spring contributions of short-lived anthropogenic sources seemed to be more variable as a function of the year (0.7-1.1 µg m^{-3}; Figs. 10 and S4). This finding suggests that these sources were largely influenced by origins of air masses, which advected to Ersa numerous emissions, potentially of variable strength and from various locations relatively close to Ersa."

As noticed by referee #2, an increase of factor 2 contributions occurred in spring 2013 and another one in summer 2012. However, compared to other factor contribution variations, occurring especially in winter, changes in factor 2 concentration levels in spring and summer appeared to be less significant. As a result, we decided not to stress on this point in the revised manuscript, in agreement with our decision to limit the discussion on factor 2 contribution variation in the revised manuscript (see referee #2 comment 52).

57/Sect. 3.5.2, Page 18, line 1:

"… which could illustrate an enhanced evaporation of gasoline, solvent inks, paints and additional applications during these months as a result of higher temperatures."
This is contradicted by the temperature data shown in figure 4(b1) which shows lower temperatures in June 2013 compared to 2012 and 2014 which have smaller factor 2 contributions shown in figure 10(b2). The authors go on to give explanation of these differences, but I feel it's important to highlight this anomaly here.

We thank the referee #2 for this feedback. For different reasons stated in referee #2 comment 52, we decided to limit the discussion on factor 2 contribution variation and hence this statement was removed in the revised manuscript. Given the numerous parameters potentially having an effect on sources associated with factor 2, the control of the temperature on some potential sources composing factor 2 cannot be examined distinctly to other influences, that is why we suggested only its effect on factor 2. Factor 2 contribution variations were supposed to be mainly driven by air mass origins, which could partly explain why lower factor 2 contributions were observed in June 2013 than in June 2012 and 2014.

58/Sect. 3.5.5, Page 20, line 17:

"… probably related to photochemical decay and dilution processes."
Earlier in this section the authors state that natural gas may be an important source for factor 5 so presumably a summer decrease in emissions may also contribute to the observed seasonal variation?

We thank the referee #2 for this suggestion. As the discussion on factor 5 contribution variations was removed from the revised Sect. 3.5.5 ("Regional background (factor 5)"). This information was added in Sect. 4.1 ("VOC concentration variations in spring and summer"; Page 20 lines 11-15):

"Moreover, regional background explained in spring and summer from 24 to 53% of the total Ersa concentration 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 occurred in the hot season, enhancing the decline in its 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."

59/Sect. 3.5.5, Page 20, line 21:

"Mean factor 5 contributions in function of air mass origins were in the same range, except that more elevated contributions were noticed under the influence of European air masses (especially those potentially connected to distant contributions; Fig. 11) compared to the ones related to others continental origins."
This is a confusing sentence; can it be re-written for improved clarity?

As proposed by referee #2, this sentence was rewritten in the revised manuscript (Page 17, lines 19-20):

"Factor 5 showed slightly higher contributions when the Ersa station was under the influence of European air masses (especially those having long trajectories and hence potentially connected to distant emission areas; Fig. 9)."

60/Sect. 4.1 The controlling factors

This whole section appears to re-cap the information given in section 3.5. In order to reduce the size of the manuscript, I would suggest these sections be combined to give a more concise explanation of the observations at the site. This could be by either including extra information in section 3.5 (and removing section 4

We thank referee #2 for this feedback. As a result, we decided to remove information in Sect. 3.5 ("Major NMHC sources") concerning factor contribution variations and to keep Sect. 4 ("Discussions on the seasonal variability of VOC concentrations") in the revised manuscript. As anthropogenic NMHC sources have shown similar seasonal variations, we thought that it was more relevant to discuss their variations conjunctly instead of individually. This decision was also motivated by referee #2 general comment. Note that monoterpenes and OVOC seasonal concentrations have been incorporated in Sect. 4 to support discussing changes in biogenic contributions and VOC depletion and to further discuss OVOC sources. We would like to inform referee #2 that we decided to reorganize Sects. 4.1 and 4.2 in the revised manuscript: on one hand (Sect. 4.1) the factors explaining the VOC concentration levels and their variations in spring and summer and on the other hand (Sect. 4.2) the factors controlling those in winter and fall. Sect. 4 has been revised as follows (from Page 19 line 24 to Page 23 line 16 in the revised manuscript):

“4. Discussions on the seasonal variability of VOC concentrations

In this section, seasonal accumulated concentrations of the 35 VOCs selected in this study (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 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. The coming discussion has been structured in two steps: on one hand the factors explain the VOC concentration levels and their variations in spring and summer, and on the other hand the factors controlling those in winter and fall.

4.1 Determination of controlling factors in spring and summer

Firstly, the 21 NMHCs have shown low concentrations during summer and spring 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 higher in these seasons (von Engeln and Teixeira, 2013), favouring vertical dispersion. OVOC concentration levels in summer and spring are in agreement with a higher 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, regional background explained in spring and summer from 24 to 53% of the total Ersa concentration 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 occurred in the hot season, enhancing the decline in its 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 and spring (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 reach the Ersa station (Sect. 3.4.3). As pinpointed by 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 sources (Sect. 3.5.2), their contributions were not reduced as sharply as those of other anthropogenic sources (Fig. S4), which can probably be related to a 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 (Sect. 3.5.4).

Looking now at the interannual variations during summer and spring periods, Fig. 10 highlights that the total 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 and spring contributions of evaporative sources, long-lived combustion sources, and regional background, were in the same range over the studied period, as well as MEK concentrations (0.3-0.4 µg m^{-3}; Fig. 10) which have been attributed 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 by pollutant depletion and vertical/horizontal dispersion during these seasons. Summer and spring contributions of short-lived anthropogenic sources were seemed to be more variable as a function of the year (0.7-1.1 µg m^{-3}; Figs. 10 and S4). This finding suggests that these sources were largely influenced by origins of air masses, which 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 to concentrations of monoterpenes during the two summer periods (Fig. 10) and consistent with temperature and solar radiation variations (Sect. 3.4.1). Higher summer concentrations of formaldehyde and acetone were also noticed in 2013 than in 2012 (difference 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 to a change in its biogenic primary/secondary contributions than in its background levels. These findings suggest, in summer 2013, enhanced emissions from the local vegetation partly related to the release of monoterpenes and/or higher biogenic secondary contributions. For similar reasons, slightly higher spring contributions of biogenic sources were 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 Determination of controlling factors in fall and winter

During fall and winter periods, total 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 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 OH concentrations owing to lower available UV light and temperatures (Fig. 3). Hence, VOCs were not removed from the atmosphere as quickly as in summer and spring. This statement is in agreement with OVOC concentration levels. PBL height also decreased during these seasons, impacting pollutant vertical dispersion. These conditions, favouring 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 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 to NMHC concentrations specifically in winter (explaining 18-24% of the total NMHC concentrations) since the typical low winter ambient temperatures (Fig. 3) may involve an increased use of residential heating (Sect. 3.5.4). To better identify regional influences, average winter and fall contributions of the NMHC anthropogenic sources were investigated in 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 occurrences were from 36% to 70%). NMHC anthropogenic sources showed higher accumulated contributions when European air masses were advected to Ersa (Fig 11), and could be attributed to potential emission areas located in Italy and possibly more distant potential emission areas in central Europe (Sect. 3.5). To a lesser extent, high anthropogenic source accumulated contributions 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 (below 0.1 µg m^{-3}). Indeed, 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 difference 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 regional background winter contributions monitored 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, 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 and hence their respective contributions, according to Fig 11. This statement is also in agreement the 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 primary sources showed higher accumulated winter contributions in 2013 (10.8-9.6 µg m^{-3}, respectively; Fig. 11) than in 2014 (8.2-7.8 µg m^{-3}). During winter 2013, the main potential emission areas for the 4 anthropogenic 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 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, potential emission areas located in the Po Valley and the southeast of France, known to experience high anthropogenic emissions, did not seem to have contributed 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, in winter 2014 than in winter 2013 (occurrences of 24 and 0%, respectively). Accumulated anthropogenic source contribution associated with Corsican-Sardinian 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 explain the lower OVOC winter concentrations observed at Ersa 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. 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). Meteorological 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. Higher temperatures along with the lack of cold nights in winter 2014 (Van Oldenborgh, 2015) may also have affected the source strength especially of long-lived combustion sources. Furthermore, 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 winter 2014 (higher by 300% than the seasonal normal value for the 1981-2010 period; see Fig. S5 of the Supplement). Abundant rainfalls were also noticed in southeast of France during winter 2014 (the highest one 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 have reduced anthropogenic source contributions from the Po Valley and the southeast of France in winter 2014."

The revised Fig. 10:

“

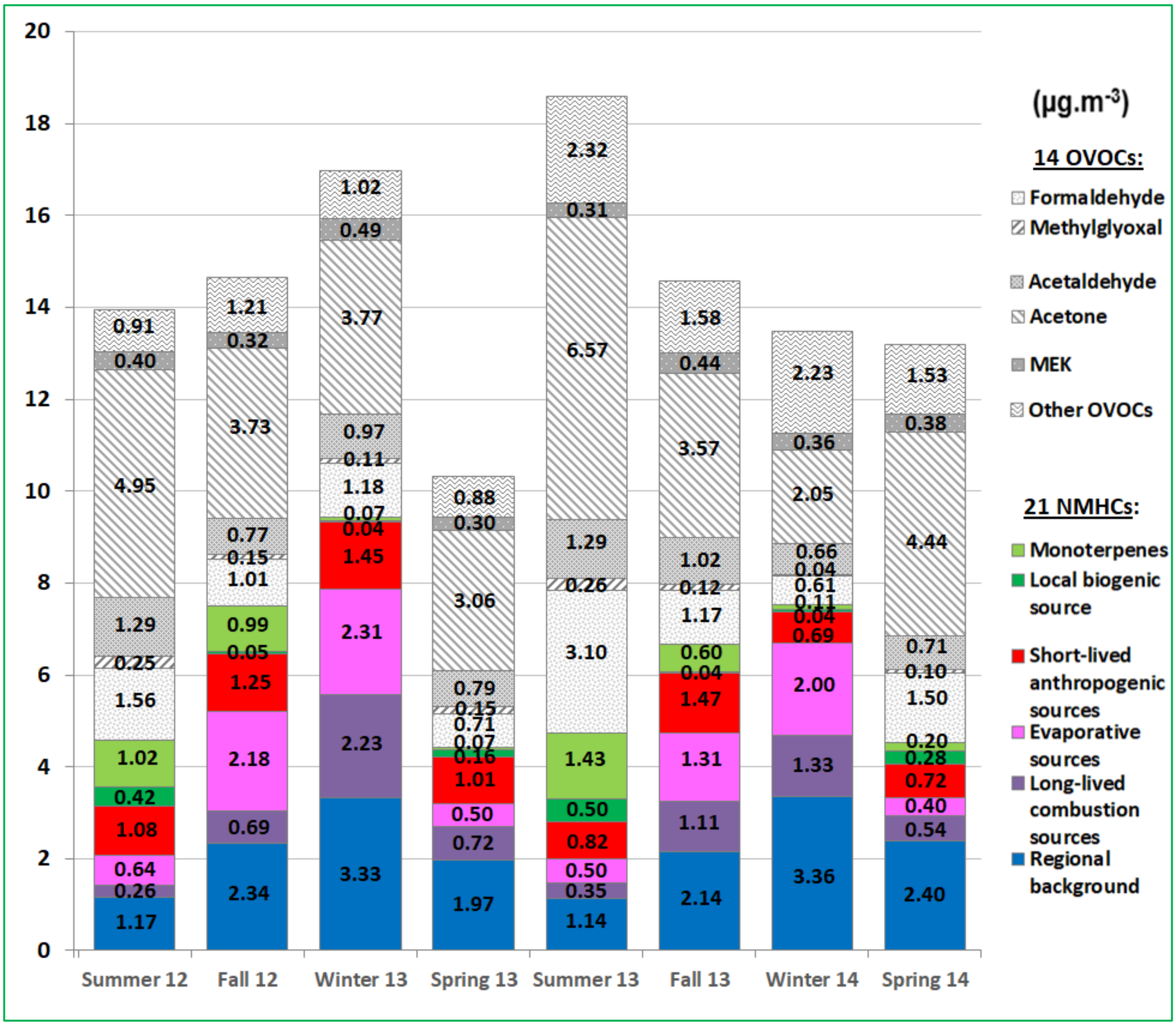


Figure 10: Variations in seasonal averaged accumulated concentrations (expressed in µg m^{-3}) of the 35 VOCs selected in this study. The 17 NMHCs selected for the factorial analysis were apportioned to the five modelled NMHC sources. NMHC seasonal measured concentrations which were not modelled by the 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).“

61/Sect. 4.1, Page 22, lines 13-14

“… favouring phenomena of vertical dispersion.”
Delete “phenomena of”, not required here: “… favouring vertical dispersion.”

As proposed by referee #2, the sentence was modified in the revised manuscript (from Page 20, lines 32 to Page 21 line 1):

“These findings can suggest that these anthropogenic sources originating from distant emission areas were largely influenced by pollutant depletion and vertical/horizontal dispersion during these seasons.”

62/Sect. 4.2, the particular case of winter

Figure 13, referred to in the text needs further explanation and a legend describing the colour scheme and the meaning of C1 – C5. These are described elsewhere, but should be included again here in the figure.

As suggested by referee #2, the figure was modified in the revised manuscript:

“

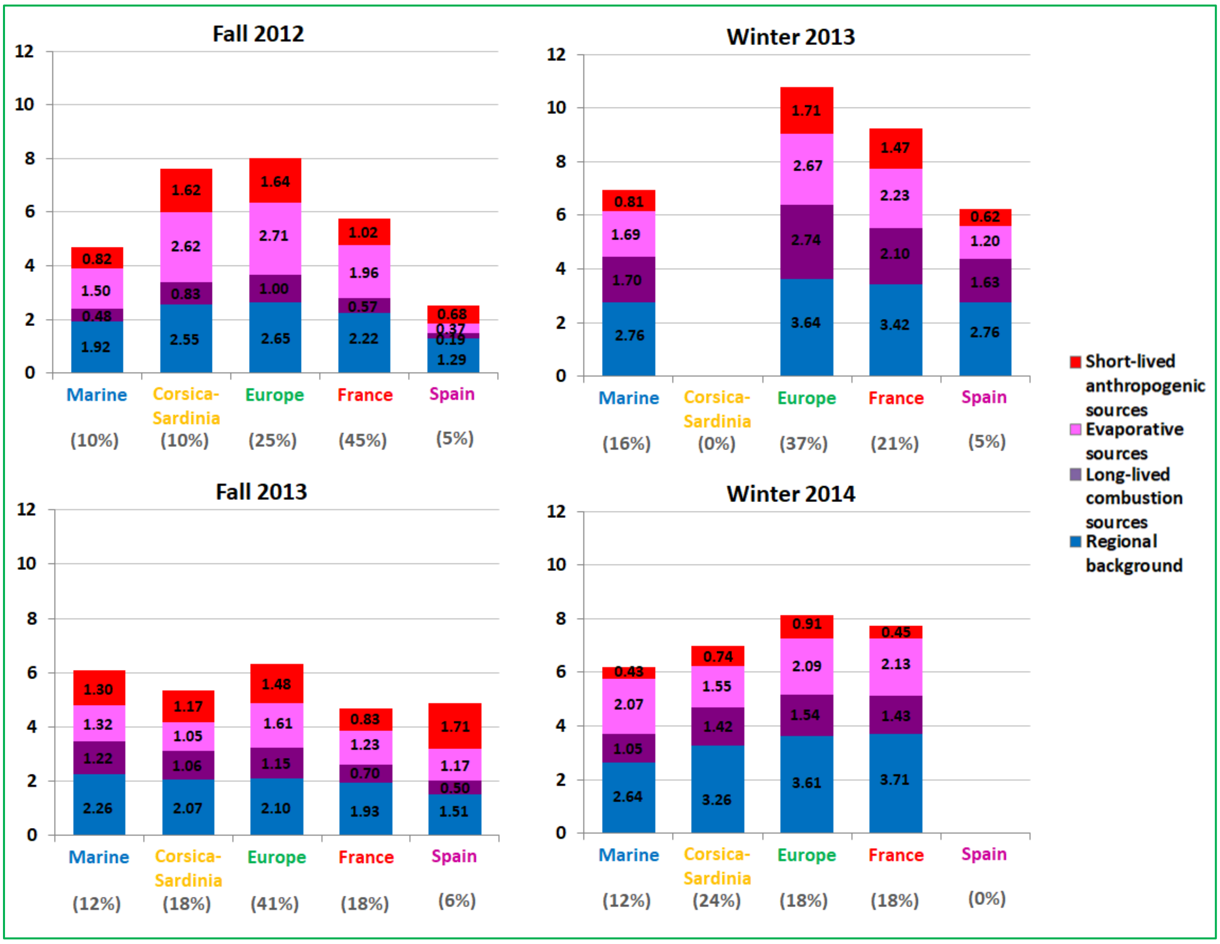


Figure 11: Accumulated average contributions (expressed in µg m^{-3}) of the NMHC anthropogenic sources (factors 2-5 which explained measured concentrations of the 16 selected NMHCs in the PMF analysis – Sect. 3.5) per season as a function of air mass origins (Sect. 3.2). Winter: 01/01-31/03 periods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

63/Sect. 4.2, Page 24, line 2

“… compared to winter 2013 ones …”
Remove “ones”, it’s not required here.

As suggested by referee #2, the sentence was modified in the revised manuscript (Page 22, lines 7-9):

“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 difference 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.”

64/Sect. 4.2, Page 24, line 34

“As a consequence, this finding also point out that shorter observation periods (i.e., up to two months) may be reflected the variability of the identified parameters under the specific meteorological conditions of the studied period.”
Sentence is poorly written and doesn’t make sense, needs to be re-written for clarity.

We thank referee #2 for this suggestion, but the sentence was removed in the revised Sect. 4.2 (“VOC concentration variations in fall and winter”). However, this information was rewritten in the conclusion for clarity (from Page 26 line 33 to Page 27 line 3) as follows:

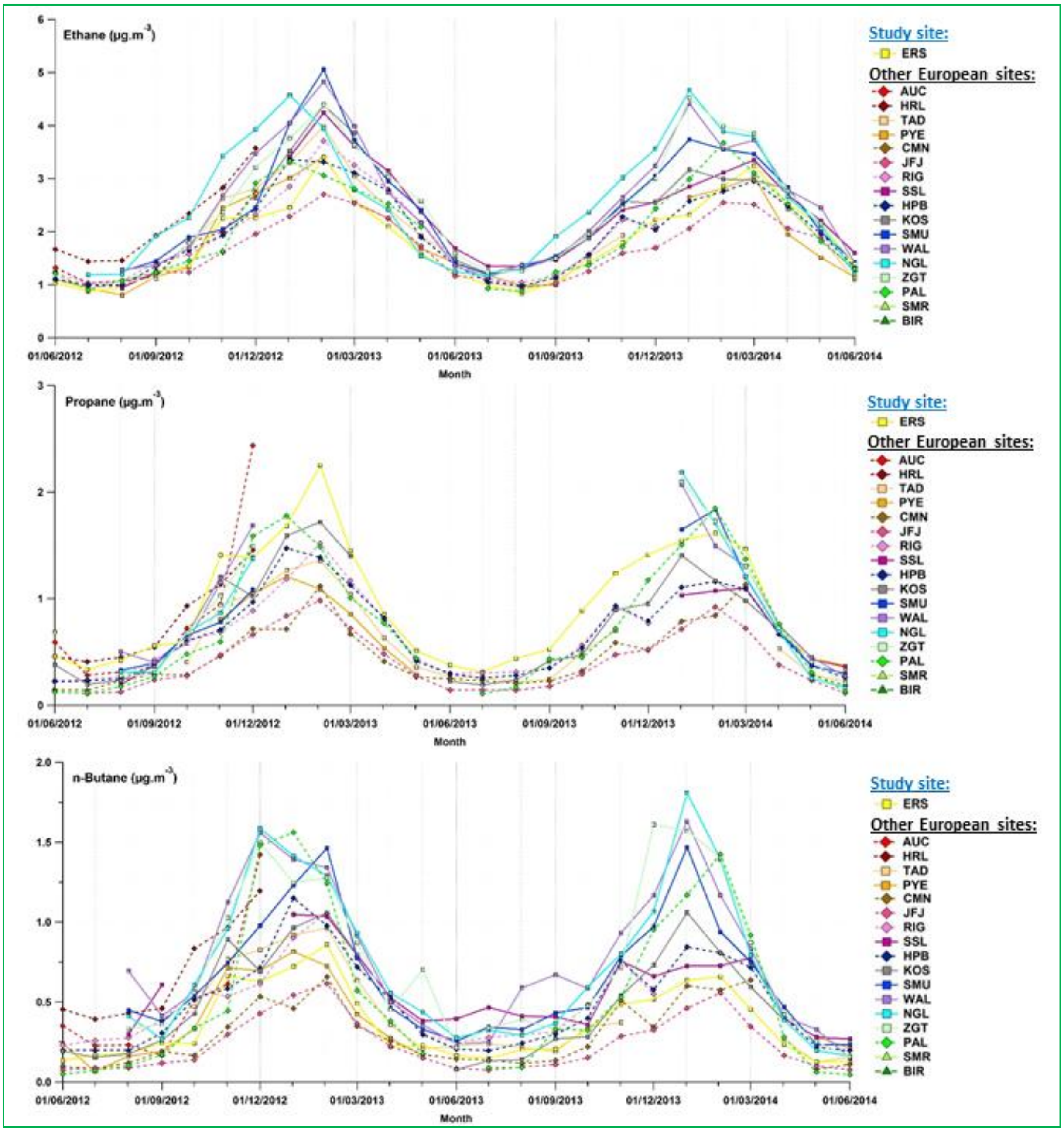
“They also pointed out that the PMF-derived factors controlling VOC concentration variations at remote sites may be mainly controlled by the meteorological conditions that occurred during the study period when issued from short observation periods (i.e. up to two months).”

65/Sect. 5, VOC concentration variations in continental Europe

Figure 15 is referred to in the text. The ERSA site should be highlighted in the caption to identify the station under study here.

As suggested by referee #2, the Ersa site was highlighted in the caption of the revised Figure 13 as follows:

“



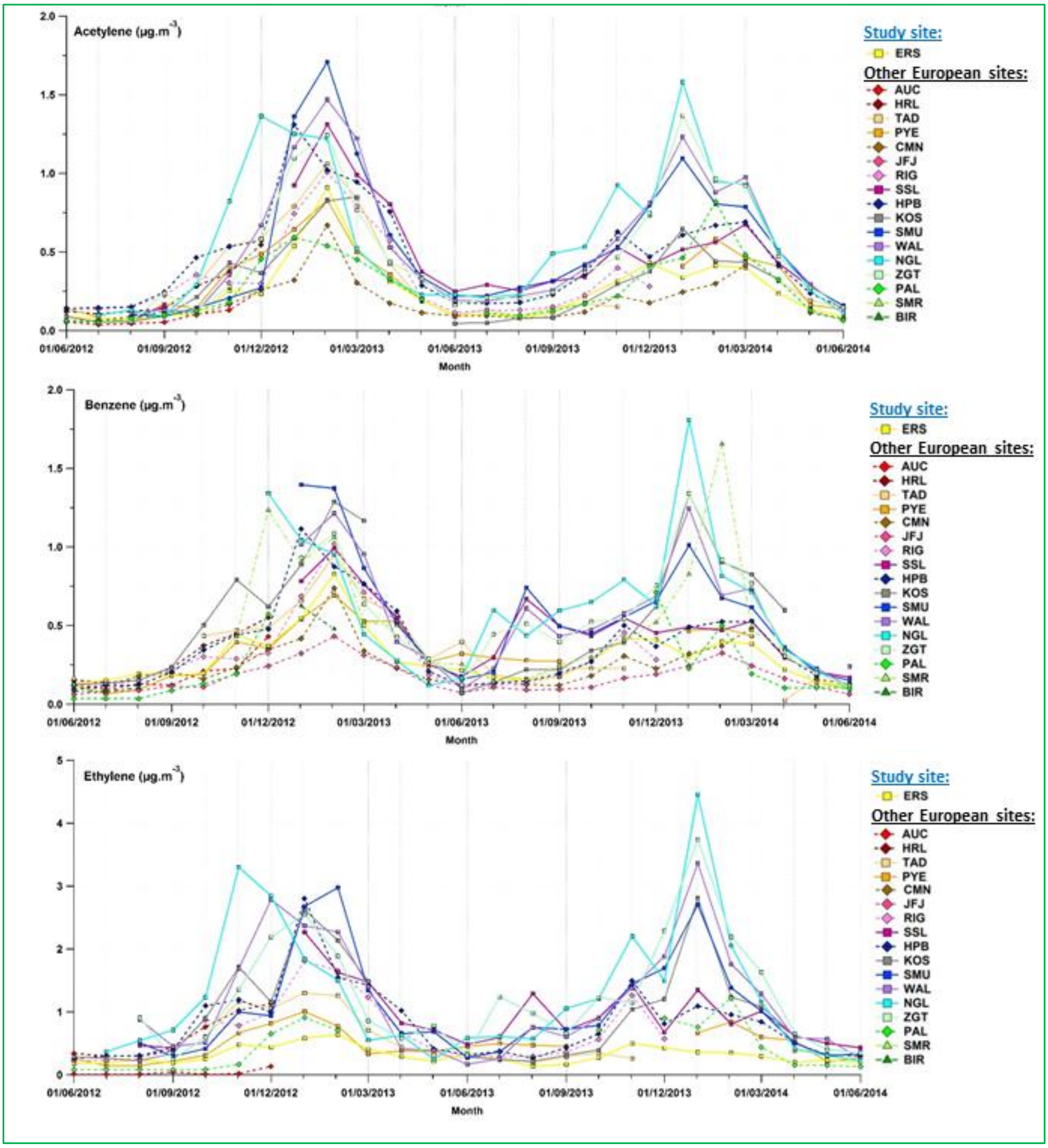


Figure 13: Monthly concentration time series of a selection of NMHCs (expressed in µg m^{-3}) measured at Ersa and 17 other European monitoring stations. Stations are indicated according to their GAW identification (Sect S7). "ERS" referred to the study site."

66/Sect. 5, Page 25, line 17

"… observed in most continental Europe …"
"… observed in most of continental Europe …"

As suggested by referee #2, the sentence was modified in the revised manuscript (From Page 23 line 31 to Page 24 line 1):

"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."

67/Sect. 5, Page 25, line 20

"… were globally lower and …"
not globally, but European wide

As suggested by referee #2, the sentence was modified in the revised manuscript (Page 24, lines 4-5):

"Monthly NMHC concentrations were European wide lower and relatively homogeneous from June to August whatever the location and the typology of the station […]."

68/Sect. 5, Page 25, line 23

"… suggesting a high importance of photochemistry processes and vertical dispersion phenomena in regulating concentration levels."
I would suggest that temperature (linked to boundary layer height) is the main driver here. As the authors state earlier in the manuscript, the majority of these compounds (with the exception of ethylene) have relatively long lifetimes and so photochemistry will likely be limited.

As suggested by referee #2, the sentence was modified in the revised manuscript (Page 24, lines 7-8):

"It suggests that the temperature was the main driver in regulating summer concentration levels, linked to photochemistry processes and vertical dispersion."

69/Sect. 5, Page 26, line 5

"Then, at stations located …"
Delete "then"

As suggested by referee #2, the sentence was modified in the revised manuscript (Page 24, lines 21-22):

"~~Then,~~ At stations located in central Europe (i.e. stations located in Switzerland, Germany and Czech Republic - see Sect. S7), […]."

70/Sect. 5, Page 26, line 22

to normal values
How do the authors conclude which is "normal"?

These normal values were obtained from the CPC (Climate Prediction Center) of NOAA (Fig. S5). The CPC produces monthly and three month maps of total precipitation and percent of normal plus average temperature and departures from normal (https://www.cpc.ncep.noaa.gov/products/monitoring_and_data/restworld.php, last access: 13/10/2020). As indicated in Fig. S5, normal values are calculated using the average of monthly (or quarterly) values for 1981-2010 period. The belonging of these normal values to NOAA is now indicated in Fig. S5 and in Sect. 5 ("VOC concentration variations in continental Europe"; Page 24, lines 27-29):

"Furthermore, precipitations in central Europe were less frequent and/or intense both in winters 2013 and 2014 compared to normal values for the 1981-2010 period (average values calculated by the NOAA – see Fig. S5 of the Supplement) […]."

71/Sect. 5, Page 27, line 6

"Then, VOC concentrations ..."
Delete "then"

As suggested by referee #2, the sentence was modified in the revised manuscript (Page 25, lines 24-25):

"~~Then,~~ NMHC winter concentrations monitored in Scandinavia (represented by PAL station results on Fig. 14) were higher in 2014 than in 2013 […]."

72/Sect. 5, Page 27, line 11

Sentence containing "... was not as warmer-than-average as ..." is poorly written, please re-write for clarity

As suggested by referee #2, the sentence was modified in the revised manuscript (Page 25, lines 29-31):

"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 normal values for the 1981-2010 period, since an intense cold wave occurred in January 2014 and was associated with a strong anticyclone centred on western Russia and extending from Finland to Crimea."

73/Sect. 6 Conclusions

This section is far too long and needs to be re-written more concisely.

As recommended by referee #2, the conclusions have been rewritten more concisely in the revised manuscript (from Page 26, line 2 to Page 27, line 11):

"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. Primary anthropogenic 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 and spring. The selected 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 and fall have favoured the advection at Ersa of air masses enriched by 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 and spring. As a result, the regional background, evaporative sources and long-lived combustion sources were identified as the dominant contributors to 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 precipitations) 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. OVOC have shown higher winter concentrations in 2013 than in 2014, as a result of the enrichment of air masses advected to Ersa by primary anthropogenic sources 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 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 seasonal variations of Ersa VOC concentrations, related to the VOC range considered and the temporal resolution of their measurements in the PMF analysis. After this work, some questions remain in terms of identification and characterization of OVOC sources and origins and of the contribution of local BVOC 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 completing the understanding of determinants governing VOC concentration variations initiated both by Michoud et al. (2017) and this study."

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

Cécile Debevec[1], Stéphane Sauvage[1], Valérie Gros[2], Thérèse Salameh[1], Jean Sciare[2,3], François Dulac[2], Nadine Locoge[1].

[1]IMT Lille Douai, Univ. Lille, SAGE - Département Sciences de l'Atmosphère et Génie de l'Environnement, 59000 Lille, France
[2] Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Unité Mixte CEA-CNRS-UVSQ, IPSL, Univ. Paris-Saclay, Gif-sur-Yvette, 91190, France
[3] Climate and Atmosphere Research Centre, the Cyprus Institute (CyI), Nicosia, 2121, Cyprus

Correspondence to: Stéphane Sauvage (stephane.sauvage@imt-lille-douai.fr) – Cecile Debevec (cecile.debevec@imt-lille-douai.fr)

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 3~~2~~5 selected VOCs, and their various associated sources. The VOC ~~speciation~~ abundance was largely dominated by oxygenated VOCs (OVOCs) along with primary anthropogenic VOCs having a long lifetime in the atmosphere. VOC temporal variations ~~are~~ were then examined. Primarily of local origin, biogenic VOCs exhibited notable seasonal and interannual variations, related to temperature and solar radiation ~~ones~~. Anthropogenic compounds ~~have shown an increasing~~showed increased concentrations ~~trend~~ in winter (JFM months) followed by a decrease in spring/summer (AMJ/JAS months), and ~~different~~ higher concentration levels in winter ~~periods of~~ 2013 than in winter ~~and~~ 2014 by up to 0.3 µg m^{-3} in the cases of propane, acetylene and benzene. OVOC concentrations were generally high~~er~~ 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 ~~anthropogenic~~ 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 ~~composed of 5 factors~~ was taken on. It includes an anthropogenic ~~biogenic~~ factor (which contributed ~~4~~39% to the total concentrations of the selected VOCs in the PMF analysis ~~mass~~) connected to the regional background pollution, ~~three~~ 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 ~~remaining~~ biogenic ~~one~~ source (~~4~~39%)~~) connected to the regional background pollution~~. Variations in these main sources impacting VOC concentrations observed at the ~~the receptor site~~Ersa station are 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 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 ~~to~~ with potential emission areas located in Italy and possibly more distant ones in central Europe. Higher VOC concentrations during winter 2013 compared to winter 2014 ~~ones~~ could be related to anthropogenic source contribution variations probably governed by the 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 from bi-weekly samples in terms of summer concentration levels and source apportionment. However, they suggested that higher sampling frequency and temporal resolution, in particular to observe VOC concentration~~s~~ variations during the daily cycle, are needed to confirm the deconvolution of the different anthropogenic sources identified by the PMF approach. Finally, comparisons of the 25 months of observations at Ersa with VOC measurements conducted at 17 other European monitoring stations highlighted the representativeness of the Ersa ~~background~~ station for monitoring seasonal variations in VOC regional pollution impacting continental Europe. Nevertheless, winter VOC 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. Interannual and spatial VOC concentration 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 ~~studied~~ 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~~; Atkinson, 2000~~). Accordingly, with a view to extensively characterize VOC sources, it is meaningful to examine their chemical composition, in addition to identifying the factors controlling their variations at different time scales.

VOC regional distributions are eminently changing 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 meteorological conditions. Therefore, these elements underline the necessity to carry out long-term VOC measurements. ~~In Europe, studies essentially focus on urban and suburban locations (e.g., Derwent et al., 2014 and von Schneidemesser et al., 2010 in United Kingdom; Salameh et al., 2019 and Waked et al., 2016 in France; Roemer et al., 1999 in the Netherlands; Fanizza et al., 2014 in Italy), reflecting concerns about the role of VOCs in urban air quality control, efficiency assessment of national VOC emission regulation implementations, and population exposure. European VOC observations in the background atmosphere are still dedicated largely to process studies and short-term research missions. However, t~~There are growing efforts now to ~~carry out~~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 multi-year studies were conducted ensuing the increasing demand for high quality VOC data, and long-term monitoring have led to international programs like the European Research Infrastructure for the observation of Aerosol, Clouds and Trace gases (ACTRIS - https://www.actris.eu/; last access: 03/04/2020), the European Monitoring and Evaluation Program (EMEP - http://www.emep.int/; last access: 03/04/2020 - 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: 03/04/2020). Regarding VOCs, t~~These research studies principally explored the emission regulation efficiency~~, and~~ links between tropospheric ozone production and changes in VOC concentrations, and assessed seasonal variations and regional distributions in VOC concentrations. Nonetheless, investigations on 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 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 through 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 concentrations 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~~s~~ to be challenging, primarily on account of the lack of extensive in-situ observations. ~~In order to improve our actual comprehension of the complexity of the Mediterranean atmosphere, it is essential to increase~~

~~the atmospheric pollutant observations, including speciated and reactive VOCs, at representative regional background sites.~~ 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: ~~03~~11/10~~04~~/2020), the project ChArMEx (the Chemistry-Aerosol Mediterranean Experiment, http://charmex.lsce.ipsl.fr, last access: ~~03~~11/10~~04~~/2020; Dulac, 2014) ~~focused on the development and coordination of regional research actions. More precisely, ChArMEx~~ 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 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.

~~The present study was designed to characterize the seasonal variations in the sources of VOCs affecting the western Mediterranean atmosphere. An extensive chemical composition dataset was collected at a receptor site considered to be representative of the northwestern basin.~~ In this article, we present and discuss factors controlling ~~ambient levels and~~ seasonal and interannual variations of a selection of VOCs observed at the Ersa station~~ of the Corsican Observatory for Research and Studies on Climate and Atmosphere-ocean environment (CORSiCA - https://corsica.obs-mip.fr/, last access: 03/04/2020; Lambert et al., 2011),~~ over more than two years~~ as part of the ChArMEx project~~ (from early June 2012 to late June 2014). ~~Selected species include alkanes, alkenes, alkyne, aromatic compounds and oxygenated VOCs (OVOCs), which were measured using off-line techniques.~~ To ~~reach its objective~~this end, this study ~~will~~ describes (i) ~~quantify~~ the concentration levels of the targeted VOCs, (ii) ~~specify~~ their temporal variations at seasonal and interannual scales, (iii) the identification ~~identify~~ and ~~characterize~~ characteristics of their main sources by statistical modelling, (iv) ~~assess and examine~~the evaluation of their source contributions on seasonal bases, together with (v) ~~examine~~ 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 the aim of providing a high quality controlled climatically relevant gas/aerosol database following the recommendations and criteria of the international atmospheric chemistry networks, i. e., the European Research Infrastructure for the observation of Aerosol, Clouds and Trace gases (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)~~ACTRIS, EMEP, and GAW~~. This 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 by air masses advected 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 ~~study site~~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. ~~Note that m~~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~~30~~/10~~05~~/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 in the surroundings 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 are also located nearby (78 % of holm oaks, with some cork oaks and chestnuts), 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 period of two years, non-methane hydrocarbons (NMHCs) and OVOCs (carbonyl compounds) were measured routinely employing complementary off-line methods. Four-hour~~s~~-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 housing the analysers. Table 1 describes ~~our~~ VOC measurements set up throughout the observation period and Fig. S1 specifies their collection periods.~~.~~

As generally realized in the EMEP network, ~~21~~ 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 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 sampling. Separation was performed by a system of dual capillary columns supplied with a switching device: the first one 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 to in-situ measurements (Sauvage et al., 2009).

About 150 ~~off-line 4-h-integrated~~ air samples were gathered using sorbent cartridges (63 air samples on multi-sorbent cartridges and 89~~91~~ 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 are 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), 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 ~~four~~ 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 250 °C and flow rate regulated at 10 mL min^{-1}. In parallel, ~~15~~ 15 additional C_1-C_8 ~~OVOCs~~ carbonyl compounds were collected ~~using the DNPH cartridges~~ at a flow rate fixed at 1.5 L min^{-1} using the DNPH cartridges.~~.~~ During the field campaign, several ozone scrubbers have been 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 using a GC-FID (for multi-adsorbent cartridges) or by high-performance liquid chromatograph connected to an ultraviolet detector (HPLC-UV; for DNPH cartridges).

The reproducibility of each analytical instrument has been 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 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 uncertainty evaluation (Reimann et al., 2018) considering precision, detection limit and systematic errors in the measurements. Evaluated relative uncertainties ranged from 7% to 43% concerning steel canisters, between 7% and ~~65~~73% for multi-sorbent cartridges and from 6% to 41% concerning 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 commercial analyser (G2401; Picarro, Santa Clara, California, USA) using a cavity ring-down spectroscopy (CRDS) at a time resolution of 5 min. O_3 was measured from 31 May 2012 to 26 December 2013 by means of a UV 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. Note that trace gases and meteorological results presented in this study are 4-hour averages concurrent to periods when the VOC sampling periods were realized (see Fig. S1).

~~2.2.3 Additional high frequency VOC measurements performed at Ersa~~

~~Additional VOC measurements were realized during summer campaigns performed in 2012, 2013 and 2014. One hundred of 3-h-integrated air samples were collected at Ersa using DNPH cartridges from 29 June to 11 July 2012 at a frequency of 8 samples per day. Additionally, the ChArMEx special observation period 1b (SOP-1b) occurred from 15 July to 5 August 2013 at Ersa. More than 80 VOCs were measured during the SOP-1b intensive field campaign using different on-line and off-line techniques, which have already been presented in Michoud et al. (2017). Furthermore, formaldehyde measurements realized during the SOP-1b field campaign with DNPH cartridges are used in this study. Finally, around 70 3h-integrated air samples were collected at Ersa from 26 June to 10 July 2014 on DNPH cartridges (54 samples realized at a frequency of 4 cartridges per day from 6h-18h UTC) and on stainless steel canisters (20 samples realized at a frequency of 3 canisters per day from 9h-18h UTC). These campaign measurements will be confronted with the two years of VOC measurements investigated in the present study, in order to examine the representativeness of the study period (see Sect. 3.4.4).~~

~~2.2.4 Concurrent VOC measurements performed at other European background monitoring stations~~

~~From June 2012 to June 2014, VOC measurements were concurrently conducted at 17 other European background monitoring stations, allowing us (i) to examine the representativeness of Ersa station in terms of seasonal variations in VOC concentrations impacting continental Europe and (ii) to provide some insights on dominant drivers for VOC concentration variations in Europe built on Ersa's VOC observations (see Sect. 5). These European stations are part of EMEP and GAW networks. Figure 2 shows their geographical distribution. They cover a large part of western and central Europe from Corsican island in the south to northern Scandinavia in the north, are located at different altitudes (up to 3580 m a.s.l.) and most of them are categorized as GAW regional stations for Europe. More information on these stations can be found on EMEP (https://www.nilu.no/projects/ccc/sitedescriptions/index.html, last access: 03/04/2020) or GAW station information system (https://gawsis.meteoswiss.ch/GAWSIS//index.html#/, last access: 03/04/2020) sites. VOC measurements were realized by different on-line (GC or proton-transfer-reaction mass spectrometer - PTR-MS) or off-line techniques (VOCs collected by steel canisters) and were reported in the EMEP EBAS database (http://ebas.nilu.no/Default.aspx, last access: 03/04/2020).~~

2.3 Identification and contribution of major sources of VOCs

In order to characterize ~~VOC~~ NMHC concentrations measured at Ersa, we apportioned ~~VOC~~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 ~~Section~~ Sect. ~~S1~~ S2 of the Supplement. We used the PMF version 5.0, an enhanced tool developed by the Environmental Protection Agency (EPA) and including a multilinear engine ME-2 (Paatero, 1999), and followed the guidance on the use of PMF (Norris et al., 2014). Using NMHC inputs composed of 152 atmospheric data points of 14 variables (13 single primary HCNMs and another one resulting of 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.

~~In order to have sufficient completeness (in terms of observation number), only VOC measurements from bi-weekly ambient air samples collected into steel canisters from 04 June 2012 to 27 June 2014 were retained in this factorial analysis. The chemical dataset includes 14 selected single or grouped VOCs, i.e. those showing significant concentration levels during the study period (see Sect. 3.3). They were divided into five compound families: alkanes (ethane, propane, i-butane, n-butane, i-pentane, n-pentane and n-hexane), alkenes (ethylene and propene), alkyne (acetylene), diene (isoprene) and aromatics (benzene, toluene, and EX, the sum of ethylbenzene, m,p-xylenes and o-xylene). The final VOC dataset encompassed 152 atmospheric data points having a time resolution of 4 hours. Input information are detailed in Table 2. Moreover, the data processing and quality analysis of the VOC dataset are presented in the supplement material of Debevec et al. (2017).~~

~~In order to optimize the PMF solution, we followed the same procedure as in Debevec et al. (2017) (see Sect. S1 in the Supplement). As a result, a five-factor PMF solution has been chosen in this study considering a F_{peak} parameter fixed at~~

~~0.8 which allowed a finer decomposition of the VOC dataset following an acceptable change of the Q-value (Norris et al., 2014).~~

~~Quality indicators provided by the EPA PMF application have been indicated in Table 2. The PMF model results reconstruct on average 99% of the total concentration of the 14 selected compounds of this study. Individually, almost all chemical species also showed both good determination coefficients and slopes (close to 1) between reconstructed and measured concentrations, apart from propene, n-pentane, n-hexane, toluene and EX. Therefore, PMF model limitations to explain these species should be kept in mind when examining PMF results.~~

~~The evaluation of rotational ambiguity and random errors in a given PMF solution can be realized with DISP (displacement) and BS (bootstrap) error estimation methods (Brown et al., 2015; Norris et al., 2014; Paatero et al., 2014). As no factor swap occurred in the DISP analysis results, the 5-factor PMF solution is considered adequately robust to be interpreted. Then, bootstrapping was realized by performing 100 runs, and considering a random seed, a block size of 18 samples and a minimum Pearson correlation coefficient of 0.6. Each modeled factor of the selected PMF solution was well mapped over at least 95% of realized runs, assuring their reproducibility.~~

2.4 Geographical origins of VOC sources~~s~~

2.4.1 Classification of air mass origins

In order to identify and classify air-mass origins, 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. ~~Firstly, h~~Having several back trajectories per sample allows us to check if air masses transported at the station over 4 hours were globally of the same origin. As a result, samples with air masses showing contrasted trajectories (e. g., due to a transitory state between two different origins) were classified as of mixed origins and discarded (9% of the air masses). Remaining air masses were then manually classified into five trajectory clusters (marine, Corsica-Sardinia, Europe, France and Spain - Fig. ~~3~~ 2 and Table ~~3~~2) in function of their pathway when they reached the ~~measurement site~~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 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 ~~3~~ 2 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, 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 ~~the receptor~~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 ~~Section~~ Sect. ~~S2~~ S3 of the Supplement.

