

Increasing influence of easterly air masses on NMHC concentrations at the Pallas-Sodankylä GAW station

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Received 26 May 2014, final version received 23 Oct. 2014, accepted 22 Oct. 2014

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

Non-methane hydrocarbons (NMHCs, C₂–C₆) have been measured at the Pallas-Sodankylä GAW station since 1994. In 2010, evacuated stainless-steel-canister sampling was replaced by an *in-situ* gas chromatograph, and parallel measurements were conducted over the period of a year. Results were in good agreement for all other compounds except propene. NMHCs at Pallas show a typical seasonal variation, with the highest mixing ratios in winter and lowest in summer. Alkanes did not show any clear diurnal variation, but ethene had a maximum at midday or during the afternoon in summer. This indicated biogenic sources. *i/n*-Butane and *n/i*-pentane ratios were higher than those typically found in urban areas or in traffic emissions, indicating other sources than these (e.g. wood combustion or natural gas) having a strong effect on mixing ratios at Pallas. Trend analysis over twenty years of measurements indicated a significant decreasing trend only for ethyne, even though emissions of NMHCs in the European Union (EU) decreased by 50% during this period. No trend was found for ozone, either. This indicated that some other source areas than the EU must play a significant role at Pallas. This was confirmed by source area estimates, which showed that eastern Europe is the main source area for high mixing ratios at Pallas.

Introduction

Non-methane hydrocarbons (NMHC) are released into the air from petrol exhaust and evaporation, stationary combustion, gas leaks, solvent use, etc. Also large amounts of VOCs are released into the atmosphere from natural sources (Tarvainen *et al.* 2007). In the air, the main sink reaction for NMHCs is that with the hydroxyl radical, but for alkenes the ozone reaction is also important (Atkinson 1994). In addition, NMHCs react with nitrate (Atkinson 1994, Penkett *et al.* 1993) and chlorine (Finlayson-Pitts *et al.* 1989) radicals. Atmospheric lifetimes of NMHCs are rather long, varying

from days to months during winter, but being much shorter in summer, when there is enough light to produce hydroxyl radicals. In winter in northern latitudes, NMHCs accumulate and maximum concentrations are measured during the dark, winter months (Hakola *et al.* 2006, Solberg *et al.* 1996). In spring, VOC concentrations start decreasing, concomitant with the increase in ozone due to efficient photochemical reactions, and minimum concentrations are reached in summer.

NMHC reactions with the OH radical can result in ozone formation when enough nitrogen oxides are present (Derwent *et al.* 2003). Reductions in the emissions of ozone precur-

sors in Europe have been followed by a downward trend in episodic ozone-level peaks (Derwent *et al.* 2003). However, background ozone levels have increased e.g. in Ireland (Simmonds *et al.* 2004). In Finland, ozone concentrations increased in the years 1990–2000, although a simultaneous decreasing trend was observed in the other Nordic countries (Laurila *et al.* 2004, Solberg *et al.* 2005). Between 1994 and 2007 mean summer concentrations of O₃ showed no significant trends at eight Finnish rural sites. Summertime peak concentrations increased slowly (but significantly) at two northernmost stations, while at the other background sites no significant trends were detected (Anttila and Tuovinen 2010).

Since 1994, light molecular weight hydrocarbons (C₂–C₆) have been measured in Finnish Lapland at the Pallas GAW (Global Atmosphere Watch) station first twice a week using canister sampling, and then since the beginning of 2010 using also *in-situ* on-line gas-chromatography. Concentration trends were studied earlier (Hakola *et al.* 2006); in these, the concentrations of the fast-reacting species (C₅–C₆ alkanes and ethyne) were found to have decreased by 10%–40% in 1994–2003, whereas the concentrations of the slowly-reacting compounds, ethane and propane, showed no change or were increasing during the ten years of measurements. Higher concentrations of all NMHCs were found in the air masses arriving at Pallas from central Europe and from Russia, while the marine air masses were the cleanest.

This paper we analyse short-term variability of the NMHC concentrations measured during 2010–2012 at Pallas, as well as the trends in the NMHCs during twenty years (1994–2013) of measurements. We also studied the source areas using the data from new *in-situ* measurements.

Experimental methods

Measurement site

The Pallas station has been part of the Global Atmosphere Watch program of the World Meteorological Organization since 1994, and is run by the Finnish Meteorological Institute (FMI).

Pallas (67°58′N, 24°07′E) is located in the sub-arctic region at the northernmost limit of the northern boreal forest zone. The station is situated on a fell-top at an elevation of 565 m a.s.l. The vegetation on the fell-top is sparse, consisting mainly of low vascular plants, moss and lichen. A more detailed description of the site can be found in Hatakka *et al.* (2003).

