Sources and trends of air pollutants at Pallas
Action 13: Pollution transport

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VACCIA - 13. Pollution transport - Pallas-Sodankylä LTER
Intermediate report 31 Dec 2010

FINNISH METEOROLOGICAL INSTITUTE

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1 Introduction

The VACCIA (Vulnerability assessment of ecosystem services for climate change impacts and adaptation) is a project funded by European Union Life+ programme for years 2009-2011. The aims of VACCIA project are to gather information about how global warming is changing ecosystem services, to find out how society can adapt to new conditions and to estimate how climate change will affect the transport of airborne pollutants to northern latitudes. The project also concentrates on informing public and decision makers about the project outcomes. The VACCIA action 13 is particularly aimed at assessing trends and source areas of atmospheric pollutants and to find out how climate change will affect pollution transport to northern areas. This report describes the trends and source areas of major pollutants measured at Finnish Meteorological Institute's Pallas GAW (Global Atmosphere Watch) station in Lapland. The second part of the report will focus on how climate change is expected to change air pollution transport to the northern areas.

2 Data and statistical methods

2.1 Data

The data in this report are from Finnish Meteorological Institute's (FMI) Pallas Global Atmosphere Watch (GAW) station. Pallas is located at the northernmost limit of the northern boreal forest zone and it represents well the continental background air of the subarctic region (Hatakka et al., 2003). There are altogether five measurement sites in this area, but the atmospheric composition measurements of this report are from the Sammaltunturi main station (67°58´24''N, 24°06´58''E) and the Matorova station (68°00´00''N, 24°14´24''E). The Sammaltunturi station resides on top of the fjeld at an elevation of 565 m a.s.l. The vegetation on the fjeld top is sparse, consisting mainly of low vascular plants, moss and lichen. Matorova lies six kilometres east-northeast of Sammaltunturi at an elevation of 340 m a.s.l. It is situated on top of a small hill covered by coniferous forest in the middle of a hectare clearing. Data from 1996 to 2009 was included and the elemental/chemical components included were: trace elements analyzed from filter samples collected from Matorova, ozone (O_3), nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and light volatile organic compounds (VOCs,

C$_2$-C$_6$) measured at Sammaltunturi. Aerosol samples for persistent organic pollutants (POP) and polycyclic aromatic hydrocarbons (PAH) analysis were collected at Matorova and analyzed in the laboratory of the IVL Swedish Environmental Research Institute. The major inorganic ions were analyzed from filter samples collected also at Matorova site.

2.2 Trend calculation

The linear trends in the concentration time series were estimated by Generalized Least Squares (GLS) regression with classical decomposition and autoregressive moving average (ARMA) errors, applied to monthly data. 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. This advanced GLS-ARMA method has been shown to be a powerful method to the identification of even the weakest trends of air pollutants (Anttila and Tuovinen, 2010).

The monthly time series between 1994/1996 and 2009 were first deseasonalized by the classical seasonal decomposition following Brockwell and Davis (2002), in which a moving average with a 13-month window (with the first and last observations averaged) was first subtracted from the original data. Next, the mean of the monthly deviations thus obtained was subtracted, to ensure that the mean of the seasonal component is zero. The seasonal component was then calculated by averaging the scaled deviations on a monthly basis. Finally, a deseasonalized time series was produced by subtracting this seasonal component from the original data.

The GLS-ARMA-based trend analysis consisted of the following steps; for additional details, see Brockwell and Davis (2002).
(*i*) A first-order OLS regression model was fitted to the deseasonalized data.
(*ii*) The autocorrelation function (ACF) of the resulting residuals was calculated. If 5% of the values of the sample ACF up to a lag of 40 were outside the bounds $\pm 1.96/\sqrt{n}$ (corresponding to the 95% confidence interval), where n is the number of observations, it was concluded that the residuals were not independent and identically-distributed random variables, and an ARMA model was introduced.

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(*iii*) The optimal ARMA(*p*, *q*) model to represent the residuals was selected. The order of the model (i.e., the *p* and *q* for the autoregressive and moving-average process, respectively) was determined based on the bias-corrected version of the information criterion of Akaike (AICC) (Hurvich and Tsai, 1989). The model producing the lowest AICC value for the combinations of $p \leq 9$ and $q \leq 9$ was selected (with 9 as an arbitrary choice).

(*iv*) The parameters of the selected ARMA(*p*, *q*) process were estimated, together with the coefficients of linear regression, by maximizing the Gaussian likelihood.

(*v*) The maximum likelihood estimation was repeated with the residuals from the updated regression parameters until the parameter values stabilized, providing the final estimates of trend and error structure.

The analyses described above were conducted with ITSM 2000-V.7.3 (Professional) software (Copyright 1999, B and D Enterprises Inc. 1 Oct 2005).