For each VOC observation, 3-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 model (version 4.4 revised in February 2016), following the same methodology as ~~those of~~that used for the 48-h back-trajectories ~~48 h~~ previously presented. The arrival time of trajectories at the Ersa station corresponds to the hour when half of the sampling was done (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, 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 3.50; Petit et al., 2017). Back-trajectories have been shortened (i.e. the ZeFir tool considered shorter back-trajectories than 72 h) ~~Note that wet deposition condition was assumed~~ when a precipitation higher than 0.1 mm was ~~reported~~ encountered along the trajectory (Bressi et al., 2014). ~~Furthermore, a~~As also done by Michoud et al. (2017), back-trajectories have been also shortened when air mass altitudes gone beyond 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 higher number of crossing trajectory points. As a result, s~~S~~ome studies applied an empirical weighing function so as to limit the possible influence of high concentrations which may be observed during occasional episodes with uncommon trajectories (e.g., Bressi et al., 2014; Waked et al., 2014, 2018) and hence could influence cells having a low number of trajectory points. We preliminary tried to apply this weighing function in this study. Exploratory t~~T~~ests revealed that CF results with the empirical weighing function only highlighted local contributions, given the ~~total~~ number of air masses considered in this study. The farther a cell is from the ~~receptor site~~Ersa station, the lower its corresponding n_{ij} value (number of points of the total number of back-trajectories contained in the ij^{th} grid cell, Sect. ~~S2~~ S3 of the Supplement), and more the weighing function tended toward downweighting the low n_{ij} value. 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 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 monthly variations are depicted in Fig. ~~4~~3. As the field measurement period covered ~~a period of~~ two years (i.e. from June 2012 to June 2014), their interannual variations are also shown in Fig. 3~~4~~b.

Air temperature observed during the observation period showed typical seasonal variations, i.e. the highest temperatures recorded in summer (i.e. from July to September) and the lowest ~~ones~~ in winter (i.e. from 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; minimal and maximal mean values ~~over the period 1981-2010~~ for Bastia available at http://www.meteofrance.fr/climat-passe-et-futur/climathd~~http://www.meteofrance.com/climat/france/bastia/20148001/normales~~, last access: ~~03~~11/~~04~~10/2020). The range of temperatures recorded in June was rather expanded over the 3 years. In fact, ~~June 2013~~ mean temperature was lower in June 2013 than in June 2012 and 2014~~ mean ones~~ (mean temperature of 24.7 ±5.8 °C, 19.4 ±4.1 °C and 22.5 ±5.4 °C for June 2012, 2013 and 2014, respectively), which could have influenced biogenic emissions. Additionally, temperatures recorded during winter 2013 were colder than in winter 2014~~ ones~~ (mean temperature of 7.0 ±4.1 °C, and 9.7 ±1.5 °C for winter 2013 and 2014, respectively). This finding could be explained by different climatic events which have occurred during these two winter periods and have concerned a large part of continental Europe. On one hand, ~~western European winter 2013 was considered rigorous and may be caused by a destabilization phenomenon of~~ the stratospheric polar vortex~~. In early January 2013, the established stratospheric polar vortex~~ underwent a sudden stratospheric warming (SSW; Coy and Pawson, 2015) in early January 2013, ~~inducing air warming inside the vortex and a weakening of the cyclonic air circulation around the vortex. Consequently, the polar vortex was moved out of its polar position towards Europe and the SSW ended up splitting the vortex into two lobes, including one setting on western Europe and the Atlantic. These events had~~having repercussions on the tropospheric polar vortex~~ which also broke~~, which collapsed~~ing~~ several times towards Europe. ~~All these elements modified~~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 2014 ~~(Photiadou et al., 2015)~~ characterized by its lack of cold outbreaks and nights, caused by an anomalous atmospheric circulation (Rasmijn et al., 2016; Van Oldenborgh et al., 2015; Watson et al., 2016). ~~In fact, the north Atlantic jet stream took a rather zonal orientation and with it the usual storm tracks shifted south. On the other side of the Atlantic Ocean, the eastern part of the USA and Canada were struck by cold polar air being advected southward due to the anomalously persistent deflection of the jet stream over the USA. The contrast between cold air advection south across the USA, and the warm tropical Atlantic was likely to have been partly responsible for the persistence and unusual strength of the north Atlantic jet stream. This situation created ideal conditions for active cyclogenesis leading to the generation of successive strong extratropical storms being carried downstream across the north Atlantic toward the British Isles .~~

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

Globally, r~~R~~elative humidity ~~globally~~ followed opposite seasonal variations ~~than~~ to temperature and solar radiation ~~ones~~. In June 2012, air was dryer compared to in June 2013 and 2014 ~~mean relative humidity values~~ (mean relative humidity of 57 ±15%, 77 ±16% and 67 ±33% for June 2012, 2013 and 2014, respectively). The wind speed did not show a clear seasonal variation over the two years studied~~,~~ . ~~except maybe~~Slightly higher wind speeds were noticed in April and May, ~~that~~ which could induce higher dispersion of air pollutants and ~~could~~ advect air pollutants from more distant sources to the ~~receptor site~~Ersa station. ~~May 2014 encountered particularly windy conditions.~~

3.2 Air mass origins

Occurrences of air mass origins which have influenced Ersa throughout the observation period are indicated in Table ~~3~~2. The ~~receptor site~~Ersa station was predominantly under the influence of 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 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) and is defined by a different transit time from continental coasts, viewed as an indicator of the potential moment when an air mass could have been ~~contaminated~~ enriched by anthropogenic sources for the last time (Table 2~~3~~), as observed by Michoud et al. (2017). Continental air masses spent less time over the sea than marine ones. Nonetheless, transit times of continental air masses over the sea differ in function of how they are categorized. Air masses originating from Corsica-Sardinia, France and Europe have spent 0-8 h (median values – Table ~~3~~2) above the sea before reaching the ~~receptor site~~Ersa station, while the air masses originating from Spain have spent about 36 h. 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 values of 6 h and 8 h, respectively; Table 2) when their trajectories are categorized as long; compared to short ones (23 h and 19 h, respectively~~; Table 3~~). These findings are based on the fact that an air mass trajectory classified as short has closer distance between two succeeding trajectory points compared to another one classified as long. Due to the Ersa location in the Mediterranean Sea, the air masses having trajectories characterized as long have spent more time to reach the Ersa site. Note that European and French air masses were more frequently characterized by long trajectories (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, marine air masses ~~categorized~~ having~~as marine~~

~~showed relatively close transport times between their~~ short and long trajectories have both shown long transit times (~~median transit times comprised between~~ 40-~~ and ~~48 h – Table ~~3~~2) and Corsican-Sardinian air masses only concerned long ~~ones~~trajectories.

3.3 VOC mixing ratios

~~Descriptive s~~Statistical results on concentrations ~~for a selection~~ of ~~25~~ 35 VOCs~~, which showed significant concentration levels during the 2-yr studied period,~~ selected in this study (see Sect. S1 in the Supplement) are summarized in Table ~~4~~3. Their average concentration levels as a function of the measurement sampling times (09:00-13:00 or 12:00-16:00) are indicated in Table S1. These VOCs were organized into three principal categories: ~~anthropogenic,~~ biogenic, anthropogenic, and ~~OVOCs~~ oxygenated VOCs (~~16,~~ 5, 16 and 14 targeted species, respectively; Table 3). Isoprene and four monoterpenes were classified into ~~biogenic compounds~~BVOCs, while primary hydrocarbons (alkanes, alkenes, alkynes and aromatic compounds)~~,~~ were included into anthropogenic ~~compounds~~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. ~~Although represented by only four compounds,~~ OVOCs were the most abundant, accounting for ~~54~~65% of the total concentration of the ~~selected~~ 35 compounds selected in this study. They were mainly composed of acetone (contribution of 51~~60~~% to the OVOC cumulated concentration). Anthropogenic ~~VOCs~~ NMHCs also contributed significantly (~~41~~26%) to the total concentration of the 35 measured VOCs and principally consisted of ethane and propane (which represented 34 and 17% of the anthropogenic ~~VOC~~ NMHC mass, respectively) as well as n-butane (7%). The high contribution of species with generally the longest lifetime in the atmosphere (see Sect. 3.4) is consistent with the remote location of the Ersa site and in agreement with Michoud et al. (2017). ~~Biogenic~~ BVOCs only contributed little to the total VOC concentration on annual average (4~~5~~%), reaching 13% in summer. They were mainly composed of isoprene and α-pinene (contribution of 44~~2~~ and 32~~23~~% to the ~~biogenic~~ 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 in summer 2013 at Ersa (Debevec et al., 2018; Kalogridis, 2014). On the contrary, a larger α-terpinene contribution was noticed during the summer intensive campaign than the 2-yr observation period. Note that speciated monoterpenes were measured differently during the summer 2013 campaign, by means of an automatic analyser (see Sect. S4 in the Supplement).

3.4 VOC variability

~~The variability in VOC concentration levels is governed by an association of factors involving source strength (e.g., emissions), dispersion, dilution processes and transformation processes (photochemical reaction rates with atmospheric oxidants; Filella and Peñuelas, 2006). At this type of remote site, it is also important to consider the origin of air masses impacting the site as distant sources can play a significant role comparatively to local sources (see Sect. 3.5).~~ Monthly and interannual variations of ~~selected~~ primary (anthropogenic and biogenic) ~~VOCs~~ NMHCs along with OVOCs observed at Ersa selected in this study (Sect.

S1) are ~~hence~~ discussed in this section. Seasonal VOC concentration levels are indicated in Table 4. In addition, ~~T~~the comparison between the VOC monitoring measurements ~~as~~ investigated in this study with concurrent campaign measurements performed during the summers ~~of~~ 2012~~, 2013 and~~ -2014 ~~is detailed~~ is presented in Sect~~ion~~. S4~~3~~ of the Supplement, in order to check the representativeness of the 2-yr observation period with regard to summer concentration levels.~~.~~

3.4.1 Biogenic VOCs

Concentration v~~V~~ariations ~~in~~ of ~~two~~ three selected BVOC~~ concentrations~~s, isoprene, ~~and~~ α-pinene and camphene, were analysed at different timescales (monthly/interannual variations; Fig. 4~~5~~). 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, –Michoud et al., (2017) and Kalogridis (2014) observed that emissions of isoprene and the sum of ~~α-pinene~~monoterpenes~~ emissions~~ were merely governed by temperature and solar radiation, considering the diurnal variations in their concentrations (Geron et al., 2000a; 2000b; Guenther et al., 2000) and their correlations with environmental parameters. Furthermore, these biogenic compounds showed significant interannual variations over the two years studied, linked to temperature and solar radiation variations. For instance, higher mean concentrations of isoprene and α-pinene were noticed in June 2012 (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 in June 2013 (0.2 ±0.2 and <0.1 µg m^{-3})~~ and June 2014 ones (0.7 ±0.5 and 0.2 µg m^{-3}),~~. Higher June concentrations of camphene (and α-terpinene; not shown) were also noticed in 2014 than in 2013 (Fig. 4). ~~which~~ These concentration levels may be related to the fact that temperature and solar radiation were more favourable to enhance biogenic emissions in June 2012 and 2014 compared to in June 2013 ~~and 2014~~ meteorological conditions (Sect 3.1). Due to the relative humidity values observed in June 2012 and 2014, which were lower than in June 2013, we cannot rule out that an increase of BVOC concentrations may be related to a transient drought stress-induced modification of BVOC emissions (Ferracci et al., 2020, Loreto and Schnitzler, 2010; Niinemets et al., 2004). -Moreover, i~~Surprisingly, i~~soprene and ~~and~~ α-pinene concentrations were ~~drastically lower~~higher in July and August 201~~2~~3 (0.~~3~~5 ±0.3 and 1~~0~~.~~9~~1 ±0.4~~3~~ µg m^{-3} ~~for isoprene and α-pinene~~, respectively) than in ~~June 2012~~July and August 2012 ~~ones~~(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). ~~Mean temperature and s~~Solar radiation ~~were~~ was ~~slightly~~ lower in July and August 2012, temperature was slightly lower in July 2012 and mean wind speed was slightly higher in July 2012 (Fig. 3~~4~~), which could affect biogenic emissions and favour 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. ~~5~~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 ~~This finding could be the result of a weaker degradation of α-pinene due to lower~~ ozone fall concentrations ~~observed from October to December compared to~~than in summer ~~ones~~ (O$_3$ concentration variations are depicted in Fig. ~~S1~~ 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 be considered cautiously given variable day-to-day and strong diurnal BVOC variations which were observed during the summer 2013 observation period (Kalogridis, 2014).

3.4.2 Anthropogenic VOCs

~~Variations~~ Variations of a selection of NMHCs, illustrating contrasted ~~primary anthropogenic sources and~~ reactivity (according to their atmospheric lifetimes considering photochemical reaction rated with OH radicals defined in Atkinson, 1990 and Atkinson and Arey, 2003), ~~were analysed at different timescales (monthly/interannual variations;~~are depicted in Fig. 5~~6)~~. Despite lifetimes in the atmosphere ranging from a few hours to some days~~ (Atkinson, 1990; Atkinson and Arey, 2003)~~, all selected NMHCs were characterized by ~~almost the same~~similar seasonal variation, 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 (the most reactive species of the NMHCs selected in this study and which have 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}.~~This seasonal trend can be explained by seasonal variations in (i) emission sources (e.g., residential heating), (ii) OH concentrations, typically higher in summer inducing higher photochemical decay, and (iii) planetary boundary layer (PBL) height, inducing enhanced accumulation of VOCs in winter.~~

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 and ethane had the longest lifetime among those selected in this study. However, ethane concentrations recorded at Ersa did not show any interannual variation over the two years studied (Fig. 5). ~~Among the selected VOCs, ethane is the species with the highest atmospheric lifetime, considering its low photochemical reaction rate with OH radicals (Atkinson and Arey, 2003). It is typically emitted by natural gas use and can be also considered as a tracer of the most distant sources. Ethane concentrations recorded at Ersa did not show any interannual variation over the two years studied, suggesting a stable influence of most distant sources. Note that ethane concentration levels were still relatively important during summer (mean concentration of 1.0 ±0.2 µg m^{-3}), suggesting a high importance of long-range transport contribution to VOC levels at Ersa during this season (its contribution during other seasons will be discussed in Sect 4). Furthermore, propane, n-butane, acetylene, and benzene are characterized by photochemical reaction rates with OH radicals from four to ten times higher than ethane one (Atkinson, 1990; Atkinson and Arey, 2003) and are tracers of various anthropogenic sources (solvent use for propane, road traffic and/or residential heating for acetylene and benzene and evaporative sources for propane and n-butane; e.g., Leuncher et al., 2015). These NMHCs exhibited different concentration levels during the two studied winter periods. Indeed, their mean concentrations during winter 2013 were from 0.1 to 0.3 µg m^{-3} higher than winter 2014 ones. Additionally, CO covaried well with acetylene and benzene, as expected for~~

~~combustion tracers of medium-to-long lifetimes (Figs. 6 and S1 of the Supplement). Ethylene has the lowest lifetime among the selected species depicted in Fig. 6 (considering its photochemical reaction rate with OH radicals referred in Atkinson and Arey, 2003), it is considered as typically emitted by combustion processes and can be used as tracer of local sources (e.g., Sauvage et al., 2009). Even ethylene showed higher concentrations during winter 2013 compared to winter 2014 ones (mean ethylene concentration of 0.6 ±0.2 and 0.3 ±0.1 µg m^{-3} during winter 2013 and 2014, respectively). As a result, winter variations of concentration levels concerned at a time close sources and more distant ones and will be more investigated thereafter (Sect. 4.2).~~

3.4.3 Oxygenated VOCs

Variations of selected OVOCs, illustrating contrasted reactivity (according to their atmospheric lifetimes considering their photochemical reaction rates with OH radicals defined in Atkinson, 1990 and Atkinson and Arey, 2003) were ~~analysed at different timescales (monthly/interannual variations;~~depicted in Fig. 6~~7)~~. Formaldehyde, acetaldehyde, glyoxal, methylglyoxal and C_6-C_{11} aldehydes have relatively short lifetime 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 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 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 were monitored in June 2012 (0.7 µg m^{-3}), similarly to isoprene (Sect. 3.4.1). 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). 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 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). ~~Identified acetone sources include primary emissions from both biogenic (green plant and litter sources) and anthropogenic origins, but its~~Acetone emissions are~~is~~ thought to be globally of biogenic rather than anthropogenic origin (Goldstein and Schade, 2000; Schade and Goldstein, 2006). Acetone can also be ~~induced by secondary (biogenic/anthropogenic) sources from~~ resulted of the ~~VOC~~ oxidation of various VOCs ~~(e.g. propane, i-butane, i-pentane, monoterpenes and methylbutanol) and biomass burning~~ (Goldstein and Schade, 2000; Jacob et al., 2002; Singh et al., 2004) and roughly half of ~~acetone~~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 concentrations 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 their concentrations both in summer and winter (Fig. 6 and Table 4), suggesting they were probably produced by several biogenic and anthropogenic sources. 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 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 concentration in February 2013 was 65-75% higher than in February 2014, confirming their links with anthropogenic sources. ~~During summer, despite their lower lifetime, these OVOCs can be significantly induced by secondary and biogenic sources, which can explain their higher concentrations.Besides photochemical production, acetaldehyde can also be released by terrestrial plants, in the process of ethanol production in leaves and roots following fermentation reactions (Jardine et al., 2008; Rottenberger et al., 2008; Winters et al., 2009).~~ These two OVOCs also showed different interannual variations in late spring and summer (Fig. 6). The glyoxal highest concentrations were monitored in June 2012 (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 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).~~formaldehyde and acetaldehyde are mainly produced through the chemical transformation of anthropogenic and biogenic VOCs (Rottenberger et al., 2004; Seco et al., 2007), particularly in clean and remote areas. Additionally, these OVOCs showed significant interannual variations.~~

~~Firstly, formaldehyde and acetaldehyde are mainly produced through the chemical transformation of anthropogenic and biogenic VOCs (Rottenberger et al., 2004; Seco et al., 2007), particularly in clean and remote areas. One of the main precursor hydrocarbons for formaldehyde is thought to be isoprene along with methane, methanol and acetaldehyde (Schade and Goldstein, 2001; Wolfe et al., 2016). Additional sources of formaldehyde are industrial processes, motor exhausts and forest~~

~~fires (Seco et al., 2007, and references therein). According to the budget estimates of Millet et al. (2010), the largest acetaldehyde source is provided by hydrocarbon oxidation, essentially alkanes and alkenes as well as isoprene and ethanol. Nevertheless, acetaldehyde is only produced as a second or higher-generation oxidation product of isoprene for all its reaction pathways with atmospheric oxidants (Millet et al., 2010). Besides photochemical production, acetaldehyde can also be released by terrestrial plants, in the process of ethanol production in leaves and roots following fermentation reactions (Jardine et al., 2008; Rottenberger et al., 2008; Winters et al., 2009). Formaldehyde and acetaldehyde have relatively short lifetime into the atmosphere, considering their photochemical reaction rate with OH radicals (9.37 10^{-12} and 15 10^{-12} cm^{3} $molecule^{-1}s^{-1}$, respectively - Atkinson and Arey, 2003) and hence they can be induced by relatively close sources. Formaldehyde and acetaldehyde concentrations showed clear seasonal variations (Fig. 7); with high summer and spring concentrations (mean concentrations of 2.1 ±1.5 and 1.1 ±0.5 μg m^{-3}, respectively). During summer, despite their lower lifetime, these OVOCs can be significantly induced by secondary and biogenic sources, which can explain their higher concentrations. During the summer field campaign of 2013 conducted at Ersa, the OH reactivity showed notable diurnal profile consistent with air temperature one, which can denotes that BVOCs, including secondary species, were greatly influencing the local atmospheric chemistry (Zannoni et al., 2017). These findings are in agreement with a large result on BVOC oxidation on the local photochemistry. Moreover, formaldehyde and acetaldehyde concentration levels remained relatively significant during fall (i.e., from October to December) and winter (mean concentration of 0.9 ±0.5 and 0.8 ±0.3 μg m^{-3}, respectively), suggesting a significant contribution of anthropogenic (primary and/or secondary) sources. Additionally, these OVOCs showed significant interannual variations. In late spring and summer, their concentrations may be dependent on temperature and solar radiation variations which can influence biogenic emissions. For instance, formaldehyde and acetaldehyde mean concentrations were higher in June 2012 (2.9 ±0.4 and 1.4 ±0.4 μg m^{-3} for formaldehyde and acetaldehyde, respectively) compared to June 2014 ones (2.2 and 0.8 μg m^{-3}), in agreement with biogenic concentration variations previously discussed in Sect 3.4.1. Formaldehyde and acetaldehyde concentrations were lower in August 2012 (2.0 ±0.6 and 1.2 ±0.2 μg m^{-3} for formaldehyde and acetaldehyde, respectively) than August 2013 ones (3.6 ±1.5 and 1.5 ±0.6 μg m^{-3}), in agreement with isoprene and α-pinene concentration variations (Fig. 5) and since meteorological conditions in August 2013 were more favorable to photochemical processes (Fig. 4). Furthermore, formaldehyde and acetaldehyde exhibited concentrations in February 2013 (1.5 ±0.7 and 1.2 ±0.3 μg m^{-3}, respectively) twice higher than February 2014 ones (each at 0.7 ±0.1 μg m^{-3}), consistent with NMHC concentration variations (Fig. 6).~~

~~Identified acetone sources include primary emissions from both biogenic (green plant and litter sources) and anthropogenic origins, but its emissions is thought to be globally of biogenic rather than anthropogenic origin (Goldstein and Schade, 2000; Schade and Goldstein, 2006). Acetone can also be induced by secondary (biogenic/anthropogenic) sources from VOC oxidation (e.g. propane, i-butane, i-pentane, monoterpenes and methylbutanol) and biomass burning (Goldstein and Schade, 2000; Jacob et al., 2002; Singh et al., 2004). Acetone is the OVOC of the selection with generally the highest atmospheric lifetime, considering its photochemical reaction rate with OH radicals (1.7 10^{-13} cm^{3} $molecule^{-1}s^{-1}$ – Atkinson and Arey, 2003), and hence acetone can result from distant sources and/or be formed within polluted air masses before they reach~~

~~the receptor site. As a result, distant sources can significantly contribute to its concentrations at Ersa. Actually, roughly half of acetone concentrations measured at diverse urban or rural sites have been assigned to regional background pollution by several studies . Acetone showed similar seasonal variations than formaldehyde and acetaldehyde, i.e. high concentrations during spring and summer (mean acetone concentration of 5.4 ±3.0 µg m^{-3}) suggesting that biogenic sources as well as secondary sources significantly contributed to its atmospheric abundance at Ersa. Acetone concentrations remained significantly high during winter and fall (mean concentration of 3.2 ±1.6 µg m^{-3} and lowest ones not below 1.5 µg m^{-3}), which can be potentially explained by significant contributions of anthropogenic sources and regional background pollution during these seasons. Similarly as formaldehyde and acetaldehyde, acetone showed significant interannual variations both in summer (mean concentrations in summer 2012 lower from 1.6 µg m^{-3} than summer 2013 one, related to meteorological parameter and biogenic VOC variabilities) and winter (mean concentrations in winter 2013 higher from 1.7 µg m^{-3} than winter 2014 one, related to NMHC variability).~~

~~Methyl ethyl ketone (MEK) can be emitted by terrestrial vegetation or by numerous anthropogenic sources, such as biomass burning, solvent evaporation as well as vehicle exhaust, and can be produced by the atmospheric oxidation of other VOCs like n-butane (Yáñez-Serrano et al., 2016 and references therein). MEK is characterized by photochemical reaction rates with OH radicals ten times higher than acetone one (1.22 10^{-12} cm^{3} molecule^{-1}s^{-1} – Atkinson and Arey, 2003) but admitted low enough to allow advection to the receptor site of MEK released by distant pollution sources or its formation during the transport of polluted air masses. MEK showed distinct variations from other OVOC ones discussed in this section. Indeed, MEK concentrations did not show seasonal variations except an increasing winter trend (mean-concentration of 0.4 ±0.1 µg m^{-3}). This finding suggests that anthropogenic (primary and secondary) sources significantly contribute to MEK concentrations. As observed for most NMHCs in Sect. 3.4.2, MEK exhibited different concentration levels during the two studied winter periods since its mean concentration in February 2013 was by 0.2 µg m^{-3} higher than its February 2014 one.~~

~~3.4.4 Comparisons with other VOC measurements performed at Ersa~~

~~The comparison between the VOC monitoring measurements as investigated in this study with concurrent campaign measurements performed during the summers of 2012, 2013 and 2014 is detailed in Section S3 of the Supplement. The purpose is to examine the representativeness of the 2-yr observation period in terms of summer concentration levels. As a synthesis of these comparisons, VOC concentration levels and variations of the three summer field campaigns were globally in consistency with those previously described in this study. This finding can suggest that the annual temporal coverage of VOC measurements realized over the two years was sufficiently adapted to well characterize VOC concentration variations (at seasonal scale). However, campaign data in the Supplement show that BVOC day to day variations can be significant especially in summer, as established by Kalogridis (2014) and Michoud et al. (2017). Interpretation of interannual variations of BVOC measurements is based on a limited number of sampling days during the studied period, it should then be considered cautiously.~~

3.5 Major ~~VOC~~ NMHC ~~factorial analysis~~sources

In the coming section, major NMHC sources which have impacted primary NMHC concentrations measured at Ersa were identified using a~~the~~ PMF 5-factor solution ~~composed of 5 factors~~ (from simulations presented in Sect. 2.3) ~~is described and examined~~and a dataset composed of 14 variables (selected NMHCs measured from steel canisters, see Sect. S2). Figure 7~~8~~ depicts factor contributions to the species chosen as inputs for the PMF tool along with ~~VOC~~ NMHC contributions to the 5 factors defined by the factorial analysis. Figure~~s~~ ~~9~~8 and Table 5 ~~and 10~~ show PMF factor contribution time series and their relative contributions to the total concentrations of the selected NMHCs in this factorial analysis, respectively ~~and their seasonal and interannual variations, respectively~~. Average factor relative contributions as a function of the measurement sampling times are also indicated in Table 5. ~~. Note that winter variations will be investigated thereafter (Sect. 4.2).~~ In the present section, lifetimes were assessed from kinetic rate constants of the reactions of selected ~~VOCs~~ 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 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 Ersa. A part of them may not be precisely associated with emission profiles but should rather be explained as aged profiles originating from several source regions comprising several source categories ~~s assimilating to several source categories~~ (Sauvage et al., 2009). The PMF analysis was hence performed to define co-variation factors of primary VOCs 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 this study, PMF result relevance was checked, benefiting from previous PMF analysis performed with the Ersa VOC summer 2013 dataset (42 variables; Michoud et al., 2017) and experimental strategies to characterize VOC concentration variations at a remote background such as Ersa are discussed in Sect. 3.5.6.

3.5.1 Local b~~B~~iogenic source (factor 1)

The average contribution of factor 1 to ~~the sum of~~ measured ~~VOC~~ concentrations of the NMHCs selected in the factorial analysis is of 0.2 ±0.4 µg m^{-3} on average during the observation period (corresponding to 4% of the sum of selected NMHCs – Table 5), peaking 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~~9~~). The chemical profile of factor 1 depicts an elevated contribution of isoprene, recognized as a chemical marker for biogenic emissions, having its variability fully related to this factor. The ~~relative load of this VOC for~~isoprene relative contribution to the factor 1 is 70%. The estimated tropospheric lifetime of isoprene ~~in the troposphere~~ was quite short (winter: 5.6 h and summer: 1.1 h), 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 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 the contributions of additional primary BVOCs (the sum of monoterpenes) and some OVOCs (carboxylic acids, methanol and acetone) and the clear diurnal variations of the local primary biogenic source.

~~Average seasonal contributions exhibited a seasonal cycle (Fig. 10a1) with high values in summer (July-September mean contribution of 0.5 ±0.4 µg m^{-3}) and spring values (April-June mean contribution of 0.3 ±0.6 µg m^{-3}), in agreement with isoprene variability investigated in Sect. 3.4.1. Biogenic emissions were directly related to ambient temperature and solar radiation (Sect. 3.4.1.), inducing these factor 1 contribution variations. As already observed for isoprene, factor 1 contributions showed significant interannual variations over the two years studied (Fig. 10b1), confirming that the biogenic source strength was dependent on meteorological conditions (Fig. 4).~~

3.5.2 Short-lived anthropogenic sources (factor 2)

19% of the sum of the selected measured ~~VOC~~NMHCs was attributed to factor 2 (Table 5). This ~~latter~~ 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 (~~EX;~~ 93%), ethylene (48%) and propene (83%), typically emitted by combustion processes and with short-to-medium lifetime (winter: 24 h-4.1 days; summer: 5-20 h). ~~, with an average contribution to the sum of measured VOC concentrations from this factor of 66%~~The relative contribution of these VOCs to factor 2 is 66%. ~~Note that factor 2 did not show a good correlation with CO (Pearson correlation coefficient only of 0.2).~~ 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 lifetime (winter: 4-6 days; summer: 21 h-1.3 day), also contributes to this factor by 19%. ~~Note that f~~Factor 2 did not show a good correlation with CO (Pearson correlation coefficient only of 0.2). Factor 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 previously investigated in Michoud et al. (2017).

~~Average seasonal contributions showed slightly higher contributions during fall (October-December mean factor 2 contribution of 1.3 ±0.6 µg m^{-3}) and winter (January-March: 1.1 ±0.7 µg m^{-3}; Fig. 10a2). As a consequence of lower available UV light and temperatures, OH concentrations decrease in fall and winter, inducing reduced chemical reaction rates. Consequently, VOCs were not depleted as rapidly as in spring/summer months. Moreover, the PBL height was significantly~~

~~lower in winter, conducting to less dilution of emissions, favouring relative accumulation of pollutants, and so increasing VOC concentrations. However, factor 2 contributions were also significant in spring and summer (mean factor 2 contributions of 0.9 ±0.4 µg m^{-3}, each), which could illustrate an enhanced evaporation of gasoline, solvent inks, paints and additional applications during these months as a result of higher temperatures. Interannual comparison of mean monthly factor 2 contributions (Fig. 10b2) pointed out no clear seasonal variation over the study period, suggesting this source was of different origins during the two years studied, probably related to air mass origin occurrences and trajectories (discussed in Sect. 4.2).~~ Regarding factor 2 contributions coupled with air mass clusters (Fig. ~~11~~9), more elevated contributions were noticed 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. Furthermore, CF analysis applied to factor 2 contributions (see Fig. S3~~2~~ 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, s~~S~~hip emission contribution cannot be discarded as well, as already suggested 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 factor 3 to the sum of selected measured ~~VOC~~NMHC concentrations is approximately estimated at 1.2 ±1.0 µg m^{-3} (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-pentane (50%), n-pentane (59%), n-hexane (42%) and propane (43%; lifetimes of 4-21 days in winter, and 21 h-4 days in summer). 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~~ – LPG~~; Sauvage et al., 2009 and references therein). Additionally, propane can be viewed as a relevant profile signature of natural gas transport, storage and use (Leu~~n~~chner et al., 2015). The cumulated relative contribution of these ~~VOCs~~ alkanes to factor 3 is up to 88%. As a result, this factor can be viewed as “evaporative sources”.

~~Average seasonal contributions exhibited a seasonal cycle (Fig. 10a3) with high winter and fall values (mean contribution of 2.2 ±0.7 and 1.9 ±1.0 µg m^{-3}, respectively). During the cold season, evaporative emissions can be expected to be lower. But, as a result of lower OH concentrations and weaker solar radiation in this period than in summer, the chemical lifetimes of the involved compounds were intensified in winter and fall, which may have favoured their advection to the site and their accumulation. Factor 3 contributions and CO concentrations were quite correlated especially in winter and fall (Pearson correlation coefficient of 0.6), similarly as factors 3 and 2 (0.5). These findings suggest that the high contributions in these seasons of evaporation tracers may be related to the combustion processes as well and factors 2 and 3 can be partly related to the same sources. Mean factor 3 contributions were only 0.5-0.6 µg m^{-3} in spring and summer. This low contribution~~

~~can be partly explained as it was mainly composed of VOCs with medium lifetimes which may rapidly react during these seasons before reaching the receptor site. Interannual comparisons of mean monthly factor 3 contributions (Fig. 10b3) pointed out a clear and reproducible seasonal variation over the two years studied. This finding could suggest that this factor was largely influenced by chemical processes and regional contributions.~~ Regarding factor contributions as a function of air mass clusters (Fig. ~~1~~9~~1~~), more elevated contributions were noticed when aged air masses originated from France and Europe and probably transported toward Ersa by relatively distant sources. According to the CF analysis applied to factor 3 contributions (Fig. ~~S2~~ 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 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 ~~VOC~~ concentration of the selected measured NMHCs is roughly evaluated at 0.9 ±0.7 µg m^{-3} (16% of the 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 average ~~total~~ cumulated relative contribution ~~to the sum~~ of ~~measured~~ these VOC ~~concentrations from~~to this factor of 80%. Aromatic compounds and acetylene are generally ~~attributed to~~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 partly aged air masses advected towards the ~~measurement site~~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.

~~Average seasonal contributions (Fig. 10a4) exhibited a clear seasonal cycle with intense winter values and really low summer ones (mean contribution of 1.8 ±0.8 and 0.3 ±0.1 µg m^{-3}, respectively). This factor 4 strength variation is consistent with an elevated use of heating systems during wintertime due to typical low temperatures. Moreover, factor 3 showed good correlation with factor 4 in winter and fall (Pearson correlation coefficient of 0.5), suggesting a contribution of these combustion sources to evaporative sources. A clear and reproducible seasonal variation of factor 4 contributions was observed over the two years studied (Fig. 10b4) that could suggest this factor was largely influenced by chemical processes and regional contributions, along with source strength.~~ Furthermore, factor 4 showed higher contributions when the Ersa station received European air masses (see Fig. ~~1~~9~~1~~), especially by ~~ones~~ those having long trajectories. The CF analysis depicted in Fig. ~~S2~~ 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. ~~Note that the CF analysis mostly highlighted factor contribution origins observed in wintertime (detailed in Sect. 4). As a reminder, the interannual variations observed in winter will be analysed in section 4.2.~~

3.5.5 Regional background (factor 5)

Contributing at 39% to the total concentration of the selected measured ~~VOCs~~NMHCs, factor 5 corresponds to the dominant ~~VOC~~NMHC ~~-~~source detected at Ersa during the study period. The profile of this factor is principally dominated by ethane, having its variability fully explained by factor 5 (Fig. 7), and is also composed of propane (18% explained). 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 ~~VOCs~~ NMHCs with shorter lifetimes are attributed to this factor, including ethylene (16% explained) and propene (12%; lifetime of 21 h to 3 days in winter and of 4-13 h in summer) despite a low contribution to factor 5 mass (~3%). Hence, the high abundance of long-lived species may result here from aged air masses advected to the ~~study site~~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 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, we associated factor 5 with the “regional background”.

~~Mean seasonal contributions (Fig. 10a5) exhibited a characteristic feature for this source with a maximum in winter (mean contribution of 3.3 ±0.6 µg m^{-3}) in link with tropospheric accumulation, succeeded by a decline in spring and summer (mean contribution of 2.1 ±0.7 and 1.2 ±0.2 µg m^{-3}, respectively) probably related to photochemical decay and dilution processes. As already observed for ethane (Sect. 3.4.2), factor 5 contributions did not show any interannual variation over the two years studied (Fig. 10b5), confirming that this factor was largely influenced by chemical and dilution processes and long-range transport. Note that factor 5 showed good correlation both with factor 4 and CO (Pearson correlation coefficient of 0.8 and 0.7, respectively), which can suggest similar origins. Mean f~~Factor 5 showed slightly higher contributions when the Ersa station was ~~in function of air mass origins were in the same range, except that more elevated contributions were noticed~~ under the influence of European air masses (especially those ~~potentially connected to distant contributions~~having long trajectories and hence potentially connected to distant emission areas; Fig. 9~~11~~)~~ compared to the ones related to others continental origins~~. As expected, the CF analysis applied to factor 5 contributions did not clearly pinpoint a specific potential emission area (Fig. S3~~2~~ 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 variation in VOC concentrations observed at a remote background site

The choice to restrain the number of VOCs in the factorial analysis, to have a better temporal representativeness of factor contributions (Sect. S2), as well as VOC measurement temporal resolution and collection periods and the number of observations, have undoubtedly had some consequences on the PMF solution results of this study (in terms of factor number, chemical profiles and variations). As a result, the 2-yr PMF results of this study 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 ~~local~~ 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 ~~cover~~examine seasonal and interannual variations of main primary sources impacting VOC concentrations observed at the ~~receptor site~~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 t~~T~~he 5-factor PMF solution~~,~~ modelled with ~~a~~ the ~~two~~ 2-y~~ea~~r ~~VOC~~ NMHC dataset (14 variables, 152 4-h resolution observations), ~~(from June 2012 to June 2014) was compared~~with ~~with~~ the 6-factor PMF solution modelled with the shorter summer ~~SOP-1b~~2013 VOC dataset ~~(from 15 July to 5 August 2013), composed of 6 factors, namely primary biogenic factor, secondary biogenic factor, short-lived anthropogenic factor, medium-lived anthropogenic factor, long-lived anthropogenic factor and oxygenated factor~~ (42 variables, 329 1.5-h resolution observations, Michoud et al., 2017) 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 factorial analyses as influencing VOC 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 concentrations over two years and suggests that these selected NMHCs included dominant tracers of these sources.

To support this statement, a summer 2013 PMF solution, realized considering only the 17 NMHCs selected in the factorial analysis of this study as inputs, was examined and compared with the summer 2013 PMF solution modelled with a higher number of VOCs by Michoud et al. (2017; Sect. S6 in the Supplement). Results 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 have depended on additional VOCs – Sect. S6). PMF factorial analyses have hence shown limitations in the investigation of short-lived anthropogenic sources influencing Ersa VOC concentrations, given 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).

Furthermore, the 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 for a better assessment of the contribution of local biogenic sources, considering BVOC day-to-day variations, as noticed in summer 2013 (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 by the fact that different interannual BVOC concentration variations were noticed between isoprene and selected speciated monoterpenes in Sect. 3.4.1. Concentrations of non-speciated monoterpenes measured in summer 2013 were mainly attributed to the same primary biogenic source as for isoprene concentrations in Michoud et al. (2017). But variations in the sum of monoterpenes may have reflected those related to abundant biogenic species such as α-pinene, and hence masked those characterizing more-reactive species such as α-terpinene (Kalogridis, 2014; Debevec et al., 2018).

The limited range of VOCs included in the PMF study had the advantage to better deconvolve 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 elevated background levels (like for ethane, methanol and acetone of the summer 2013 VOC dataset; Michoud et al., 2017). These low concentrations thus represented a higher proportion on 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~~they~~ also raised the importance of the consideration of a finer time resolution and a higher temporal coverage of VOC measurements conducted at a remote background site such as Ersa~~s~~ to ~~comfort~~support results from source apportionment, in terms of deconvolution of anthropogenic sources~~,~~. Indeed, anthropogenic sources identified with the 4-h observations in this study have~~ which can~~ shown some significant correlations between them (Sect. S5), as a consequence of their similar seasonal variations (Sects. 3.4.2 and 4). The consideration in the 2-yr factorial analysis of diurnal variations ~~c~~would help ~~to limit~~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 of main primary sources influencing VOC concentrations observed at the Ersa station (Sects. S5 and S6), but can modify their relative contributions, emphasizing the contribution of local biogenic/anthropogenic sources and decreasing the contribution of regional anthropogenic sources (Michoud et al, 2017). ~~Note that the SOP-1b PMF source apportionment was performed considering a dataset composed of 42 VOCs, comprising six oxygenated compounds and collected with three different on-line techniques (see Sect. S3 of the Supplement). Chemical profile, variability and origin of these summer factors were examined in Michoud et al. (2017). Benefiting from these results, the two source apportionment analyses can be confronted to evaluate the representativeness of their source composition and contributions. Comparison results are hence presented in Sect. S4 of the Supplement, supporting the investigation of the contribution of both experimental strategies to characterize the main sources influencing VOC levels observed at the receptor site of long-range transported pollution impacting the western Mediterranean region.~~ ~~On one hand, the SOP-1b intensive field campaign occurred in summer and~~

~~offered good conditions to (i) monitor at a specific period anthropogenic sources, influenced by several geographic origins along with biogenic local 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 cover seasonal and interannual variations of main primary sources impacting VOC concentrations observed at the receptor site. Globally, sources identified as influencing VOC concentrations at Ersa had similar chemical compositions. The longer time scale of VOC measurements (i.e. the 2-yr period) presented here helped to deconvolve long-lived combustion sources from regional background. Nevertheless, the time resolution of VOC measurement of the 2-yr period (4 hours compared to 1 hour and a half during the SOP-1b period) and the limited number of sampling days during this study period did not help to support the clear deconvolution of the 5 factors, as factors related to anthropogenic sources were quite correlated between them (as a consequence of their seasonal variations – see Sect. 3.5; and unlike SOP-1b anthropogenic sources showing between them Pearson correlation factors from -0.5 to 0.1). Finally, the incorporation of OVOCs in the source apportionment had little impact on the identification of main primary sources influencing VOC concentrations observed at the receptor site but can modify their relative contributions, emphasizing the contribution of local biogenic/anthropogenic sources and decreasing the contribution of regional anthropogenic sources.~~

The VOCs observed at Ersa were largely dominated 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 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 primary sources, but the limited number of samples realized with DNPH cartridges did not favor it (Fig. S1 and Sect. S2). Formaldehyde has shown high concentration levels (Table 3) and clear seasonal variation (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 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. 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 and fall.

4.1 ~~Determination of controlling factors~~VOC concentration variations in spring and summer

~~In this section, source contributions are examined regarding their seasonal variations so as to identify the prevailing drivers for VOC concentration variations. Benefiting from two years of observations, the discussion will also be focused on interannual variations. Seasonal accumulated contributions of the main sources identified as contributing to the total VOC mass observed at Ersa during the study period were summarized in Fig. 12. Note that spring 2012 data are not presented in Fig. 12, since the monitoring period started in June 2012 and did not cover the whole season. During this particular month, the biogenic source was determined to be the largest contributor to the cumulated VOC concentrations (34% of the total VOC mass explained) since its emissions were enhanced by the high temperatures monitored (Fig. 4).~~

Firstly, ~~low total contributions of~~ the ~~five VOC factors~~21 NMHCs ~~were observed~~have shown low concentrations during summer and spring periods (average seasonal accumulated concentration of ~~mean total contributions of~~ 4~~3~~.6~~4~~ ±0.1~~8~~ ~~and 4.4 ±0.9~~ μg m^{-3}; Fig. 10~~, respectively~~)~~.~~ while the 14 OVOCs exhibited high concentrations (8.0 ±1.8 μg m^{-3}). PBL height can be higher in these seasons (von Engeln and Teixeira, 2013), favouring vertical dispersion. OVOC concentration levels in summer and spring are in agreement with a higher 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, ~~The regional background and the short-lived anthropogenic sources were identified as the largest contributors to the total VOC concentrations monitored at Ersa in spring and summer.~~ regional background ~~The regional background contributed~~explained in spring and summer from ~~30~~ 24 to 53~~5~~% of the total Ersa ~~VOC~~ concentration of the NMHCs selected in this study~~observed at the Ersa station in these seasons~~. 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 ~~Especially since this source is principally constituted of long-lived compounds, it~~ also suggest~~s~~ that aged -emissions ~~air masses~~ advected by air masses to the ~~study site~~Ersa station significantly influenced VOC concentrations observed during these seasons. This statement is also in agreement with the high acetone concentration levels in summer and spring (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 reach the Ersa station (Sect. 3.4.3). As pinpointed by 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). ~~Additionally, s~~Short-lived anthropogenic sources explained in spring and summer from ~~19~~ 16 to ~~30~~24% of the ~~total VOC~~NMHC concentrations ~~mass~~. Despite the high reactivity of the VOCs composing these sources (Sect. 3.5.2)~~As the short-lived anthropogenic sources were composed of VOCs with short to medium lifetimes (Sect. 3.5.2), they can be rapidly depleted in spring and summer. Additionally, PBL height can be higher in these seasons (von Engeln and Teixeira, 2013), favouring~~

~~phenomena of vertical dispersion. However~~, their contributions were not reduced as sharply as those of other anthropogenic sources~~were elevated~~ (Fig. S4), which can ~~be~~ probably be ~~attributed~~ related to high influences of ship transport and relatively close potential emission areas (~~e.g. Italian coastline areas – see Fig. S2 of the Supplement~~Sect. 3.5.2). Evaporative and long lived combustion sources only contributed from ~~7~~ 6 to ~~17~~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). ~~Evaporative sources were mainly composed of VOCs with medium lifetimes along with of regional origins (Sect. 3.5.3), and hence, during these seasons, these compounds can have reacted and/or been dispersed before reaching the receptor site.~~ Low contributions of long-lived combustion sources can also be partly explained by a lower source strength (Sect. 3.5.4).