Sampling and analysis of NMHCs

From 1994 to 2011, NMHC samples were collected at Pallas into evacuated stainless-steel canisters twice a week between 9:00 and 16:00 and analyzed at the laboratory of the Finnish Meteorological Institute with a gas chromatograph-flame ionization detector (GC-FID). These measurements are described in detail by Hakola *et al.* (2006).

In-situ measurements of NMHCs started at Pallas in 2010 using a Perkin-Elmer thermal desorption-gas chromatography system with flame ionization detection. The GC system is composed of two columns and a heart-cut device. The first column is a BP-1 dimethyl polysiloxane column (50 m × 0.22 mm × 1 μm) followed by the heart-cut device and an alumina/Na₂SO₄ PLOT column (50 m × 0.32 mm). The heart-cut device is used to separate the analytes into two fractions; the more-volatile fraction elutes from the BP-1 and is directed into the PLOT column for further chromatography and detection on FID2. After the volatile fraction has passed through the BP-1 column, the heart-cut is switched to the other position and the later-eluting compounds are directed to FID1. The temperature program of the oven was 46 °C for 16 min, from 10 to 170 °C with 5 °C min⁻¹; from 170 °C to 200 °C with 15 °C min⁻¹; 200 °C for 6 min. The analysis lasted for 47 min. The inlet consists of a heated stainless-steel line (temperature 70 °C, length 5 m, outer diam. 0.25 inch, flow 2 l min⁻¹) connected the station main gas line with a flow of 90 m³ h⁻¹. After passing a Nafion drier, NMHCs are trapped on a Perkin-Elmer Air Toxic Trap held at –40 °C. The sampling time is 30 minutes and the sampling flow is 20 ml min⁻¹. About every 100th sample is a calibration sample (National Physical Laboratory, 32 VOC mix at 4 ppb level). The

sampling interval varies from one hour to one day. Limits of detection (LODs) are calculated as three times the standard deviation of blank levels and from the signal-to-noise ratio for the compounds with no blank. Uncertainties are calculated from partial uncertainties.

Canister versus on-line sampling

During the first year of the *in-situ* NMHC measurements, parallel canister samples were also collected and analyzed. Altogether 50 canister samples were taken during daytime at the same time with *in-situ* measurements in 2010. The detection limits for the *in-situ* measurements were higher for all compounds (Table 1), and these measurements showed somewhat higher mixing ratios, but were generally very well correlated (Pearson's correlations) with the canister analyses. Propene was the only compound that showed a lot of deviation. This may be due to its instability when stored in the canisters and the high background for the *in-situ* measurements.

Trend calculations

Linear trends in the concentration time series were estimated using a Generalized Least Squares (GLS) regression with classical decomposition and autoregressive moving average (ARMA) errors. This advanced GLS-ARMA method has been shown to be a powerful tool

in the identification of even the weakest trends in air pollutants (Anttila and Tuovinen 2010). In this statistical model, the autocorrelation typically present in air pollution concentration time series is accounted for by iteratively applying an ARMA-based correlation structure to the residuals of the fitted linear model. Details of this trend analysis method are given in Anttila and Tuovinen (2010); here we just summarize the procedure.

First, all mixing-ratio data from 1994–2013 were averaged into monthly means. Missing values (only four months of a total of 238 months) were replaced by the means of the previous and following monthly mixing ratio values. These monthly time series were then deseasonalized by the classical seasonal decomposition, and a first-order ordinary least squares (OLS) regression model was fitted to this deseasonalized data.

Following this, the autocorrelation function (ACF) of the resulting residuals was calculated and an ARMA model was introduced. The order of the ARMA model (i.e., the p and q for the autoregressive and moving-average process, respectively) was determined by minimizing the second order Akaike Information Criterion (AIC_c) (see e.g. Brockwell and Davis 2002). The parameters of the selected ARMA(p,q) process were estimated, together with the coefficients of a linear regression, by maximizing the Gaussian likelihood. The analyses described above were conducted using a ITSM 2000-V.7.3 software (B and D Enterprises Inc.).

Table 1. Detection limits of the *in-situ* and canister analyses of NMHCs in 2010 together with slopes, intercepts and correlations (r^2) of 50 parallel canister analyses with *in-situ* measurements.