Looking now at the interannual variations during summer and spring periods, Fig. ~~12~~10 highlights that the total ~~contributions~~ concentrations of the ~~five VOC factors~~selected NMHCs were in the same range during the two summer periods as well as the two spring ones (absolute difference was of 0.~~3~~2 µg m^{-3} between summers 2012 and 2013 ~~total contributions~~ and below 0.1 µg m^{-3} between springs 2013 and 2014 ~~ones~~). As depicted in Fig. S4~~10~~, summer and spring contributions of ~~monthly contributions of~~ evaporative sources, long-lived combustion sources, and regional background, were in the same range ~~and followed the same variation from April to September~~ over the studied 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). Th~~ei~~se findings can suggest that these anthropogenic sources originating from distant emission areas were largely influenced by ~~chemical processes,~~ pollutant depletion and vertical/horizontal dispersion ~~phenomena and regional contributions in spring and summer~~during these seasons. Summer and spring c~~C~~ontributions of short-lived anthropogenic sources ~~were in the same range~~ seemed to be more variable as a function of the year (0.7-1.1 µg m^{-3}; Figs 10 and S4)~~during spring and summer (0.7-1.1 µg m^{-3}; Fig. 12) but did not seem to follow a specific variation (Fig. 10)~~. This finding suggests that these sources were largely influenced by origins of air masses, which advected to Ersa ~~some relatively close~~ numerous ~~source~~ 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 to concentrations of monoterpenes during the two summer periods (Fig. 10) and consistent with temperature and solar radiation variations (Sect. 3.4.1). Higher summer concentrations of formaldehyde and acetone were also noticed in 2013 than in 2012 (difference 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 to a change in its biogenic primary/secondary contributions than in its background levels. These findings suggest, in summer 2013, enhanced emissions from the local vegetation partly related to the release of monoterpenes and/or higher biogenic secondary contributions. For similar reasons, slightly higher spring contributions of biogenic sources were 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).

~~As a result, main parameters influencing VOC concentrations in spring and summer were meteorological conditions (i.e. high temperatures/solar radiation enhancing biogenic source contributions), OH concentrations (typically high especially~~

~~in summer) inducing higher photochemical decay, PBL height (typically high in summer) favouring vertical dispersion of pollutants and long-range transport.~~

~~During fall and winter periods, total contributions of the five VOC factors depicted in Fig. 12 were comprised between 6.1 and 9.4 µg m^{-3}. Several parameters can explain these levels. Firstly, chemical reaction rates dropped in fall and winter as a consequence of decreased OH concentrations owing to lower available UV light and temperatures (Fig. 4). Hence, VOCs were not removed from the atmosphere as quickly as in the summer/spring months. PBL height also decreased during these seasons, impacting vertical dispersion phenomena. Moreover, the regional background and evaporative sources were identified as the dominant contributors to the VOC concentrations collected at Ersa in fall and winter (contribution of 35-45% and of 24-33% to the total VOC concentration, respectively), suggesting that regional contributions significantly influenced Ersa's VOC concentrations during these seasons. Long-lived combustion sources also contributed significantly to VOC concentrations specifically in winter (explaining 18-24% of the total VOC concentration) since the typical low ambient temperatures during these seasons (Fig. 4) may involve an increased use of residential heating. To better identify regional influences, average seasonal contributions of the anthropogenic sources were investigated in function of air mass origins in Fig. 13. During fall and winter, the receptor site was mostly influenced by continental air masses coming from Europe and France. Anthropogenic sources showed higher accumulated contributions when European air masses were advected to Ersa (Figs. 11 and 13), and could be attributed to potential emission areas located in Italy (the Po Valley and Central Italy) and possibly more distant potential emission areas in central Europe (western Hungary, Croatia, Slovenia - Fig. S2 of the Supplement). To a lesser extent, high anthropogenic source contributions were also noticed when Ersa received air masses originating from continental France (potential emission areas located in the southeast of France) and Corsica-Sardinia.~~

~~Concerning the interannual variations during fall and winter periods, Fig. 12 shows that total contributions of the five VOC factors were in the same range during the two fall periods (absolute difference of 0.4 µg m^{-3} between fall 2012 and 2013 total contributions). Contrariwise, the five factors total contribution in winter 2013 (9.4 ±2.5 µg m^{-3}) was higher by 1.9 µg m^{-3} than winter 2014 one on average. Looking now at source contributions during these two winter periods individually, regional background contributions were in the same range (absolute difference below 0.1 µg m^{-3}; Fig. 12), while contributions of long-lived combustion sources, short-lived anthropogenic sources and to a lesser extent evaporative sources were higher during winter 2013 compared to winter 2014 ones (absolute difference from 0.3 to 0.9 µg m^{-3}; Fig. 12).~~

4.2 ~~The particular case of winter~~VOC concentration variations in fall and winter

During fall and winter periods, total 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 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 OH concentrations owing to lower available UV light and temperatures (Fig. 3). Hence, VOCs were not removed from the atmosphere as quickly as in summer and spring. 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 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 to NMHC concentrations specifically in winter (explaining 18-24% of the total NMHC concentrations) since the typical low winter ambient temperatures (Fig. 3) may involve an increased use of residential heating (Sect. 3.5.4). To better identify regional influences, average winter and fall contributions of the anthropogenic sources 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 occurrences were from 36% to 70%). NMHC anthropogenic sources showed higher accumulated contributions when European air masses were advected to Ersa (Fig 11), and could be attributed to potential emission areas located in Italy and possibly more distant potential emission areas in central Europe (Sect. 3.5). To a lesser extent, high anthropogenic source accumulated contributions 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 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 difference 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 regional background winter contributions monitored 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~~T~~he ~~difference~~ interannual variations ~~of~~ in ~~contributions~~ VOC winter concentrations ~~between the two winter periods~~ could be partly explained by occurrences and origins of air masses advected to the Ersa station, their ~~origin occurrences~~ enrichment in different anthropogenic sources 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 ~~during~~ in winter 2013 than ~~during~~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 ~~winter~~ 2013 (10.8-9.6 µg m^{-3}, respectively; Fig. 11~~3~~) ~~compared to~~than in ~~winter~~ 2014 ~~ones~~ (8.2-7.8 µg m^{-3}). During 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 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, potential emission areas located in the Po Valley and the southeast of France, known to experience high anthropogenic emissions, did not seem to have contributed significantly to VOC concentrations in winter 2014. On the other hand, the Ersa~~the~~ station more frequently received air masses originating from Corsica-Sardinia, i.e. relatively close potential emission areas, in winter 2014 than in winter 2013 (occurrences of 24 and 0%, respectively). A~~ and hence was influenced by closer anthropogenic sources in winter 2014~~ccumulated anthropogenic source contribution associated with Corsican-Sardinian influence in winter 2014 was only 7.0 µg m^{-3} (Fig. 12). ~~Otherwise~~These findings can suggest less aged (but rather low) emissions have influenced Ersa concentrations in winter 2014 and can partly explain the lower OVOC winter concentrations observed at Ersa in 2014 than in 2013.~~, the average accumulated anthropogenic source contribution associated to Corsican-Sardinian influence was only 7.0 µg m^{-3} in winter 2014 (Fig. 13).~~

~~Moreover, Fig. 14 presents the CF analyses realized for the 4 anthropogenic sources using only winter 2013 and 2014 observations. These analyses globally showed that Ersa station was influenced by air masses of different potential origins in winters 2013 and 2014. During winter 2013, the main potential emission areas for the 4 anthropogenic 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. On the other hand, VOC concentrations observed at Ersa during winter 2014 were mostly influenced by contributions from relatively close (but rather low) potential emission areas located in Corsica and Sardinia (Fig. 14). Moreover, in winter 2014, Ersa did not seem to be influenced at all by air masses originating from central Europe (especially from Slovenia and Hungary - Fig. 14), that could partly explain the difference of VOC concentrations observed at the receptor site during the two winter periods. Surprisingly, potential emission areas located in the Po Valley and the southeast of France, known to experience high anthropogenic emissions, did not seem to have contributed significantly to VOC concentrations in winter 2014.~~

~~Even though contributions of long-lived combustion sources, short-lived anthropogenic sources and evaporative sources were significantly reduced in winter 2014 compared to winter 2013 ones (Sect. 4.1), the shape of their variations remained similar in winters 2013 and 2014, as depicted in Fig. 9, despite different potential origins have influenced VOC concentrations monitored at Ersa between these two winter periods. These findings could be an evidence of homogenous regional background pollution distribution at synoptic scale. Mean regional background contributions monitored in winters 2013 and 2014 (Sect. 4.1) are also in agreement with this suggestion. Moreover, t~~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 ~~source~~ emission strengths as well as chemical transformations occurring inside air masses all along their transport to the ~~receptor site~~Ersa station. These statements are consistent with interannual variations in OVOC winter concentrations. ~~.~~

To support these suggestions, we can notice that most countries of western Europe experienced different winters in 2013 and 2014~~, induced by different climatological events occurring during these two winter periods~~ (see Sect. 3.1 and Fig. S5 of the Supplement). As a reminder, w~~W~~inter 2013 was considered rather rigorous~~ (Fig. S3 of the Supplement)~~, 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~~03~~/10~~04~~/2020). On the other hand, winter 2014 was rather mild and temperatures were the hottest of the ~~1981~~1951-~~2010~~ 2014 period (mean temperature for Europe ~~reached 11.2 °C, i.e.~~was ~2.6~~1~~ °C higher than ~~the normal value~~the pre-industrial period; ~~Photiadou et al., 2015~~EEA, 2015~~ and Fig. S3 of the Supplement~~). ~~This difference of temperatures between the two winters studied could have affected OH concentrations. Indeed, m~~Meteorological winter conditions ~~in winter 2014~~ were probably more favourable to induce higher OH concentrations in 2014 than in ~~winter~~ 2013~~ ones~~, leading to higher photochemical decay, and so lower ~~VOC~~ NMHC concentrations observed at the ~~receptor site~~Ersa station. Higher temperatures along with the lack of cold nights in winter 2014 (Van Oldenborgh~~Photiadou et al.~~, 2015) may also have affected the source strength especially of long-lived combustion sources~~ in winter 2014~~. Furthermore, 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~~ observed at the receptor site~~. Note that in northern Italy, a very high monthly rainfall was recorded in winter 2014 (higher by 300% than the seasonal normal value for the 1981-2010 period; see Fig. S5~~3~~ of the Supplement). Abundant rainfalls were also noticed in southeast of France during winter 2014 (the highest one 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~~03~~/10~~04~~/2020). As a consequence, these meteorological conditions should have reduced anthropogenic source contributions from the Po Valley and the southeast of France in winter 2014.

~~As a summary, the main parameters governing VOC concentration variations in winter seem to be the emission strength of the main anthropogenic sources identified in this study, and the continental regional background level constrained by external parameters, i.e. dispersion phenomena (long-range transport, enrichment in anthropogenic sources of continental air masses advected to the site as well as air mass origin occurrences) and pollutant depletion (in relation to the oxidizing capacity of the environment). This study also highlights that meteorological conditions can significantly affect the importance of these parameters in controlling VOC concentration variations in winter. As a consequence, this finding also point out that shorter observation periods (i.e., up to two months) may be reflected the variability of the identified parameters under the specific meteorological conditions of the studied period.~~

5. VOC concentration variations in continental Europe

From June 2012 to June 2014, ~~VOC~~ NMHC measurements were concurrently conducted at 17 other European background monitoring stations (described in ~~Sect. 2.2.4~~Sect. S7), allowing us (i) to examine the representativeness of the Ersa station in terms of seasonal variations in ~~VOC~~ 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~~5~~ depicts monthly concentration time series of a selection of NMHCs measured at the 18 ~~considered~~ European monitoring stations (including Ersa).

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 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 ~~VOCs~~ 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 by regional background for ethane, by long-lived combustion sources for propane, acetylene and benzene, and by evaporative sources for n-butane (see ~~Section~~ Sect. 3.5 and Fig. 7~~8~~). As a result, the study of concentration variations of these source tracers may help to highlight~~ing~~ temporal and spatial variations in source contributions to ~~VOC~~ NMHC concentrations observed in most of continental Europe. In addition, despite its shorter lifetime compared to other ~~VOCs~~ NMHCs of the selection, ethylene concentration variations were also ~~also be taken into account~~examined in this study to investigate short-lived anthropogenic source importance and variability in continental Europe.

Monthly NMHC concentrations were ~~globally~~ European wide lower and relatively homogeneous from June to August whatever the location and the typology of the ~~considered~~ station (the highest absolute difference between anthropogenic ~~VOC~~ NMHC 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 suggests that~~, suggesting~~ the temperature was the main driver in regulating summer concentration levels, linked to~~ a high importance of~~ photochemistry processes and the vertical dispersion~~ phenomena in regulating concentration levels~~. ~~Note that e~~Ethane concentration levels were still relatively important during summer (mean concentrations > 1.0 µg m^{-3}) suggesting long-range transport (up to intercontinental pollution transport) was among the main parameters governing VOC summer concentration~~s in summer~~ in continental Europe. On the other hand, anthropogenic NMHC~~VOC~~ monthly concentration levels appear to be more spatially variable in continental Europe in winter. Indeed, the highest absolute differences between VOC winter concentrations measured at two stations ~~in winter was~~ 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 probably highlight spatial variations in anthropogenic source contributions to ~~VOC~~ NMHC concentrations observed in continental Europe in winter. Lower winter concentrations of the selected NMHCs ~~in winter~~ were observed at stations located in southern and western Europe, including Ersa, other French sites and high-altitude ones (see Fig~~s. 2 and~~ 13 and Sect. S7~~5~~). Note that high-altitude sites may have the particularity, compared to the other European sites, of being frequently in free-tropospheric conditions. Additionally, southwestern France and Po valley experienced a wet winter both in 2013 and 2014 (see Fig. S5~~3~~ of the Supplement) that may have had a significant impact on the enrichment in NMHC~~VOC~~ anthropogenic sources of air masses advected to these regions and hence can have participated in the decrease in~~of~~ ~~VOC~~NMHC concentrations monitored at nearby stations. ~~Then, a~~At stations located in central Europe (i.e. stations located in Switzerland, Germany and Czech Republic - see

Sect. S7~~Fig 2~~), NMHC concentrations tended to be more elevated in winter compared to southern and western European observations, especially for ~~VOC~~NMHC species potentially mainly explained by long-lived combustion sources, evaporative sources and short-lived anthropogenic sources, which could suggest these stations were under different influences. These findings are consistent with ~~VOC~~ NMHC primary source contribution~~concentration~~ variations as a function of air mass origins observed at Ersa and CF analyses examined in this study (Sect. 4.2 ~~-~~and Figs. 11~~3~~ and S3~~2~~ of the Supplement). Furthermore, precipitations in central Europe were less frequent and/or intense both in winters 2013 and 2014 compared to normal values for the 1981-2010 period (average values calculated by the NOAA – see Fig. S5~~3~~ of the Supplement) which may have favoured VOC source contribution accumulation and transport and hence can have induced higher VOC concentrations measured at nearby monitoring stations. Additionally, high NMHC winter concentrations were also observed in northern Europe ~~in winter~~, especially for ~~VOC~~NMHCs mainly explained by evaporative sources and long-lived combustion sources.

To go further, Fig. 1~~6~~4 depicts accumulated concentrations of a selection of 15 ~~VOCs~~ NMHCs measured 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 ~~in winter~~ build on what we have learned from Ersa's VOC observations in Sect. 4.2. These selected ~~VOCs~~ NMHCs are those taken into account in the PMF analysis applied to Ersa 2-yr ~~VOC~~ NMHC measurements (at the exception of ethylbenzene and o-xylene; Sect. ~~2.3.2~~S2). Stations located in southwestern France and Po Valley showed relatively ~~stable~~similar ~~VOC~~ NMHC concentrations in winters 2013 and 2014 (total differences ranged from -0.1 to 0.4 µg m^{-3}). At these sites, winter concentrations of ~~VOCs~~ NMHCs potentially explained by long-lived combustion sources have slightly decreased in ~~winter~~ 2014 compared to ~~winter~~in 2013 ~~ones~~ (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 normal values for the 1981-2010 period (Fig. ~~S3~~ S5 of the Supplement). However, ~~VOC~~ NMHC concentrations and their variations observed at Ersa and in northwestern France were more similar to central European ones than southwestern French and southern European ones. ~~VOC~~ NMHC winter concentrations measured in central Europe were generally significantly higher in ~~winter~~ 2013 ~~compared to~~than in ~~winter~~ 2014 ~~ones~~ (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 ~~-~~ ~~Fig.~~ Sect. S7~~2~~; total differences of -2.8-0.7 µg m^{-3}). As observed at Ersa again, in central Europe, NMHC~~VOC~~ winter concentrations potentially related to anthropogenic sources that have influenced Ersa winter ~~VOC observatio~~concentrations were higher in ~~winter~~ 2013 ~~compared to winter~~than in 2014 ~~ones~~, especially for those influenced by long-lived combustion sources (reduction of 0.7-1.1 µg m^{-3}, corresponding to 21-44% of winter 2013 concentrations) and short-lived anthropogenic source contributions (reduction of 0.6-1.3 µg m^{-3}, i.e. of 21-43%). ~~VOC~~ NMHC winter concentrations related to evaporative sources also decreased 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 when air masses were advected to the site from central Europe (Sect. 4.2~~Fig. 13~~). They also highlight interannual variations in local contributions to ~~VOC~~ NMHC winter concentrations observed in central Europe ~~in winter~~. Furthermore, 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 were respectively colder and warmer compared to normal values for the 1981-2010 period (Fig. ~~S3~~ S5 of the Supplement). That could partly explain NMHC~~VOC~~ winter concentration variations in central Europe in 2013 and 2014~~these winters~~. Winter m~~Note that m~~eteorological differences compared to normal values for the 1981-2010 period in ~~winters~~ 2013 and 2014 were more marked in central Europe compared to in southern France and southern Europe (Fig. S5~~3~~ of the Supplement), which could partly explain their respective interannual variations. ~~Then,~~ NMHC~~VOC~~ winter concentrations monitored in Scandinavia (represented by PAL station results~~observations~~ on Fig. ~~1~~14~~6~~) were higher in ~~winter~~ 2014 ~~compared to~~than in ~~winter~~ 2013 ~~ones~~ (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 ~~VOCs~~ 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~~3~~ of the Supplement), early winter 2014 in northern Europe ~~was not as warmer-than-average as in central Europe~~was also colder than normal values for the 1981-2010 period, since an intense cold wave occurred in January 2014 and was associated with a strong anticyclone ~~centered~~centred on western Russia and extending from Finland to Crimea. Additionally, winter precipitations in these regions were less frequent and/or intense than normal values for the 1981-2010 period (Fig. S5~~3~~ of the Supplement) in ~~winter~~ 2014 ~~compared to winter~~than in 2013 which may have favoured accumulation and transport and hence induced higher NMHC~~VOC~~ concentrations measured at nearby monitoring stations.

~~In conclusion, the study of NMHC variabilities in continental Europe showed that Ersa can be considered as a good regional representative station. Summer VOC concentration levels did not vary much spatially in Europe suggesting that photochemistry, vertical dispersion phenomena and long-range transport were the main drivers of VOC concentration variations in Europe in summer. Nevertheless, winter concentration levels can significantly vary temporally (at interannual scale) and spatially (lower concentrations in southern and western Europe than in central and northern Europe), pointing out local influence and spatial variations in anthropogenic source contributions to VOC concentrations observed in continental Europe. Ersa concentration variations in winter were more representative of central Europe than southern/western or northern Europe. These comparisons also revealed that meteorological conditions, especially in winter, can significantly influence anthropogenic source contributions by acting on their emission strengths, accumulation, transport or deposition, and hence they can affect VOC concentration levels impacting continental Europe.~~

6. Conclusions

~~The western Mediterranean is known as a sensitive region sorely affected by air pollution, making this region relevant for investigation. This atmospheric pollution is partly owing to the conjunction of intense local anthropogenic emissions, specifically concentrated in coastal cities, natural emissions enhanced by favourable climatic conditions as well as contributions of more distant sources. This complex mixture of air pollutants will have impacts on human health, ecosystems and climate. However, to clearly assess the various incidences of this complex pollution impacting the Mediterranean region,~~

~~supplementary observational data collected in the region were needed, since they remained scarce, especially long-term measurements.~~

~~Considering the variability of VOCs at different timescales, it is particularly interesting to carry out measurements over long periods to better understand seasonal and interannual variations in VOC sources impacting the region, especially in the view of the expected progression of climate change with regional warming. As a result, w~~Within the framework of the ChArMEx project, a ~~background~~ 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~~. Around 300 atmospheric measurements of a wide range of VOCs (primary anthropogenic and biogenic species as well as oxygenated compounds) were conducted at Ersa with different off-line techniques. This study presents~~ in order to examine seasonal variabilities of ~~25~~ 35 selected VOCs (21 NMHCs and 14 carbonyl compounds)~~, which showed significant concentration levels during the study period, and their various associated sources~~.

~~Particular attention in this study was brought to identifying and evaluating the respective contributions of the various potential sources influencing VOC observations at Ersa. Apportionment factorial analysis was hence conducted on the database composed of 14 primary VOCs (or grouped VOCs) using the positive matrix factorization technique. The objective was to define and examine covariation factors of VOCs that were characteristic of aged or local primary emissions. The selected PMF solution was composed of 5 factors, including a biogenic factor (average relative contribution of 4% to the total concentration of measured VOCs), three anthropogenic factors (short-lived anthropogenic sources, evaporative sources and long-lived combustion sources; cumulated contribution of 57%),-determined as originate from either local or more distant emission zones (e.g. Italy and potentially central Europe); and a remaining one (39%) related to regional background pollution (aged air masses advected to the site from a large part of continental Europe).~~

~~Five primary biogenic compounds were measured (including isoprene and α-pinene).~~ Biogenic ~~compounds~~ VOCs were principally imputed to ~~a local origin~~the local vegetation and exhibited high concentrations ~~from June to August~~and interannual variations in late spring and summer, related to temperature and solar radiation variations~~consistent with temperature and solar radiation variations~~. ~~During late spring/summer periods, biogenic source was one of the main sources impacting VOC concentrations observed at the receptor site (16% on average and up to 53%). Biogenic compounds also showed significant interannual variations, related to temperature and solar radiation variations.~~

A~~16~~ nthropogenic ~~selected primary anthropogenic species~~NMHCs, having atmospheric lifetimes ranging from a few hours to some days~~ and tracers of various sources~~, ~~were monitored at the receptor site~~have shown~~. Anthropogenic VOC concentrations observed at the receptor site were~~ low concentrations in spring and summer since the Ersa station was mostly influenced by aged advected air masses. Primary anthropogenic sources identified in this study ~~were~~were hence largely influenced by the ~~chemical processes~~pollutant depletion (in relation to the oxidizing capacity of the environment) and~~,~~ vertical dispersion before reaching the Ersa station~~phenomena and regional contributions~~, 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 and spring. ~~The regional background contributed from 30 to 55% to the total~~

~~measured VOC concentration observed at the Ersa station in these seasons. Short-lived anthropogenic sources also explained from 19 to 30% of the total measured VOC mass possibly contributed by ship transport and relatively close potential emission areas (southeastern French and Italian industrialized and populated coastline areas). Furthermore, a~~The~~ll~~ selected anthropogenic ~~compounds~~ 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 and fall have favoured the advection at Ersa of air masses enriched by 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 and spring. As a result, the regional background, evaporative sources and long-lived combustion sources were identified as the dominant contributors to 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 precipitations) occurring before they reached the Ersa station~~During these seasons, the regional background and evaporative sources were identified as the dominant contributors to VOC concentrations monitored at the study site (contributions of 35-45% and of 24-33% to the total VOC concentration, respectively), suggesting that regional contributions significantly influenced VOC concentrations in fall and winter. Long-lived combustion sources also contributed significantly to VOC concentrations especially in wintertime (explaining 18-24% of the total measured VOC mass), partly due to an increased use of residential heating in the cold season. Anthropogenic sources showed higher accumulated contributions when European air masses were advected to Ersa and could be attributed to potential emission areas located in Italy (the Po Valley and central Italy) and possibly more distant ones in central Europe (western Hungary, Croatia and Slovenia). To a lesser extent, high anthropogenic source contributions were also noticed when Ersa received air masses originating from France (potential emission areas located in the southeast of France) and Corsica-Sardinia. Interannual variations in anthropogenic VOC concentrations highlighted significant differences between winter periods of 2013 and 2014. VOC concentrations were particularly higher during winter 2013 compared to winter 2014 ones, associated with anthropogenic source contribution variations. Main parameters governing VOC concentration variations in winters 2013 and 2014 seem to be the emission strength of the main anthropogenic sources identified in this study, continental regional background together with external parameters, i.e. dispersion phenomena (long-range transport, enrichment in anthropogenic sources of continental air masses advected to the site as well as air mass origin occurrences) and pollutant depletion (in relation to the oxidizing capacity of the environment)~~. ~~This study also highlights that meteorological conditions can significantly affect the importance of these parameters in controlling VOC concentration variations in winter.~~

~~Moreover, four oxygenated VOCs (such as acetone)~~The OVOCs selected in this study largely prevailed in the VOC ~~speciation~~ abundance during the 2-yr monitoring period. They have also shown different seasonal and interannual variations, suggesting several source contributions. ~~OVOC sources can include primary emissions from both biogenic and anthropogenic origins and OVOCs may also be induced by secondary (biogenic/anthropogenic) sources from oxidation of various VOCs.~~ 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 ~~anthropogenic~~ primary/secondary anthropogenic sources, more specifically for MEK and glyoxal. OVOC have shown higher winter concentrations in 2013 than in 2014, as a result of the enrichment of air masses advected to Ersa by primary anthropogenic sources from regional origins.

~~Concurrent datasets of VOC concentrations from 3 summer campaigns performed at Ersa help to comfort the representativeness of the 2-yr monitoring period in terms of summer concentration levels, variations and source apportionment. The consistency in VOC concentration levels between the 2-yr monitoring period and the three summer ones can suggest that the annual temporal coverage of VOC measurements realized over the two years of the observation period was sufficiently adapted to well characterize VOC concentration variations (at seasonal scale). Moreover, sources identified in this study and those for the summer 2013 Ersa monitoring period showed globally similar chemical compositions, regarding VOCs in common between the two factorial analyses. These comparisons also pointed out the contribution of the larger time scale of VOC measurements to deconvolve long lived combustion sources from regional background and to highlight interannual variations in anthropogenic source contributions. However, they also raised the importance of the consideration of a finer time resolution and higher temporal coverage of VOC measurements conducted at remote background sites to comfort results from source apportionment, in terms of deconvolution of anthropogenic sources, which can show some significant correlations between them, as a consequence of their similar seasonal variations. The consideration in the factorial analysis of diurnal variations could help to limit this potential statistical bias.~~

~~Finally, during the same 25-month period as the Ersa monitoring campaign, VOC measurements were conducted at 17 other European monitoring stations, allowing us to examine the representativity of Ersa station in terms of seasonal and interannual variations in VOC concentrations impacting continental Europe and to provide some insights on dominant drivers for VOC concentration variations in Europe built on what we have learned from Ersa's VOC observations. T~~She study of elected NMHC variabilities in continental Europe ~~showed~~ supported that Ersa can be considered as a good regional representative station. ~~Summer VOC concentration levels did not vary much spatially, suggesting that photochemistry processes, vertical dispersion phenomena and long-range transport were the main drivers of VOC concentration variations in continental Europe in summer. Nevertheless~~However, ~~winter VOC~~NMHC winter concentration levels can significantly vary temporally ~~(at interannual scale)~~ and spatially ~~(lower concentrations in southern and western Europe than in central and northern Europe)~~, pointing out spatial variations in anthropogenic source contributions to ~~VOC~~ NMHC concentrations observed in continental Europe, in relation to~~.~~ ~~These comparisons also revealed that~~ meteorological conditions~~, especially in winter, can significantly influence anthropogenic source contributions by acting on their emission strengths, accumulation, transport or deposition, and hence they can affect VOC concentration levels impacting continental Europe.~~ Ersa winter concentration variations ~~in winter~~ were found more representative of central Europe than southern/western or northern Europe. ~~These comparisons also revealed that meteorological conditions, especially in winter, can significantly influence anthropogenic source contributions by acting on their emission strengths, accumulation, transport or deposition, and hence they can affect VOC concentration levels impacting continental Europe. As a result, t~~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. ~~As a consequence, this finding~~They also pointed out that the PMF-derived factors controlling VOC concentration variations at remote sites ~~shorter observation periods (i.e., up to two months)~~ may ~~reflect~~be mainly controlled by the ~~the variability of the identified parameters under the specific~~ meteorological conditions that occurred during the study period when issued from short observation periods (i.e. up to two months) ~~of the studied period~~.

Concurrent datasets of VOC concentrations from 3 summer campaigns performed at Ersa helped to ~~comfort~~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 seasonal variations in Ersa VOC concentrations, related to the VOC range and the temporal resolution of their measurements considered in the PMF analysis. After this ~~study~~work, some questions remain in terms of identification and characterization of OVOC sources and origins ~~at seasonal and interannual scales~~and of the contribution of local BVOC sources at seasonal and interannual scales. ~~Hence, i~~It would be interesting to conduct ~~at Ersa~~ 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~~,~~. ~~which~~ This would help ~~to~~ completing~~e~~ the understanding of determinants governing ~~O~~VOC concentration variations initiated both by Michoud et al. (2017) and this study.

Data availability

Access to EOP 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~~03~~/10~~04~~/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 field. TS calculated uncertainties related to VOC measurements conducted with DNPH cartridges and canisters and validated them following the ACTRIS protocol. CD, SS, VG and NL analyzed 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.

Acknowledgements

This study received financial support from the MISTRALS/ChArMEx programme funded by CNRS/INSU, CEA, and Météo-France, from ADEME, the French Environmental Ministry, the CaPPA projects, and the Communauté Territoriale de Corse (CORSiCA project). The CaPPA project (Chemical and Physical Properties of the Atmosphere) is funded by the French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir) under contract ANR-11-LABX-0005-01 and by the Regional Council Nord-Pas de Calais and the European Funds for Regional Economic Development (FEDER). This research was also funded by the European Union Seventh Framework Programme under grant agreement number 293897, the DEFI-VOC project, CARBO-SOR/Primequal and SAF-MED (ANR grant number ANR-12-BS06-0013-02). The authors are thankful for the O_3 and CO datasets made available, respectively, by François Gheusi from Laboratoire d'Aérologie and by ICOS-France monitoring network. The authors also want to thank Thierry Leonardis, Emmanuel Tison, Vincent Gaudion, Laurence Depelchin and Isabelle Fronval for their contributions to obtaining of VOC datasets, from the organization and the setting of instruments at Ersa to the analysis of VOC samples at the laboratory, but also Thierry Bourianne and Qualitair Corse team for their involvement on site concerning VOC sample routines as well as the associated logistic procedure. The authors finally thank the ChArMEx project manager Eric Hamonou for his logistical help.

References

Ait-Helal, W., Borbon, A., Sauvage, S., De Gouw, J. A., Colomb, A., Gros, V., Freutel, F., Crippa, M., Afif, C., Baltensperger, U., Beekmann, M., Doussin, J. F., Durand-Jolibois, R., Fronval, I., Grand, N., Leonardis, T., Lopez, M., Michoud, V., Miet, K., Perrier, S., Prévôt, A. S. H., Schneider, J., Siour, G., Zapf, P., and Locoge, N.: Volatile, and intermediate volatility organic compounds in suburban Paris: Variability, origin, and importance for SOA formation, Atmos. Chem. Phys., 14, 10439–10464, doi:10.5194/acp-14-10439-2014, 2014.

Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds: a review, Atmos. Environ., 24A, 1–41, doi:10.1016/j.atmosenv.2007.10.068, 1990.

Atkinson, R.: Atmospheric chemistry of VOCs, and NO(x), Atmos. Environ., 34, 2063–2101, doi:10.1016/S1352-2310(99)00460-4, 2000.

Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds., Chem. Rev., 103, 4605–4638, doi:10.1021/cr0206420, 2003.

Badol, C., Locoge, N., and Galloo, J.: Using a source-receptor approach to characterise VOC behaviour in a French urban area influenced by industrial emissions Part II : Source contribution assessment using the Chemical Mass Balance (CMB) model, Sci. Total Environ., 9, 429–440, doi:10.1016/j.scitotenv.2007.09.002, 2008.

Borbon, A., Coddeville, P., Locoge, N., and Galloo, J. C.: Characterising sources, and sinks of rural VOC in eastern France, Chemosphere, 57, 931–942, doi:10.1016/j.chemosphere.2004.07.034, 2004.

Bressi, M., Sciare, J., Ghersi, V., Mihalopoulos, N., Petit, J. E., Nicolas, J. B., Moukhtar, S., Rosso, A., Féron, A., Bonnaire, N., Poulakis, E., and Theodosi, C.: Sources, and geographical origins of fine aerosols in Paris (France), Atmos. Chem. Phys., 14, 8813–8839, doi:10.5194/acp-14-8813-2014, 2014.

~~Brown, S. G., Eberly, S., Paatero, P., and Norris, G. A.: Methods for estimating uncertainty in PMF solutions: Examples with ambient air, and water quality data, and guidance on reporting PMF results, Sci. Total Environ., 518–519, 626–635, doi:10.1016/j.scitotenv.2015.01.022, 2015.~~

Buzcu, B., and Fraser, M. P.: Source identification, and apportionment of volatile organic compounds in Houston, TX, Atmos. Environ., 40, 2385–2400, doi:10.1016/j.atmosenv.2005.12.020, 2006.

Cachier, H., Aulagnier, F., Sarda, R., Gautier, F., Masclet, P., Besombes, J. L., Marchand, N., Despiau, S., Croci, D., Mallet, M., Laj, P., Marinoni, A., Deveau, P. A., Roger, J. C., Putaud, J. P., Van Dingenen, R., Dell'Acqua, A., Viidanoja, J., Martins-Dos Santos, S., Liousse, C., Cousin, F., Rosset, R., Gardrat, E., and Galy-Lacaux, C.: Aerosol studies during the ESCOMPTE experiment: An overview, Atmos. Res., 74, 547–563, doi:10.1016/j.atmosres.2004.06.013, 2005.

Charron, A., Plaisance, H., Sauvage, S., Coddeville, P., Galloo, J. C., and Guillermo, R.: A study of the source-receptor relationships influencing the acidity of precipitation collected at a rural site in France, Atmos. Environ., 34, 3665–3674, doi:10.1016/S1352-2310(00)00096-0, 2000.

Cholakian, A., Beekmann, M., Colette, A., Coll, I., Siour, G., Sciare, J., Marchand, N., Couvidat, F., Pey, J., Gros, V., Sauvage, S., Michoud, V., Sellegri, K., Colomb, A., Sartelet, K., Langley DeWitt, H., Elser, M., Prévot, A. S. H., Szidat, S., and Dulac, F.: Simulation of fine organic aerosols in the western Mediterranean area during the ChArMEx 2013 summer campaign, Atmos. Chem. Phys., 18, 7287-7312, doi.org:10.5194/acp-18-7287-2018, 2018.

Colette, A., Granier, C., Hodnebrog, Ø., Jakobs, H., Maurizi, A., Nyiri, A., Rao, S., Amann, M., Bessagnet, B., D'Angiola, A., Gauss, M., Heyes, C., Klimont, Z., Meleux, F., Memmesheimer, M., Mieville, A., Rouïl, L., Russo, F., Schucht, S., Simpson, D., Stordal, F., Tampieri, F., and Vrac, M.: Future air quality in Europe: a multi-model assessment of projected exposure to ozone, Atmos. Chem. Phys., 12, 10613–10630, doi:/10.5194/acp-12-10613-2012, 2012.

Colette, A., Bessagnet, B., Vautard, R., Szopa, S., Rao, S., Schucht, S., Klimont, Z., Menut, L., Clain, G., Meleux, F., Curci, G., and Rouïl, L.: European atmosphere in 2050, a regional air quality and climate perspective under CMIP5 scenarios, Atmos. Chem. Phys., 13, 7451–7471, doi:10.5194/acp-13-7451-2013, 2013.

Coy, L., and Pawson, S.: The major stratospheric sudden warming of January 2013: Analyses, and forecasts in the GEOS-5 data assimilation system, Mon. Weather Rev., 143, 491–510, doi:10.1175/MWR-D-14-00023.1, 2015.

Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., and Locoge, N.: Origin, and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus), Atmos. Chem. Phys., 17, 11355–11388, doi:10.5194/acp-17-11355-2017, 2017.

Debevec, C., Sauvage, S., Gros, V., Sellegri, K., Sciare, J., Pikridas, M., Sarda-esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., and Locoge, N.: Driving parameters of biogenic volatile organic compounds, and consequences on new particle formation observed at an eastern Mediterranean background site, Atmos. Chem. Phys., 18, 14297–14325, doi:10.5194/acp-18-14297-2018, 2018.

~~Derwent, R. G., Dernie, J. I. R., Dollard, G. J., Dumitrean, P., Mitchell, R. F., Murrells, T. P., Telling, S. P., and Field, R. A.: Twenty years of continuous high time resolution volatile organic compound monitoring in the United Kingdom from 1993 to 2012, Atmos. Environ., 99, 239–247, doi:10.1016/j.atmosenv.2014.10.001, 2014.~~

Detournay, A.: Etude de COV oxygénés et biogéniques en milieu rural : du développement métrologique à l'évaluation de l'impact sur la chimie atmosphérique, Université Lille 1; http://www.theses.fr/2011LIL10139, 2011.

Detournay, A., Sauvage, S., Locoge, N., Gaudion, V., Leonardis, T., Fronval, I., Kaluzny, P., and Galloo, J. C.: Development of a sampling method for the simultaneous monitoring of straight-chain alkanes, straight-chain saturated carbonyl compounds, and monoterpenes in remote areas, J. Environ. Monit., 13, 983–990, doi:10.1039/c0em00354a, 2011.

Detournay, A., Sauvage, S., Riffault, V., Wroblewski, A., and Locoge, N.: Source, and behavior of isoprenoid compounds at a southern France remote site, Atmos. Environ., 77, 272–282, doi:10.1016/j.atmosenv.2013.03.041, 2013.

Doche, C., Dufour, G., Foret, G., Eremenko, M., Cuesta, J., Beekmann, M., and Kalabokas, P.: Summertime tropospheric-ozone variability over the Mediterranean basin observed with IASI, Atmos. Chem. Phys., 14, 10589–10600, doi:10.5194/acp-14-10589-2014, 2014.

Dollard, G. J., Dumitrean, P., Telling, S., Dixon, J., and Derwent, R. G.: Observed trends in ambient concentrations of C2-C8 hydrocarbons in the United Kingdom over the period from 1993 to 2004, Atmos. Environ., 41, 2559–2569, doi:10.1016/j.atmosenv.2006.11.020, 2007.

Draxler, R. R., and Hess, G. D.: An overview of the HYSPLIT_4 modelling system for trajectories, dispersion, and deposition, Aust. Meteorol. Mag., 47, 295–308, 1998.

Dulac, F.: An overview of the Chemistry-Aerosol Mediterranean Experiment (ChArMEx), Geophysical Research Abstracts, p. 11441, EGU General Assembly 2014, Vienna. [online] Available from: http://adsabs.harvard.edu/abs/2014EGUGA..1611441D, 2014.

EEA: Global and European temperatures, https://www.eea.europa.eu/data-and-maps/indicators/global-and-european-temperature-1/assessment (last access: 11/10/2020), 2015.

Elbir, T., Cetin, B., Cetin, E., Bayram, A., and Odabasi, M.: Characterization of volatile organic compounds (VOCs), and their sources in the air of Izmir, Turkey, Environ. Monit. Assess., 133, 149–160, doi:10.1007/s10661-006-9568-z, 2007.

Encyclopædia Britannica: Corsica, https://www.britannica.com/place/Corsica (last access: 11~~8~~/10~~04~~/2020), 2018.

Eyring, V., Köhler, H. W., Van Aardenne, J., and Lauer, A.: Emissions from international shipping: 1. The last 50 years, J. Geophys. Res. Atmos., 110, D17305, doi:10.1029/2004JD005619, 2005.

~~Fanizza, C., Incoronato, F., Baiguera, S., Schiro, R., and Brocco, D.: Volatile organic compound levels at one site in Rome urban air, Atmos. Pollut. Res., 5, 303–314, doi:10.5094/APR.2014.036, 2014.~~Ferracci, V., Bolas, C. G., Freshwater, R. A., Staniaszek, Z., King, T., Jaars, K., Otu-Larbi, F., Beale, J, Malhi, Y., William Waine, T., Jones, R. L., Ashworth, K. and Harris, N. R. P.: Continuous isoprene measurements in a UK temperate forest for a whole growing season: Effects of drought stress during the 2018 heatwave, Geophysical Research Letters,47, e2020GL088885, https://doi.org/10.1029/2020GL088885, 2020.

Filella, I., and Peñuelas, J.: Daily, weekly, and seasonal time courses of VOC concentrations in a semi-urban area near Barcelona, Atmos. Environ., 40, 7752–7769, doi:https://doi.org/10.1016/j.atmosenv.2006.08.002, 2006.

Finlayson-Pitts, B. J., and Pitts, J. N., Jr: Overview of the chemistry of polluted and remote atmospheres, in Chemistry of the Lower and Upper Atmosphere - Theory, Experiments and Applications, Academic Press, San Diego, CA, USA, 1-14, 2000.

Friedrich, R., and Obermeier, A.: Anthropogenic emissions of volatile organic compounds, in Reactive Hydrocarbons in the Atmosphere, Academic. Press, San Diego, CA, USA, 1-39, https://doi.org/10.1016/B978-012346240-4/50002-3, 1999.

Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal , and implications for formation of secondary organic aerosols, J. of Geophys. Res., 13, D15303, 2008.

Geron, C., Rasmussen, R., Arnts, R. R., and Guenther, A.: A review and synthesis of monoterpene speciation from forests in the United States, Atmos. Environ., 34, 1761–1781, doi:10.1016/S1352-2310(99)00364-7, 2000a.

Geron, C., Guenther, A., Sharkey, T. O. M., and Arnts, R. R.: Temporal variability in basal isoprene emission factor, Tree Physiol., 20, 799–805, doi:10.1093/treephys/20.12.799, 2000b.

Giorgi, F.: Climate change hot-spots, Geophys. Res. Lett., 33, L08707, doi:10.1029/2006GL025734, 2006.

Goldstein, A. H., and Schade, G. W.: Quantifying biogenic, and anthropogenic contributions to acetone mixing ratios in a rural environment, Atmos. Environ., 34, 4997–5006, doi:10.1016/S1352-2310(00)00321-6, 2000.

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, J. Geophys. Res. D Atmos., 110, 1–22, doi:10.1029/2004JD005623, 2005.

Grant, A., Yates, E. L., Simmonds, P. G., Derwent, R. G., Manning, A. J., Young, D., Shallcross, D. E., and O’Doherty, S.: A five year record of high-frequency in situ measurements of non-methane hydrocarbons at Mace Head, Ireland, Atmos. Meas. Tech., 4, 955–964, doi:10.5194/amt-4-955-2011, 2011.

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., and Fall, R.: Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America, Atmos. Environ., 34, 2205–2230, doi:10.1016/S1352-2310(99)00465-3, 2000.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases, and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

Hakola, H., Hellén, H., and Laurila, T.: Ten years of light hydrocarbons (C2-C6) concentration measurements in background air in Finland, Atmos. Environ., 40, 3621–3630, doi:10.1016/j.atmosenv.2005.08.019, 2006.

Hellén, H., Hakola, H., and Laurila, T.: Determination of source contributions of NMHCs in Helsinki (60°N, 25°E) using chemical mass balance, and the Unmix multivariate receptor models, Atmos. Environ., 37, 1413–1424, doi:10.1016/S1352-2310(02)01049-X, 2003.

Hellén, H., Kouznetsov, R., Anttila, P., and Hakola, H.: Increasing influence of easterly air masses on NMHC concentrations at the Pallas-Sodankylä GAW station, Boreal Environ. Res., 20, 542–552, 2015.

Helmig, D., Tanner, D. M., Honrath, R. E., Owen, R. C., and Parrish, D. D.: Nonmethane hydrocarbons at Pico Mountain, Azores: 1. Oxidation chemistry in the North Atlantic region, J. Geophys. Res. Atmos., 113, D20S91, doi:10.1029/2007JD008930, 2008.

Jacob, D. J., Field, B. D., Jin, E. M., Bey, I., Li, Q., Logan, J. A., Yantosca, R. M., and Singh, H. B.: Atmospheric budget of acetone, J. Geophys. Res. Atmos., 107, ACH 5-1, doi:10.1029/2001JD000694, 2002.

Jaidan, N., El Amraoui, L., Attié, J.-L., Ricaud, P., and Dulac, F.: Future changes in surface ozone over the Mediterranean Basin in the framework of the Chemistry-Aerosol Mediterranean Experiment (ChArMEx), Atmos. Chem. Phys., 18, 9351–9373, doi:10.5194/acp-18-9351-2018, 2018.

Jardine, K., Harley, P., Karl, T., Guenther, A., Lerdau, M., and Mak, J. E.: Plant physiological, and environmental controls over the exchange of acetaldehyde between forest canopies, and the atmosphere, Biogeosciences, 5, 1559–1572, doi:10.5194/bg-5-1559-2008, 2008.

Kalogridis, A.: Caractérisation des composés organiques volatils en région méditerranéenne, Université Paris Sud - Paris XI. [online] Available from: https://tel.archives-ouvertes.fr/tel-01165005, 2014.

~~Kendon, M., and McCarthy, M.: The UK ’s wet, and stormy winter of 2013/2014, R. Meteorol. Soc., 70, 40–47, doi:10.1002/wea.2474, 2015.~~

Kopf, S.: World Development Report 2010: Development, and Climate Change, edited by T. W. Bank, [online] Available from: https://siteresources.worldbank.org/INTWDR2010/Resources/5287678-1226014527953/WDR10-Full-Text.pdf, 2010.

Lambert, D., Mallet, M., Ducrocq, V., Dulac, F., Gheusi, F., and Kalthoff, N.: CORSiCA: A mediterranean atmospheric, and oceanographic observatory in Corsica within the framework of HyMeX, and ChArMEx, Adv. Geosci., 26, 125–131, doi:10.5194/adgeo-26-125-2011, 2011.

Lanz, V. A., Henne, S., Staehelin, J., Hueglin, C., Vollmer, M. K., Steinbacher, M., Buchmann, B., and Reimann, S.: Statistical analysis of anthropogenic non-methane VOC variability at a European background location (Jungfraujoch, Switzerland), Atmos. Chem. Phys., 9, 3445–3459, doi:10.5194/acp-9-3445-2009, 2009.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D., and Hewitt, C.N.: Biogenic volatile organic compounds in the Earth sys-tem, New Phytol., 183, 27–51, https://doi.org/10.1111/j.1469-8137.2009.02859.x, 2009.

Legreid, G., Lööv, J. B., Staehelin, J., Hueglin, C., Hill, M., Buchmann, B., Prevot, A. S. H., and Reimann, S.: Oxygenated volatile organic compounds (OVOCs) at an urban background site in Zürich (Europe): Seasonal variation, and source allocation, Atmos. Environ., 41, 8409–8423, doi:10.1016/j.atmosenv.2007.07.026, 2007.

Legreid, G., Folini, D., Staehelin, J., Lööv, J. B., Steinbacher, M., and Reimann, S.: Measurements of organic trace gases including oxygenated volatile organic compounds at the high alpine site Jungfraujoch (Switzerland): Seasonal variation, and source allocations, J. Geophys. Res. Atmos., 113, D05307, doi:10.1029/2007JD008653, 2008.

Lelieveld, J., Hadjinicolaou, P., Kostopoulou, E., Giannakopoulos, C., Pozzer, A., Tanarhte, M., and Tyrlis, E.: Model projected heat extremes, and air pollution in the eastern Mediterranean, and Middle East in the twenty-first century, Reg. Environ. Chang., 14, 1937–1949, doi:10.1007/s10113-013-0444-4, 2014.

Leuchner, M., Gubo, S., Schunk, C., Wastl, C., Kirchner, M., Menzel, A., and Plass-Dülmer, C.: Can positive matrix factorization help to understand patterns of organic trace gases at the continental Global Atmosphere Watch site Hohenpeissenberg?, Atmos. Chem. Phys., 15, 1221–1236, doi:10.5194/acp-15-1221-2015, 2015.

Loreto, F. and Schnitzler, J.-P.: Abiotic stresses and induced BVOCs, Trends Plant Sci.,15,154–166,https://doi.org/10.1016/j.tplants.2009.12.006, 2010.

Malley, C. S., Braban, C. F., Dumitrean, P., Cape, J. N., and Heal, M. R.: The impact of speciated VOCs on regional ozone increment derived from measurements at the UK EMEP supersites between 1999, and 2012, Atmos. Chem. Phys., 15, 8361–8380, doi:10.5194/acp-15-8361-2015, 2015.

Matsunaga, S., Mochida, M. and Kawamura, K.: Growth of organic aerosols by biogenic semi-volatile carbonyls in the forestal atmosphere, Atmos. Env., 37, 2045-2050, 2003.

Michoud, V., Sciare, J., Sauvage, S., Dusanter, S., Léonardis, T., Gros, V., Kalogridis, C., Zannoni, N., Féron, A., Petit, J. E., Crenn, V., Baisnée, D., Sarda-Estève, R., Bonnaire, N., Marchand, N., Dewitt, H. L., Pey, J., Colomb, A., Gheusi, F., Szidat, S., Stavroulas, I., Borbon, A., and Locoge, N.: Organic carbon at a remote site of the western Mediterranean Basin: Sources, and chemistry during the ChArMEx SOP2 field experiment, Atmos. Chem. Phys., 17, 8837–8865, doi:10.5194/acp-17-8837-2017, 2017.

~~Millet, D. B., Guenther, A., Siegel, D., Nelson, N., Singh, H., De Gouw, J., Warneke, C., Williams, J., Eerdekens, G., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., Palmer, P. I., and Barkley, M.: Global atmospheric budget of acetaldehyde: 3-D model analysis, and constraints from in-situ, and satellite observations, Atmos. Chem. Phys., 10, 3405–3425, doi:10.5194/acp-10-3405-2010, 2010.~~

Nabat, P., Somot, S., Mallet, M., Chiapello, I., Morcrette, J. J., Solmon, F., Szopa, S., Dulac, F., Collins, W., Ghan, S., Horowitz, L. W., Lamarque, J. F., Lee, Y. H., Naik, V., Nagashima, T., Shindell, D., and Skeie, R.: A 4-D climatology (1979-2009) of the monthly tropospheric aerosol optical depth distribution over the Mediterranean region from a comparative evaluation, and blending of remote sensing, and model products, Atmos. Meas. Tech., 6, 1287–1314, doi:10.5194/amt-6-1287-2013, 2013.

Navazo, M., Durana, N., Alonso, L., Gómez, M. C., García, J. A., Ilardia, J. L., Gangoiti, G., and Iza, J.: High temporal resolution measurements of ozone precursors in a rural background station. A two-year study, Environ. Monit. Assess., 136, 53–68, doi:10.1007/s10661-007-9720-4, 2008.

Niinemets, Ü., Loreto, F., and Reichstein, M.: Physiological and physicochemical controls on foliar volatile organic compound emissions, Trends Plant Sci., 9, 180–186, https://doi.org/10.1016/j.tplants.2004.02.006, 2004.

Norris, G., Duvall, R., Brown, S., and Bai, S.: EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals, and User Guide Prepared for the US Environmental Protection Agency Office of Research, and Development, Washington, DC. [online] Available from: https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf, 2014.

Van Oldenborgh, G. J., Haarsma, R., De Vries, H., and Allen, M. R.: Cold extremes in North America vs. mild weather in Europe, Bull. Am. Meteorol. Soc., 96, 707–714, doi:10.1175/BAMS-D-14-00036.1, 2015.

Owen, S. M., Boissard, C., and Hewitt, C. N.: Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species : VOC speciation, and extrapolation to habitat scale, Atmos. Environ., 35, 5393–5409, 2001.

Paatero, P.: Least squares formulation of robust non-negative factor analysis, Chemom. Intell. Lab. Syst., 37, 23–35, doi:10.1016/S0169-7439(96)00044-5, 1997.

Paatero, P.: The Multilinear Engine—A Table-Driven, Least Squares Program for Solving Multilinear Problems, Including the n-Way Parallel Factor Analysis Model, J. Comput. Graph. Stat., 8, 854–888, doi:10.1080/10618600.1999.10474853, 1999.

Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111–126, doi:10.1002/env.3170050203, 1994.

~~Paatero, P., Eberly, S., Brown, S. G., and Norris, G. A.: Methods for estimating uncertainty in factor analytic solutions, Atmos. Meas. Tech., 7, 781–797, doi:10.5194/amt-7-781-2014, 2014.~~

Pang, Y., Fuentes, M., and Rieger, P.: Trends in the emissions of Volatile Organic Compounds (VOCs) from light-duty gasoline vehicles tested on chassis dynamometers in Southern California, Atmos. Environ., 83, 127–135, doi:10.1016/j.atmosenv.2013.11.002, 2014.

Petit, J. E., Favez, O., Albinet, A., and Canonaco, F.: A user-friendly tool for comprehensive evaluation of the geographical origins of atmospheric pollution: Wind, and trajectory analyses, Environ. Model. Softw., 88, 183–187, doi:10.1016/j.envsoft.2016.11.022, 2017.

~~Photiadou, C., van der Schrier, G., van Oldenborgh, G. J., Verver, G., Tank, A. K., Plieger, M., Mänchel, H., Bissoli, P., and Rössner, S.: 2014 warmest year on record in Europe - EURO4M Climate Indicator Bulletin, [online] Available from: http://cib.knmi.nl/mediawiki/index.php/2014_warmest_year_on_record_in_Europe (last access: 18/04/2020), 2015.~~

Plass-Dülmer, C., Michl, K., Ruf, R., and Berresheim, H.: C2-C8 Hydrocarbon measurement, and quality control procedures at the Global Atmosphere Watch Observatory Hohenpeissenberg, J. Chromatogr. A, 953, 175–197, doi:10.1016/S0021-9673(02)00128-0, 2002.

Rasmijn, L. M., van der Schrier, G., Barkmeijer, J., Sterl, A., and Hazeleger, W.: Simulating the extreme 2013/2014 winter in a future climate, J. Geophys. Res., 121, 5680–5698, doi:10.1002/2015JD024492, 2016.

Reimann, S., Wegener, R., Claude, A., and Sauvage, S.: ACTRIS-2 WP3 - Deliverable 3 . 17 . Updated Measurement Guideline for NOx, and VOCs., 2018.

~~Roemer, M., Builtjes, P., Esser, P., Guicherit, R., and Thijsse, T.: C2-C5 Hydrocarbon measurements in the Netherlands 1981-1991, Atmos. Environ., 33, 3579–3595, 1999.~~

Rottenberger, S., Kuhn, U., Wolf, A., Schebeske, G., Oliva, S. T., Tavares, T. M., and Kesselmeier, J.: Exchange of short-chain aldehydes between Amazonian vegetation, and the atmosphere, Ecol. Appl., 14, 247–262, 2004.

Rottenberger, S., Kleiss, B., Kuhn, U., Wolf, A., Piedade, M. T. F., Junk, W., and Kesselmeier, J.: The effect of flooding on the exchange of the volatile C2-compounds ethanol , acetaldehyde, and acetic acid between leaves of Amazonian floodplain tree species, and the atmosphere, Biogeosciences, 5, 1085–1100, doi:www.biogeosciences.net/5/1085/2008, 2008.

Royer, P., Raut, J. C., Ajello, G., Berthier, S., and Chazette, P.: Synergy between CALIOP, and MODIS instruments for aerosol monitoring: Application to the Po Valley, Atmos. Meas. Tech., 3, 893–907, doi:10.5194/amt-3-893-2010, 2010.

Safieddine, S., Boynard, A., Coheur, P. F., Hurtmans, D., Pfister, G., Quennehen, B., Thomas, J. L., Raut, J. C., Law, K. S., Klimont, Z., Hadji-Lazaro, J., George, M., and Clerbaux, C.: Summertime tropospheric ozone assessment over the Mediterranean region using the thermal infrared IASI/MetOp sounder, and the WRF-Chem model, Atmos. Chem. Phys., 14, 10119–10131, doi:10.5194/acp-14-10119-2014, 2014.

~~Salameh, T., Sauvage, S., Locoge, N., Gauduin, J., Perrussel, O., and Borbon, A.: Spatial and temporal variability of BTEX in Paris megacity : Two-wheelers as a major driver, Atmos. Environ. X, 1, 100003, doi.org:10.1016/j.aeaoa.2018.100003, 2019.~~

Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P., and Galloo, J. C.: Long term measurement, and source apportionment of non-methane hydrocarbons in three French rural areas, Atmos. Environ., 43, 2430–2441, doi:10.1016/j.atmosenv.2009.02.001, 2009.

Schade, G. W., and Goldstein, A. H.: Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation, J. Geophys. Res., 106, 3111–3123, 2001.

Schade, G. W., and Goldstein, A. H.: Seasonal measurements of acetone, and methanol: Abundances, and implications for atmospheric budgets, Global Biogeochem. Cycles, 20(1), GB1011, doi:10.1029/2005GB002566, 2006.

~~von Schneidemesser, E., Monks, P. S., and Plass-duelmer, C.: Global comparison of VOC, and CO observations in urban areas, Atmos. Environ., 44, 5053–5064, doi:10.1016/j.atmosenv.2010.09.010, 2010.~~

Seco, R., Peñuelas, J., and Filella, I.: Short-chain oxygenated VOCs: Emission, and uptake by plants, and atmospheric sources, sinks, and concentrations, Atmos. Environ., 41, 2477–2499, doi:10.1016/j.atmosenv.2006.11.029, 2007.

Seco, R., Peñuelas, J., Filella, I., Llusià, J., Molowny-Horas, R., Schallhart, S., Metzger, A., Müller, M., and Hansel, A.: Contrasting winter, and summer VOC mixing ratios at a forest site in the Western Mediterranean Basin: The effect of local biogenic emissions, Atmos. Chem. Phys., 11, 13161–13179, doi:10.5194/acp-11-13161-2011, 2011.

Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D. T., and Schwikowski, M.: Trajectory analysis of high-alpine air pollution data, in Air Pollution Modeling, and Its Application X, edited by S.-E. Gryning, and M. M. Millán, pp. 595–596, Springer, Boston, MA., 1994.

Singh, H. B., Salas, L., Chatfield, R. B., Czech, E., Fried, A., Walega, J., Evans, M. J., Field, B. D., Jacob, D. J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J. H., Avery, M. A., Sandholm, S., and Fuelberg, H.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, J. Geophys. Res. Atmos., 109, D15S07, doi:10.1029/2003JD003883, 2004.

Solberg, S., Dye, C., Schmidbauer, N., Herzog, A., and Gehrig, R.: Carbonyls, and Nonmethane Hydrocarbons at Rural European Sites from the Mediterranean to the Arctic, J. Atmos. Chem., 25, 33–66, doi:10.1007/BF00053285, 1996.

Solberg, S., Dye, C., Walker, S. E., and Simpson, D.: Long-term measurements, and model calculations of formaldehyde at rural European monitoring sites, Atmos. Environ., 35, 195–207, doi:10.1016/S1352-2310(00)00256-9, 2001.

Spivakovsky, C. M., Logan, J. A., Montzka, S. A., Balkanski, Y. J., Foreman-Fowler, M., Jones, D. B. A., Horowitz, L. W., Fusco, A. C., Brenninkmeijer, C. A. M., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Three-dimensional climatological distribution of tropospheric OH: Update, and evaluation, J. Geophys. Res. Atmos., 105, 8931–8980, doi:10.1029/1999JD901006, 2000.

Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., and Ngan, F.: Noaa's hysplit atmospheric transport, and dispersion modeling system, Bull. Am. Meteorol. Soc., 96, 2059–2077, doi:10.1175/BAMS-D-14-00110.1, 2015.

Tørseth, K., Aas, W., Breivik, K., Fjeraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring, and Evaluation Programme (EMEP), and observed atmospheric composition change during 1972-2009, Atmos. Chem. Phys., 12, 5447–5481, doi:10.5194/acp-12-5447-2012, 2012.

von Engeln, A., and Teixeira, J.: A planetary boundary layer height climatology derived from ECMWF reanalysis data, J. of Climate, 26, 6575-6590, doi:10.1175/JCLI-D-12-00385.1, 2013.

Lo Vullo, E., Furlani, F., Arduini, J., Giostra, U., Cristofanelli, P., Williams, M. L., and Maione, M.: Non-methane volatile organic compounds in the background atmospheres of a Southern European mountain site (Mt. Cimone, Italy): Annual, and seasonal variability, Aerosol Air Qual. Res., 16, 581–592, doi:10.4209/aaqr.2015.05.0364, 2016.

Waked, A., Bourin, A., Michoud, V., Perdrix, E., Alleman, L. Y., Sauvage, S., Delaunay, T., Vermeesch, S., Petit, J.-E., and Riffault, V.: Investigation of the geographical origins of PM10 based on long, medium and short-range air mass back-trajectories impacting Northern France during the period 2009–2013, Atmos. Environ., 193, 143-152, doi :10.1016/j.atmosenv.2018.08.015, 2018.

Waked, A., Favez, O., Alleman, L. Y., Piot, C., Petit, J. E., Delaunay, T., Verlinden, E., Golly, B., Besombes, J. L., Jaffrezo, J. L., and Leoz-Garziandia, E.: Source apportionment of PM10 in a north-western Europe regional urban background site (Lens, France) using positive matrix factorization, and including primary biogenic emissions, Atmos. Chem. Phys., 14, 3325–3346, doi:10.5194/acp-14-3325-2014, 2014.

Waked, A., Sauvage, S., Borbon, A., Gauduin, J., Pallares, C., Vagnot, M.-P., Léonardis, T., and Locoge, N.: Multi-year levels, and trends of non-methane hydrocarbon concentrations observed in ambient air in France, Atmos. Environ., 141, 263–275, doi:10.1016/j.atmosenv.2016.06.059, 2016.

Watson, P. A. G., Weisheimer, A., Knight, J. R., and Palmer, T. N.: The role of the tropical West Pacific in the extreme Northern Hemisphere winter of 2013/2014, J.Geophys. Res. Atmos., 121, 1698–1714, doi:10.1002/2015JD024048.Received, 2016.

Winters, A. J., Adams, M. A., Bleby, T. M., Rennenberg, H., Steigner, D., Steinbrecher, R., and Kreuzwieser, J.: Emissions of isoprene, monoterpene, and short-chained carbonyl compounds from Eucalyptus spp. in southern Australia, Atmos. Environ., 43, 3035–3043, doi:10.1016/j.atmosenv.2009.03.026, 2009.

Wolfe, G. M., Kaiser, J., Hanisco, T. F., Keutsch, F. N., De Gouw, J. A., Gilman, J. B., Graus, M., Hatch, C. D., Holloway, J., Horowitz, L. W., Lee, B. H., Lerner, B. M., Lopez-Hilifiker, F., Mao, J., Marvin, M. R., Peischl, J., Pollack, I. B., Roberts, J. M., Ryerson, T. B., Thornton, J. A., Veres, P. R., and Warneke, C.: Formaldehyde production from isoprene oxidation across NOx regimes, Atmos. Chem. Phys., 16, 2597–2610, doi:10.5194/acp-16-2597-2016, 2016.

Yáñez-Serrano, A. M., Nölscher, A. C., Bourtsoukidis, E., Derstroff, B., Zannoni, N., Gros, V., Lanza, M., Brito, J., Noe, S. M., House, E., Hewitt, C. N., Langford, B., Nemitz, E., Behrendt, T., Williams, J., Artaxo, P., andreae, M. O., and Kesselmeier, J.: Atmospheric mixing ratios of methyl ethyl ketone (2-butanone) in tropical, boreal, temperate, and marine environments, Atmos. Chem. Phys., 16, 10965–10984, doi:10.5194/acp-16-10965-2016, 2016.

~~Zannoni, N., Gros, V., Sarda Esteve, R., Kalogridis, C., Michoud, V., Dusanter, S., Sauvage, S., Locoge, N., Colomb, A., and Bonsang, B.: Summertime OH reactivity from a receptor coastal site in the Mediterranean Basin, Atmos. Chem. Phys., 17, 12645–12658, doi:10.5194/acp-17-12645-2017, 2017.~~

Zhang, J., Sun, Y., Wu, F., Sun, J., and Wang, Y.: The characteristics, seasonal variation, and source apportionment of VOCs at Gongga Mountain, China, Atmos. Environ., 88, 297–305, doi:10.1016/j.atmosenv.2013.03.036, 2014.

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.

~~[a] ethane, ethylene, propane, propene, i-butane, n-butane, acetylene, i-pentane and n-pentane, n-hexane, isoprene, benzene, toluene, ethylbenzene, m,p-xylenes, o-xylene~~

~~[b] formaldehyde, acetaldehyde, acetone, acrolein, propanal, methyl vinyl ketone (MVK), methacrolein (MACR), methyl ethyl ketone (MEK), i-/n-/butanals, benzaldehyde, glyoxal, methylglyoxal, hexanal~~

Instrument	Steel canisters	DNPH cartridges – Chemical desorption (acetonitrile) – HPLC-UV	Multi-~~Solid ad~~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-~~65~~73]
Species	2~~1~~4 C_2 - ~~$C_5{}^a$~~C_5 ~~VOCs~~NMHCs	15 C_1 - ~~C_6~~C_6~~^{b}~~ ~~OVOCs~~carbonyl compounds	~~6 C_6 - C_{11} n-aldehydes~~ ~~28~~ 44 C_5 - ~~C_{16}~~C_{16} ~~alkanes/alkenes~~NMHCs ~~10 C_6 - C_9 aromatics~~ ~~6 Monoterpenes~~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 ~~3~~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 ~~4~~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 ~~ALKANES~~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: Seasonal average VOC 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

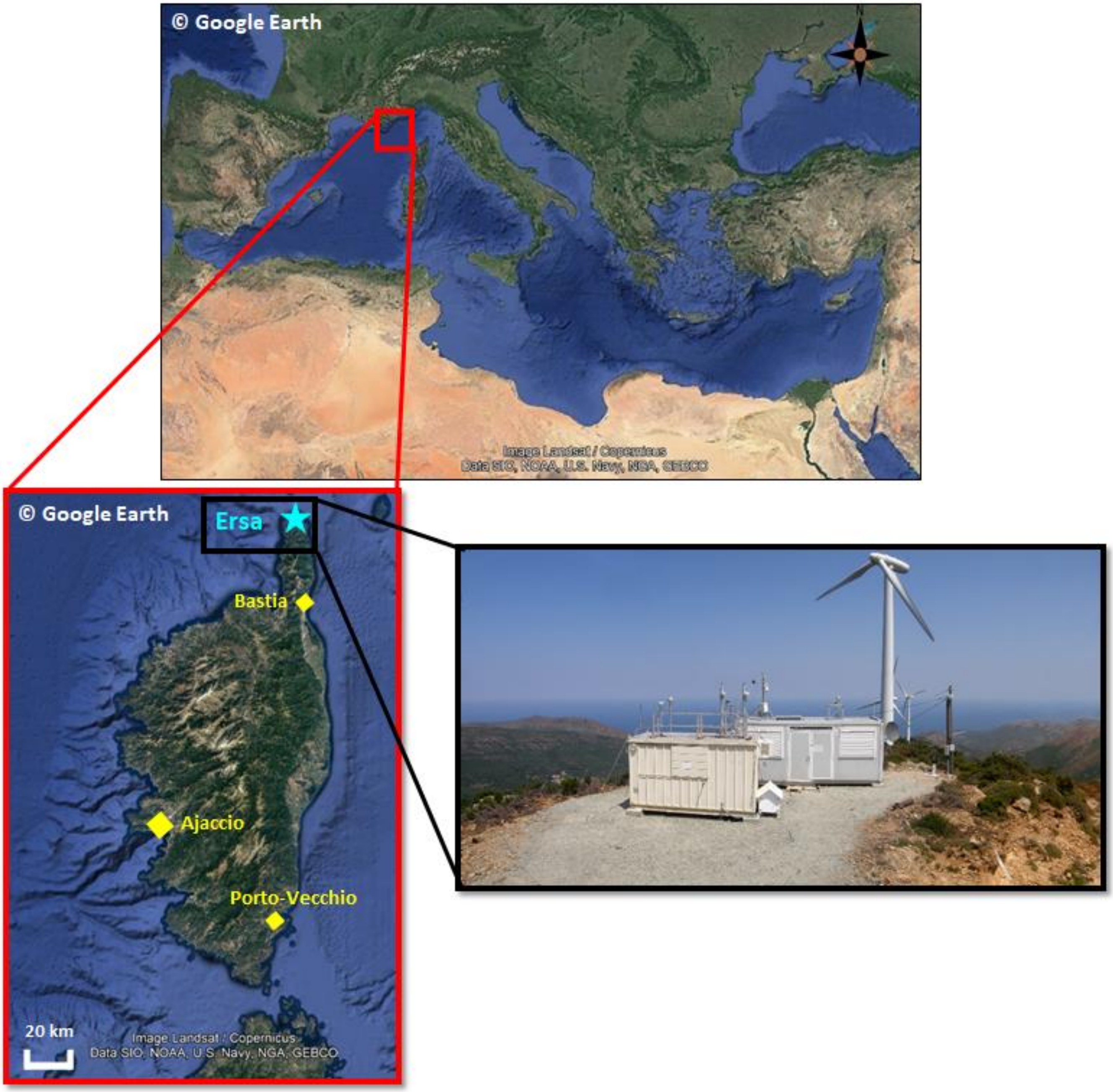


Figure 1: Maps of the Mediterranean region and Corsica (source Google earth) and view of the sampling station. (a) Position of Corsican island in the Mediterranean region. (b) The sampling site and major Corsican agglomerations are displayed as a blue star and yellow diamonds, respectively. (c) Picture of the sampling site, during the observation period. Maps provided by Google Earth Pro software (v.7.3.3; image Landsat/Copernicus; data SIO, NOAA, U.S, Navy, NGA, GEBCO; © Google Earth).

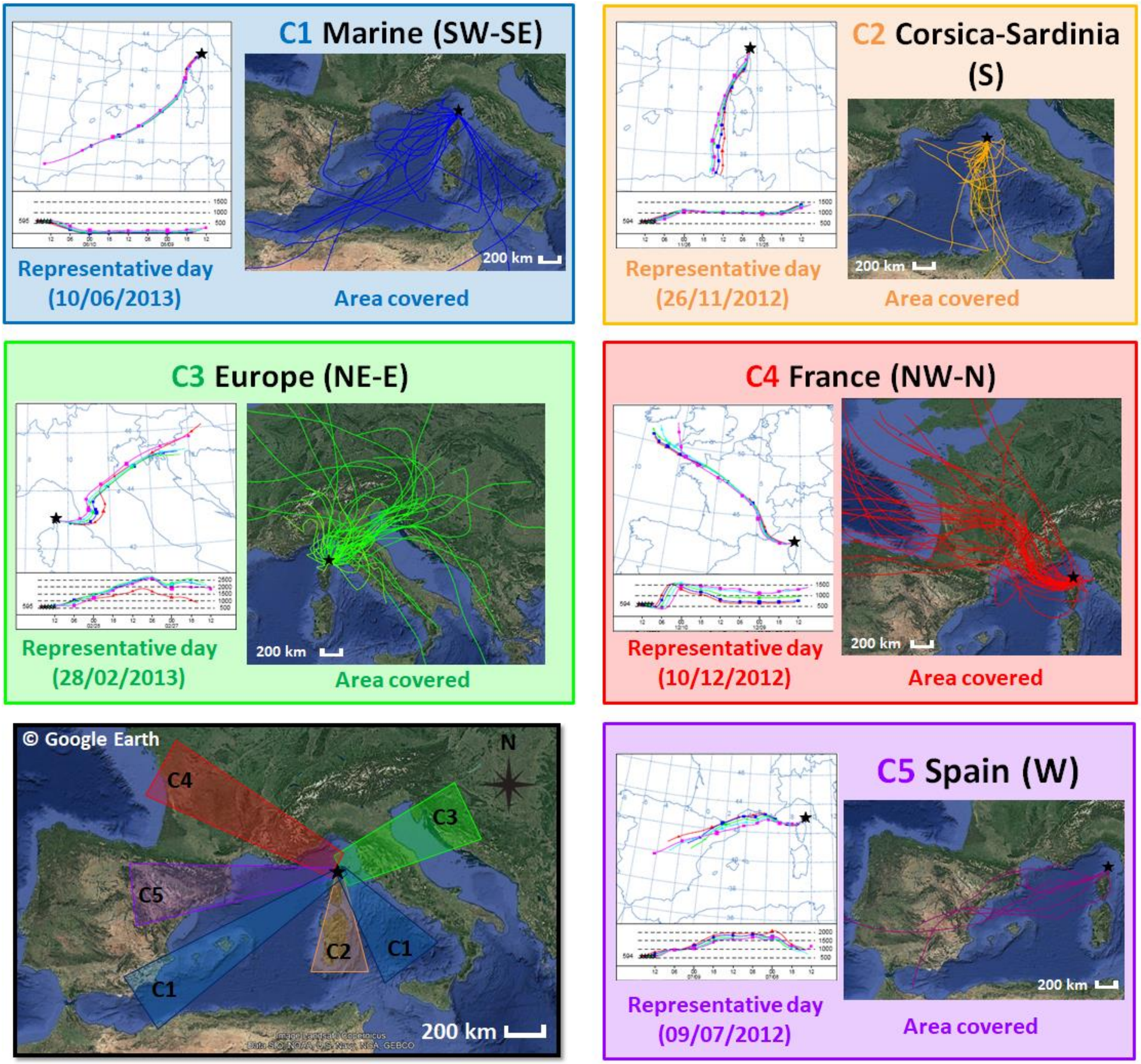


Figure ~~3~~2: Classification of air masses which impacted the Ersa site during the observation field campaign as a function of their trajectory. Back trajectories simulated with the HYSPLIT model (NOAA-ARL) were classified into five clusters: Marine (cluster 1 – wind sectors SW & SE), Corsica-Sardinia (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 of trajectory, ~~receptor~~ the Ersa ~~site~~ station represented by a black star) for five single days representative of an isolated cluster. To complete, 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, NOAA, U.S, Navy, NGA, GEBCO; © Google Earth).

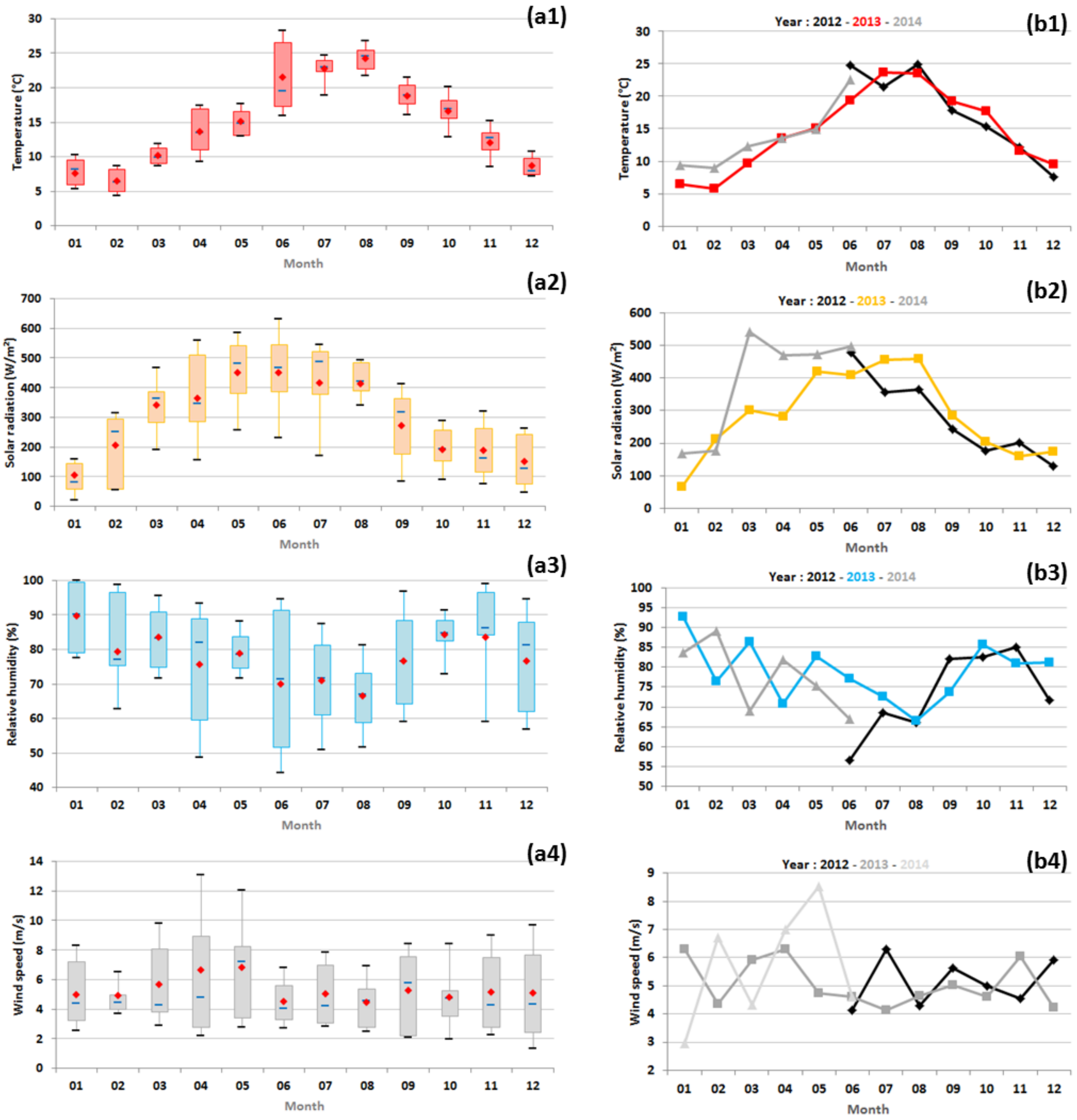


Figure ~~4~~3: (a) Monthly variations in meteorological parameters (temperature expressed in °C, global solar radiation in W m^{-2}, relative humidity in % and wind speed in m s^{-1}) represented by box plots~~ ~~;~~and (b) their average values as a function of the year.~~ the b~~B~~lue solid line~~ represents the median value~~, the red marker, ~~represents the mean value ~~and the box ~~shows ~~represent the median, the mean, and the interquartile range of the values, respectively. The bottom and ~~the ~~top of the box depict the first and~~ the~~ third quartiles (i.e. Q1 and Q3) and~~.~~ t~~T~~he ends of the whiskers correspond to the first and ~~the ~~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.

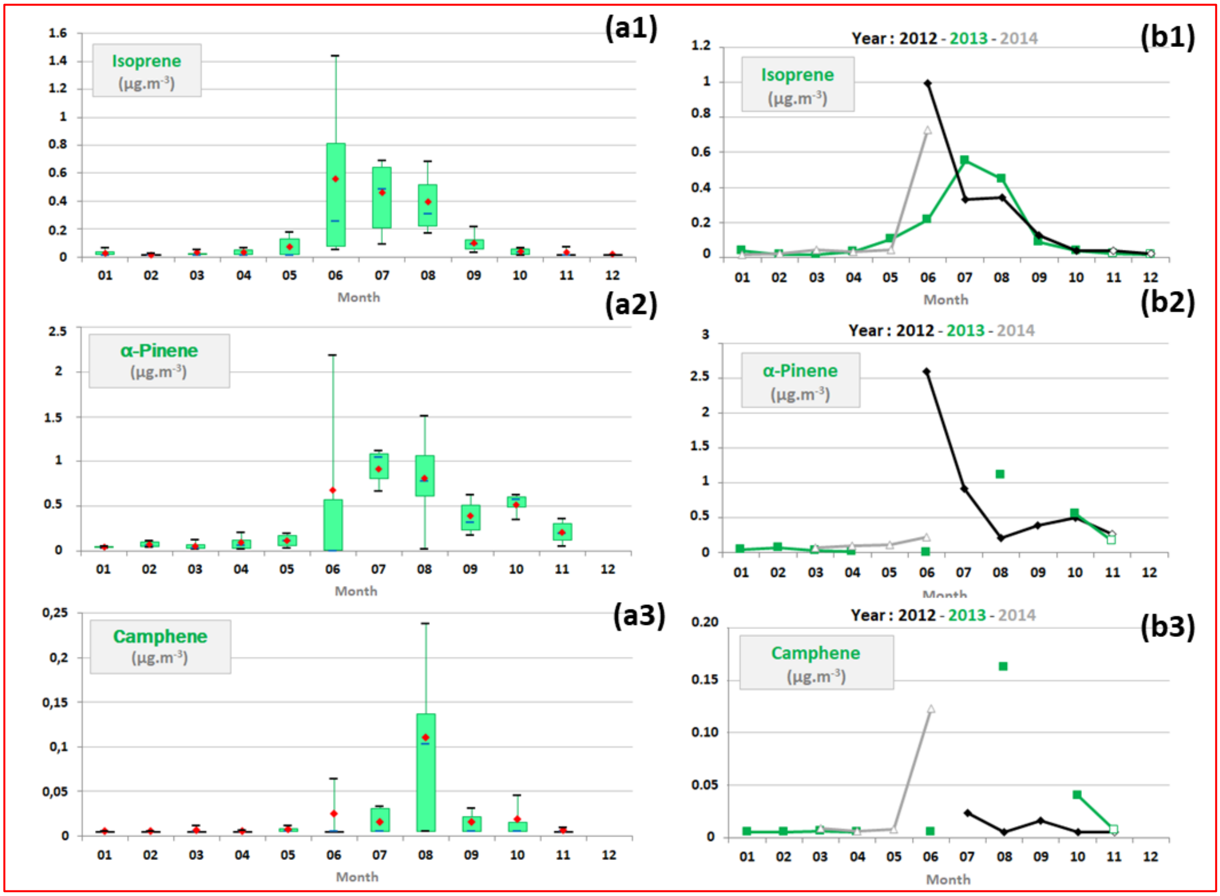
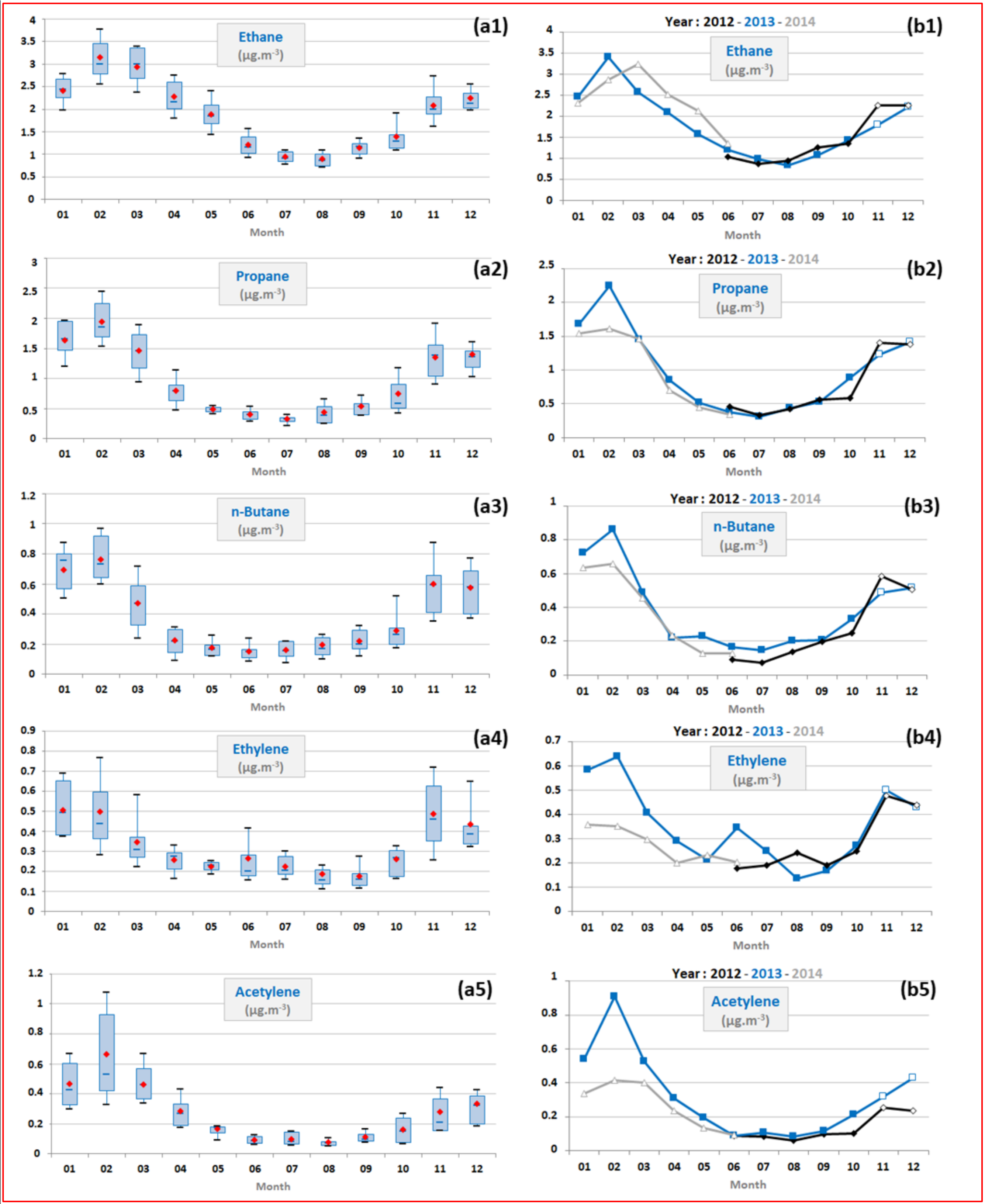


Figure ~~5~~4: (a) Monthly variations in a selection of biogenic VOC concentrations (expressed in µg m^{-3}) represented by box plots~~ and (b) their average monthly concentrations as a function of the year.~~; the ~~B~~blue solid line~~ represents the median value~~, the red marker, ~~represents the mean value~~ and the box ~~shows the interquartile range~~represent the median, the mean, and the interquartile range of the values, respectively. The bottom and ~~the~~ top of the box depict the first and ~~the~~ third quartiles (i.e. Q1 and Q3) and ~~.~~ t~~T~~he ends of the whiskers correspond to the first and ~~the~~ 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)
(b1)
Year : 2012 - 2013 - 2014
Ethane
(µg.m-3)
(a2)
Propane
(µg.m-3)
(b2)
Year : 2012 - 2013 - 2014
Propane
(µg.m-3)
(a3)
n-Butane
(µg.m-3)
(b3)
Year : 2012 - 2013 - 2014
n-Butane
(µg.m-3)
(a4)
Ethylene
(µg.m-3)
(b4)
Year : 2012 - 2013 - 2014
Ethylene
(µg.m-3)
(a5)
Acetylene
(µg.m-3)
(b5)
Year : 2012 - 2013 - 2014
Acetylene
(µg.m-3)
01
02
03
04
05
06
07
08
09
10
11
12
Month

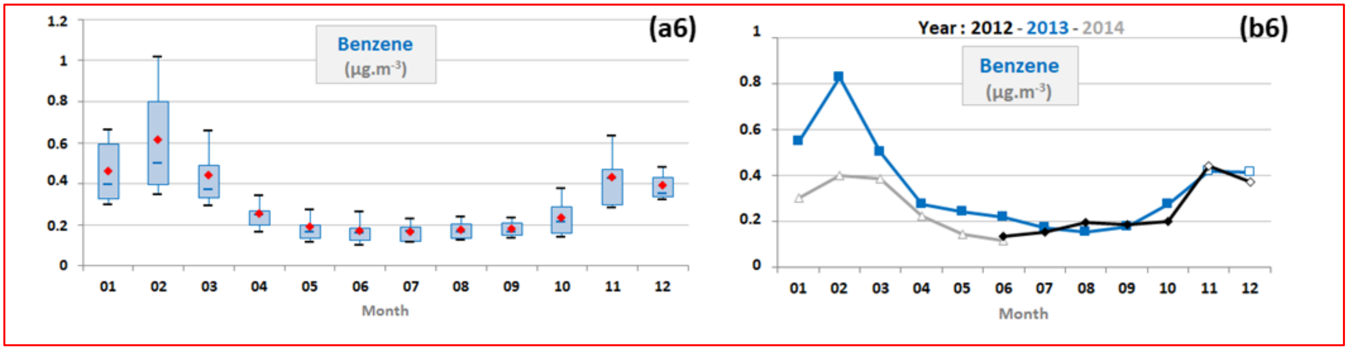
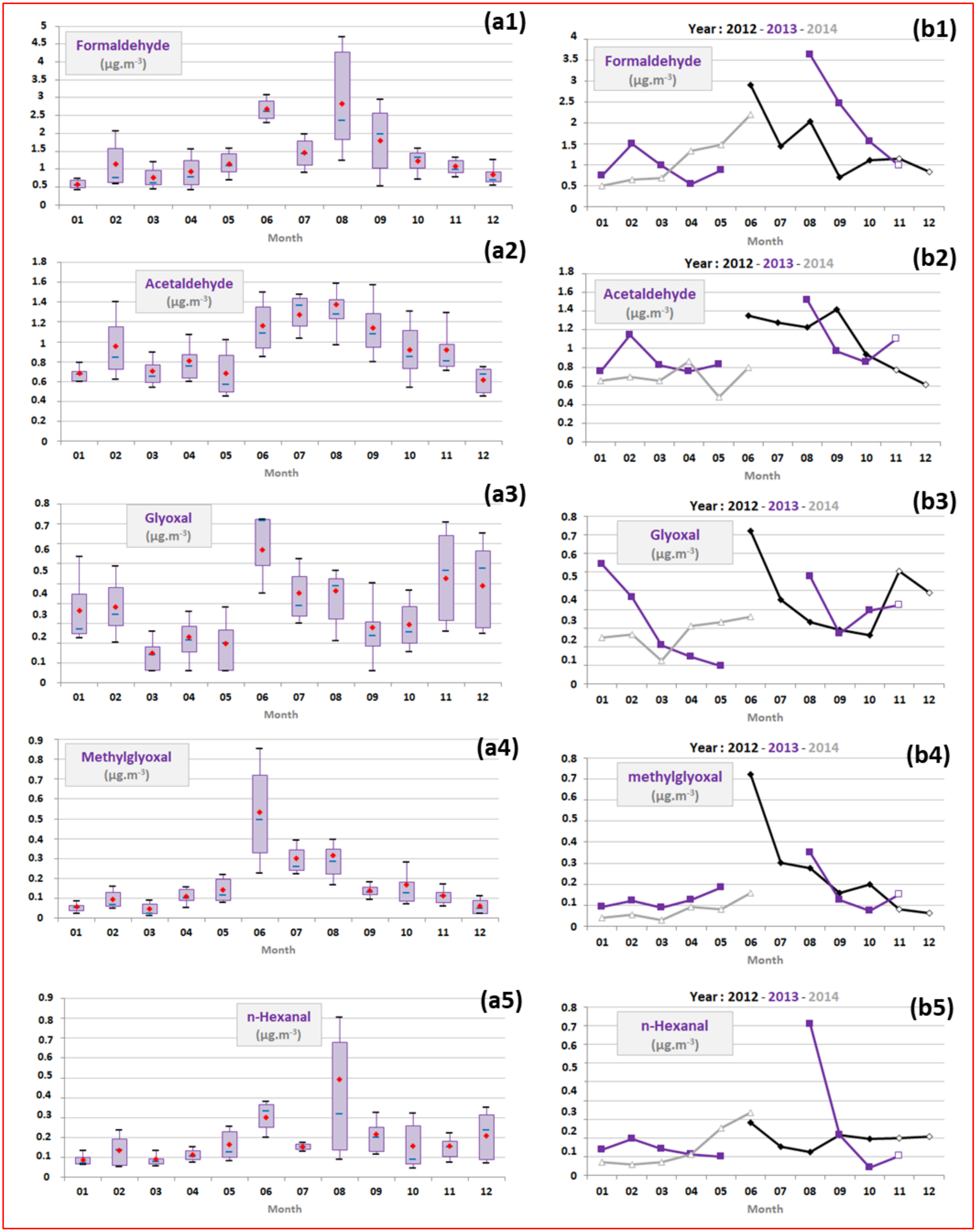