	Detection limits (pptv)		Slope	Intercept	r^2
	<i>In situ</i>	Canister			
Ethane	35	6	0.77	66	0.86
Ethene	87	8	0.95	10	0.81
Ethyne	38	20	0.78	-8	0.91
Propane	86	7	0.95	-35	0.95
Propene	69	10			
<i>i</i> -Butane	31	8	0.98	-59	0.81
<i>n</i> -Butane	66	7	1.17	-43	0.88
<i>i</i> -Pentane	56	7	0.94	0.9	0.89
<i>n</i> -Pentane	65	7	1.01	-5	0.92

Source area estimates

To identify the source areas of ambient VOCs at Pallas we used adjoint dispersion simulations for the hourly-averaged concentrations measured in winter in 2010–2012. The method is quite similar to the one used by Meinander *et al.* (2013), but for the sake of completeness, we describe it below.

A qualitative analysis of the origins of airborne substances can be done using simple backward trajectories. This approach needs a very large number of trajectories to provide reliable results. For quantitative assessment in the case of limited observational information, so-called “footprint” computations can be used (e.g. Prank *et al.* 2010). This approach is based on solving the adjoint-dispersion equation for each measurement to obtain a field of sensitivity for each observation to a source location in space and time: same source located at different points would result in different concentrations measured, and the ratio of the concentrations equals to the ratio of sensitivities in these points.

The modeling was performed with SILAM (System for Integrated modeLing of Atmospheric cOmposition) v5_4. The system uses the Eulerian non-diffusive advection scheme of Galperin (2000) and the adaptive vertical diffusion algorithm of Sofiev (2002). For a more detailed description *see* Sofiev *et al.* (2008) and <http://silam.fmi.fi>.

Verification of the model was performed within the scope of the EU-GEMS project (<http://www.ecmwf.int/gems>) and is continued on a routine basis within EU-MACC (<http://www.gmes-atmosphere.eu>).

The SILAM model was driven by ERA-interim (Dee *et al.* 2011) meteorological fields that have a 0.72° spatial resolution. The adjoint simulations were performed with a resolution of 1° × 1° over the domain, with 8 vertical layers of thickness varying from 30 m at the surface to 2000 m over a height range from the surface to 6 km. The observations in the simulations were located at Pallas at a height of 250 m a.g.l., corresponding to the hill-top location of the station. A passive tracer with source timing corresponding to the original measurements had been used for calculations. For each 1-hour-long measure-

ment period, a 4D sensitivity to source location in space and time was calculated. Then, for each of the species, the surface time-integrated sensitivity fields were grouped with respect to the observed concentration into “high”, “medium”, and “low” and summed up within each group. The margins were taken at approximately the 10th and 90th percentiles of the observed values (Table 2).

Comparison of the sensitivity maps for “clean” and “polluted” samples allows one to identify the areas that of likely locations of powerful sources. The areas of high sensitivity for “clean” samples do not contain persistent powerful sources. Thus the likely source areas can be identified as those missing from “clean” maps, but are highly represented in “polluted” ones.

Results

Seasonal and diurnal variation of NMHCs in 2012

All compounds showed a typical seasonal variation, with the highest mixing ratios in winter and the lowest in summer, when lifetimes are shortest due to higher abundance of OH radicals (Table 3). Summer mixing ratios at Pallas were close to the values measured in a very clean Arctic area (Hellén *et al.* 2012), but winter mixing ratios were higher (Swanson *et al.* 2003).

During the winter or spring months, the mixing ratios did not show any diurnal variations (Fig. 1). This was expected, due to the remote location of the site and relatively long lifetime of the compounds (Table 3). In July, ethene mixing ratios had a clear maximum in the afternoon, indicating a biogenic source. Ethene, a growth

Table 2. Grouping limits for the concentration samples.

	“Low” (pptv)	“High” (pptv)
Ethane	< 1500	> 3000
Ethyne	< 250	> 700
Propane	< 700	> 1700
Butane	< 200	> 800
<i>i</i> -Butane	< 150	> 500
<i>i</i> -Pentane	< 100	> 350
<i>n</i> -Pentane	< 75	> 250

hormone, is known to be emitted by vegetation (Goldstein *et al.* 1996).

Ratios of isomeric pairs of NMHCs

The ratios of isomeric pairs (*i*-butane and *n*-butane or *i*-pentane and *n*-pentane) are not expected to change during their transport due to OH oxidation since the reaction rate constants are very similar. Subsets of the data for the four seasons showed no obvious change in the ratios (Fig. 2), indicating that the main sources remained the same throughout the year 2012.