Figure ~~6~~5: (a) Monthly variations in a selection of anthropogenic VOC concentrations (expressed in µg m^{-3}) represented by box ~~plots~~ plots~~and (b) their average monthly concentrations as a function of the year.~~; the ~~B~~blue solid line~~ represents the median value~~, the red marker, ~~represents the mean value~~ and the box ~~shows the interquartile range~~represent the median, the mean, and the interquartile range of the values, respectively. The bottom and ~~the~~ top of the box depict the first and ~~the~~ third quartiles (i.e. Q1 and Q3) and~~.~~ t~~T~~he ends of the whiskers correspond to the first and ~~the~~ 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)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
01 02 03 04 05 06 07 08 09 10 11 12
Month
(b1)
Year : 2012 - 2013 - 2014
Formaldehyde
(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)
Acetaldehyde
(µg.m-3)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
01 02 03 04 05 06 07 08 09 10 11 12
Month
(b2)
Year : 2012 - 2013 - 2014
Acetaldehyde
(µg.m-3)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
01 02 03 04 05 06 07 08 09 10 11 12
Month
(a3)
Glyoxal
(µg.m-3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
01 02 03 04 05 06 07 08 09 10 11 12
Month
(b3)
Year : 2012 - 2013 - 2014
Glyoxal
(µg.m-3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
01 02 03 04 05 06 07 08 09 10 11 12
Month
(a4)
Methylglyoxal
(µg.m-3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
01 02 03 04 05 06 07 08 09 10 11 12
Month
(b4)
Year : 2012 - 2013 - 2014
methylglyoxal
(µg.m-3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
01 02 03 04 05 06 07 08 09 10 11 12
Month
(a5)
n-Hexanal
(µg.m-3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
01 02 03 04 05 06 07 08 09 10 11 12
Month
(b5)
Year : 2012 - 2013 - 2014
n-Hexanal
(µg.m-3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
01 02 03 04 05 06 07 08 09 10 11 12
Month

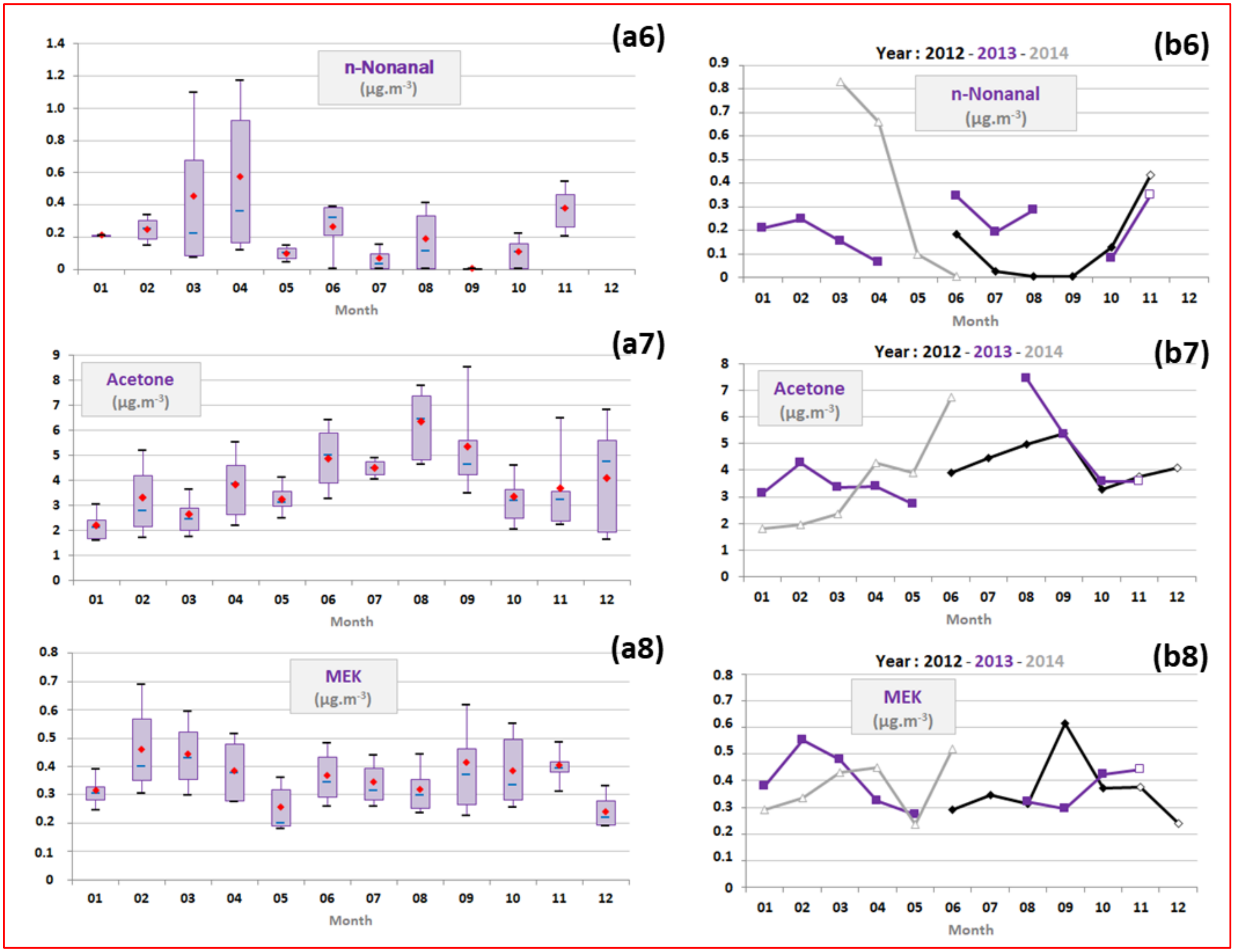


Figure ~~7~~6: (a) Monthly variations in a selection of oxygenated VOC concentrations (expressed in µg m^{-3}) represented by box plots ~~;and (b) their average monthly concentrations as a function of the year.~~ the b~~B~~lue solid line~~ represents the median value~~, the red marker~~, represents the mean value~~ and the box ~~shows~~ represent the median, the mean, and the interquartile range of the values, respectively. The bottom and ~~the~~ top of the box depict the first and ~~the~~ third quartiles (i.e. Q1 and Q3) and~~.~~ t~~T~~he ends of the whiskers correspond to the first and ~~the~~ 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.

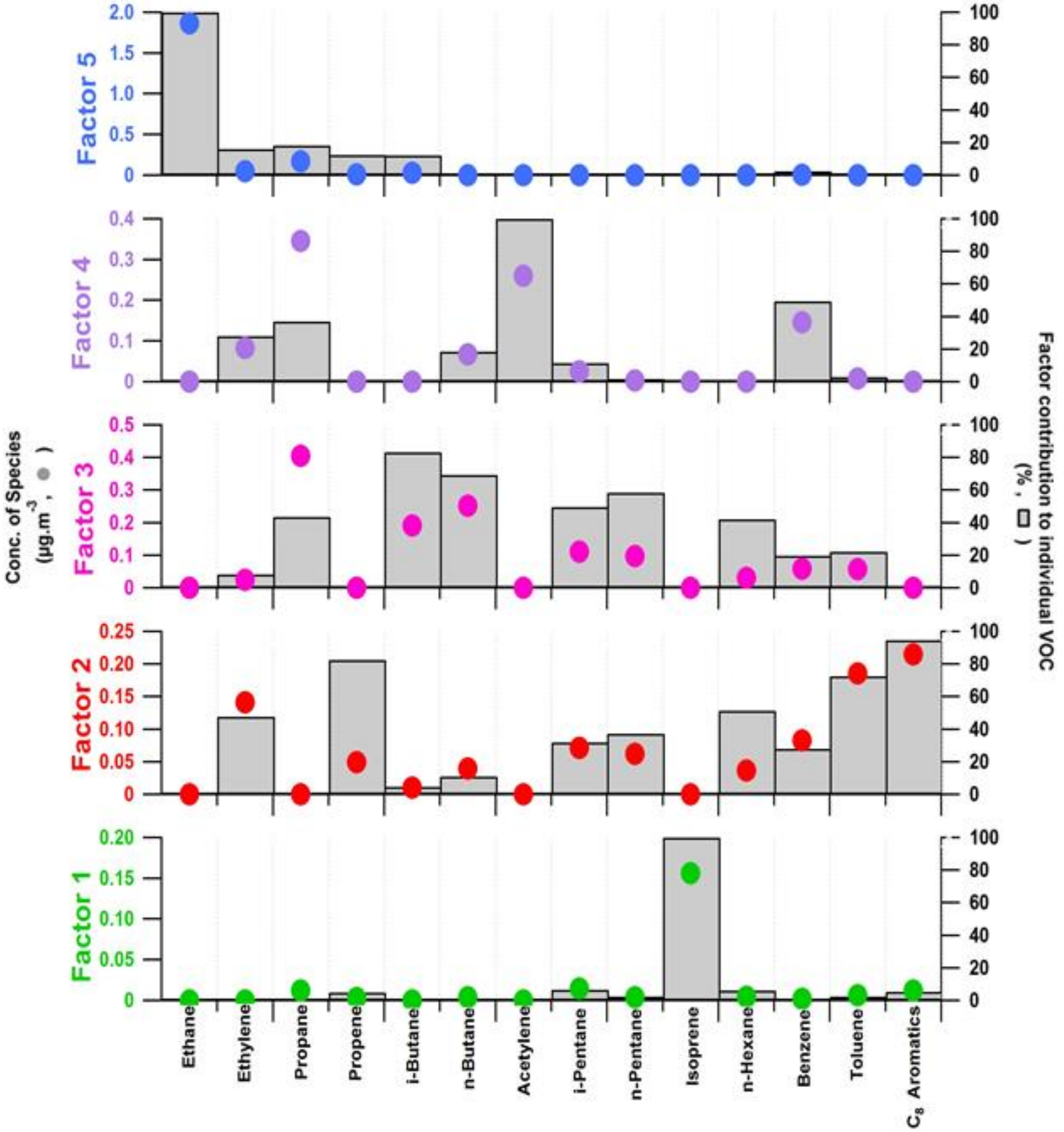


Figure ~~8~~7: Chemical profiles of the 5-factor PMF solution (14 ~~VOCs~~variables). Factor contributions to each species (µg m^{-3}) and the percent of each species apportioned to the factor are displayed as a grey bar and a color circle, respectively. Factor 1 ~~-~~– local biogenic source; factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background.

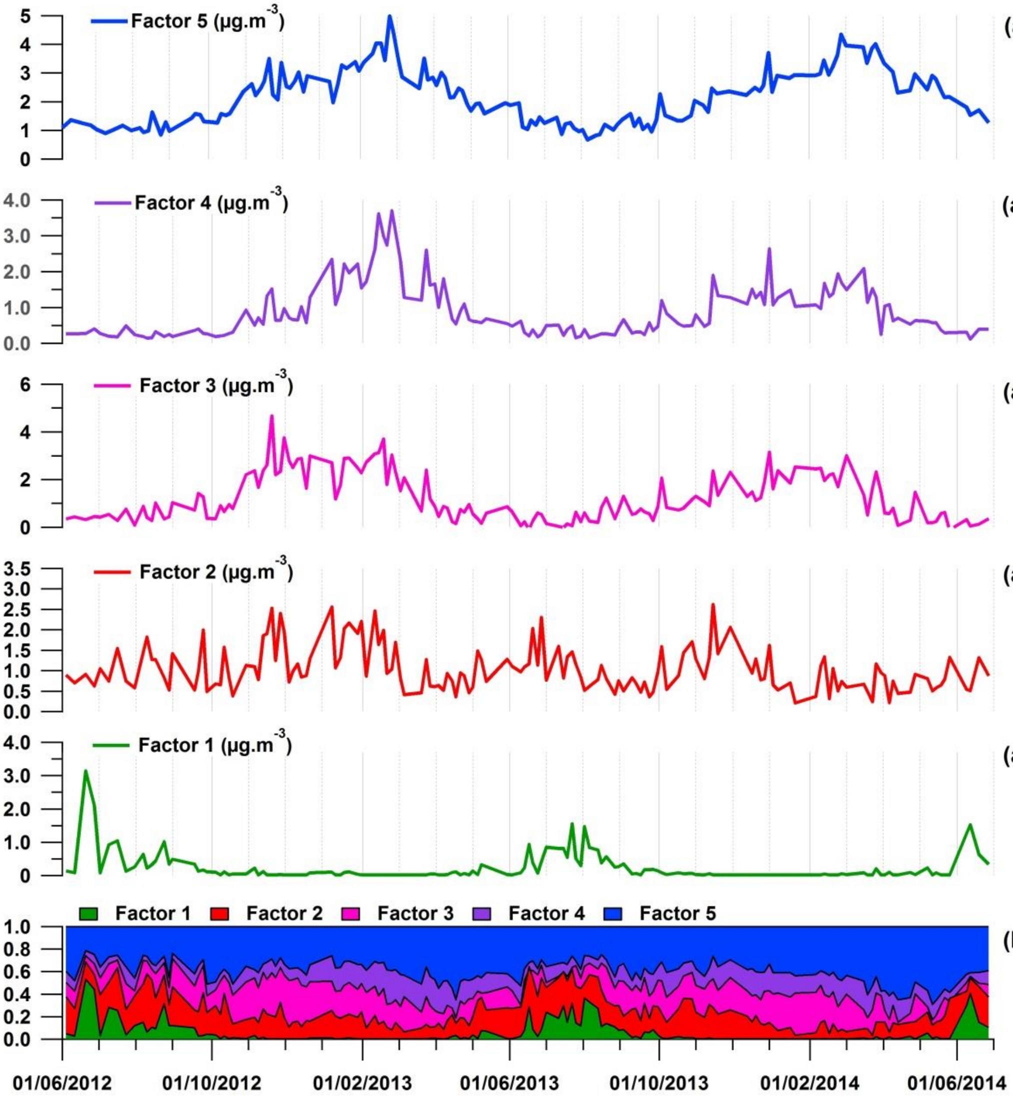


Figure ~~9~~8: (a) Time series of ~~VOC~~ NMHC factor contributions (µg m^{-3}) and (b) accumulated relative ~~VOC~~ NMHC contributions. Factor 1 - local biogenic source; factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – 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).

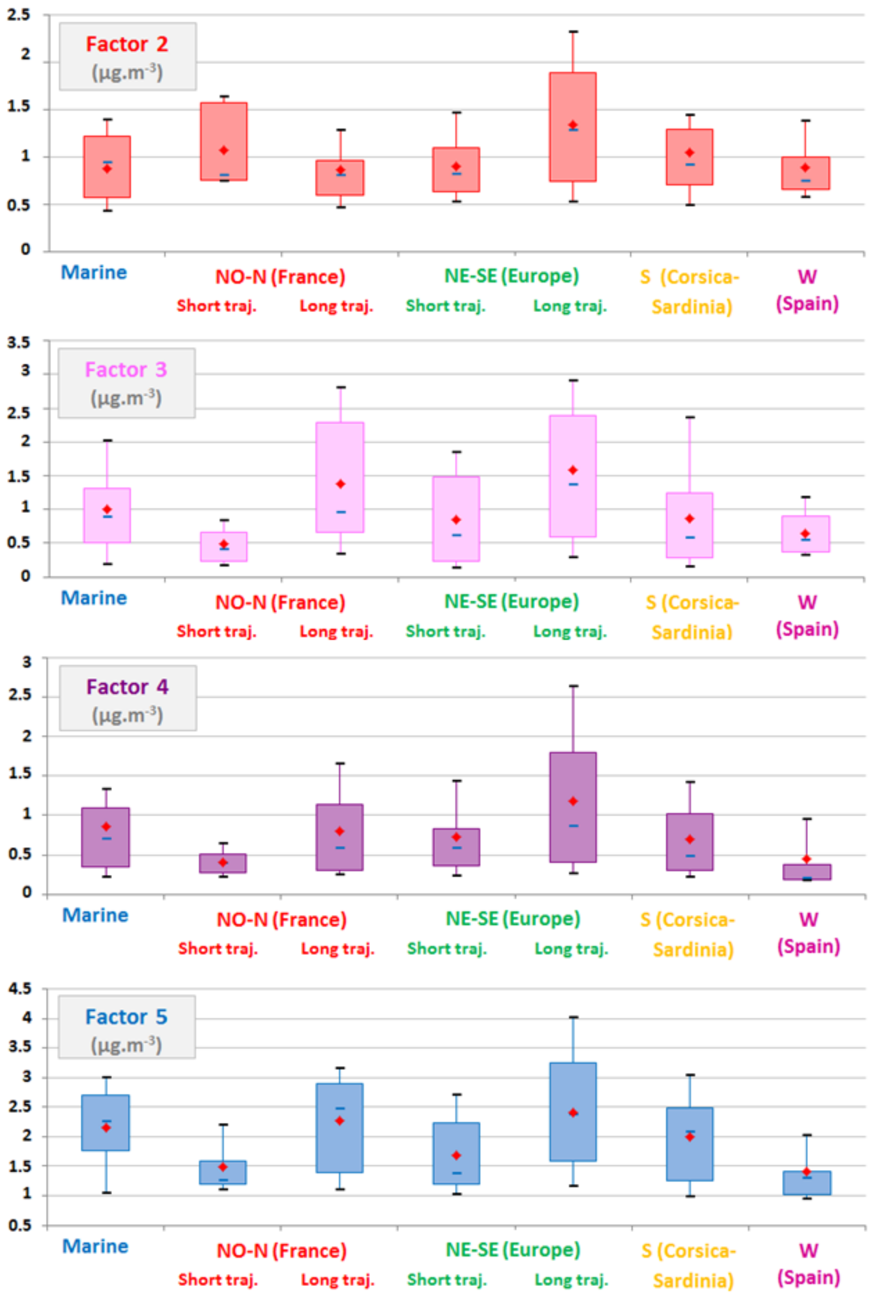


Figure ~~11~~9: ~~VOC~~ NMHC factor contributions (µg m^{-3}) as a function of air mass origins represent by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box depict the first 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~~VOC~~ factors: 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).

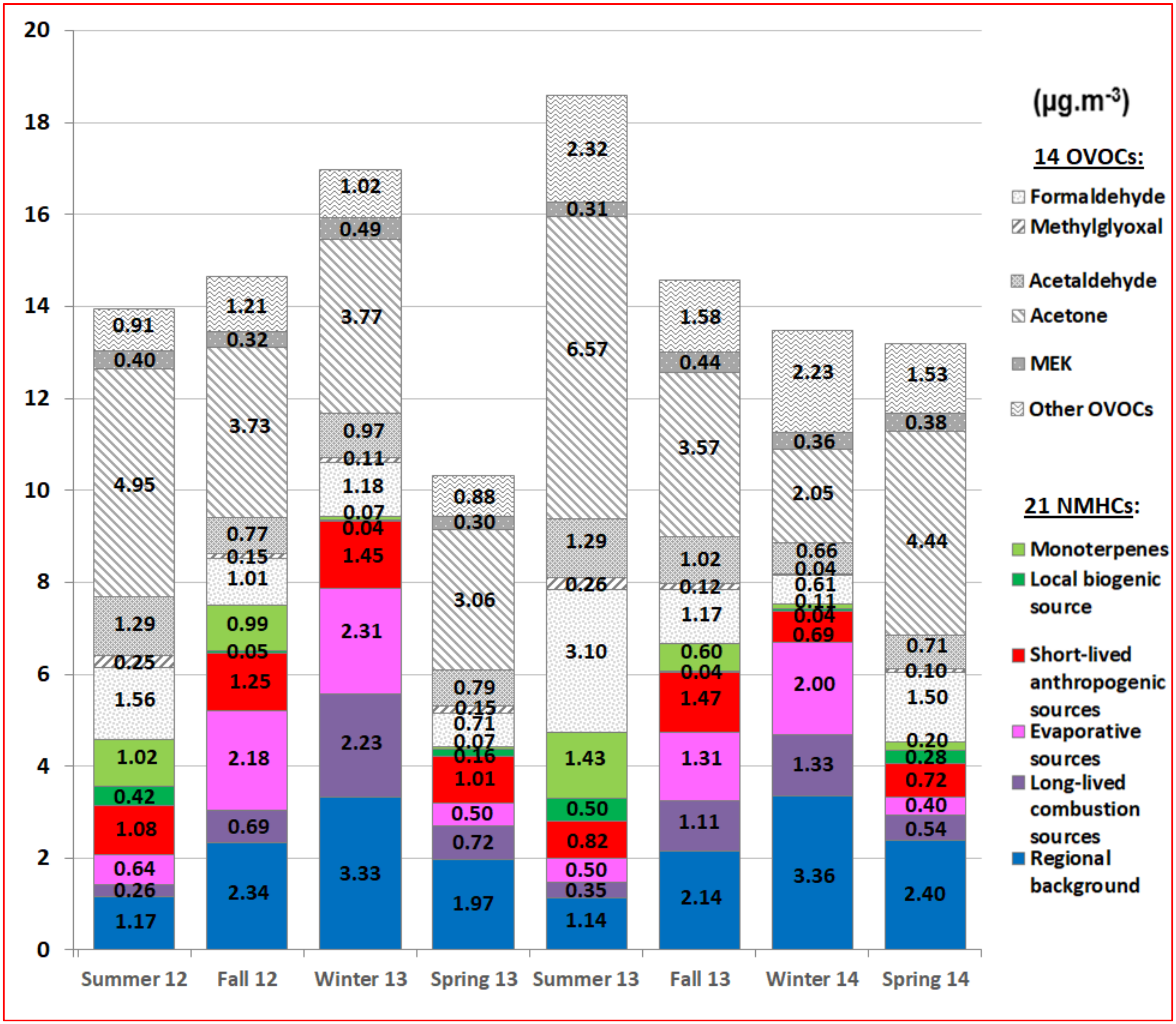


Figure ~~12~~10: Variations in~~of~~ seasonal averaged accumulated ~~contributions~~ concentrations (expressed in µg m^{-3}) of the 35 VOCs selected in this study. The 17 NHMCs selected for the factorial analysis were apportioned to~~of the~~ the five modelled ~~VOC~~ NMHC sources~~ (expressed in µg m^{-3})~~. 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. ~~Factor 1 - biogenic source; 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 – 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).

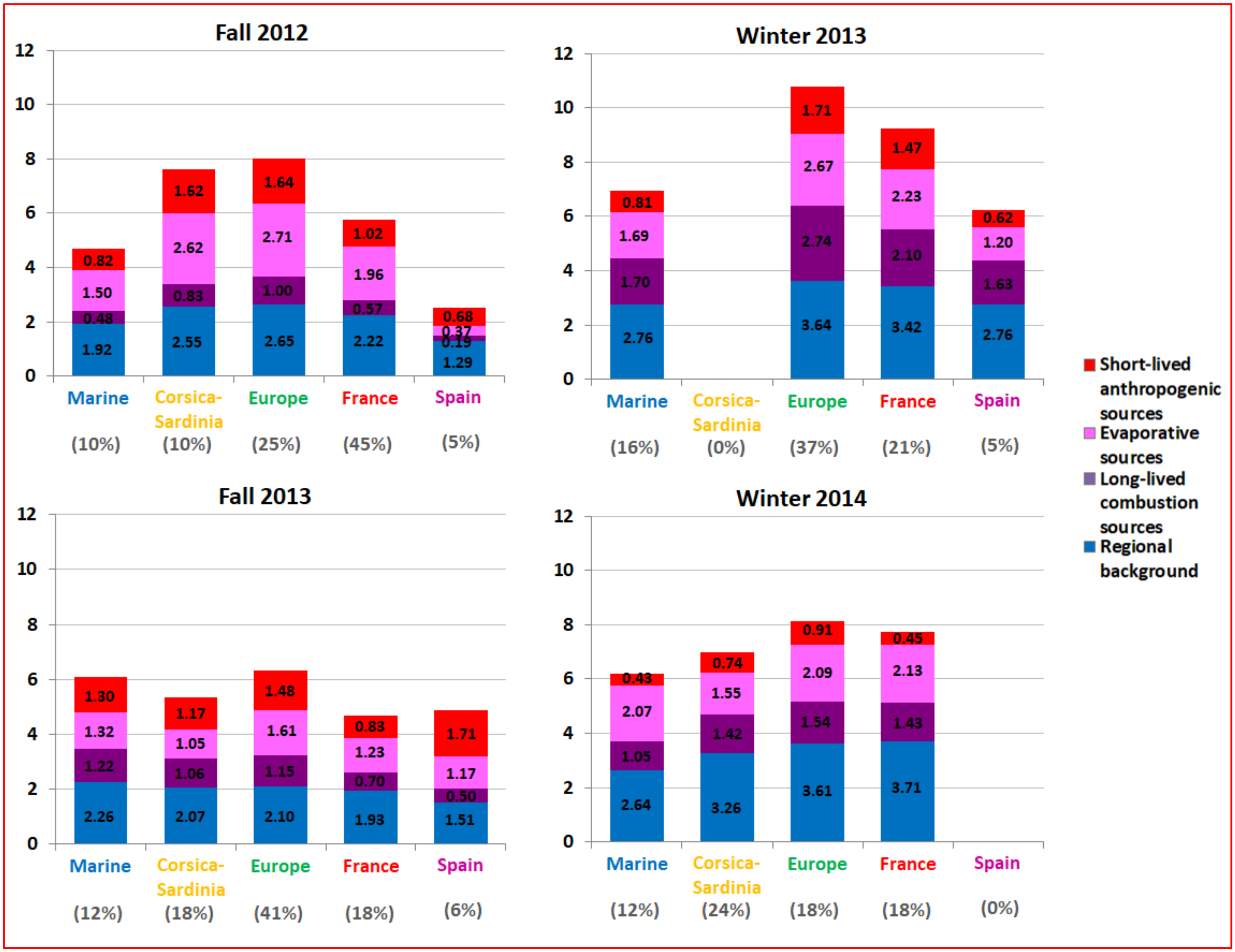


Figure ~~13~~11: Accumulated average contributions (expressed in µg m^{-3}) of the ~~anthropogenic VOC~~NMHC anthropogenic sources (factors 2-5 which explained measured concentrations of the 16 selected NMHCs in the PMF analysis – Sect. 3.5)~~factors~~ per season as a function of air mass origins (Sect. 3.2). ~~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.

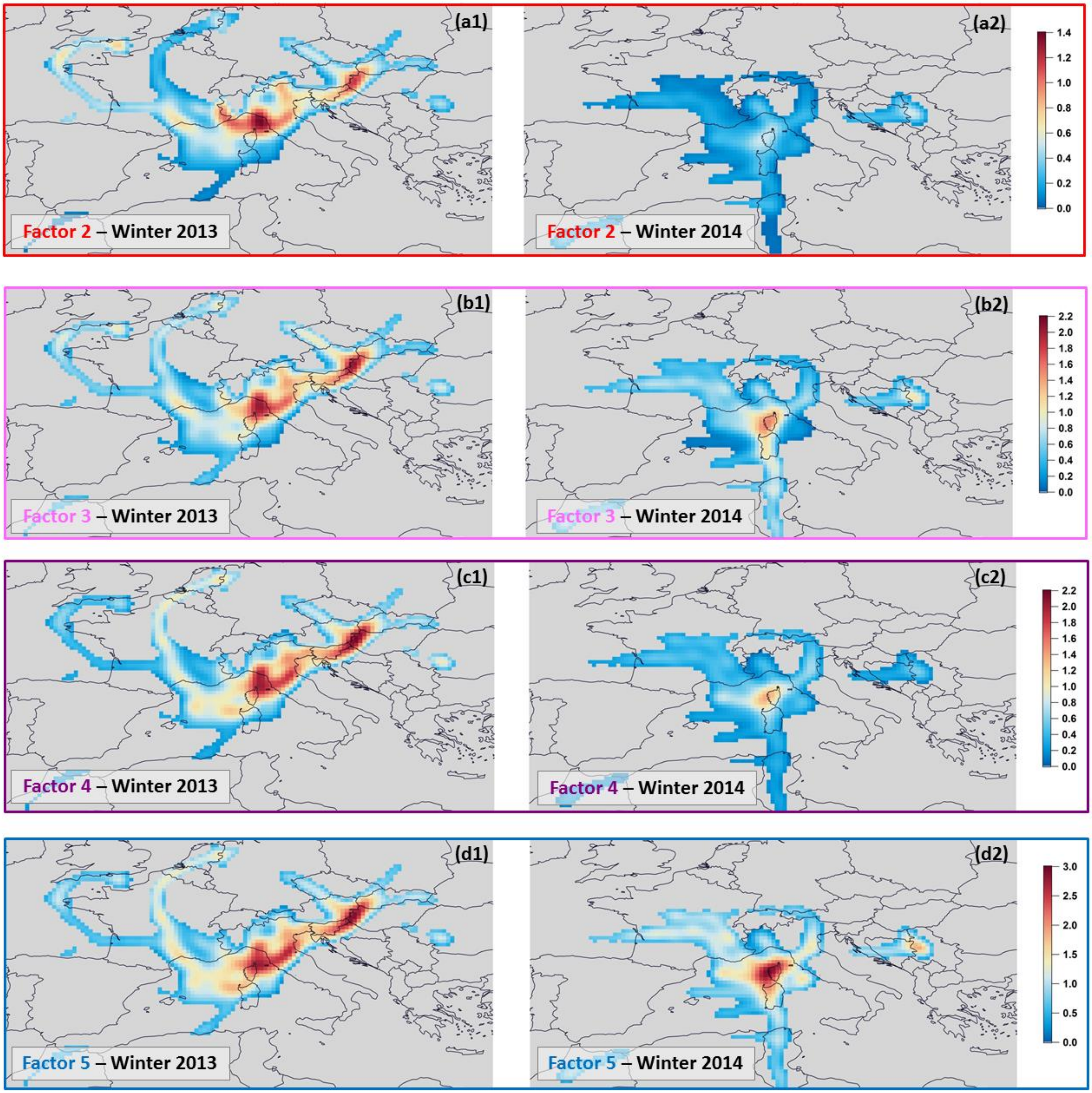
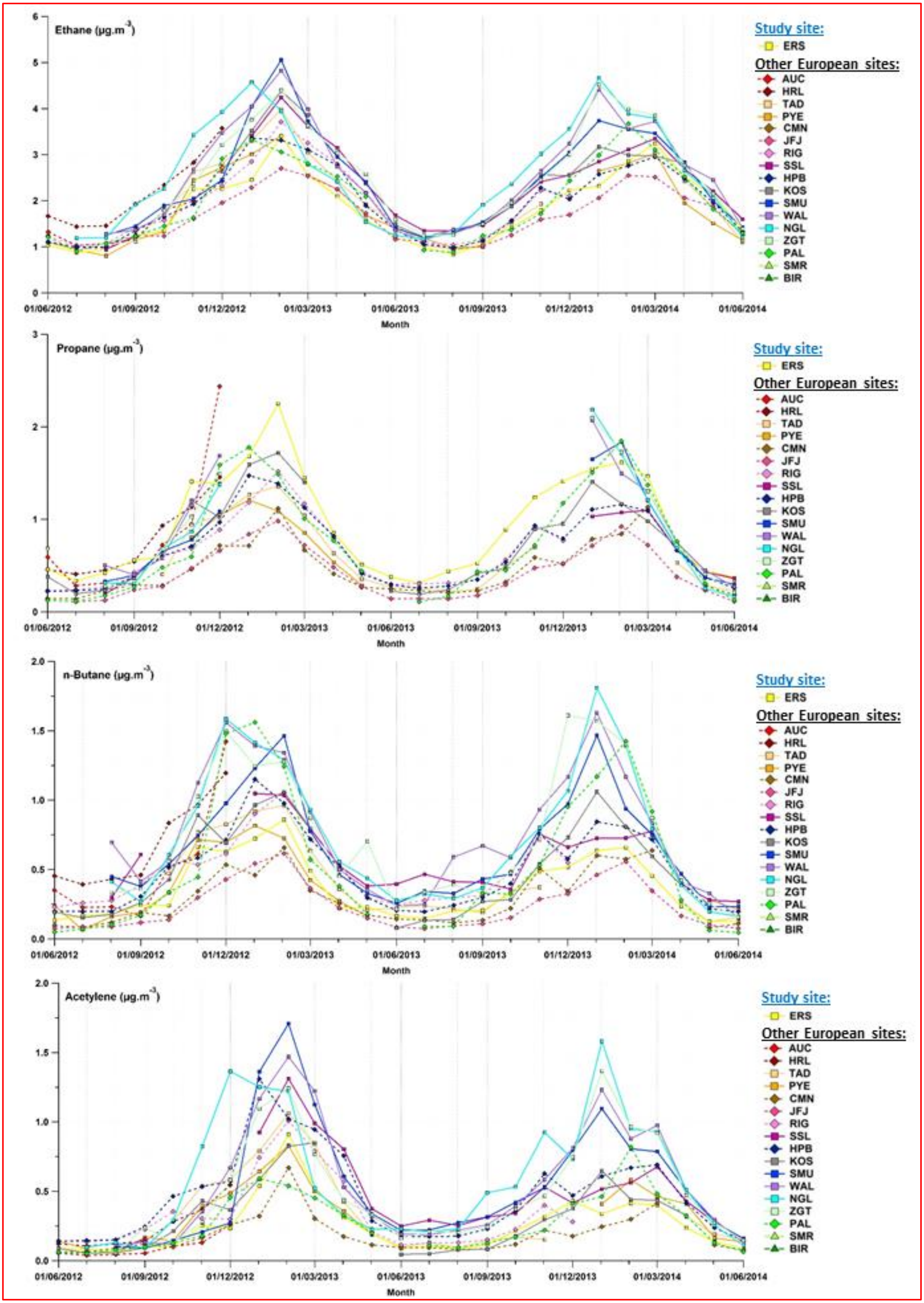


Figure ~~14~~12: Potential source areas contributions to factors 2-5 during winters 20013 and 2014. Contributions are expressed in µg m^{-3}. Factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background. Winter: 01/01-31/03 periods – fall: 01/10-31/12 periods.


Ethane (µg.m⁻³)
Propane (µg.m⁻³)
n-Butane (µg.m⁻³)
Acetylene (µg.m⁻³)
0
1
2
3
4
5
6
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

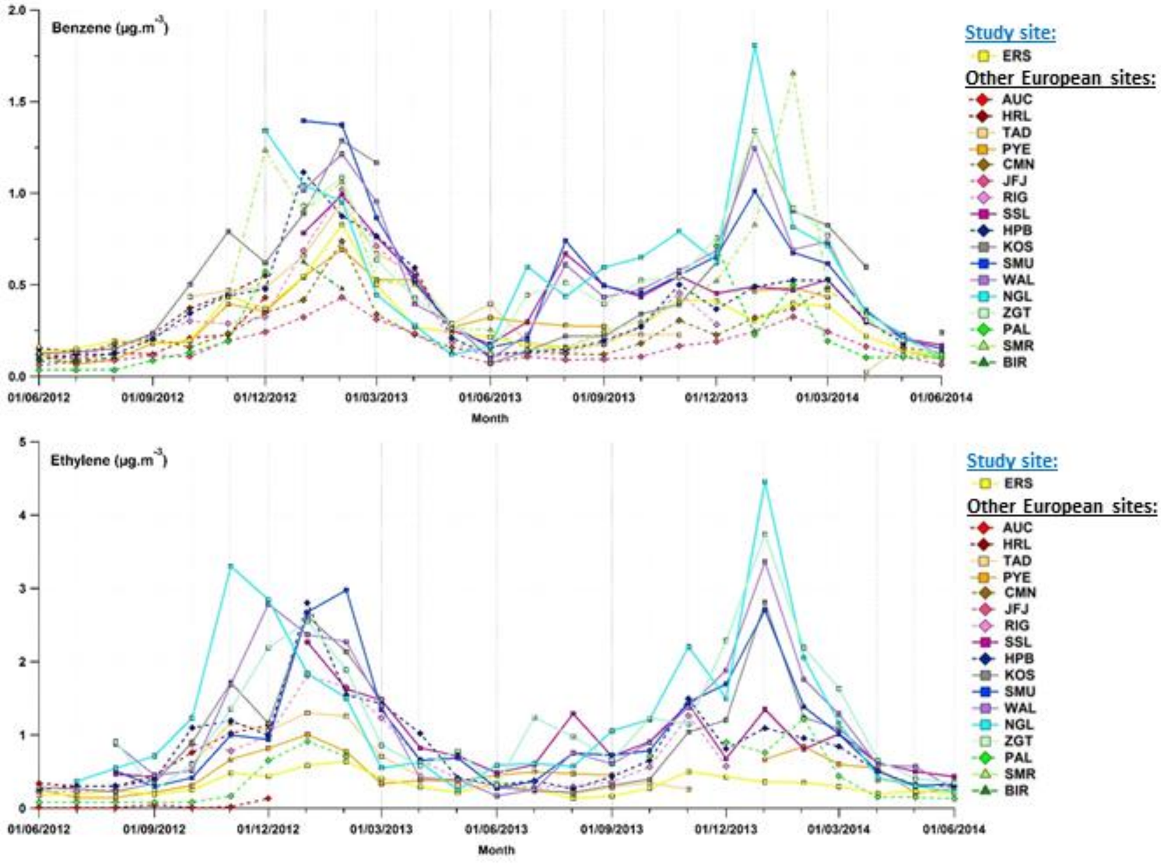


Figure ~~15~~13: Monthly concentration time series of a selection of NMHCs (expressed in µg m^{-3}) measured at Ersa and 17 other~~18~~ European monitoring stations. Stations are indicated according to their GAW identification (see Sect. S7). "ERS" refers to the study site.~~ (see Sect. 5)~~

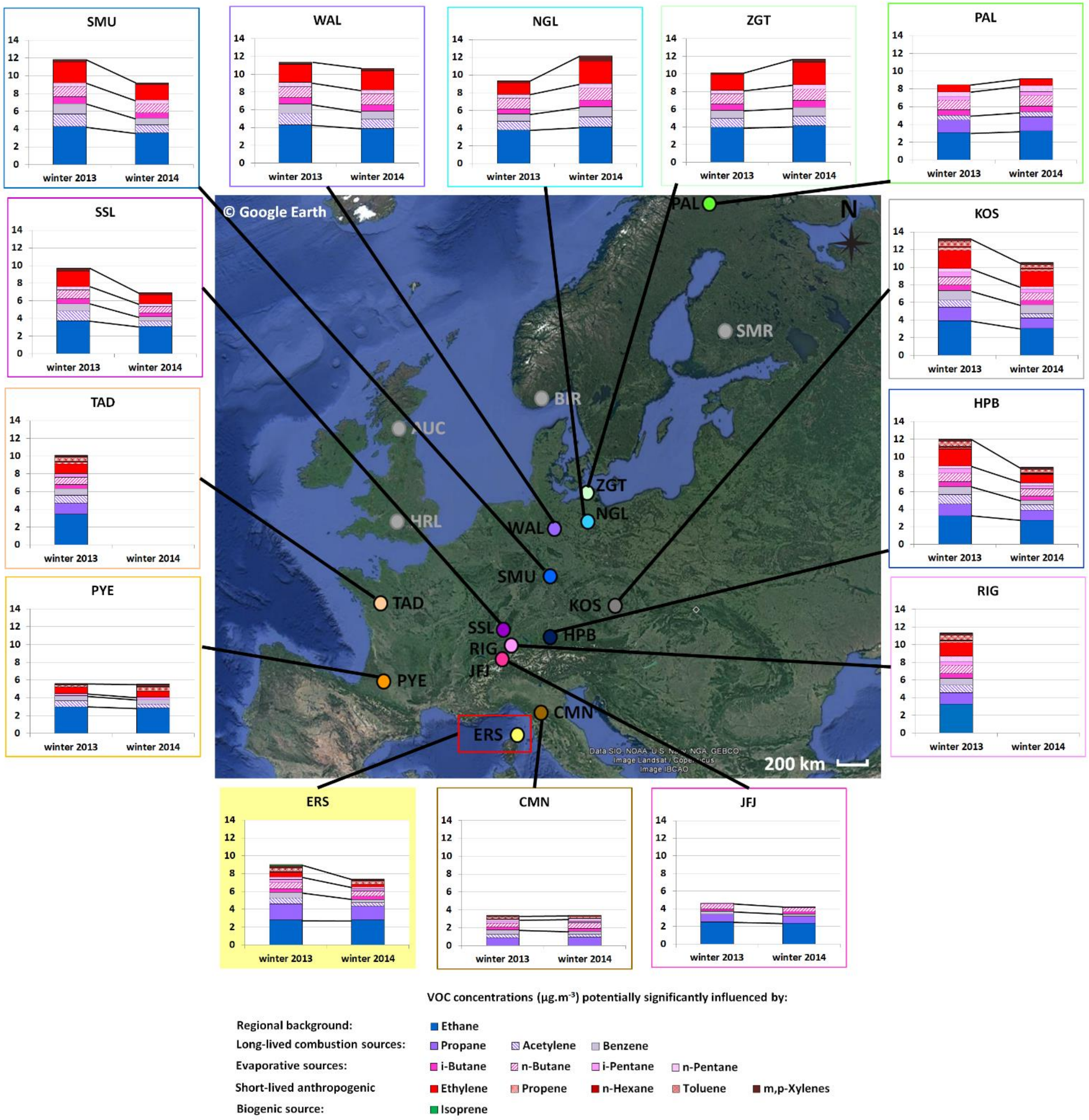


Figure ~~16~~14: Accumulated average concentrations of a selection of 15 VOCs (expressed in µg m^{-3}) measured at Ersa and 13 other~~4~~ European monitoring stations ~~(see Sect. 5)~~ in winters 2013 and 2014. Stations are indicated according to their GAW identification (see Sect. S7). "ERS" refers 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 ~~VOC~~ NMHC dataset. 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, ~~VOC~~ NMHC measurements did not cover winter 2014 period, that’s why accumulated concentrations were only indicated for winter 2013 period. For AUC, HRL, BIR and SMR stations, represented by grey markers, ~~VOC~~ 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 ~~VOC~~ NMHC winter concentrations ~~variations~~. ~~Ersa location and results are highlighted.~~ Map provided by Google Earth Pro software (v.7.3.3 image Landsat/Copernicus – IBCAO; data SIO, NOOA, U.S, Navy, NGA, GEBCO; © Google Earth).

Supplement materials to:

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

Cécile Debevec[1], Stéphane Sauvage[1], Valérie Gros[2], Thérèse Salameh[1], Jean Sciare[2,3], François Dulac[2], Nadine Locoge[1].

[1]IMT Lille Douai, Univ. Lille, SAGE - Département Sciences de l'Atmosphère et Génie de l'Environnement, 59000 Lille, France
[2] Equipe CAE, Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Unité Mixte CEA-CNRS-UVSQ, Gif sur Yvette, 91190, France
[3] Climate and Atmosphere Research Centre, the Cyprus Institute (CyI), Nicosia, 2121, Cyprus

Correspondence to: Stéphane Sauvage (stephane.sauvage@imt-lille-douai.fr) – Cecile Debevec (cecile.debevec@imt-lille-douai.fr)

Table S1: Average concentrations ± standard deviations (µg m^{-3}) of selected VOCs measured at Ersa from June 2012 to June 2014 as a function of the measurement sampling times (see Table 1).

	Species	Samples collected from 09:00-13:00	Samples collected from 12:00-16:00
BVOCs	**Isoprene**	0.08 ± 0.21	0.21 ± 0.35
	α-Pinene	0.13 ± 0.11	0.49 ± 0.71
	Camphene	0.01 ± 0.03	0.03 ± 0.07
	α-Terpinene	0.02 ± 0.03	0.09 ± 0.18
	Limonene	0.08 ± 0.17	0.24 ± 0.34
Anthropogenic NMHCs	**Ethane**	2.43 ± 0.70	1.57 ± 0.80
	Propane	1.28 ± 0.62	0.81 ± 0.62
	i-Butane	0.36 ± 0.25	0.19 ± 0.16
	n-Butane	0.51 ± 0.29	0.31 ± 0.25
	i-Pentane	0.32 ± 0.26	0.26 ± 0.22
	n-Pentane	0.27 ± 0.28	0.23 ± 0.21
	n-Hexane	0.09 ± 0.06	0.08 ± 0.05
	Ethylene	0.38 ± 0.20	0.30 ± 0.18
	Propene	0.07 ± 0.04	0.07 ± 0.04
	Acetylene	0.31 ± 0.20	0.25 ± 0.27
	Benzene	0.35 ± 0.16	0.30 ± 0.22
	Toluene	0.37 ± 0.26	0.30 ± 0.24
	Ethylbenzene	0.06 ± 0.07	0.05 ± 0.07
	m,p-Xylenes	0.14 ± 0.15	0.15 ± 0.14
	o-Xylene	0.07 ± 0.09	0.09 ± 0.09
OVOCs	**Formaldehyde**	0.96 ± 0.48	1.82 ± 1.44
	Acetaldehyde	0.68 ± 0.17	1.11 ± 0.44
	i,n-Butanals	0.13 ± 0.07	0.34 ± 0.69
	n-Hexanal	0.15 ± 0.10	0.26 ± 0.32
	Benzaldehyde	0.15 ± 0.12	0.15 ± 0.12
	n-Octanal	0..07 ± 0.05	0.13 ± 0.24
	n-Nonanal	0.49 ± 0.43	0.18 ± 0.15
	n-Decanal	0.43 ± 0.34	0.14 ± 0.13
	n-Undecanal	0.09 ± 0.06	0.06 ± 0.06
	Glyoxal	0.07 ± 0.04	0.07 ± 0.05
	Methylglyoxal	0.07 ± 0.04	0.21 ± 0.16
	Acetone	3.32 ± 1.77	4.84 ± 2.95
	MEK	0.34 ± 0.11	0.37 ± 0.16

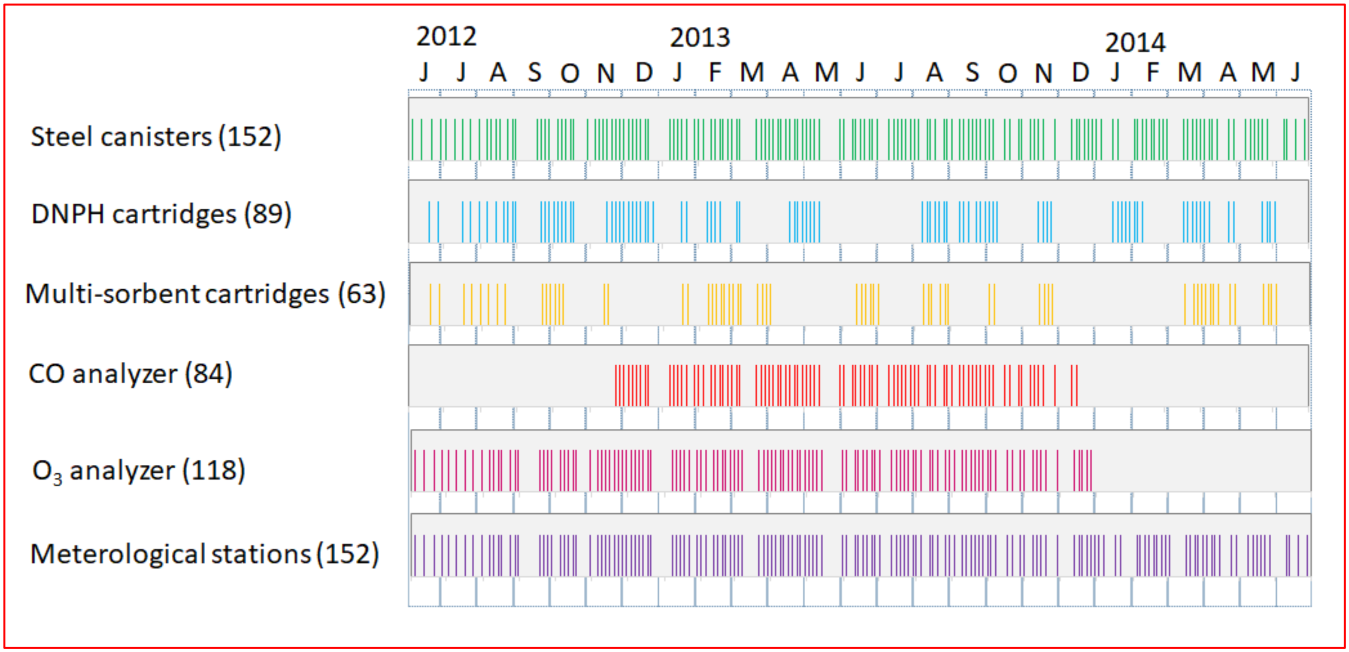


Figure S1: Data collection status indicating when VOC samples were carried out over the two-year period and when concurrent ancillary measurements were realized. The numbers indicated within parentheses correspond to the total number of data observations.

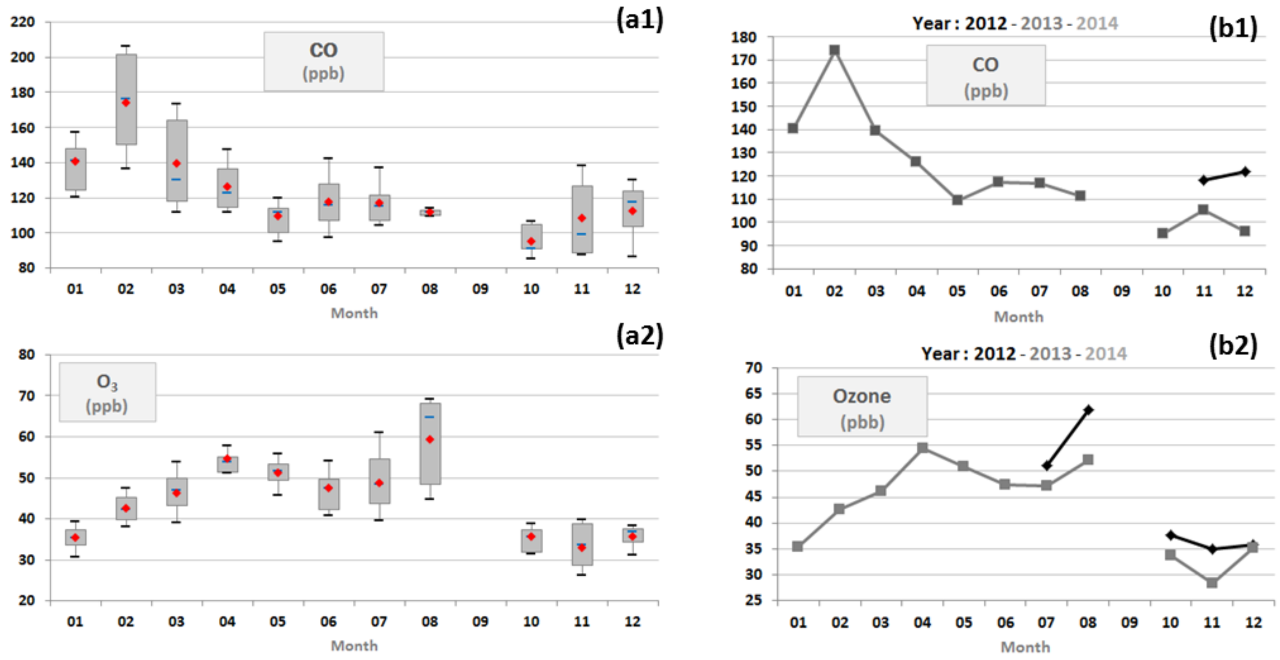


Figure S2: (a) Monthly variations in gas concentrations (CO and O_3 expressed in ppb) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean and the interquartile range of the values, respectively. The bottom and top of the box depict the first and third 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, gas data used in this study were restricted to periods when VOC measurements were realized.

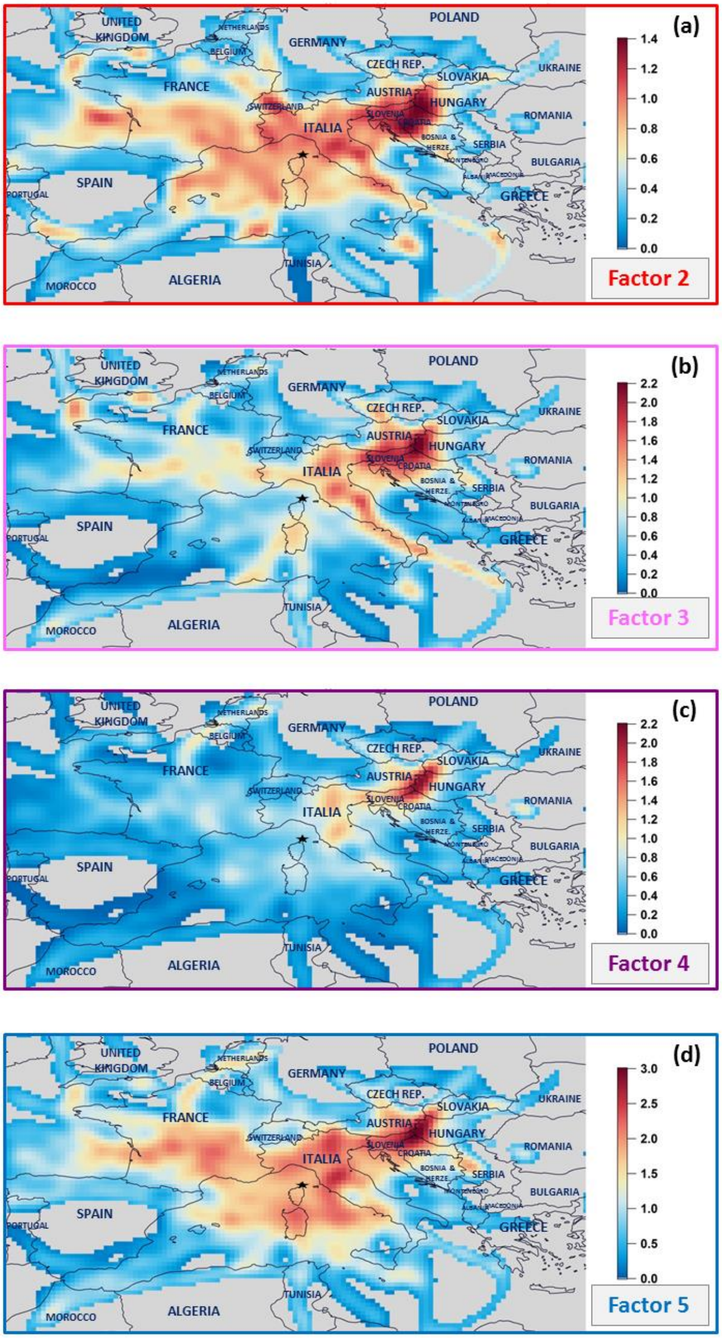
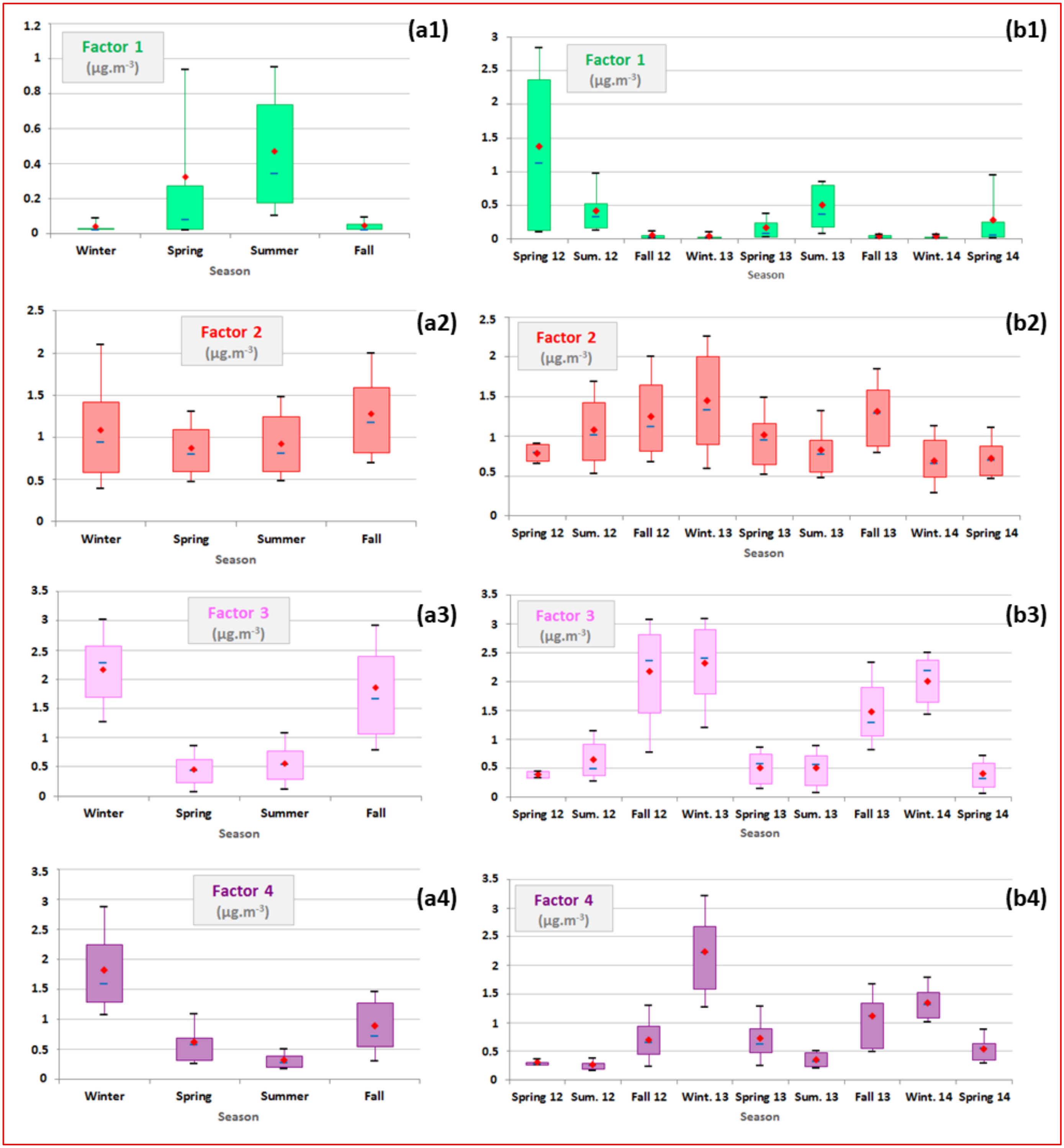


Figure S3: Potential source area contributions to factors 2-5 using the CF model. Contributions are expressed in µg m^{-3}. NMHC factors: factor 2 - short-lived anthropogenic sources; factor 3 – evaporative sources; factor 4 – long-lived combustion sources; factor 5 – regional background.


(a1)
Factor 1
(μg.m-3)
1.2
1
0.8
0.6
0.4
0.2
0
Winter
Spring
Summer
Fall
Season
(b1)
Factor 1
(μg.m-3)
3
2.5
2
1.5
1
0.5
0
Spring 12
Sum. 12
Fall 12
Wint. 13
Spring 13
Sum. 13
Fall 13
Wint. 14
Spring 14
Season
(a2)
Factor 2
(μg.m-3)
2.5
2
1.5
1
0.5
0
Winter
Spring
Summer
Fall
Season
(b2)
Factor 2
(μg.m-3)
2.5
2
1.5
1
0.5
0
Spring 12
Sum. 12
Fall 12
Wint. 13
Spring 13
Sum. 13
Fall 13
Wint. 14
Spring 14
Season
(a3)
Factor 3
(μg.m-3)
3.5
3
2.5
2
1.5
1
0.5
0
Winter
Spring
Summer
Fall
Season
(b3)
Factor 3
(μg.m-3)
3.5
3
2.5
2
1.5
1
0.5
0
Spring 12
Sum. 12
Fall 12
Wint. 13
Spring 13
Sum. 13
Fall 13
Wint. 14
Spring 14
Season
(a4)
Factor 4
(μg.m-3)
3.5
3
2.5
2
1.5
1
0.5
0
Winter
Spring
Summer
Fall
Season
(b4)
Factor 4
(μg.m-3)
3.5
3
2.5
2
1.5
1
0.5
0
Spring 12
Sum. 12
Fall 12
Wint. 13
Spring 13
Sum. 13
Fall 13
Wint. 14
Spring 14
Season

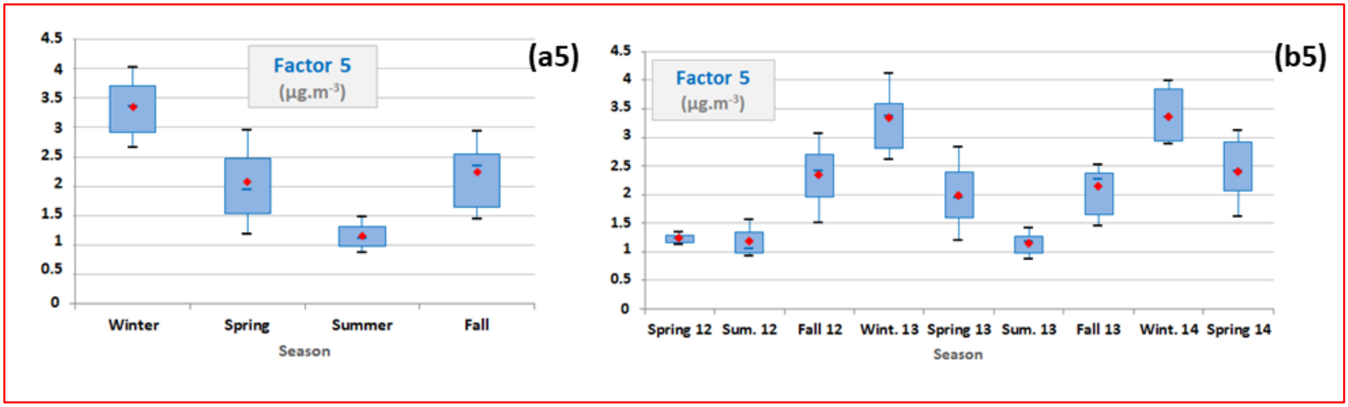
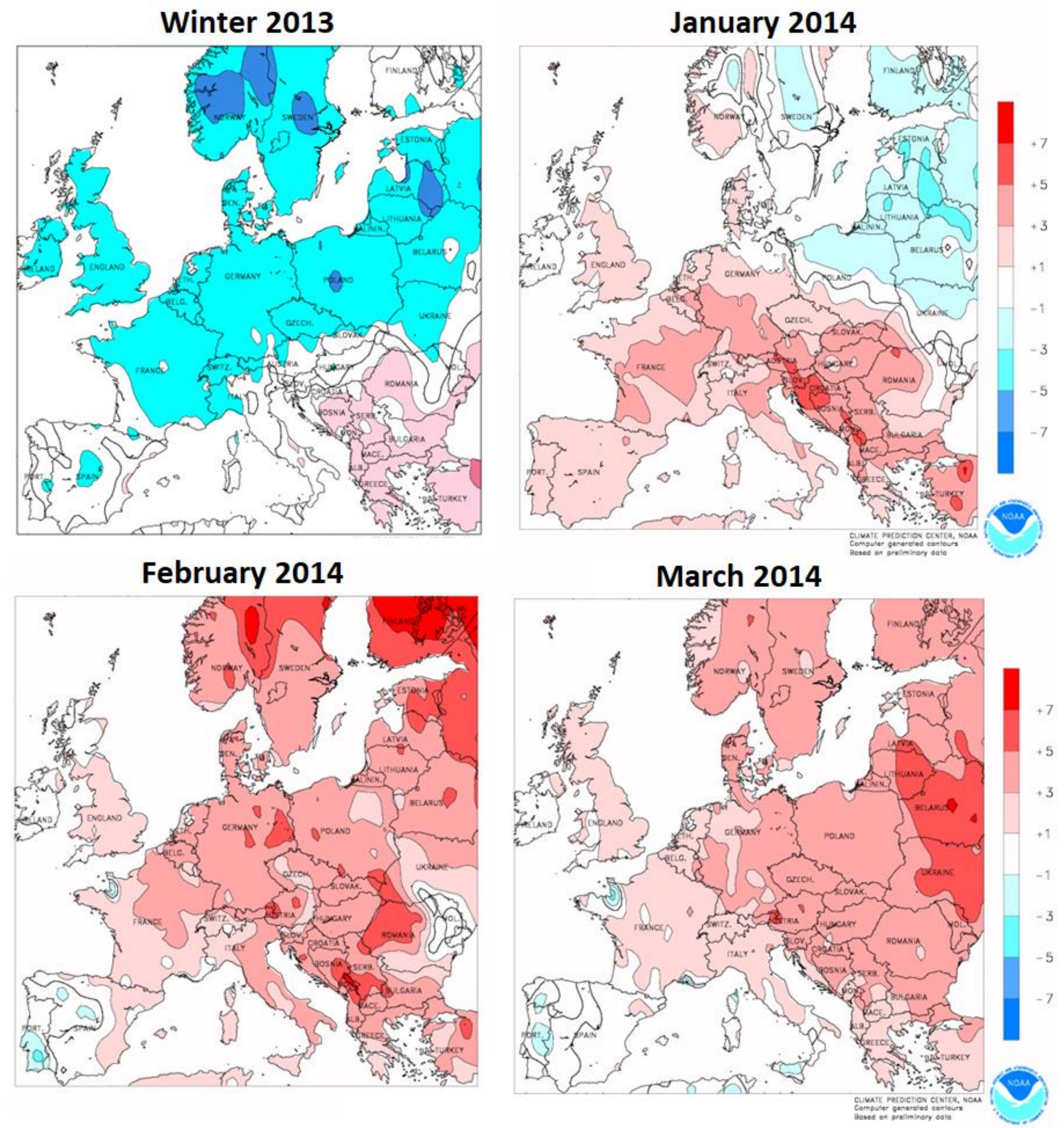


Figure S4: Seasonal (a) and interannual (b) variations in NMHC factor contributions (expressed in µg m^{-3}) represented by box plots; the blue solid line, the red marker, and the box represent the median, the mean, and the interquartile range of the values, respectively. The bottom and top of the box 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). NMHC factors: 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. 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 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).

Temperature anomalies (in °C)



Winter 2013

January 2014

February 2014

March 2014

CLIMATE PREDICTION CENTER, NOAA
Computer generated contours
Based on preliminary data

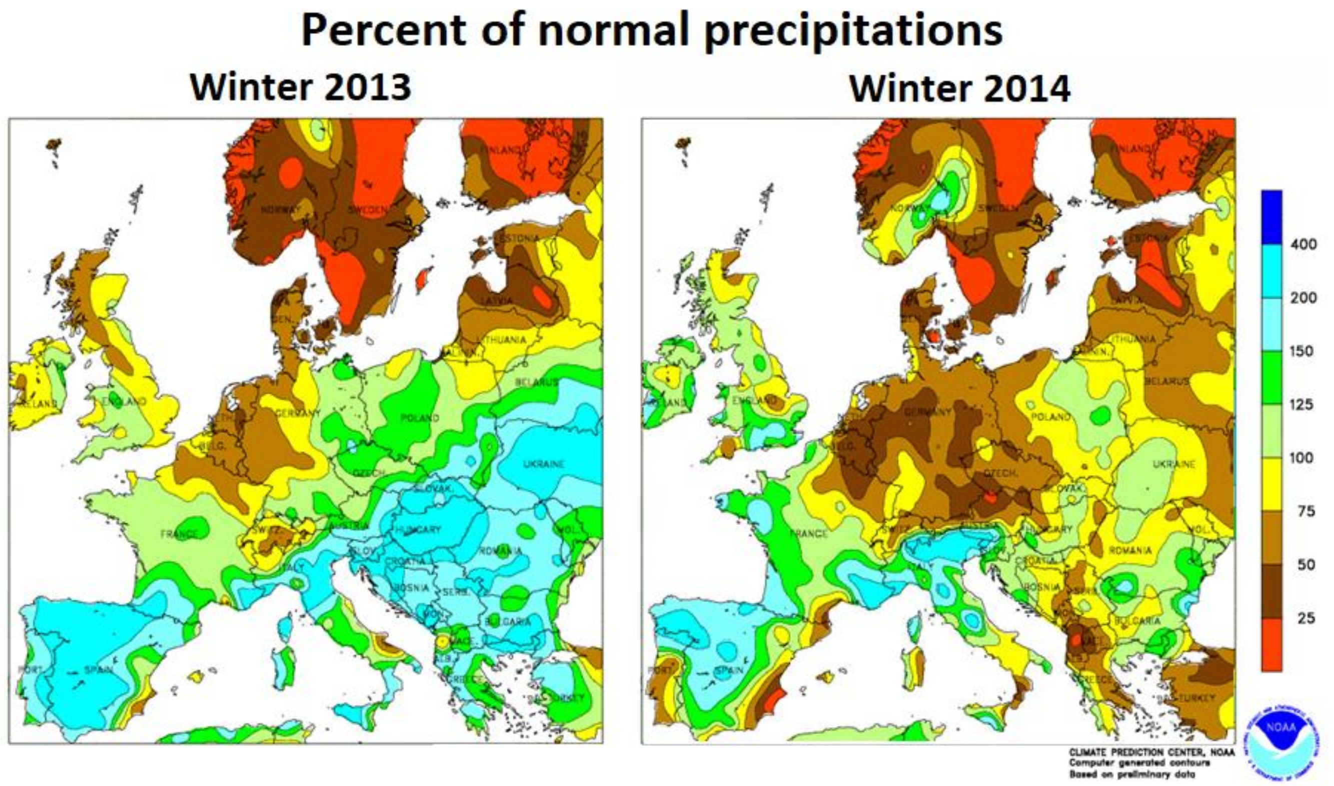


Figure S5: Normalized temperature anomalies and percent of precipitations in winters 2013 and 2014 in Continental Europe. Simulations realized by the Climate Prediction Center (CPC) of the National Oceanic and Atmospheric Administration (https://www.cpc.ncep.noaa.gov/products/analysis_monitoring/regional_monitoring/europe.html, last access: 11/10/2020). Normal values for the 1981-2010 period were calculated by the CPC using the average of monthly (or quarterly) values.

Section S1: VOCs selected in this study

In this section, the selection of the VOCs retained for this study among those measured (see Table S2) is presented. Co-eluted VOCs, i.e. n-pentanal+o-tolualdehyde measured from DNPH cartridges and 2,3-dimethylbutane+cyclopentane measured from multi-sorbent cartridges, were not considered in this study. Concentrations of b-pinene resulting from multi-sorbent cartridges were also not considered in this study for analytical reasons.

17 NMHCs were measured from both steel canisters and multi-sorbent cartridges (underlined species in Table S2) and n-hexanal was measured from both DNPH cartridges and multi-sorbent cartridges. Note that, consistency between recovery species was checked during the intensive field campaign of summer 2013 (see Michoud et al., 2017) and was not checked a second time due to the low temporal recovery of the instruments in terms of data points. In this study, the concentrations of the 17 NMHCs measured from steel canisters were retained given their higher number of observations and lower uncertainties compared to those measured with multi-sorbent cartridges. Concentrations of n-hexanal measured using DNPH cartridges were retained in this study for the same reason.

Then, to select the VOCs examined in this study, their percentages of values below their detection limit (DL) were examined and VOCs having more than 50% of their concentrations below their DL were discarded. This criteria has concerned four NMHCs measured from steel canisters (2,2-dimethylbutane, i-octane, n-octane and 1,2,4-trimethylbenzene), one carbonyl compound from DNPH cartridges (acrolein) and seven VOCs measured from multi-sorbent cartridges (2-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, 2,3,4-trimethylpentane and 1,3,5-trimethylbenzene). Furthermore, VOC average signal-to-noise (S/N) ratios were examined. This parameter determines the average relative difference between concentrations and their corresponding uncertainties, thus pondering the results in function of their quality (Norris et al, 2014). Species having a S/N ratio below 1.2 were discarded (see Debevec et al, 2017). This criteria has concerned three additional NMHCs measured from canisters (2-methylpentane, 3-methylpentane and n-heptane), two additional carbonyl compounds measured from DNPH cartridges (propanal and methacrolein) and 14 additional VOCs measured from multi-sorbent cartridges (cyclohexane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexanedecane, 1-hexene, cyclopentene, g-terpinene, styrene and n-heptanal).

Table S2: Listed VOCs as a function of family compounds and instruments. Underlined VOCs were measured by several instruments. Retained VOCs in this study are indicated in bold.

Family compounds	**Steel canisters**	**DNPH cartridges – Chemical desorption (acetonitrile) – HPLC-UV**	**Solid adsorbent – Adsorption/thermal desorption – GC-FID**
ALKANES	**Ethane, propane, i-butane, n-butane, i-pentane, n-pentane,** 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, **n-hexane,** n-heptane, i-octane, n-octane		i-Pentane, n-pentane, 2,2-dimethylbutane, 2,3-dimethylbutane+cyclopentane, 2-methylpentane, 3-methylpentane, n-hexane, cyclohexane, 2-methylhexane, 2,2,3-trimethylbutane, 2,2dimethylpentane, 2,4-dimethylpentane, 2,3-dimethylpentane, n-heptane, 2,3,4-trimethylpentane, i-octane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentandecane, n-hexadecane
ALKENES	**Ethylene, propene**		Cyclopentene, 1-hexene
ALKYNE	**Acetylene**		
DIENE	**Isoprene**		Isoprene
TERPENES			**a-Pinene,** b-pinene, **camphene, limonene, a-terpinene,** g-terpinene
AROMATICS	**Benzene, toluene, ethylbenzene, m,p-xylenes, o-xylene,** 1,2,4-trimethylbenzene		Benzene, toluene, ethylbenzene, m,p-xylenes, o-xylene, styrene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene
CARBONYL COMPOUNDS		**Formaldehyde, acetaldehyde,** propanal, **i,n-butanals,** n-pentanal+o-tolualdehyde, **hexanal, benzaldehyde, acetone, MEK,** acrolein, methacrolein, **glyoxal, methylglyoxal**	Hexanal, n-heptanal, **n-octanal, n-nonanal, n-decanal, n-undecanal**

Section S2~~1~~: Identification and contribution of major sources of ~~VOCs~~ NMHCs by EPA PMF 5.0 approach

S2.1 PMF approach

PMF is a tool elaborated for a multivariate factor analysis and used for the identification and the characterization of the “p” independent sources of "n” species measured “m” times at a given site. Note that the PMF mathematical theory is detailed elsewhere (Paatero, 1997; Paatero and Tapper, 1994). Concisely, the PMF method is based on the decomposition of a matrix of chemically speciated sample data (of dimension n x m) into two matrices of factor profiles (n x p) and factor contributions (p x m), interpreting each factor as a different source type. Species profiles of each source identified represent the repartition of each species into each given factor, and the amount of mass contributed by each factor to each successive individual sample represents the evolution in time of the contribution from each factor to the various species. The principle can be condensed as:

$$x_{ij} = \sum_{k=1}^{p} g_{jk} \times f_{ki} + e_{ij} = c_{ij} + e_{ij} , \qquad (1)$$

where x_{ij} is the ith species measured concentration (in µg m^{-3} here) in the jth sample, f_{ki} the ith mass fraction from kth source, g_{jk} the kth source contribution of the jth sample, e_{ij} the residual resulting of the decomposition and c_{ij} the species reconstructed concentration. The Eq. (1) can be solved iteratively by minimizing the residual sum of squares Q following Eq. (2):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{s_{ij}}\right)^2 , \qquad (2)$$

with s_{ij}, the extended uncertainty (in µg m^{-3}) related to the measured concentration of the ith species in the jth sample. A user-provided uncertainty following the procedure presented in Polissar et al. (1998) is also required by the PMF tool to weight individual points. Moreover, negative source contributions are not allowed.

S2.2 VOC dataset and data preparation

In order to have sufficient completeness (in terms of observation number), only ~~VOC~~ primary HCNM measurements from bi-weekly ambient air samples collected into steel canisters from 04 June 2012 to 27 June 2014 were retained in this factorial analysis. The ~~final VOC~~NMHC dataset encompassed 152 atmospheric data points having a time resolution of 4 hours. VOC observations resulting from DNPH and multi-sorbent cartridges were not considered in the PMF analysis since they were sampled only 73 and 52 days concurrently to the collection of steel canisters (Fig. S1). Reconstruction of missing data points would significantly affect the dataset quality. Additionally, the restriction of the number of data points to those common to the three datasets (36 data points) would significantly impact the temporal representativeness of the VOC inputs of the study period and hence limit the discussion on interannual and seasonal variations for statistical robustness reasons. Note that no outlier was removed from the dataset.

NMHC inputs were built using the concentrations of the 17 HCNMs selected in this study (see Sect. S1). The chemical dataset includes 13 single variables and a grouped one. This latter named “EX” grouped the concentrations of C_8 aromatic compounds, in order to maximize its concentration levels.

~~14 selected single or grouped VOCs, i.e. those showing significant concentration levels during the study period (see Sect. 3.3). They were divided into five compound families: alkanes (ethane, propane, i-butane, n-butane, i-pentane, n-pentane and n-hexane), alkenes (ethylene and propene), alkyne (acetylene), diene (isoprene) and aromatics (benzene, toluene, and EX, the sum of ethylbenzene, m,p-xylenes and o-xylene). The final VOC dataset encompassed 152 atmospheric data points having a time resolution of 4 hours.~~ Moreover, the data ~~processing~~ preprocessing and quality analysis of the VOC dataset are presented in the supplement material of Debevec et al. (2017). Since signal-to-noise (S/N) ratios of the 14 variables retained for the factorial analysis are all higher than 1.2, in this study no variable was categorized as “weak”, and hence downweighted (categorize variables in “weak” means to triple their original uncertainties; Norris et al, 2014).

S2.3 Selected PMF Solution

In order to identify the optimal number of factors for the PMF solution selected in this study, the first step consisted in carrying out numerous successive base runs considering an incremented factor number according to the protocol defined by Sauvage et al. (2009). As a result, PMF solutions composed from 2 to 10 factors, considering 100 runs and a random start, were explored.

Firstly, the selection of the solution among PMF solutions of 2 to 10 factors is based on the analysis of diverse exploratory statistical parameters (Table S3 and Fig. S6) which are as follows:

- Variations in Q_{true} and $Q_{theorical}$ as a function of the factor number of the PMF solution. Qtrue is provided by the EPA PMF tool (Norris et al., 2014) following the launch of a base model run. $Q_{theorical}$ is a calculated parameter following the equation (3). Q_{true} and $Q_{theorical}$ tend to decrease when the factor number increases. A PMF user can choose the PMF solution having a lower Q_{true} compared to the associated $Q_{theorical}$.
- Variation in IM and IS (maximum individual standard deviation and maximum individual column mean, respectively) as a function of the factor number of the PMF solution. IM and IS can be defined following equations (4) and (5), respectively. A PMF user can choose the PMF solution corresponding to a significant break in the slope of IM and/or IS (see also the relative differences d(IM) and d(IS) in Table S3) as a function of the factor number.
- Variations in average determination coefficients between reconstructed concentrations of the total variable (called in this study TVOC, see Norris et al., 2014) and measured ones (R^2(TVOC)). A PMF user can choose the PMF solution of p factors corresponding to a significant increase of R^2(TVOC) compared to the PMF solution of p-1 factors.
- An optimal PMF solution should also present a symmetrical distribution of residual values related to the total variable as well as a large proportion of them ranging between -2 and 2, especially between -0.3 and 0.3.

$$for\ p \in [2, 10], Q_{theorical} = M \times N - p \times (M + N), \qquad (3)$$

with M=152 and N=14 in this study (Sect. S2.2).

$$IM = \max\left(\frac{1}{M}\sum_{j=1}^{M}\frac{e_{ij}}{s_{ij}}\right),\ among\ i \in [1, N] \qquad (4)$$

$$IS = \max\left(\sqrt{\frac{1}{M-1}\sum_{j=1}^{M}\left[\frac{e_{ij}}{s_{ij}} - \overline{\left(\frac{e_{iJ}}{s_{iJ}}\right)}\right]^2}\right),\ among\ i \in [1, N] \qquad (5)$$

The visual inspection of statistical indicators was realized following Fig. S6. Significant breaks in slope of variations of IM as a function of the factor number of the PMF solution were noticed for PMF solutions composed from 3 to 5 factors, from 4 to 6 factors and from 7 to 9 factors (Fig. S6c). Moreover, a significant break in slope of variations of IS as a function of the factor number of the PMF solution was only noticed for PMF solutions composed from 5 to 7 factors (Fig. S6d). R²(TVOC) increases significantly between PMF solutions of 3 and 4 factors and to a lesser extent between PMF solutions from 4 to 7 factors (Fig. S6e). Contrarily, R²(TVOC) decreases significantly between PMF solutions of 7 and 8 factors. However, Q_{true} is lower than $Q_{theorical}$ from a PMF solution of 8 factors (Fig. S6a). From a PMF solution of 4 factors, the proportion of residual values ranging between -2 and 2 is higher than 90% and from a PMF solution of 5 factors, the proportion of residual values ranging between -0.3 and 0.3 is higher than 40% (Fig. S6b). As a result, we oriented our choice of optimal PMF solution from 4 to 6 factors.

In order to refine this choice, we also examined correlations between reconstructed concentrations and measured ones for individual species of the selected PMF solutions (Figs S7-S9 and Table S4), their distribution of residual values (Fig S10), the physical meaning of their factor profiles (Fig S11), their factor contribution time series (Fig S11) and correlations between their factors. From a PMF solution of 4 factors, the model identified a factor related to a biogenic source (factor 1 depicted in Fig. S11 and related to isoprene concentrations). A better reconstruction of ethane, acetylene and isoprene concentrations was noticed for a PMF solution of 4 factors (Fig S7). We did not observe any correlation between factors composing the 4-factor PMF solution. From a PMF solution of 5 factors, the model distinguished a factor related to the more reactive species (factor 2 profile composed of ethylene, propene, toluene and EX - Fig. S11) from the factor associated with evaporation sources (factor 3 profile composed of propane, i,n-butanes and i,n-pentanes - Fig. S11). These two factors are not correlated (determination coefficient: 0.35). This deconvolution notably improved the reconstruction by the PMF model of concentrations of ethylene, propene, toluene and EX (Figs. S7 and S9 and Table S4) and slightly improved the distribution of residual values for propene and toluene (Fig. S10). Ethane and isoprene concentrations are fully reconstructed with the PMF solution of 5 factors (Fig. S8 and Table S4) and their residual values were more symmetrical and gathered between -1 and 1 (Fig. S10). The additional factor composing the 6-factor PMF solution compared to the 5-factor one results from the split of the factor related to the more reactive species into two factors. The first one (factor 2 – Fig. S11) is mostly composed of ethylene and propene while the second one (factor 3 – Fig. S11) is composed of propene, i,n-pentanes, toluene and EX. These two factors are not correlated (determination coefficient: 0.02 – Fig. S11). This deconvolution notably improved the reconstruction of ethylene concentrations (Fig. S9 and Table S4), slightly improved the reconstruction of i,n-pentanes, toluene and EX concentrations but degraded propene ones. In terms of residual value distribution, the 6-factor PMF solution mostly improved the ethylene one (Fig. S10). However, ethylene, propene, i,n-pentanes, toluene and EX concentrations observed at Ersa in summer 2013 were mainly explained by the same factor according to Michoud et al. (2017), which comforted our choice of a 5-factor PMF solution for this study.

~~Diverse statistical indicators and the physical meaning of factor profiles have also to be taken into account in the selection of the optimal solution.~~

Table S3: Exploratory statistical parameters for the identification of the optimal number of factors of the PMF solution.

Factor number	Q theorical	Q robust mod	Q true	IM	IS	Proportion of residuals between [-2 ;2]	Proportion of residuals > abs(0,3)	Determination coefficient PMF results vs Meas. (R^2)	d(IM) = (IM(p) - IM(p-1)) / IM(p-1)	d(IS) =(IS(p) - IS(p-1)) / IS(p-1)
2	1796	6557	7472	0.9249	3.1160	0.7904	0.8008	0.9653	-	-
3	1630	4352	4749	0.8838	2.5538	0.8604	0.7702	0.9746	0.0444	0.1804
4	1464	3057	3169	0.4239	1.9464	0.9037	0.7049	0.9879	0.5204	0.2378
5	1298	2092	2120	0.2659	1.5157	0.9441	0.6109	0.9920	0.3727	0.2213
6	1132	1545	1547	0.2260	1.1361	0.9615	0.5550	0.9939	0.1503	0.2504
7	966	1161	1162	0.2255	1.0810	0.9737	0.5028	0.9952	0.0021	0.0485
8	800	777	777	0.1153	0.9373	0.9864	0.4384	0.9883	0.4885	0.1329
9	634	558	558	0.1133	0.8282	0.9915	0.3435	0.9873	0.0180	0.1164
10	468	380	380	0.0939	0.7596	0.9953	0.2740	0.9836	0.1713	0.0828

Table S4: Evaluation of reconstructed NMHC concentrations of PMF solutions from 4 to 6 factors as a function of measured NMHC concentrations.

	r^2			slope			intercept		
VOC	**4 factors**	**5 factors**	**6 factors**	**4 factors**	**5 factors**	**6 factors**	**4 factors**	**5 factors**	**6 factors**
(0) TVOC	0.988	0.992	0.994	1.003	1.013	1.013	-0.034	-0.072	-0.060
(1) Ethane	0.992	0.998	0.999	0.977	0.994	1.000	0.037	0.009	-0.001
(2) Ethylene	0.666	0.771	0.985	0.618	0.722	0.938	0.086	0.065	0.017
(3) Propane	0.950	0.968	0.969	0.990	1.002	1.007	-0.010	-0.013	-0.016
(4) Propene	0.275	0.454	0.411	0.350	0.534	0.488	0.034	0.024	0.026
(5) i-Butane	0.894	0.909	0.913	0.820	0.833	0.842	0.033	0.030	0.028
(6) n-Butane	0.946	0.969	0.969	0.953	0.969	0.968	0.009	0.005	0.006
(7) Acetylene	0.989	0.993	0.989	0.952	0.971	0.973	0.008	0.006	0.006
(8) i-Pentane	0.657	0.654	0.712	0.692	0.687	0.743	0.053	0.054	0.046
(9) n-Pentane	0.328	0.331	0.378	0.421	0.419	0.470	0.082	0.082	0.077
(10) Isoprene	0.568	0.995	0.995	0.362	0.998	1.009	0.054	-0.0004	-0.002
(11) n-Hexane	0.560	0.537	0.582	0.546	0.546	0.583	0.029	0.029	0.027
(12) Benzene	0.898	0.918	0.908	0.858	0.896	0.867	0.031	0.022	0.029
(13) Toluene	0.539	0.600	0.630	0.467	0.597	0.677	0.113	0.090	0.083
(14) EX	0.342	0.536	0.623	0.332	0.548	0.665	0.134	0.102	0.079

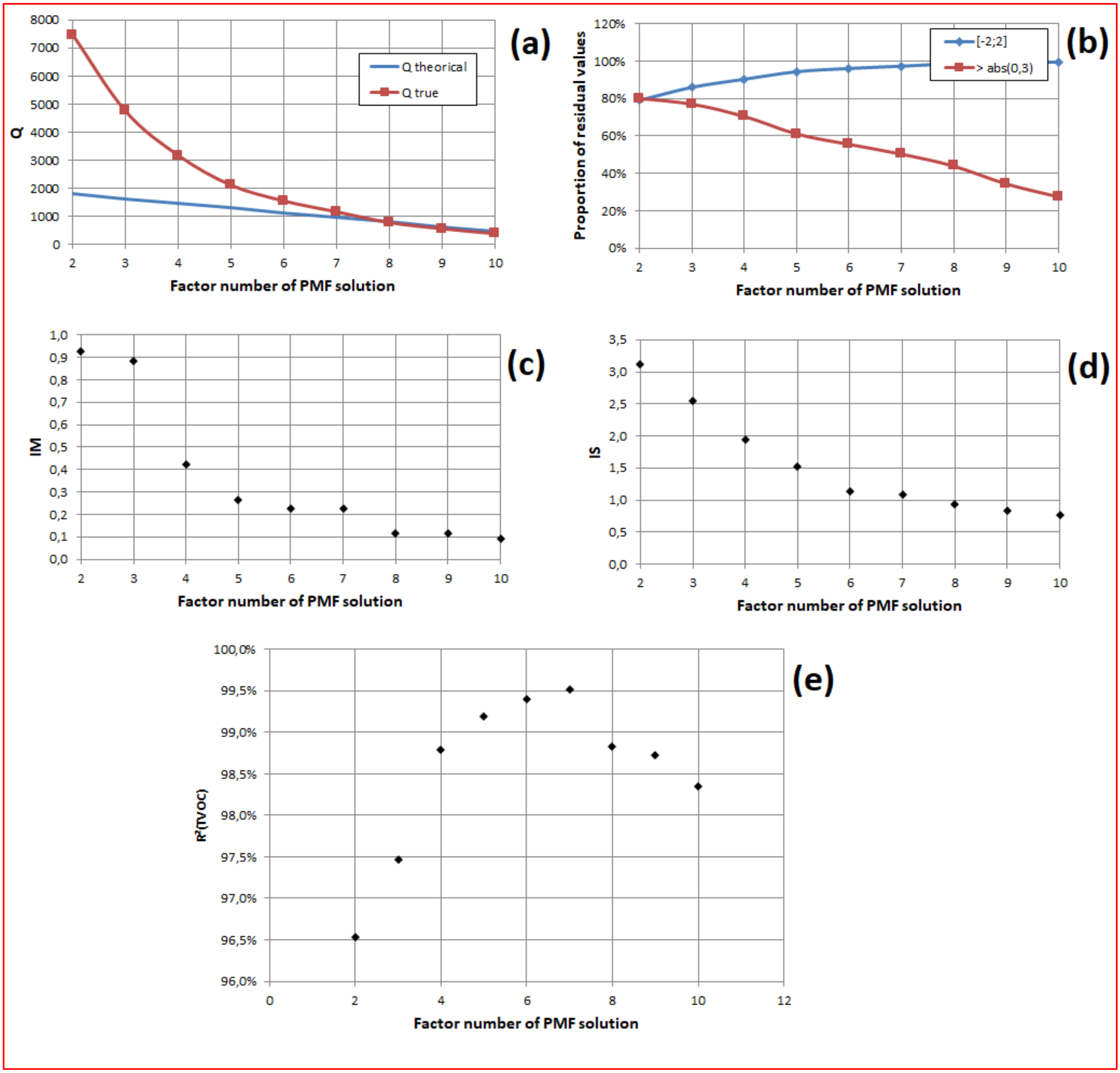


Figure S6: Variations of exploratory statistical parameters as a function of the number of factors of PMF solutions.