The overall *i/n*-butane ratio for Pallas in 2012 was 0.59 (coefficient of determination $r^2 = 0.99$). The mean urban *i/n*-butane ratio found by Hellén *et al.* (2006) in Helsinki, Finland, in 2004 was 0.51. The ratio at Pallas is very similar to that at other EMEP stations in Europe (Hakola *et al.* 2006). The *i*-butane/*n*-butane ratio of monthly mean mixing ratios for the years 1994–2012 measured at Pallas was higher at the end of the 2000s as compared with that during the 1990s (Fig. 3). Reconstructed histories of NMHCs by Helmig *et al.* (2014) also showed an increase in the *i/n*-butane ratio for the northern hemisphere. The lifetime of *n*-butane is a little

shorter than that of *i*-butane: in more remote air masses, the ratio is thus expected to be somewhat higher, indicating, therefore, more distant sources. Increases in this ratio have also been explained by chlorine atom oxidation, which is 50% faster for the *n*-butane isomer (Hopkins *et al.* 2002). However, halogen atom chemistry has only been found to have a major effect in spring (Jobson *et al.* 1994). Different emission sources are also a possible explanation for different ratios, but compared with the urban ratio of 0.51, the ratios for traffic and the distribution of fossil fuels and for solvent use are even lower (Hellén *et al.* 2006, Fujita *et al.* 1995). For commercial natural gas emissions, higher ratios of 0.68 and 0.90 have been found by Fujita *et al.* (1995) and Hellén *et al.* (2006), respectively.

The overall *n/i*-pentane ratio was 0.74 ($r^2 = 0.96$), which is in good agreement with the values determined for, e.g., Mace Head (0.74, $r^2 = 0.95$) by Yates *et al.* (2010), and at the Pico Mountains, Azores (0.69, $r^2 = 0.93$) by Helmig *et al.* (2008). The pentane ratio remained at the same level during 1994–2012 (Fig. 3). The mean urban ratio of *n/i*-pentane determined by Hellén *et al.* (2006) in Helsinki, Finland, in 2004 was 0.51. For traffic, a ratio of 0.38 was found, but for evaporated and liquid gasoline and for commercial natural gas

Table 3. Limits of detection (LOD), uncertainties (*U*) and atmospheric lifetimes (τ , days) in reaction with OH radicals, as well as mean winter (Dec–Feb), spring (Mar–May), summer (Jun–Aug), autumn (Sep–Nov) and annual mixing ratios of NMHCs at Pallas in 2012. The concentrations of OH radicals (summer 0.052 pptv and winter 0.002 pptv) are daytime averages calculated for northern Europe by Hakola *et al.* 2003.

	LOD* (pptv)	<i>U</i> (%)	τ_{winter} (d)	τ_{summer} (d)	Winter	Spring	Summer	Autumn	Whole year
Ethane	28	4	1074	41	2580	1880	890	1200	1650
Ethene**	87	9	28	1.1	370	< LOD	< LOD	< LOD	130
Propane	52	12	205	8	1500	660	110	420	680
Propene	116	9	8.9	0.3	< LOD	< LOD	< LOD	< LOD	< LOD
<i>i</i> -Butane	17	4	101	3.9	390	120	18	80	150
<i>n</i> -Butane	29	6	93	3.6	670	200	30	150	260
Ethyne	38	10	290	11	500	240	60	140	240
<i>i</i> -Pentane	13	3	60	2.3	280	60	13	60	100
<i>n</i> -Pentane	9	4	59	2.3	220	50	12	50	80
<i>i</i> -Hexane	30	4	42	1.6	51	< LOD	< LOD	< LOD	< LOD
<i>n</i> -Hexane	30	14	42	1.6	48	< LOD	< LOD	< LOD	< LOD
Benzene	21	8	178	6.9	135	60	< LOD	50	65
Toluene	37	3	39	1.5	63	< LOD	< LOD	< LOD	< LOD

* Calculated as $3 \times \text{SD}$ of blank levels or $3 \times \text{signal-to-noise ratio}$ for the compounds with no blank.

** Calculated as $3 \times \text{signal-to-noise ratio}$. However, if in chromatograms peaks standing out from the background were found for the values below the detection limit, LOD was calculated as $2 \times \text{signal-to-noise ratio}$.

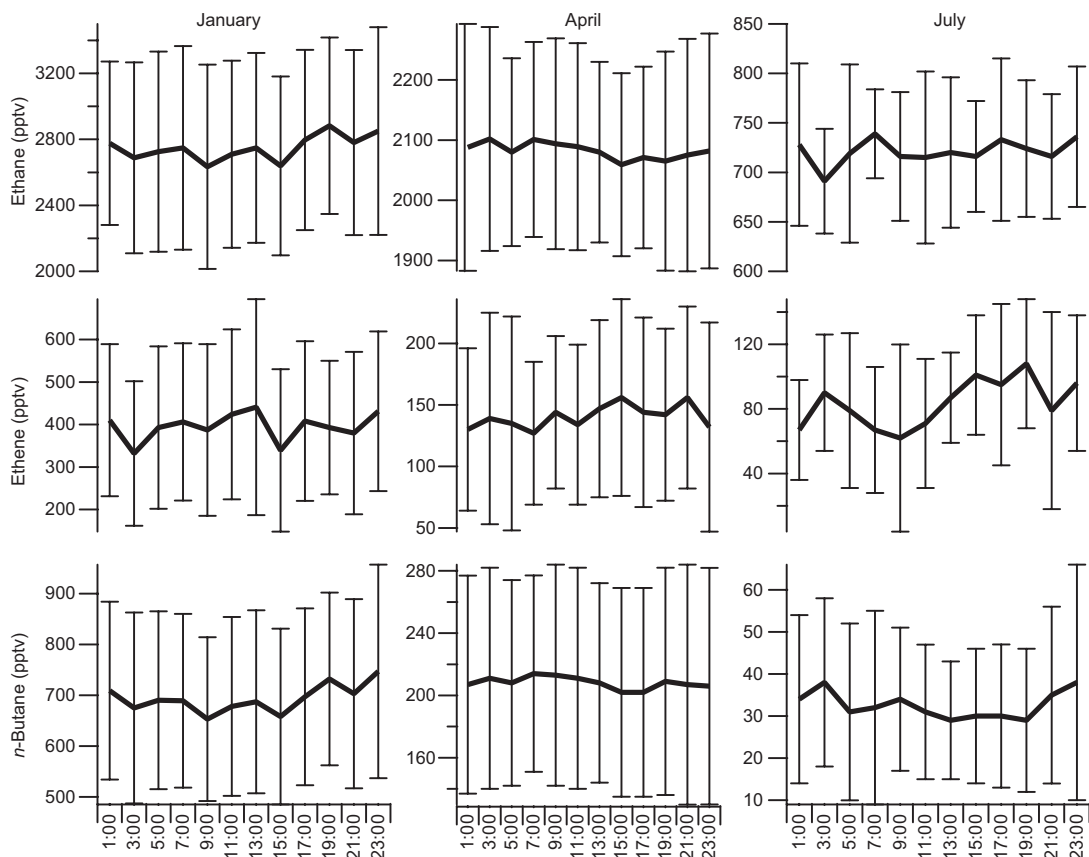


Fig. 1. Diurnal variation (local winter time) of mixing ratios of ethane, ethene (concentrations are used for samples from July; see Table 3) and *n*-butane at Pallas in January, April and July in 2012.

emissions the ratio was clearly higher (1.1–1.9). Also for wood combustion emissions, a higher value (0.84) has been found (Schauer *et al.* 2001). This suggests that wood combustion, the extraction and distribution of fossil fuels or natural gas emissions may be the sources of the pentanes found at Pallas. Wood combustion has been found to be a significant source of VOCs in residential areas in Finland (Hellén *et al.* 2006, 2008).

NMHC and ozone trends

In the trend analysis, small negative slopes were detected for most alkanes and benzene, but a decreasing trend was significant only for ethyne (Table 4). This is not in accordance with reconstructed NMHC trends for the northern hemisphere, which show a clear downward trend (1%–5% year⁻¹) during that period (Helmig *et*

al. 2014). According to the EMEP emission database (Fig. 4), emissions of NMVOCs also decreased in the European Union by over 50% during this period. At a rural French site significant decreasing trends of benzene and *i*-pentane concentrations were found in the period 1997–2006 (Sauvage *et al.* 2009). The persistently high levels of mixing ratios measured at Pallas indicate that, as compared with the EU area, some other sources or source areas dominated there. The lifetimes of these NMHCs (Table 3) are relatively long, especially in winter, and therefore they may have been transported over long distances.

Despite the decreased emissions of ozone precursors in the EU area, the mean ozone concentration at Pallas also did not show any downward trend. Similarly, background ozone levels measured at Mace Head in Ireland even increased during 1987–2003 (Simmonds *et al.* 2004). How-