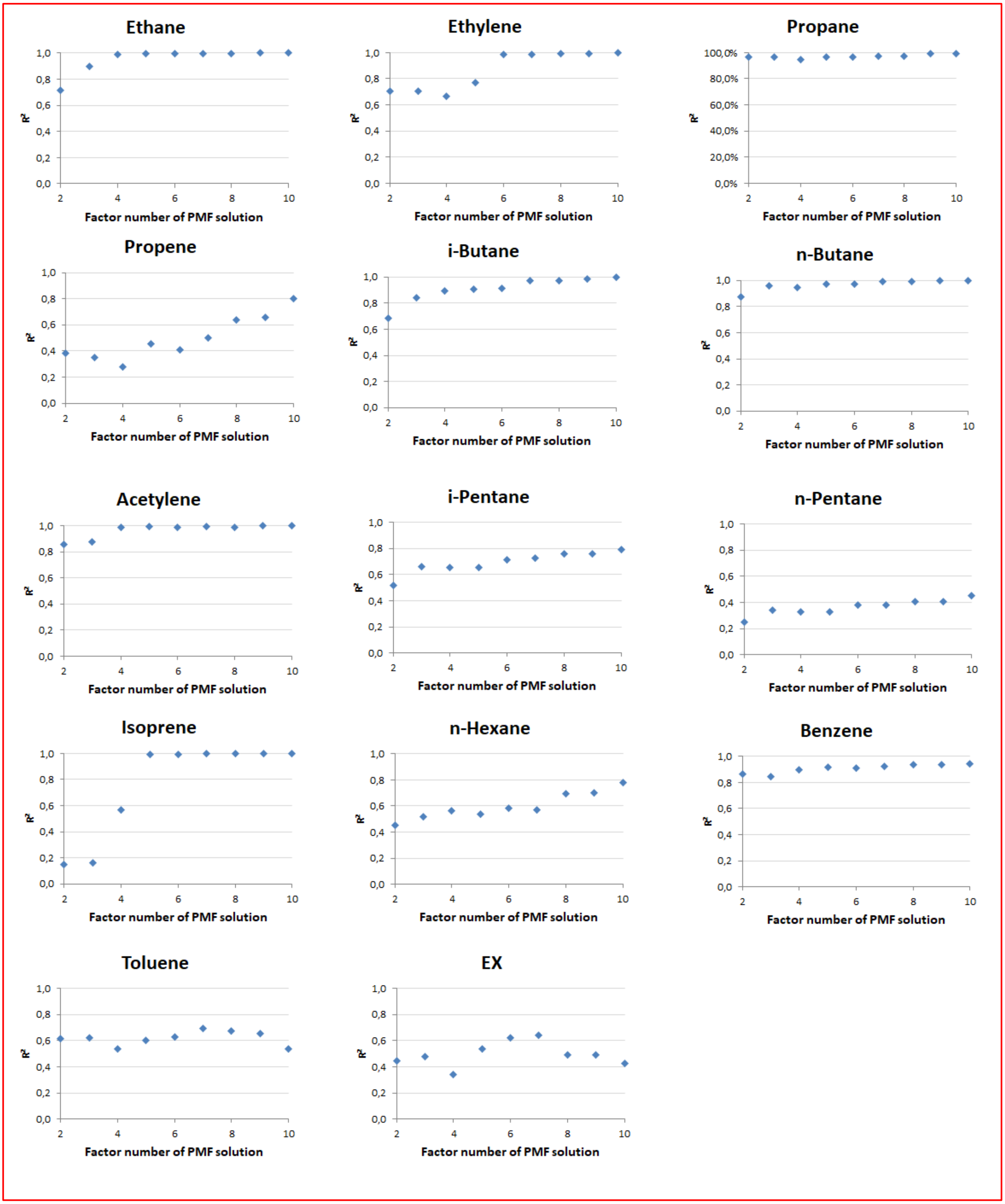
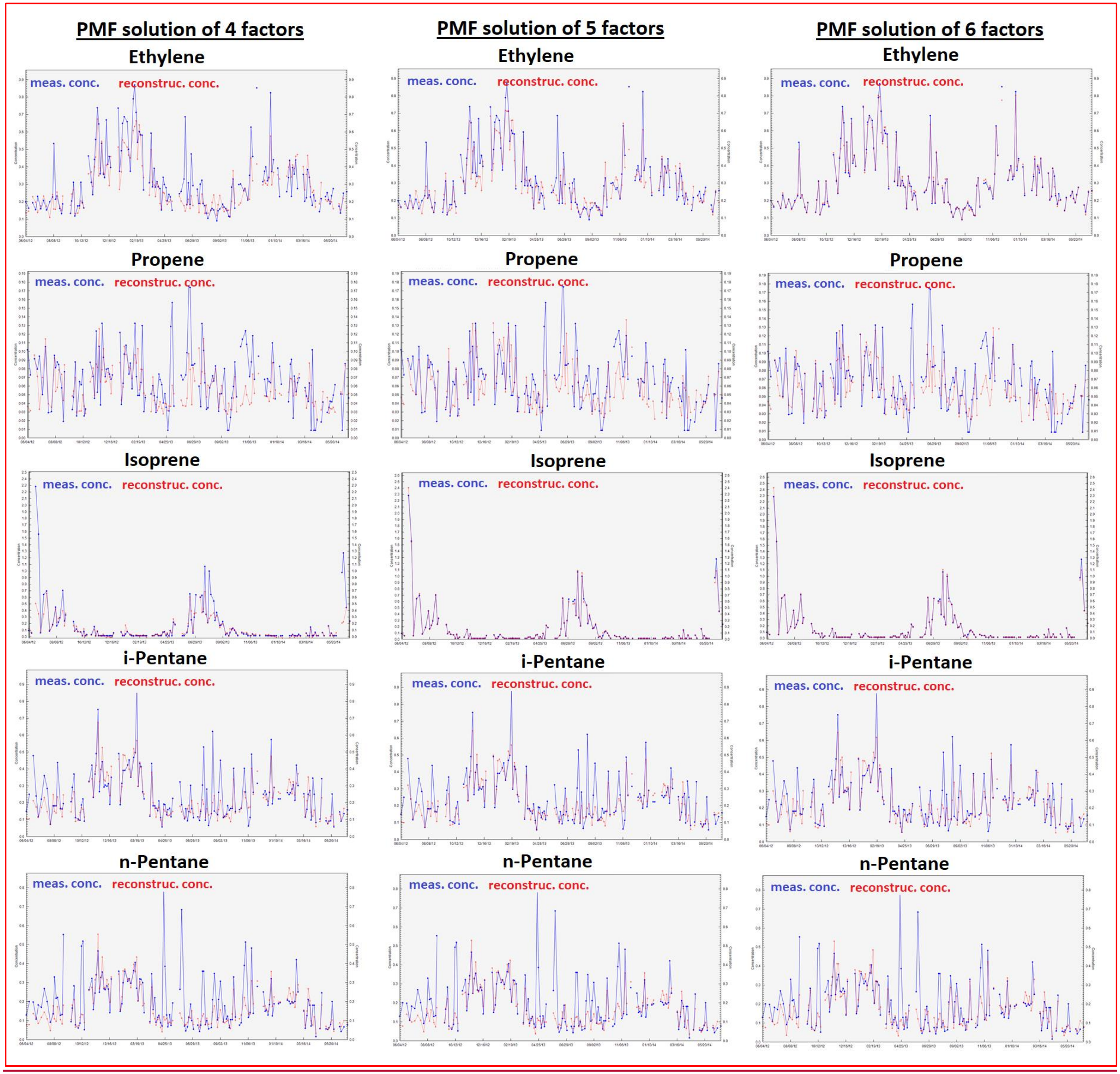


Figure S7: Correlations between reconstructed NMHC concentrations by the PMF model and measured ones as a function of the factor number of PMF solutions.


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
Ethylene
Propene
Isoprene
i-Pentane
n-Pentane
meas. conc.
reconstruc. conc.
Concentration
06/04/12
08/08/12
10/12/12
12/16/12
02/19/13
04/25/13
06/29/13
09/02/13
11/06/13
01/10/14
03/16/14
05/20/14

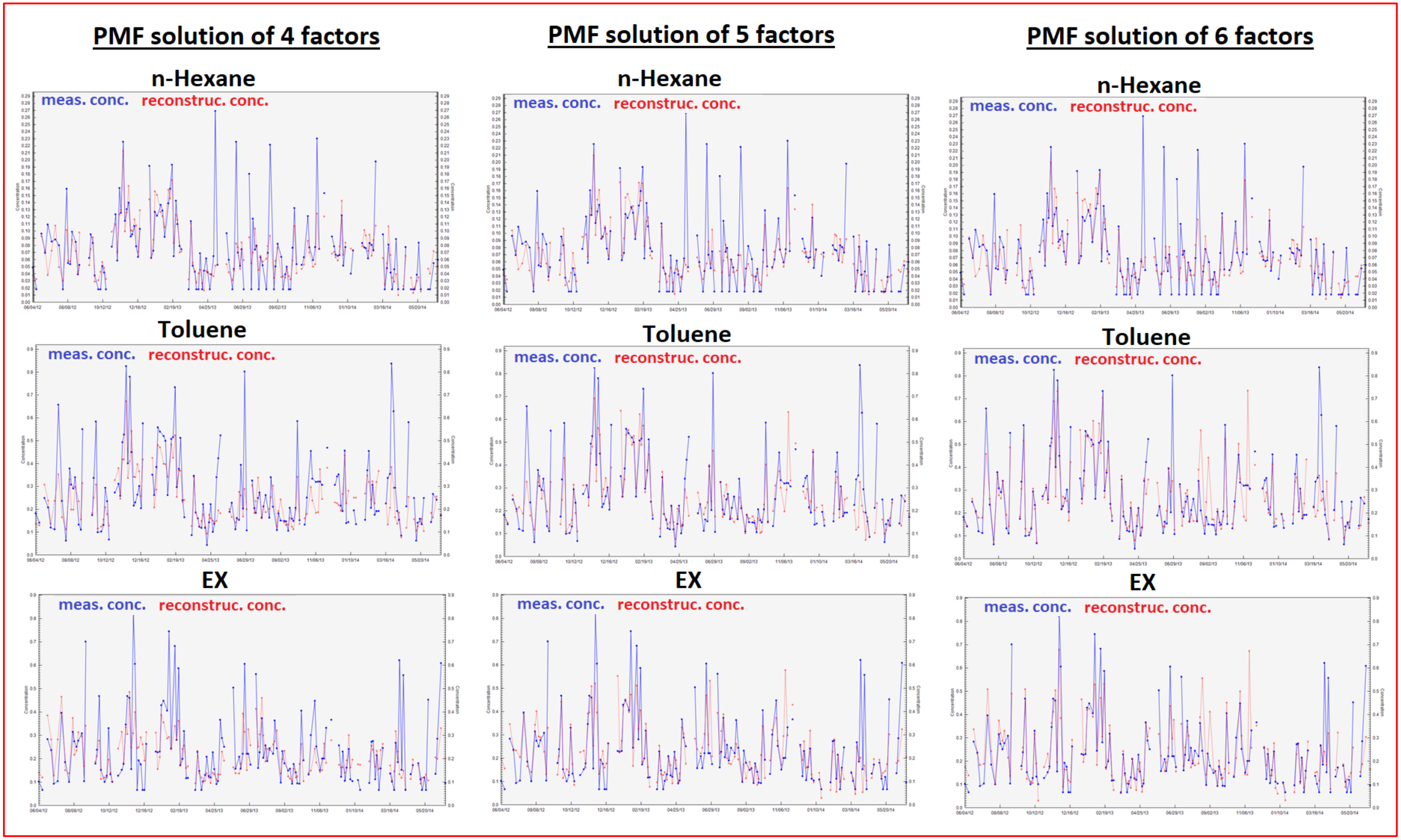
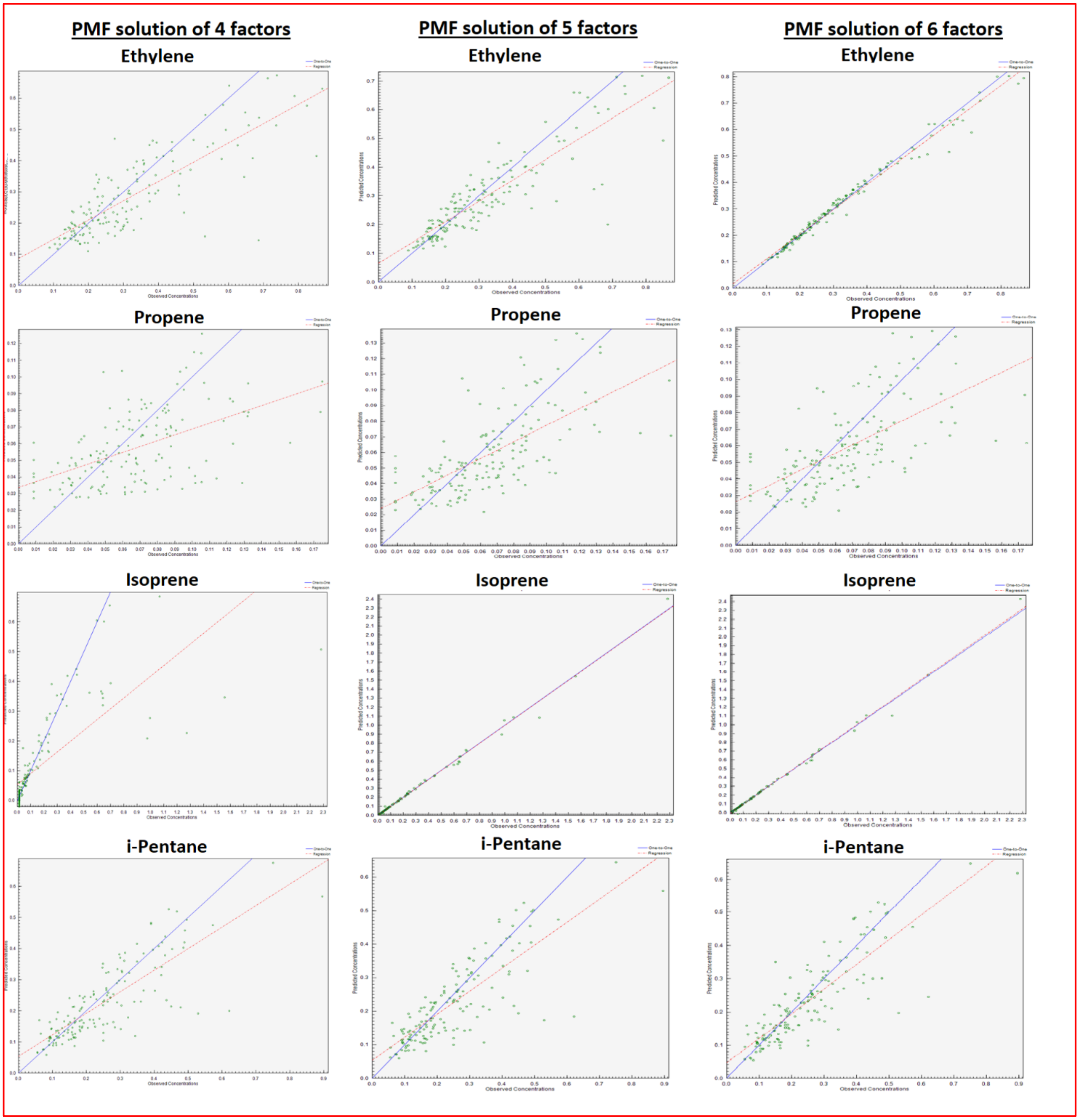


Figure S8: Time series of reconstructed NMHC concentrations for PMF solutions from 4 to 6 factors compared to NMHC measured concentrations. Note that only results of NMHCs not well reconstructed by the PMF model ($r^2 < 0.85$, see Table S4) are presented.


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
Ethylene
Propene
Isoprene
i-Pentane
One-to-One
Regression
Observed Concentrations
Predicted Concentrations

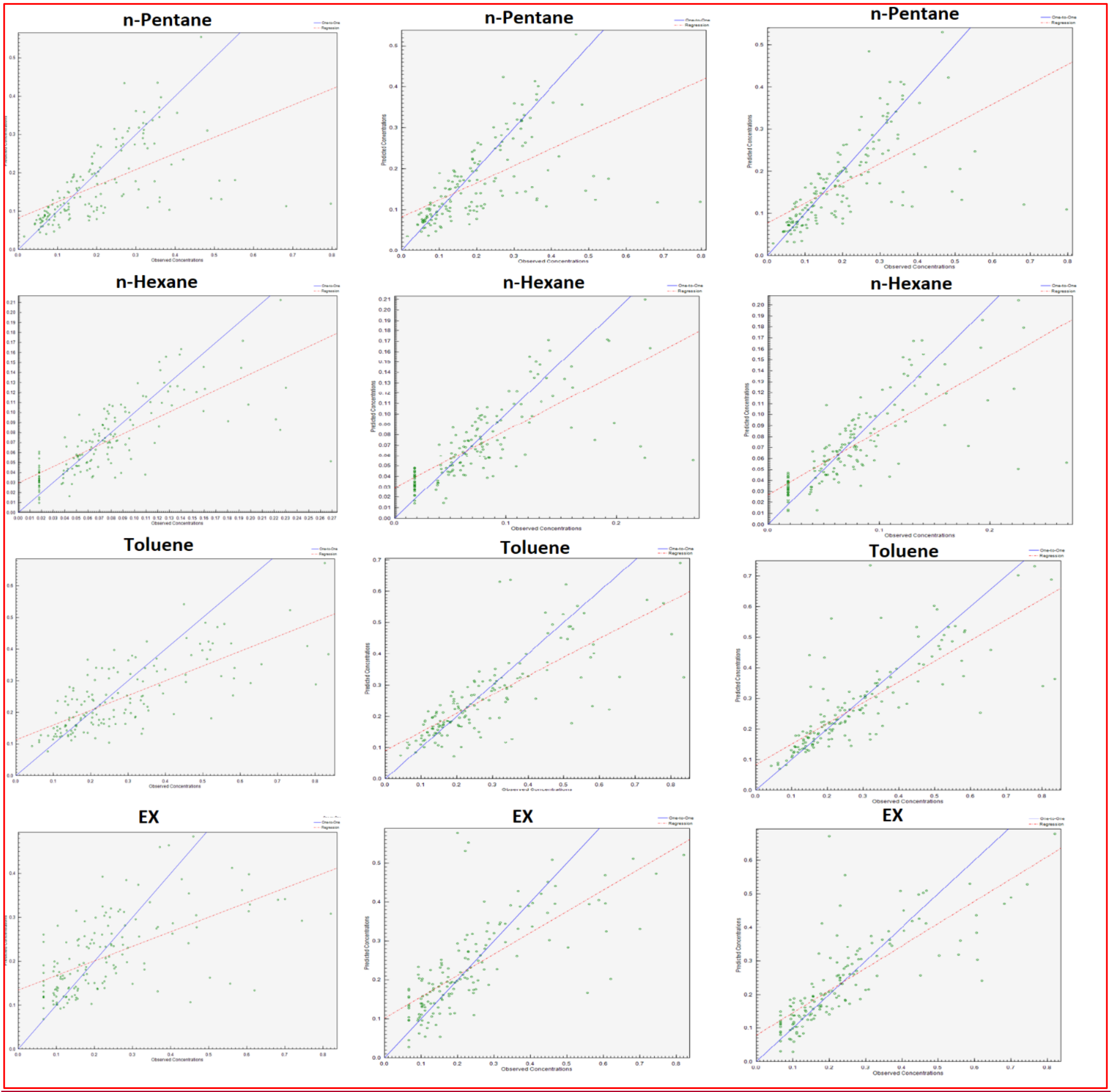
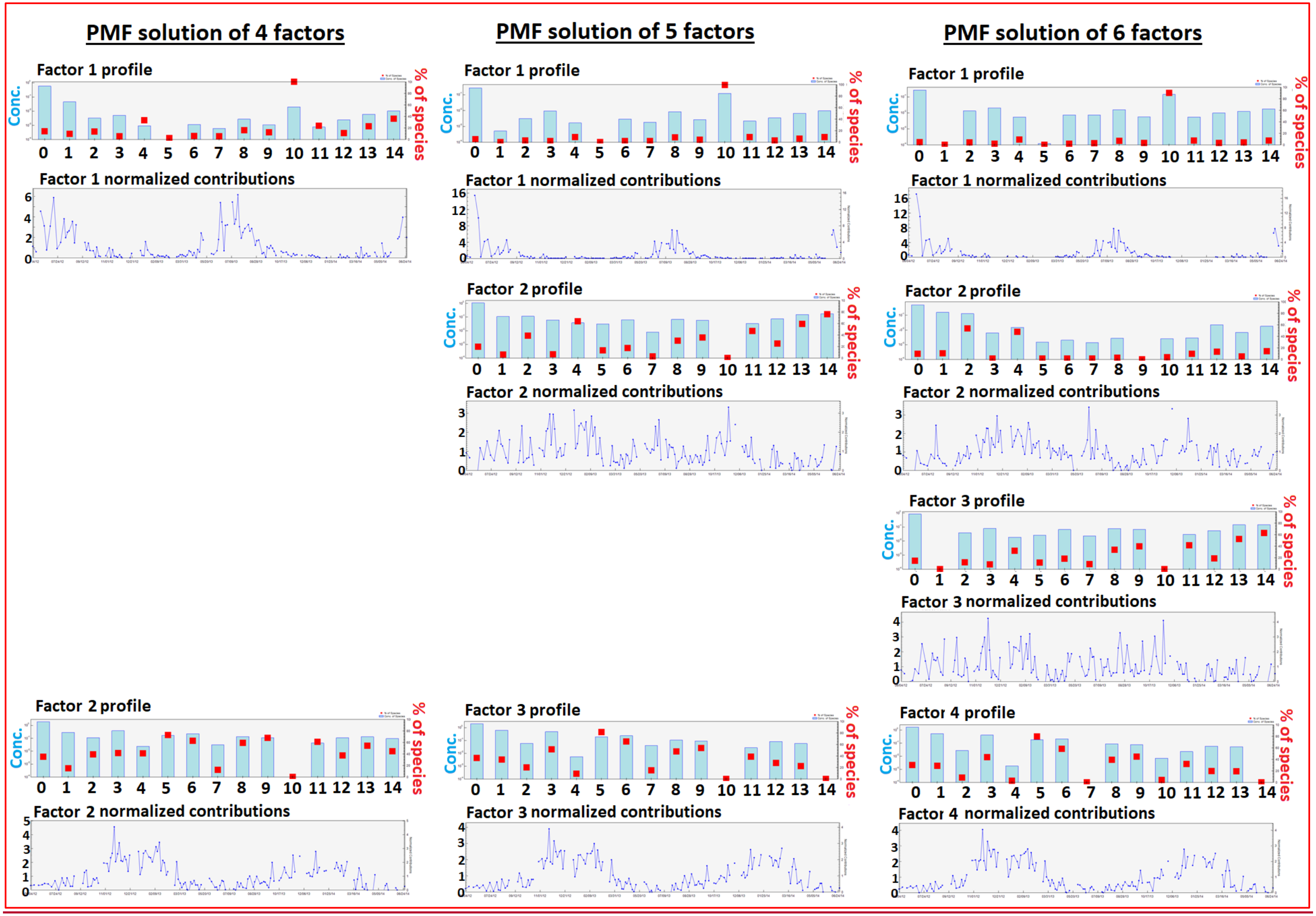


Figure S9: Scatter plots of reconstructed NMHC concentrations for PMF solutions from 4 to 6 factors and NMHC measured concentrations. Note that only results of NMHCs not well reconstructed by the PMF model ($r^2 < 0.85$, see Table S4) are presented.


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
Ethane
Ethylene
Propane
Propene
i-Butane
n-Butane
Acetylene
scaled residuals
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
i-Pentane
-4 -3 -2 -1 0 1 2 3 4 5
scaled residuals
i-Pentane
-4 -3 -2 -1 0 1 2 3 4 5
scaled residuals
i-Pentane
-4 -3 -2 -1 0 1 2 3 4
scaled residuals
n-Pentane
-3 -2 -1 0 1 2 3 4 5
scaled residuals
n-Pentane
-3 -2 -1 0 1 2 3 4 5
scaled residuals
n-Pentane
-3 -2 -1 0 1 2 3 4 5
scaled residuals
Isoprene
-3 -2 -1 0 1 2 3 4 5 6 7
scaled residuals
Isoprene
-3 -2 -1 0 1 2 3
scaled residuals
Isoprene
-3 -2 -1 0 1 2 3
scaled residuals
n-Hexane
-3 -2 -1 0 1 2 3 4 5
scaled residuals
n-Hexane
-3 -2 -1 0 1 2 3 4
scaled residuals
n-Hexane
-3 -2 -1 0 1 2 3 4
scaled residuals
Benzene
-3 -2 -1 0 1 2 3
scaled residuals
Benzene
-3 -2 -1 0 1 2 3
scaled residuals
Benzene
-3 -2 -1 0 1 2 3
scaled residuals
Toluene
-4 -3 -2 -1 0 1 2 3 4
scaled residuals
Toluene
-3 -2 -1 0 1 2 3 4
scaled residuals
Toluene
-3 -2 -1 0 1 2 3 4
scaled residuals
EX
-4 -3 -2 -1 0 1 2 3 4 5
scaled residuals
EX
-3 -2 -1 0 1 2 3 4
scaled residuals
EX
-3 -2 -1 0 1 2 3 4
scaled residuals

Figure S10: Distributions of scaled residuals as a function of NMHC for PMF solutions composed from 4 to 6 factors.


PMF solution of 4 factors
PMF solution of 5 factors
PMF solution of 6 factors
Factor 1 profile
Factor 1 normalized contributions
Factor 2 profile
Factor 2 normalized contributions
Factor 3 profile
Factor 3 normalized contributions
Factor 4 profile
Factor 4 normalized contributions
Conc.
% of species
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
0
2
4
6
8
12
16
0
1
2
3
4
5

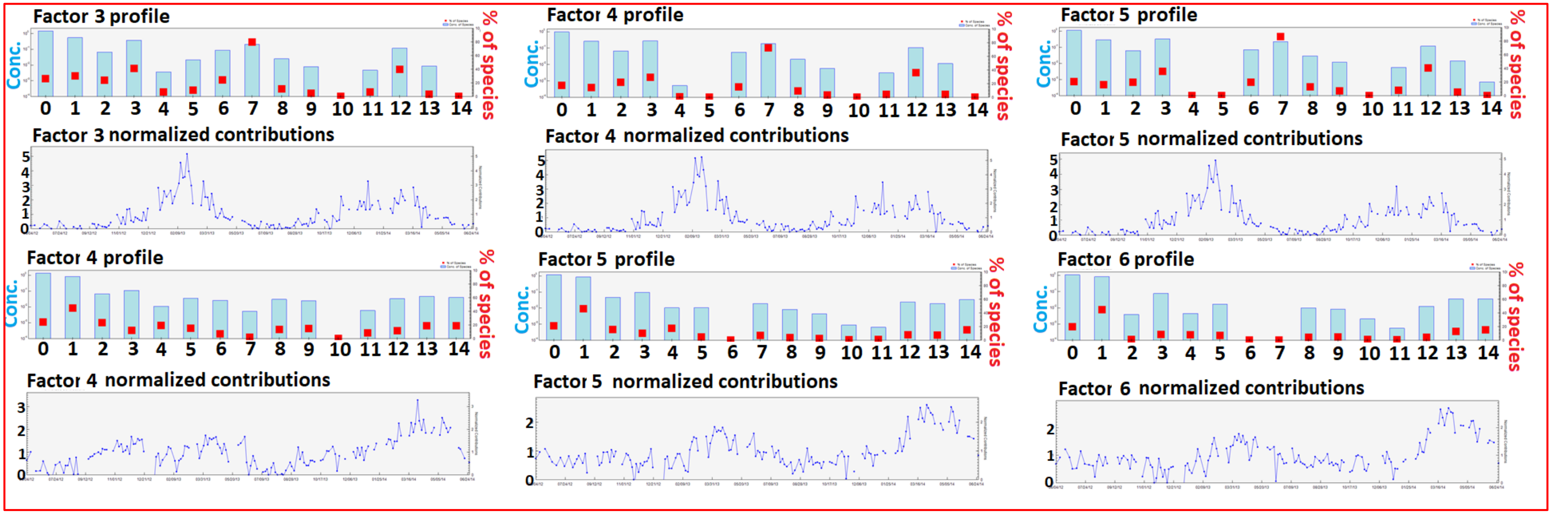


Figure S11: Factor profiles and normalized contribution time series of PMF solutions from 4 to 6 factors. Note that NMHCs 0-14 are listed in Table S4.

S2.4 Optimization of the selected PMF solution

~~In order to optimize the PMF solution, the first step consisted in carrying out numerous successive base runs considering an incremented factor number. Results were analysed so as to identify the optimal number of factors according to the protocol defined by Sauvage et al. (2009). Diverse statistical indicators and the physical meaning of factor profiles have also to be taken into account in the selection of the optimal solution.~~ Generally, the non-negativity constraint alone is considered not enough to obtain a unique solution. To reduce the number of solutions, one possible approach is to rotate a given solution and assess the obtained results with the initial solution. Consequently, ~~the second step~~ the optimization of the selected 5-factor PMF solution relies on the exploration of the rotational freedom of the selected PMF solution ~~selected~~ by acting on the F_{peak} parameter (Paatero et al., 2005; Paatero et al., 2002) following recommendations of Norris et al. (2014) so as to reach an optimized final solution. As a result, ~~a five-factor PMF solution has been chosen in this study considering~~ a F_{peak} parameter fixed at 0.8 was applied to the selected PMF solution which allowed a finer decomposition of the ~~VOC~~ NMHC dataset following an acceptable change of the Q-value (Norris et al., 2014).

Quality indicators provided by the EPA PMF application have been indicated in Table S5. The PMF model results reconstruct on average 99% of the total concentration of the 14 selected compounds of this study. Individually, almost all chemical species also showed both good determination coefficients and slopes (close to 1 – Table S4) between reconstructed and measured concentrations, apart from propene, n-pentane, n-hexane and EX (see Fig. S9). The PMF model reconstructs well the variations of these species over long periods (Fig. S8) but not over short-periods, explaining their lower determination coefficients and slopes farther from 1 (Table S4). Therefore, PMF model limitations to explain these species should be kept in mind when examining PMF results.

Table S5: Input information and mathematical diagnostic for the results of PMF analysis.

Input information		
Samples	N	152
Species	M	14
Factors	P	5
Runs		100
Nb. Species indicated as weak		0
F_{peak}		0.8
Model quality		
Q robust	Q(r)	2589.7
Q true	Q(t)	2119.9
Maximum individual standard deviation	IM	0.27
Maximum individual column mean	IS	1.52

Mean ratio (modelled vs. measured)	Slope(TVOC)	1.01
$TVOC_{modelled}$ vs. $TVOC_{measured}$	R^2(TVOC)	0.99
Nb. of species with $R^2 > 0.6$		10
Nb. of species with $1.1 > slope > 0.6$		9

The evaluation of rotational ambiguity and random errors in a given PMF solution can be realized with DISP (displacement) and BS (bootstrap) error estimation methods (Brown et al., 2015; Norris et al., 2014; Paatero et al., 2014). As no factor swap occurred in the DISP analysis results, the 5-factor PMF solution is considered adequately robust to be interpreted. Then, bootstrapping was realized by performing 100 runs, and considering a random seed, a block size of 18 samples and a minimum Pearson correlation coefficient of 0.6. Each modeled factor of the selected PMF solution was well mapped over at least 95% of realized runs, assuring their reproducibility.

Moreover, since sampling time of NMHC measurements from canister shifted several times during the two studied years (Table 1), correlations between reconstructed and observed NMHC concentrations as a function of sampling periods were investigated (Table S6). Slightly different correlation results were observed for observations resulting from samples collected from 12:00-16:00 UTC (from early June 2012 to late October 2012 and from early January 2013 to late October 2013) compared to those from 09:00-13:00 UTC (from early November 2012 to late December 2012 and from early November 2013 to late June 2014). The PMF model slightly overestimated TVOC concentrations resulting from samples collected from 09:00-13:00 and slightly underestimated those collected from 12:00-16:00, mostly due to reconstruction of ethane and propane concentrations in both cases. Concerning more reactive NMHCs, ethylene, i-butane, isoprene, toluene and EX concentrations are better reconstructed for samples collected from 12:00-16:00 while propene, i-pentane, n-pentane and n-hexane concentrations are better reconstructed for those from 09:00-13:00. The most impacted species by the sampling time shift was n-pentane, since the PMF model did not identify the sources influencing the high concentrations of n-pentane observed over short periods (see Fig S9) and this was mostly noticeable with the 12:00-16:00 sample set. More generally, the influence of the sampling time shift on PMF results also depends on the frequency and the amplitude of NMHC concentration variations over short periods for the two sample sets.

Table S6: Evaluation of reconstructed NMHC concentrations by the PMF model as a function of the sampling time shift.

	All period			Samples collected from 09:00-13:00 UTC			Samples collected from 12:00-16:00 UTC		
	slope	intercept	r^2	slope	intercept	r^2	slope	intercept	r^2
Ethane	0.997	0.006	0.999	0.986	0.029	0.996	1.002	0.001	0.999
Ethylene	0.727	0.064	0.779	0.593	0.111	0.673	0.796	0.044	0.827
Propane	1.000	-0.011	0.968	0.929	0.052	0.949	1.046	-0.035	0.977
Propene	0.534	0.024	0.438	0.632	0.018	0.489	0.497	0.026	0.418
i-Butane	0.832	0.029	0.897	0.761	0.056	0.869	0.893	0.015	0.904
n-Butane	0.967	0.004	0.963	0.954	0.010	0.957	0.975	0.002	0.961
Acetylene	0.952	0.008	0.975	0.991	0.003	0.991	0.941	0.007	0.972
i-Pentane	0.686	0.053	0.644	0.783	0.054	0.765	0.623	0.052	0.600
n-Pentane	0.421	0.081	0.332	0.852	0.032	0.788	0.295	0.085	0.238
Isoprene	0.956	0.005	0.996	0.872	0.005	0.996	0.971	0.006	0.998
n-Hexane	0.510	0.032	0.519	0.668	0.026	0.738	0.419	0.035	0.410
Benzene	0.889	0.022	0.895	0.918	0.027	0.849	0.873	0.018	0.911
Toluene	0.582	0.092	0.599	0.526	0.105	0.501	0.626	0.083	0.669
EX	0.527	0.103	0.515	0.452	0.112	0.431	0.582	0.095	0.578
TVOC	1.004	-0.186	0.992	0.988	-0.083	0.987	1.009	-0.213	0.993

Section S~~2~~3: Identification of potential emission areas by CF approach

In order to investigate potential emission regions contributing to long-distance pollution transport to the receptor site, source type contributions from the PMF were coupled with back-trajectories under a statistical approach. To achieve this, the concentration field (CF) statistical method established by Seibert et al (1994) was chosen in the present study.

The CF approach relies on the attribution of concentrations of a variable measured at a receptor site along respective back-trajectories arriving at this site. In a second step, the trajectory map is gridded in order for the attributed concentrations in a given cell to be weighted by the residence time that air parcels spent in the considered cell (Eq. (3); Michoud et al., 2017):

$$\log\left(\overline{C_{ij}}\right) = \frac{\sum_{L=1}^{M}\log(C_L)\times n_{ij-L}}{\sum_{L=1}^{M} n_{ij-L}} = \frac{1}{n_{ij}}\sum_{L=1}^{M}\log(C_L)\times n_{ij-L}, \qquad (3)$$

with $\overline{C_{ij}}$ the attributed concentration of the ij^th^ grid cell, C_L the concentration observed when the back-trajectory L reached the measurement site, n_{ij-L} the number of points of the back-trajectory L contained in the ij^th^ grid cell, n_{ij} the number of points of the total number of back-trajectories contained in the ij^th^ grid cell, and M the total number of trajectories.

Section S4~~3~~: Comparisons of VOC measurements with other ones performed at Ersa

Additional VOC measurements were realized during summer campaigns performed in 2012, 2013 and 2014. One hundred of 3-h-integrated air samples were collected at Ersa on DNPH cartridges from 29 June to 11 July 2012 at a frequency of 8 samples per day. These air samples were collected and analyzed following the same protocol as the one presented in Sect. 2.2.1. Additionally, the ChArMEx SOP-1b (special observation period 1b) field campaign took place from 15 July to 5 August 2013 at Ersa. During this intensive field campaign, more than 80 VOCs were measured by different on-line and off-line techniques which were deeply presented in Michoud et al. (2017) and summarized in Table ~~S3~~S~~-1~~7. Furthermore, formaldehyde measurements realized during the SOP-1b field campaign with DNPH cartridges are used in this study. Finally, around 70 3-h-integrated air samples were collected at Ersa from 26 June to 10 July 2014 on DNPH cartridges (54 samples realized at a frequency of 4 cartridges per day from 6h-18h UTC) and on stainless steel canisters (20 samples realized at a frequency of 3 canisters per day from 9h-18h UTC). These air samples were collected and analyzed following the same protocol as the one presented in Sect. 2.2.1. Benefiting from all these measurements, they were confronted with the two years of VOC measurements investigated in this study, in order to examine the representativeness of the study period in terms of summer concentration levels and variations. Time series of concentrations of selected VOCs, biogenic and anthropogenic compounds and OVOCs, are depicted in Figs ~~S3~~S12-S14~~-1, S3-2 and S3-3~~, respectively.

Table S~~3-1~~7: Technical details of the set-up for VOC measurement during the intensive field campaigns realized at Ersa in summers 2012, 2013 and 2014.

Field campaign	Instrument	Time resolution	Species observations used in this study	References
Summer 2012	**Off-line DNPH**	180 min	formaldehyde, acetaldehyde, acetone and MEK	Detournay, 2011; Detournay et al., 2013
Summer 2013 (SOP-1b)	**On-line PTR-TOF-MS**	10 min	isoprene, acetaldehyde, acetone and MEK	Michoud et al., 2017
	On-line GC-FID-FID	90 min	ethane, propane, n-butane, n-pentane, ethylene, acetylene, benzene	Michoud et al., 2017
	On-line GC-FID-MS	90 min	α-pinene, β-pinene and limonene	Michoud et al., 2017
	Off-line DNPH	180 min	formaldehyde	Detournay, 2011; Detournay et al., 2013
Summer 2014	**Off-line DNPH**	180 min	formaldehyde, acetaldehyde, acetone and MEK	Detournay, 2011; Detournay et al., 2013
	Off-line steel canisters	180 min	ethane, propane, n-butane, n-pentane, ethylene, acetylene, benzene, isoprene	Sauvage et al., 2009

During the intensive field campaign of summer 2013, biogenic compounds were measured on-line by different techniques (PTR-TOF-MS or GC-FID-MS - Table ~~S3~~S~~-1~~7). Significant concentration levels of biogenic VOCs were measured during this summer field campaign (e.g. isoprene concentrations up to 3.5 µg ~~.~~m^{-3} – Fig. ~~S1~~S12~~-1~~). α-Pinene concentrations during the SOP-1b campaign were of the same range than summer concentrations measured off-line during the observation field campaign while isoprene concentrations were observed at higher concentrations during the SOP-1b, which can be partly related to the better time resolution and the temporal coverage of measurements. Note that isoprene daily maximal concentrations measured during the summer 2013 campaign were variable in relation to temperature variations (Kalogridis, 2014; Michoud et al., 2017). Additionally, isoprene concentrations measured during the summer 2014 field campaign were low but were in consistency with isoprene concentrations observed in June 2014.

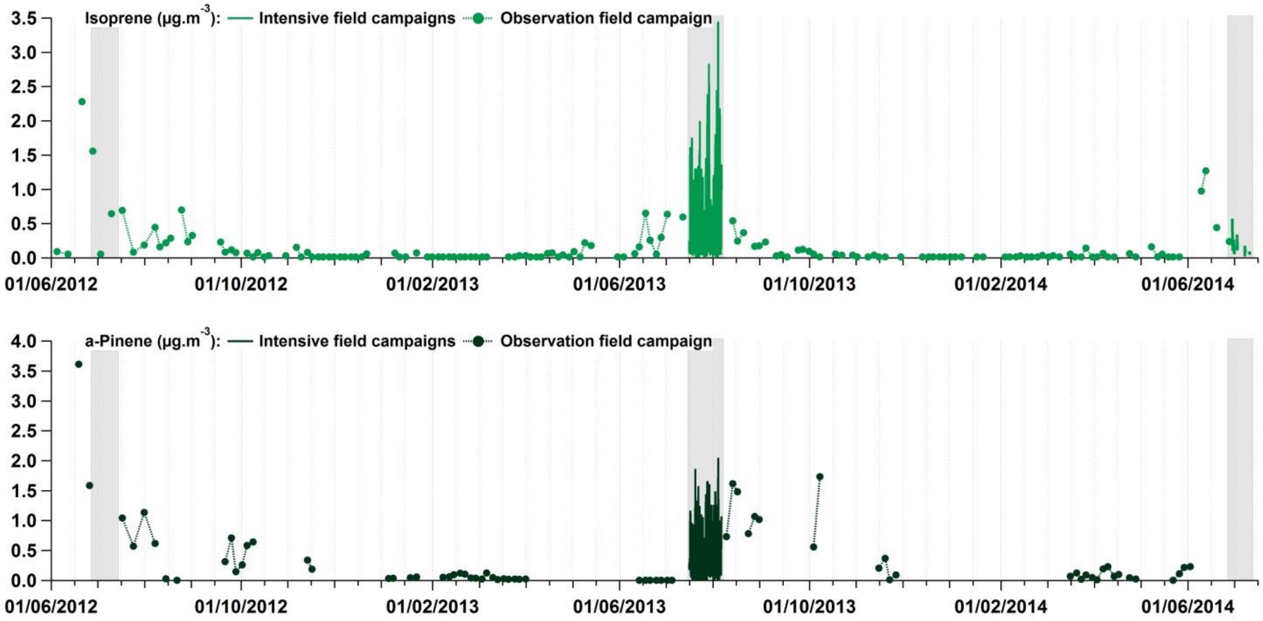
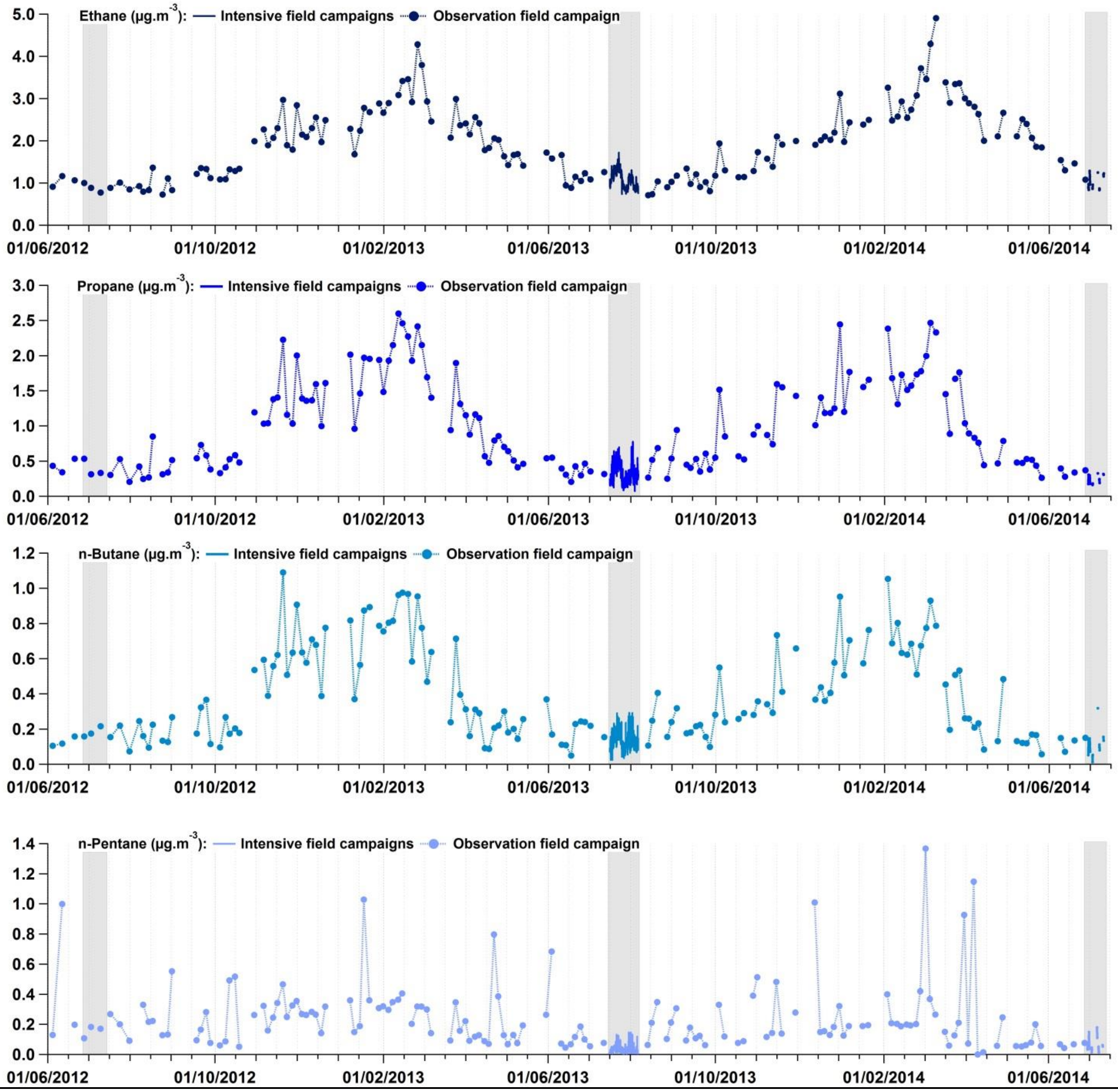


Figure ~~S3~~S12~~-1~~: Time series of concentrations of a selection of biogenic VOCs (expressed in µg m^{-3}) measured during the different field campaigns conducted at Ersa. Grey rectangles pinpoint periods when intensive field campaigns were realized. Time is given in UTC.

Anthropogenic VOC concentrations were measured with an on-line GC-FID-FID during the SOP-1b campaign and with stainless steel canister during the summer 2014 field campaign (Table ~~S3~~S~~-1~~7). Low anthropogenic VOC concentration levels were noticed during the summer 2013 and 2014 field campaigns (Fig. ~~S3~~S13~~-2~~) and, whatever their lifetime in the atmosphere, these concentrations were in consistency with seasonal variations described in Sect. 3.4.2. These findings can suggest that the annual temporal coverage of VOC measurements realized over the two years was sufficiently adapted to well characterize VOC concentration variations (at seasonal scale).


Ethane (µg.m-3): Intensive field campaigns Observation field campaign
5.0
4.0
3.0
2.0
1.0
0.0
Propane (µg.m-3): Intensive field campaigns Observation field campaign
3.0
2.5
2.0
1.5
1.0
0.5
0.0
n-Butane (µg.m-3): Intensive field campaigns Observation field campaign
1.2
1.0
0.8
0.6
0.4
0.2
0.0
n-Pentane (µg.m-3): Intensive field campaigns Observation field campaign
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
01/06/2012
01/10/2012
01/02/2013
01/06/2013
01/10/2013
01/02/2014
01/06/2014

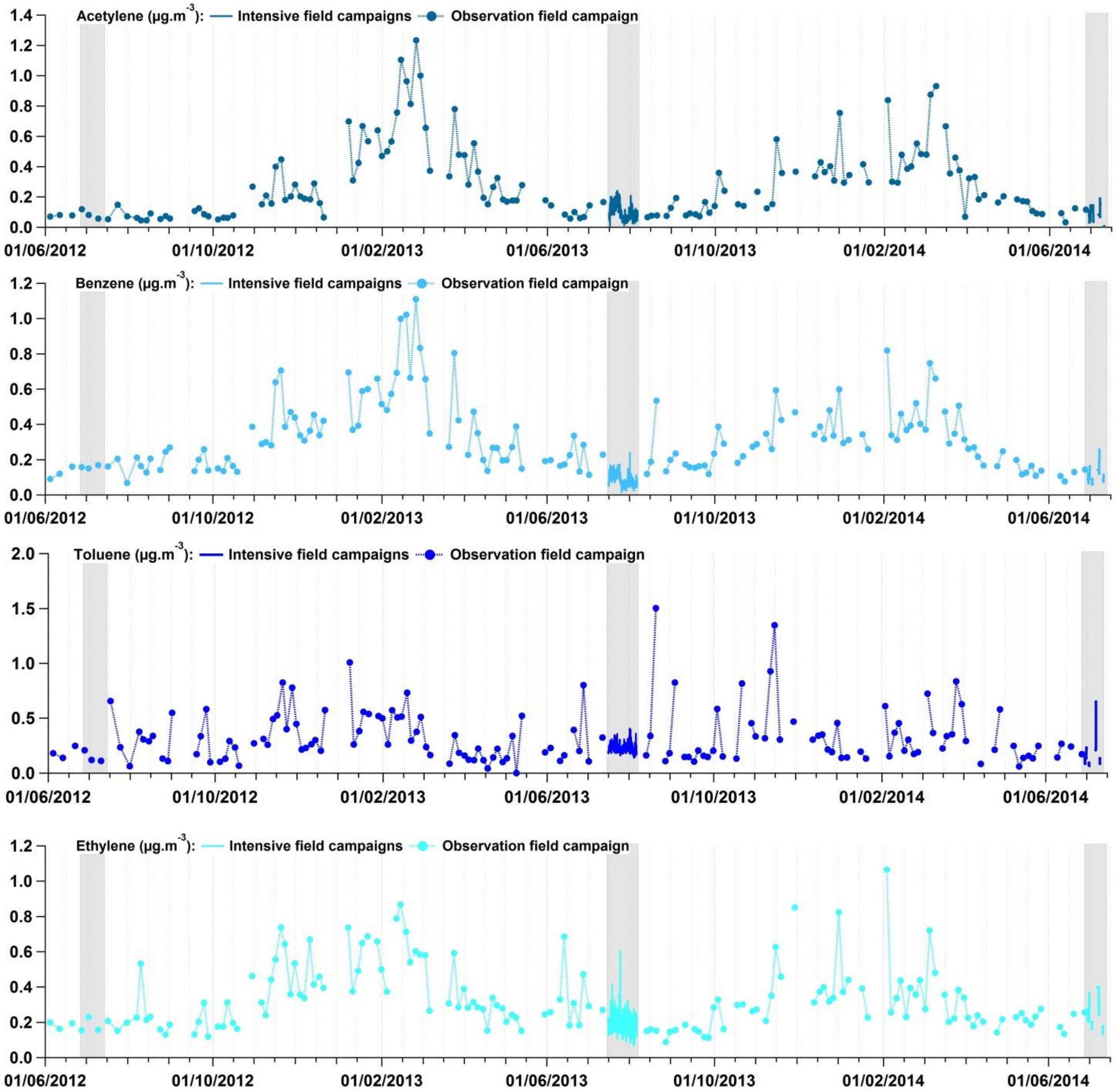


Figure ~~S3~~S13~~-2~~: Time series of concentrations of a selection of anthropogenic VOCs (expressed in µg m^{-3}) measured during the different field campaigns conducted at Ersa. Grey rectangles pinpoint periods when intensive field campaigns were realized. Time is given in UTC.

During the summer 2012 and 2014 field campaigns, OVOCs were measured off-line using DNPH cartridges. During the summer 2013 campaign, they were also measured with proton transfer reaction time-of-flight mass spectrometer (PTR-

TOF-MS - Table S~~3 1~~7). OVOC concentration levels during the three summer field campaigns (Fig. S14~~3 3~~) were in consistency with seasonal variations described in Sect. 3.4.3.

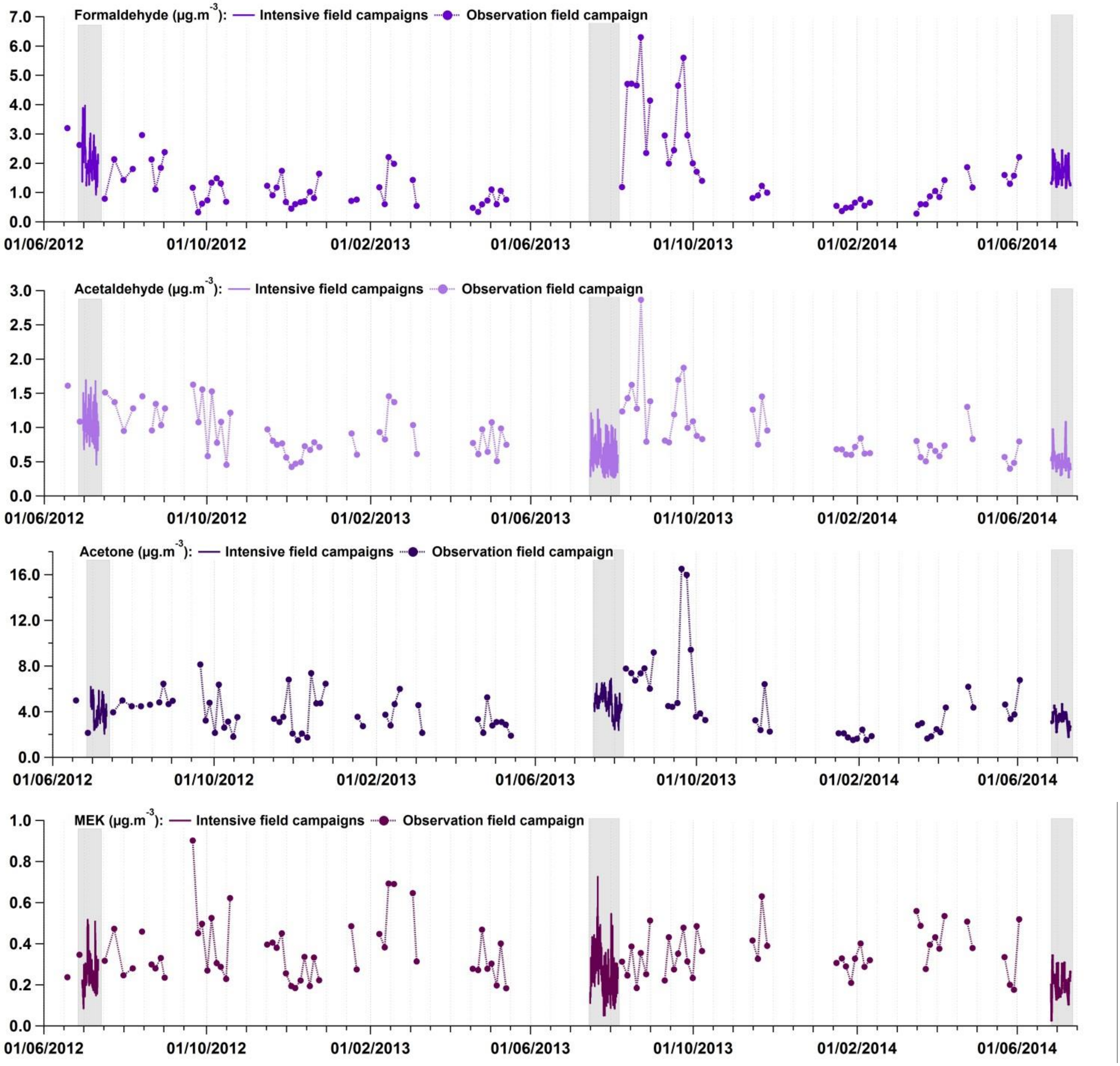


Figure ~~S3~~S14 ~~3~~: Time series of concentrations of a selection of oxygenated VOCs (expressed in µg m^{-3}) measured during the different field campaigns conducted at Ersa. Grey rectangles pinpoint periods when intensive field campaigns were realized. Time is given in UTC.

Section ~~S4~~S5: Comparisons of VOC source apportionment with previous one performed at Ersa

~~The 5-factor PMF solution, modelled with the two year observation field campaign VOC dataset (from June 2012 to June 2014) was compared with the PMF solution modelled with the SOP-1b VOC dataset (from 15 July to 5 August 2013 - Michoud et al., 2017), composed of 6 factors, namely primary biogenic factor, secondary biogenic factor, short-lived anthropogenic factor, medium-lived anthropogenic factor, long-lived anthropogenic factor and oxygenated factor. Note that the SOP-1b PMF source apportionment was performed on a dataset of 42 VOCs, including oxygenated compounds and collected with three different on-line techniques (see Sect. S3 and Michoud et al., 2017).~~ Figure ~~S4~~S15~~-1~~ compares the average relative contribution of each factor to VOC concentrations monitored during the ~~two field campaigns~~two-year and summer 2013 campaigns.

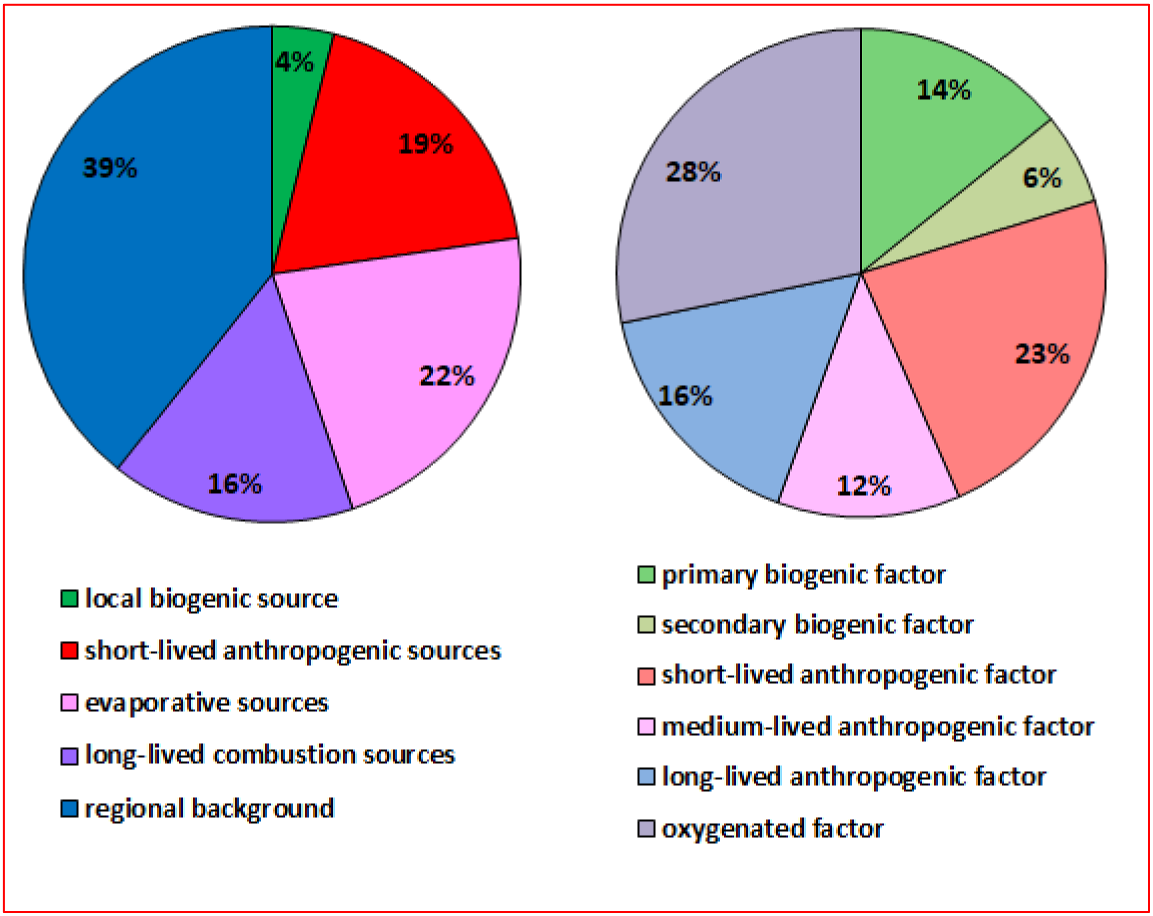


Figure ~~S4~~S15~~-1~~: Relative factor contributions (expressed in %) to the ~~two year~~2-yr VOC concentrations (on the left) compared to relative factor contributions to the SOP-1b VOC concentrations (on the right).

Firstly, the local biogenic source (factor 1 – this study) was mainly composed of isoprene like the SOP-1b primary biogenic factor. The latter also explained a large portion of monoterpene concentrations along with from 11 to 15% of some

OVOC concentrations (carboxylic acids, methanol and acetone). Even if monoterpenes were not integrated to the PMF analysis realized with the two years of VOC observations, considering the number of samples realized, α-pinene ~~VOC~~ concentration variations discussed in Sect. 3.4.1 highlighted that α-pinene showed significant concentrations in fall while isoprene concentrations were low, suggesting that an additional source could influence α-pinene concentrations observed at Ersa. Moreover, the SOP-1b primary biogenic factor contributed of 14% to the VOC total mass measured in summer 2013, partly considering the contribution of OVOCs to this factor (~60% of the factor contribution). On the other hand, the local biogenic source contribution was only of 4% to the total ~~VOC~~ mass of the selected NMHCs measured during the two study years ~~studied~~ but its contribution was higher in summer (12 and 15% during summers 2012 and 2013, respectively).

The observation field campaign PMF solution identified three anthropogenic factors (factors 2-4) and the regional background (factor 5) as among the main contributors to ~~VOC~~ NMHC concentrations impacting Ersa during two years, despite the reduced number of atmospheric data observations and the fact that primary anthropogenic ~~VOCs~~ NMHCs were characterized by almost the same seasonal variation (Sect. 3.4.2). These factors have proved to be globally in consistency with primary anthropogenic VOC factors identified by Michoud et al. (2017), despite the different number of VOCs considered in the two PMF analyses. Indeed, the summer 2013 analysis was realized considering additional primary NMHCs (2-methyl-2-butene+1-pentene, 2,2-dimethylbutane, undecane+camphor, C9-aromatics which represented 2% of the total NMHC mass of the NMHCs considered in the summer 2013 PMF analysis) and non-speciated monoterpenes (19%) owing to the deployment of automatic analysers during the summer 2013 field campaign (Sect. S4).

Short-lived anthropogenic sources (factor 2 – this study) explained a large portion of ethylene, propene, toluene and C_8 aromatic compound~~s~~ concentrations observed at Ersa during two years similarly as the SOP-1b short-lived anthropogenic factor during summer 2013. The two factors contributed similarly to the VOC total mass (19 and 23% for observation field campaign short-lived anthropogenic sources and SOP-1b short-lived anthropogenic factor, respectively) observed at ~~the receptor site~~the Ersa station. Note that some OVOCs contributed significantly to SOP-1b short-lived anthropogenic factor, such as carboxylic acids~~formic acid, acetic acid, propionic acid~~ and acetone (~ 61% of the factor contribution), enhancing its relative contribution to the VOC total mass. Furthermore, short-lived anthropogenic sources from the two-year NMHC~~VOC~~ dataset revealed different origins according to seasons.

Evaporative sources (factor 3 – this study) and the SOP-1b medium-lived anthropogenic factor have chemical profiles marked by C_4-C_6 alkanes. Nevertheless, evaporative sources explained a higher portion of i-butane and n-butane concentrations observed at Ersa during the two years ~~studied~~ compared to the SOP-1b medium-lived anthropogenic factor contributions to these concentrations during summer 2013. SOP-1b medium-lived anthropogenic factor contributed of 12% to VOC concentrations during summer 2013 while evaporative source contribution was of 22% to ~~VOC~~NMHC concentrations during the two years studied, partly considering their higher contribution especially in winter. Evaporative sources and SOP-1b medium-lived anthropogenic factor were of the same origins as they showed higher contributions when Ersa received French and European air masses.

SOP-1b long-lived anthropogenic factor was mainly composed of ethane, acetylene, propane and benzene and was consistent with chemical profiles characterizing long-lived combustion sources (factor 4 – this study) and regional background (factor 5 – this study). Regional background and long-lived combustion sources explained the integrality of ethane and acetylene concentrations, respectively while SOP-1b long-lived anthropogenic factor explained 58% of ethane concentrations and 44% of acetylene concentrations (Michoud et al., 2017). These findings can suggest that the PMF model, applied to the ~~two years of~~2-yr ~~VOC~~NMHC dataset, mostly pinpointed distant origins impacting ethane and acetylene concentrations measured at Ersa, which may be related to the temporal coverage and the time resolution of VOC measurements realized during two years. Moreover, the ~~two year~~2-yr PMF solution allowed to deconvoluate long-lived combustion sources, partly attributed to residential heating and with regional origins, from the regional background and showed a higher contribution of regional background (39% to ~~VOC~~ total mass of selected NMHCs) than the long-lived combustion sources (16%). The high temperature in summer probably induced a limited use of heating systems that could explain why the PMF model performed with the SOP-1b VOC dataset~~base~~ did not identify separately these two distant sources and the relatively low contribution of SOP-1b long-lived anthropogenic factor to the total VOC mass (16%). Note that, regional background contributions were of the same range in winters 2013 and 2014 (Figs. ~~9~~ 10 and ~~10~~S4) while long-lived combustion sources showed higher contributions in winter 2013 compared to winter 2014 ones, which may have participated to the deconvolution of these sources by the PMF model. The SOP-1b long-lived anthropogenic factor, 2-yr long-lived combustion sources and 2-yr regional background were of the same origins as they showed higher contributions especially when Ersa received European air masses.

Nevertheless, the time resolution of VOC measurement of the 2-yr period (4 hours compared to 1 hour and a half during the SOP-1b period) and the limited number of sampling days during this study period did not help to support the clear deconvolution of the 5 factors, as factors related to anthropogenic sources were quite correlated between them (as a consequence of their seasonal variations – see Sect. 3.5) while SOP-1b anthropogenic sources were not (Pearson correlation factors from -0.5 to 0.1).

Finally, the incorporation of OVOCs in the SOP-1b source apportionment analysis allowed to identify and characterize two secondary sources, namely secondary biogenic factor and oxygenated factor. SOP-1b secondary biogenic factor only contributed ~~of~~ 6% to VOC mass measured in summer 2013 and was mainly composed of methyl vinyl ketone (MVK), methacrolein (MACR), pinonaldehyde and nopinone. These compounds are specific oxidation products of primary biogenic VOCs (isoprene, α-pinene and β-pinene) which were emitted in the vicinity of the Ersa site (Michoud et al., 2017). Oxygenated factor was mainly composed of carboxylic acids (explained 54, 43 and 28% of formic acid, acetic acid and propionic acid concentrations, respectively), alcohols (e.g. 49% of methanol concentrations) and carbonyl compounds (e. g. 57, 18 and 21% of acetone, acetaldehyde and MEK concentrations, respectively). Most of these species can result from the photochemical oxidation of both anthropogenic and biogenic VOCs. Oxygenated factor was found to be the largest contributor to VOC concentrations observed at Ersa in summer 2013 (28% of the total VOC mass). Therefore, the measured OVOCs at Ersa were approximately half oxidation products of VOCs and half primary VOCs (Michoud et al., 2017).

Section S6: Examination of a summer 2013 PMF solution realized considering the 17 NMHCs selected in this study

To check the relevance of the 17 NMHCs selected as inputs in the PMF analysis presented in this study, we benefited from the PMF analysis previously conducted with the larger summer 2013 VOC dataset. The PMF solution selected by Michoud et al. (2017) was realized considering a larger number of VOCs (42). In this section, we selected a summer 2013 PMF solution composed of 4 factors, as 4 primary sources were identified in Michoud et al. (2017), and considering a VOC dataset of 13 variables (those selected for the 2-yr PMF solution, at the exception of propene which was not measured in summer 2013 with at a 90-min time resolution – Sect. S4). The two PMF solution comparison results are presented in Figs. S16 and S17. The same species dominantly composed the paired factors of the two PMF solutions (Fig. S16) suggesting that the 13 variables selected in this study comprised dominant tracers of the primary sources influencing VOC concentrations observed at Ersa in summer 2013. The primary biogenic source of the PMF solution with the VOC subset (factor 4 – Fig. S16) is composed of a lower proportion of anthropogenic NMHCs and a higher isoprene one. Species composing anthropogenic sources in low proportion tend to have been reduced with the 4-factor PMF solution (factors 1-3 – Fig. S16), suggesting a better deconvolution of the sources, at the exception of ethane proportion in the chemical profile of short-lived anthropogenic sources (factor 3) which increased. Concerning factor contribution variations (Fig. S17), medium-lived anthropogenic sources and the biogenic source showed the same variability in the two PMF solutions (determination coefficients: 0.85-0.89). Similar results were noticed for long-lived anthropogenic sources (determination coefficient: 0.72), at the exception of the last days of the special observation period. However, short-lived anthropogenic sources have shown different day-to-day variations as a function of the PMF solution, even if factor contribution variations globally followed the same pattern (Fig. S17). This factor contribution variability seems to be not only influenced by the variations in concentrations of reactive selected NMHCs composing it (Fig. S16) but can be by other species such as ethane (for the one of the 4-factor PMF solution), C_9 aromatics, 2-methylfuran and OVOCs (carboxylic acids, acetone, isopropanol and n-hexanal; Michoud et al., 2017). Note that formic and acetic acids, and acetone concentrations corresponded to 42% of the total measured concentrations of the VOCs selected for the factorial analysis (Michoud et al., 2017).

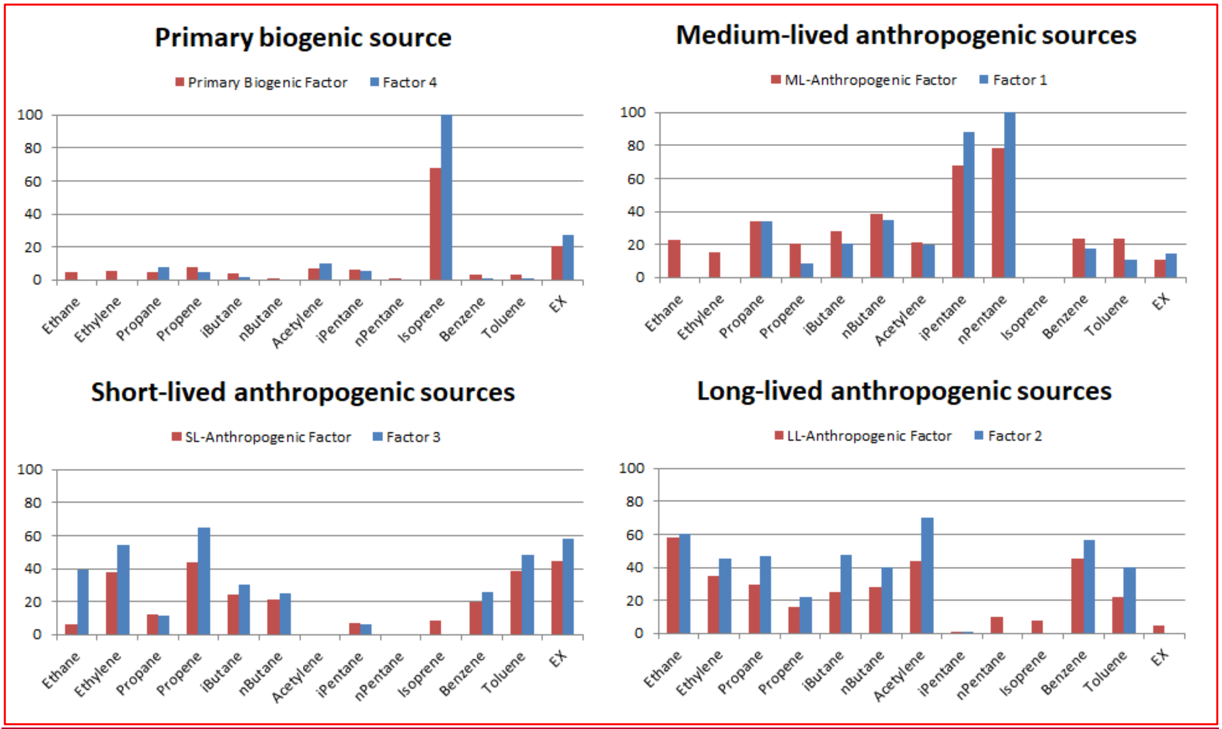


Figure S16: Chemical profiles (percent of each species apportioned to each factor - %) of the 4-factor PMF solution (13 variables; blue bars) compared to a selection of VOCs composing chemical profiles of the 4 primary sources identified in Michoud et al. (2017) owing to a 6-factor PMF solution (42 VOC dataset; red bars).

5

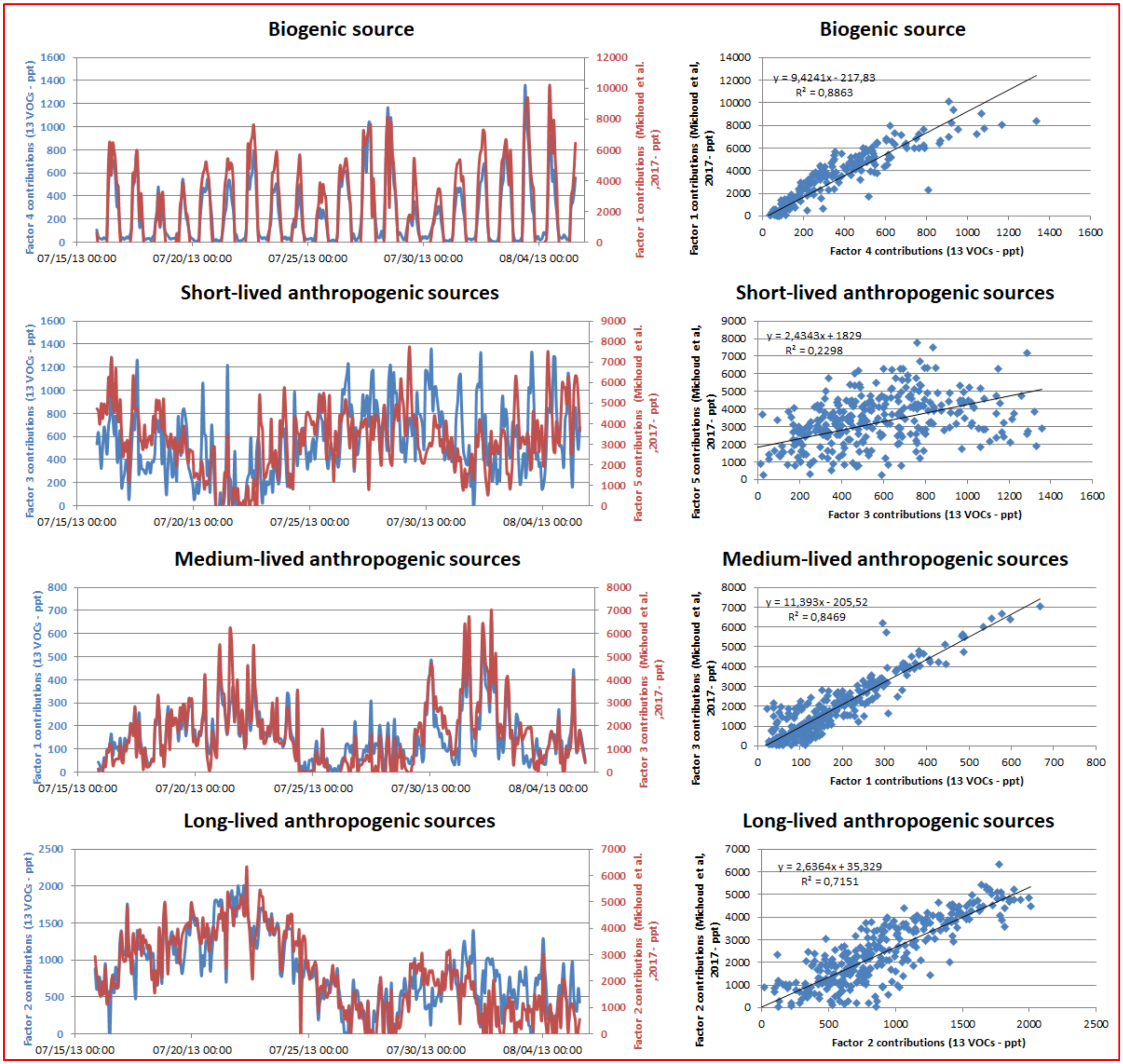


Figure S17: Times series (on the left) and scatter plots (on the right) of contributions (in ppt) of factors composing the 4-factor PMF solution (13 variables; blue lines) compared to the 4 primary sources identified in Michoud et al. (2017) owing to a 6-factor PMF solution (42 VOC dataset; red lines).

~~As a conclusion, the contribution of both experimental strategies, to characterize the main sources influencing VOC levels observed at the receptor site of pollution impacting the Western Mediterranean region, was hence investigated in this section. On one hand, the SOP-1b intensive field campaign occurred in summer and offered good conditions to monitor at a time anthropogenic sources, influenced by several geographic origins, along with biogenic local sources and secondary oxygenated sources, and to assess to their diurnal variations. On the other hand, the observation field campaign had the advantage to cover two complete years in order to monitor seasonal and interannual variations of main primary sources~~

~~impacting VOC concentrations observed at the receptor site. This larger time scale of VOC measurements also helped to deconvoluate long-lived combustion sources from regional background. Nevertheless, the time resolution of VOC measurement of the 2-yr period (4 hours compared to 1 hour and a half during the SOP-1b period) and the limited number of sampling days during this study period did not help to support the clear deconvolution of the 5 factors, as factors related to anthropogenic sources were quite correlated between them (as a consequence of their seasonal variations – see Sect. 3.5; and unlike SOP-1b anthropogenic sources showing Pearson correlation factors from -0.5 to 0.1). Finally, the incorporation of OVOCs in the source apportionment had little impact on the identification of main primary sources influencing VOC concentrations observed at the receptor site but can modify their relative contributions, emphasizing the contribution of local biogenic/anthropogenic sources and decreasing the contribution of regional anthropogenic sources.~~

Section ~~S5~~S7: Concurrent ~~VOC~~ NMHC measurements performed at other European background monitoring stations

From June 2012 to June 2014, NMHC measurements were concurrently conducted at 17 other European background monitoring stations. These European stations are part of EMEP and GAW networks. Figure S18 shows their geographical distribution. They cover a large part of western and central Europe from Corsica Island in the south to northern Scandinavia in the north, are located at different altitudes (up to 3580 m a.s.l.) and most of them are categorized as GAW ‘regional stations for Europe’. More information on these stations can be found on EMEP (https://www.nilu.no/projects/ccc/sitedescriptions/index.html, last access: 11/10/2020) or GAW station information system (https://gawsis.meteoswiss.ch/GAWSIS//index.html#/, last access: 11/10/2020) sites. NMHC measurements were realized by different on-line (GC or proton-transfer-reaction mass spectrometer - PTR-MS) or off-line techniques (VOCs collected by steel canisters) and were reported in the EMEP EBAS database (http://ebas.nilu.no/Default.aspx, last access: 11/10/2020).

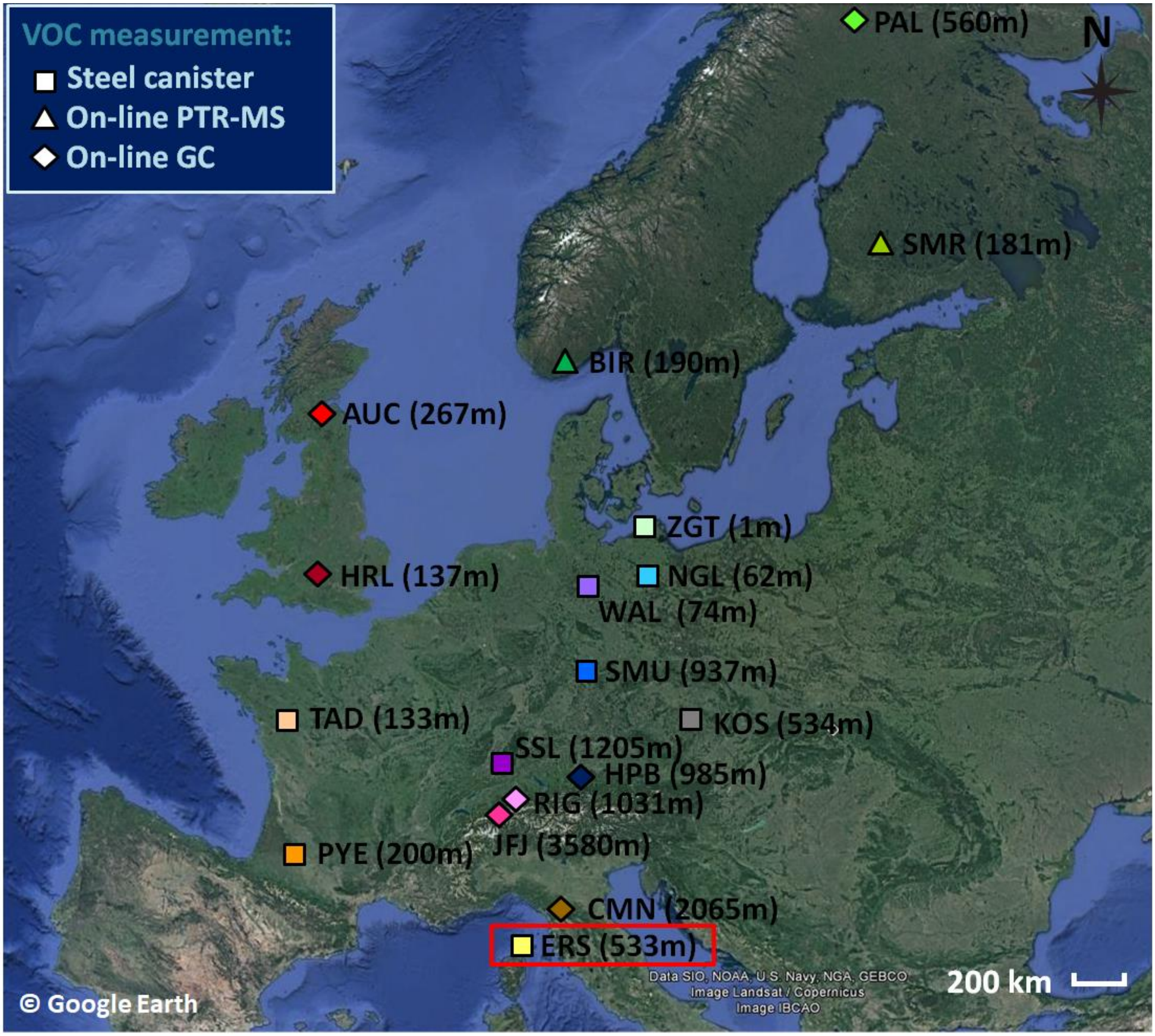


Figure S18: Locations of 18 European monitoring stations that included NMHC measurements conducted from June 2012 to June 2014. These stations are part of EMEP/GAW networks. They are characterized by their GAW identification and the altitudes are given within brackets in reference to standard sea level. AUC, BIR, ERS, KOS, NGL, PYE, RIG, SMR, SSL and TAD are categorized as GAW 'regional stations for Europe'. CMN, HPB, JFJ and PAL are categorized as GAW 'global stations'. AHRL, SMU, WAL and ZGT are considered as GAW 'other elements stations in Europe', more precisely, ZGT is a 'coastal station' while HRL, SMU and WAL are 'rural stations'. Note that high-altitude stations such as CMN and HPB could be frequently in free-tropospheric conditions. The Ersa site (GAW identification: ERS) is underlined in red. Square markers indicate that VOCs were collected by steel canisters and analysed thereafter at laboratories (i.e. off-line measurements). Triangle and diamond markers indicate that VOC measurements were conducted in-situ using PTR-MS or GC systems, respectively. NMap provided by Google Earth Pro software (v.7.3.3 image Landsat/Copernicus – IBCAO; data SIO, NOOA, U.S, Navy, NGA, GEBCO; © Google Earth).

References

Brown, S. G., Eberly, S., Paatero, P., and Norris, G. A.: Methods for estimating uncertainty in PMF solutions: Examples with ambient air, and water quality data, and guidance on reporting PMF results, Sci. Total Environ., 518–519, 626–635, doi:10.1016/j.scitotenv.2015.01.022, 2015.

Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., and Locoge, N.: Origin, and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus), Atmos. Chem. Phys., 17, 11355–11388, doi:10.5194/acp-17-11355-2017, 2017.

Detournay, A., Sauvage, S., Locoge, N., Gaudion, V., Leonardis, T., Fronval, I., Kaluzny, P., and Galloo, J. C.: Development of a sampling method for the simultaneous monitoring of straight-chain alkanes, straight-chain saturated carbonyl compounds, and monoterpenes in remote areas, J. Environ. Monit., 13, 983–990, doi:10.1039/c0em00354a, 2011.

Detournay, A., Sauvage, S., Riffault, V., Wroblewski, A., and Locoge, N.: Source, and behavior of isoprenoid compounds at a southern France remote site, Atmos. Environ., 77, 272–282, doi:10.1016/j.atmosenv.2013.03.041, 2013.

Kalogridis, A.: Caractérisation des composés organiques volatils en région méditerranéenne, Université Paris Sud - Paris XI. [online] Available from: https://tel.archives-ouvertes.fr/tel-01165005, 2014.

Michoud, V., Sciare, J., Sauvage, S., Dusanter, S., Léonardis, T., Gros, V., Kalogridis, C., Zannoni, N., Féron, A., Petit, J. E., Crenn, V., Baisnée, D., Sarda-Estève, R., Bonnaire, N., Marchand, N., Dewitt, H. L., Pey, J., Colomb, A., Gheusi, F., Szidat, S., Stavroulas, I., Borbon, A., and Locoge, N.: Organic carbon at a remote site of the western Mediterranean Basin: Sources, and chemistry during the ChArMEx SOP2 field experiment, Atmos. Chem. Phys., 17, 8837–8865, doi:10.5194/acp-17-8837-2017, 2017.

Norris, G., Duvall, R., Brown, S., and Bai, S.: EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals, and User Guide Prepared for the US Environmental Protection Agency Office of Research, and Development, Washington, DC. [online] Available from: https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf, 2014.

Paatero, P.: Least squares formulation of robust non-negative factor analysis, Chemom. Intell. Lab. Syst., 37, 23–35, doi:10.1016/S0169-7439(96)00044-5, 1997.

~~Paatero, P.: The Multilinear Engine—A Table-Driven, Least Squares Program for Solving Multilinear Problems, Including the n-Way Parallel Factor Analysis Model, J. Comput. Graph. Stat., 8, 854–888, doi:10.1080/10618600.1999.10474853, 1999.~~

Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111–126, doi:10.1002/env.3170050203, 1994.

Paatero, P., Eberly, S., Brown, S. G., and Norris, G. A.: Methods for estimating uncertainty in factor analytic solutions, Atmos. Meas. Tech., 7, 781–797, doi:10.5194/amt-7-781-2014, 2014.

Paatero, P., Hopke, P. K., Song, X. H., and Ramadan, Z.: Understanding, and controlling rotations in factor analytic models, Chemom. Intell. Lab. Syst., 60, 253–264, doi:10.1016/S0169-7439(01)00200-3, 2002.

Paatero, P., Hopke, P. K., Begum, B. A., and Biswas, S. K.: A graphical diagnostic method for assessing the rotation in factor analytical models of atmospheric pollution, Atmos. Environ., 39, 193–201, doi:10.1016/j.atmosenv.2004.08.018, 2005.

~~Paatero, P., Hopke, P. K., Begum, B. A., and Biswas, S. K.: A graphical diagnostic method for assessing the rotation in factor analytical models of atmospheric pollution, Atmos. Environ., 39, 193–201, doi:10.1016/j.atmosenv.2004.08.018, 2005.~~

Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., and Sisler, J. F.: Atmospheric aerosol over Alaska 2. Elemental composition, and sources, J. Geophys. Res. Atmos., 103, 19045–19057, doi:10.1029/98JD01212, 1998.

Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P., and Galloo, J. C.: Long term measurement, and source apportionment of non-methane hydrocarbons in three French rural areas, Atmos. Environ., 43, 2430–2441, doi:10.1016/j.atmosenv.2009.02.001, 2009.

Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D. T., and Schwikowski, M.: Trajectory analysis of high-alpine air pollution data, in Air Pollution Modeling, and Its Application X, edited by S.-E. Gryning, and M. M. Millán, pp. 595–596, Springer, Boston, MA., 1994.