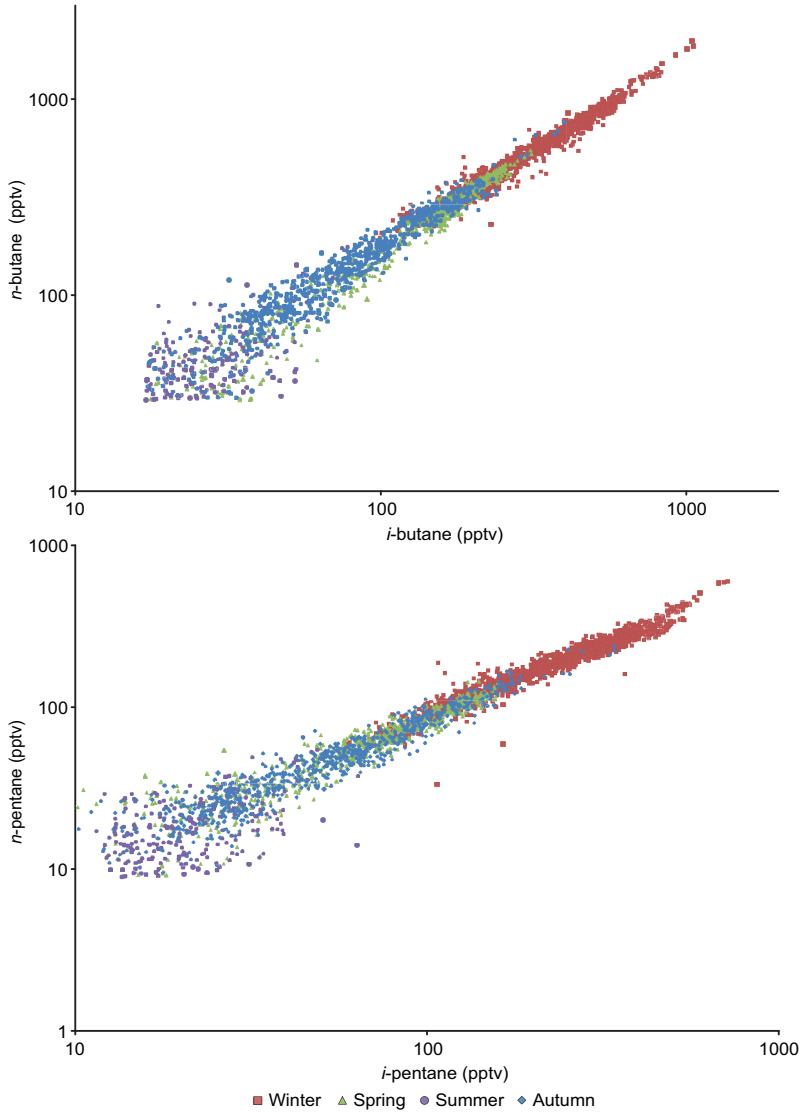


Fig. 2. Seasonal butane and pentane isomer ratios in 2012.

Table 4. Results of the trend analysis of NMHCs and ozone concentrations at Pallas in 1994–2013. Standard errors are given in parentheses. *** significant at $p < 0.001$.

	Start	Months	Intercept (pptv)	Slope (pptv month ⁻¹)	Change ± 95%CI (% year ⁻¹)
Ethane	Jan. 1994	238	1552 (75)	-0.36 (0.54)	-0.3 ± 0.8
Propane	Jan. 1994	238	649 (25)	-0.30 (0.18)	-0.5 ± 0.7
Ethyne	Jan. 1994	238	392 (21)	-0.54 (0.16)	-1.6 ± 0.9***
<i>i</i> -Butane	Jan. 1994	238	128 (7.3)	0.004 (0.05)	0.0 ± 1.0
<i>n</i> -Butane	Jan. 1994	238	257 (18)	-0.17 (0.13)	-0.8 ± 1.2
<i>i</i> -Pentane	Jan. 1994	238	97 (2.5)	-0.02 (0.02)	-0.3 ± 0.5
<i>n</i> -Pentane	Jan. 1994	238	74 (6.9)	-0.03 (0.05)	-0.5 ± 1.6
<i>n</i> -Hexane	Jan. 1994	215	23 (1.4)	-0.01 (0.01)	-0.6 ± 1.2
Benzene	Jan. 1994	215	129 (8.6)	-0.09 (0.07)	-0.8 ± 1.3
Ozone (ppbv)	Mar. 1994	192	37 (0.7)	-0.01 (0.01)	-0.4 ± 0.5

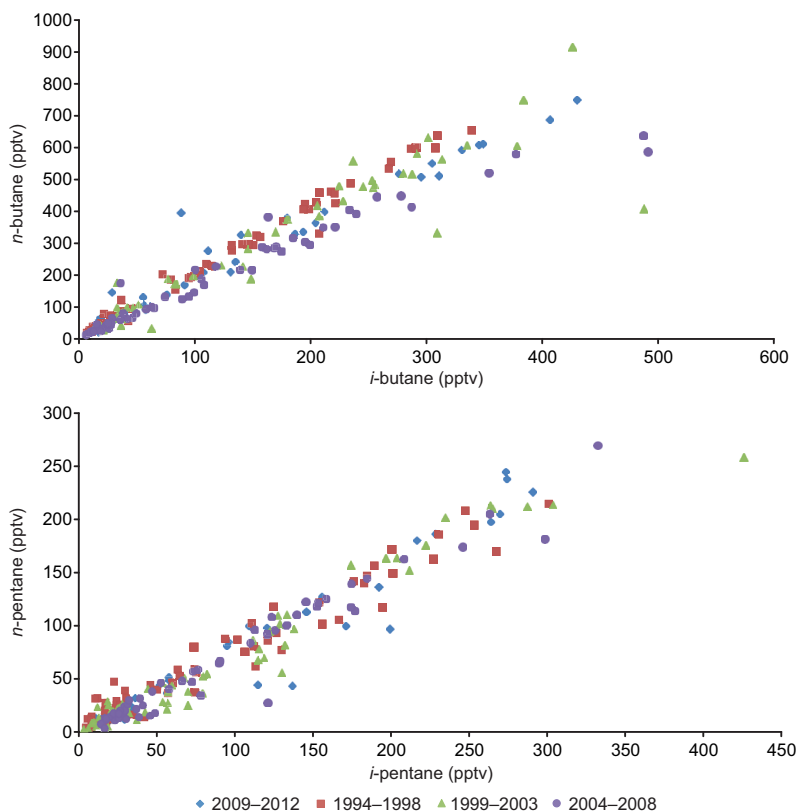


Fig. 3. *n*-Butane versus *i*-butane, and *n*-pentane versus *i*-pentane monthly mean mixing ratios (pptv) for the years 1994–2012 divided into five-year periods.

ever, a downward trend of episodic peak ozone levels was found in Europe (Derwent *et al.* 2003). The lack of a downward trend in background ozone at Pallas is in accordance with the trend in background NMHCs.

Source areas of NMHCs

A comparison of “clean” and “polluted” patterns of NMHCs clearly shows that air masses coming from eastern Europe are more polluted than air masses arriving from the other areas (Fig. 5). There are several large cities (e.g. Helsinki, St. Petersburg and Moscow), which are likely to be responsible for the pollution from that area. For compounds (butanes and pentanes) with a shorter lifetime and therefore a lower background concentration, the source area is clearer than for compounds with higher background concentrations (e.g. ethane).

The northern part of central Europe does not contribute to higher concentrations. As men-

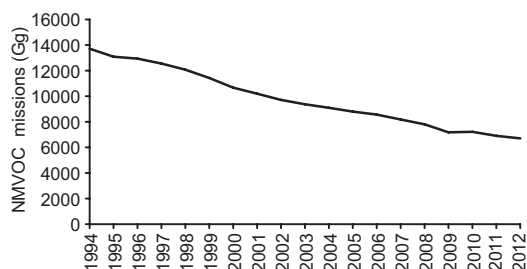


Fig. 4. Officially-reported emissions of non-methane volatile organic compounds (NMVOCs) for European Union (EMEP database accessed 24 Sep. 2014).

tioned earlier, emissions of NMHCs in the EU decreased by 50% during the studied period (Fig. 2). However, this was not the case for the concentrations of most of the alkanes at Pallas, where concentrations did not decrease between 1994 and 2013 (Table 4). This could be explained by the fact that the main source area for higher concentrations lies in the southeast. Increased eastern emissions may explain the missing decreasing trends in the NMHC mixing ratios.

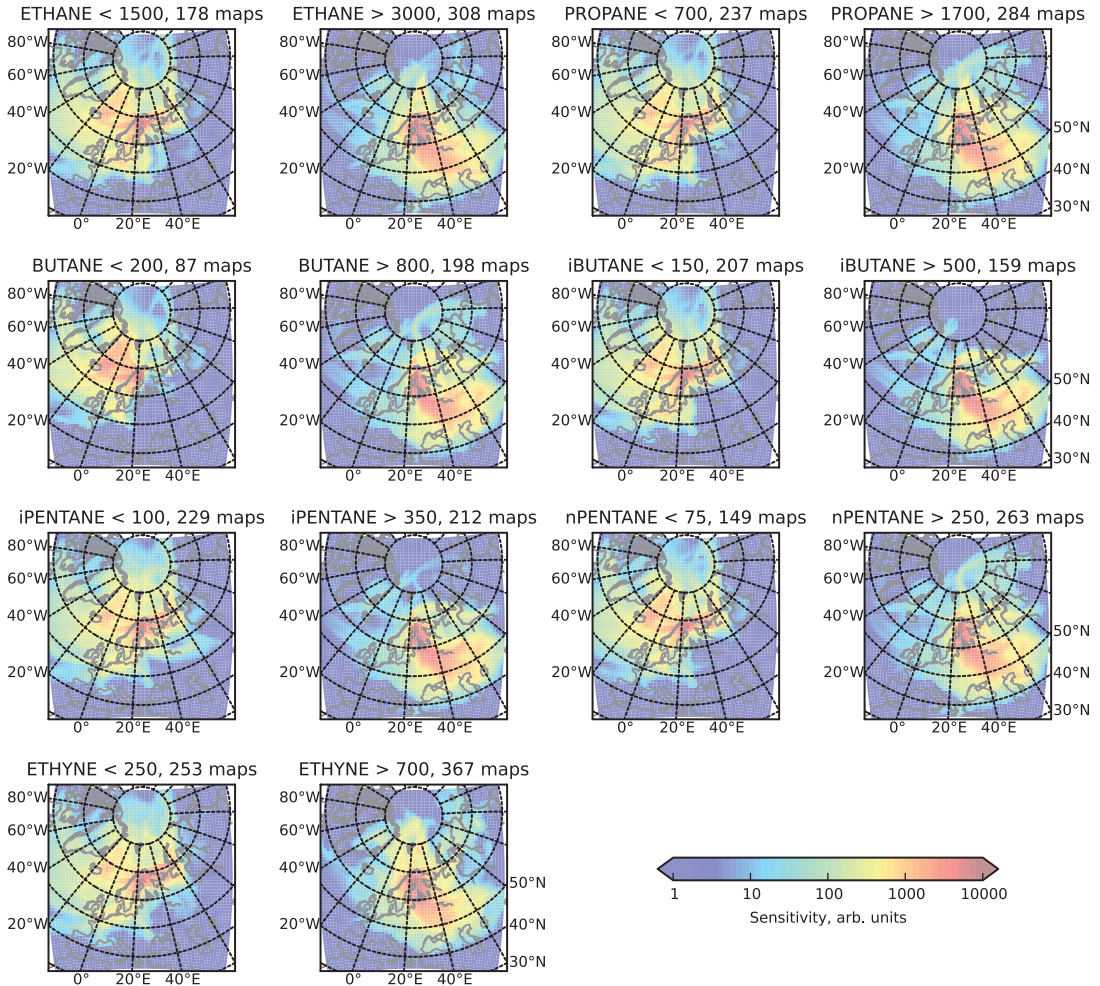


Fig. 5. The average sensitivities for “clean” (left panel) and “polluted” (right panel) samples.

Also in an earlier study at Pallas (Hakola *et al.* 2006), the highest concentrations were found in air masses coming from the east. However, air masses coming from central Europe had high concentrations too. Those measurements were conducted in 1994–2003 and, as mentioned above, emissions in the EU area were decreasing during that period.

Conclusions

NMHC mixing ratios have been measured at the Pallas-Sodankylä GAW station in northern Finland since 1994. From 1994 until 2010, the samples were collected in stainless steel canis-

ters and analyzed later in the laboratory. Since then *in-situ* GC-FID has been used. One year of parallel measurements of NMHCs showed that the canister samples are well-correlated with the *in-situ* measurements.

All compounds showed a typical seasonal variation, with highest mixing ratios in winter and lowest in summer. A more detailed study of the *in-situ* GC-FID in 2012 did not find any diurnal variation of the mixing ratios in winter. In summer, all alkanes showed a daytime minimum due to faster photochemical reactions, but ethene had its highest mixing ratios at midday. This indicated its possible biogenic sources.

The seasonal butane and pentane ratios at Pallas indicated that the main sources remained

the same throughout the year 2012. The *i/n*-butane ratio was somewhat higher than in urban areas, and has increased since 1994. This may indicate that the contribution of wood burning and natural gas emissions has increased in relation to traffic emissions. Another reason for the increasing ratio could be that the air masses had been transported over longer distances. No change of the pentane ratio was found.

Emissions of NMHCs in EU decreased by 50% in 1994–2012, but this was not reflected in the mixing ratios at Pallas. Only for ethyne a significant decreasing trend in 1994–2013 was found. Despite the decreased emissions of ozone precursors in the EU, there was no downward trend in ozone at Pallas.

Source area studies of NMHCs indicate that the EU is no longer a significant source area for NMHCs at Pallas. The main source area is located in eastern Europe to the southeast of Pallas. Increased eastern emissions may explain lack of downward trends in the NMHC mixing ratios.

Acknowledgements: “ECMWF ERA-interim” data used in this study have been provided by ECMWF. The financial support of the Academy of Finland Centre of Excellence program (project no. 1118615), Nordic ministry of research CarboNord project and Academy of Finland A4 project is gratefully acknowledged.

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