2.3 Source analyses

2.3.1 Positive Matrix Factorisation

The source apportionment of the multielemental concentrations measurements at Pallas was carried out with the Positive Matrix Factorization method. PMF is a factor analysis tool which decomposes a sample data matrix into two matrices, i.e., factor contributions and factor profiles. The PMF method is described elsewhere (Anttila et al., 1994, Paatero and Tapper 1994, Paatero 1997); and the model principle is explained only briefly here. The equation to be solved by PMF is

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (1)$$

where x_{ij} is the *j*th species concentration measured in the *i*th sample, g_{ik} is the particulate mass concentration from the *k*th source contributing to the *i*th sample, f_{kj} is the mass fraction of the *j*th species from the *k*th source, and e_{ij} is the residual associated with the *j*th species concentration measured in the *i*th sample, and *p* is the total number of independent sources. The results are constrained so that there are no

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negative source contributions. The goal of the analysis is to identify a user-specified number of factors.

Each data point is individually weighted using the uncertainty estimates for each species. The uncertainties for each sample were calculated using measurement uncertainties (MU%) and minimum detection limits (MDL) in an equation-based uncertainty procedure from Polissar et al. (1998). For PAHs, LOQs were used as MDL and for other components, LODs were used.

The conditional probability function (CPF) (Kim et al., 2003) was used for daily PMF dataset to estimate the local source impacts from various wind directions. The CPF was calculated for each factor using relative source contributions and average wind factors for each sampling day. CPF was defined as the function (2)

$$CPF_\theta = \frac{m_\theta}{n_\theta}$$

(2)

where m_θ is the number of average wind vectors (days) that fall in the wind sector θ and exceed the threshold criteria (80 percentile), while n_θ is the total number of vectors that fall in same wind sector.

Air mass trajectory analysis was used to weekly PMF dataset in order to indentify possible source areas. The daily sector values were based on 96 h 2-dimensional 925 hPa backwards trajectories obtained by EMEP MSC-W (Stohl et al.,1995, http://www.emep.int/SR_data/index_sr.html 2.12.2010). The area around the arrival point was divided into 8 equal sectors. The criteria for allocation of trajectories to one sector was that at least 50% of trajectory points' given positions were found within that sector.

Then four to five weeks with the largest peak contributions, which did not overlap on each other, were selected for each factor for further study. The air mass trajectory sectors occurring (ca. 25) during these peaking weeks describe the source directions of the high factor contributions. The sector frequency distribution plots show the different source directions for each factor.

2.3.2 Concentration field method

The source receptor relationships of pollutants detected at Pallas were studied applying the concentration field method after Seibert et al. (1994). In this method the air mass backward trajectory statistics are combined with the high time resolution concentration data detected at the receptor site.

Briefly, eight EMEP Flextra 120h back-trajectories (Pallas as the endpoint) per day for a height of 500 m above ground level were superimposed on a $1° \times 1°$ geographical grid (Stohl et al., 1995; Stohl and Seibert, 1998). The 3hour-concentration mean measured at Pallas was then attributed to all grid cells crossed by the appropriate trajectory. And finally from all realizations, average concentration fields were calculated. A high concentration value in a grid cell means that, on average, air masses crossing over this cell result in high concentrations at Pallas measurement site.

3 Results

3.1 Sulphur and trace elements

The Russian copper-nickel industry at Nikel, Zapoljarniy and Monchegorsk on Kola Peninsula is an important anthropogenic source of sulphur dioxide and heavy metal emissions to the atmosphere within the Arctic and has influence on the ambient concentrations at Pallas, too. Historical emission estimates of metal emissions, in particular, on Kola Peninsula have suffered from significant deficiencies (Boyd et al. 2009; Prank et al., 2010). The emissions for 1994 have recently been re-assessed (Table 1; Boyd et al., 2009).

Table 1. Emission estimates of SO$_2$ and heavy metals (tonnes/a) in 1994 on Kola Peninsula (Boyd et al. 2009).

	SO$_2$	Ni	Cu	Co	As	Cd	Cr	Pb	V	Zn
Kola	296 000	1916	1097	92.1	6.3	0.9	11.8	13	43.7	27

SO$_2$, Ni and Cu are the prime pollutants emitted on Kola peninsula. Prank et al. (2010) estimate that SO$_2$ emissions in this region have been fairly constant throughout

the 1990s and 2000s; no reliable emission trend estimates of heavy metals are available.

Table 2 summarizes the trend analysis results of atmospheric sulphur dioxide and trace element concentrations at Pallas between 1996 and 2009.

Table 2. Results of the trend analysis of the trace element and SO_2 concentrations at Pallas in 1996-2009. Standard error is shown in parentheses. The yearly change is shown with its 95% confidence intervals.

Component	Start	n	Intercept ng/m^3	Slope ng/m^3 /month	Change %/year	Significance
SO2 (in µg/m^3)	01/96	168	0.8 (0.1)	-0.003 (0.001)	-4.4 ± 2.7	**
Aluminium	01/96	168	21.0 (2.6)	-0.021 (0.027)	-1.2 ± 3.0	-
Arsenic	01/96	168	0.3 (0.0)	-0.001 (0.000)	-4.3 ± 2.4	**
Cadmium	01/96	168	0.0 (0.0)	-0.000 (0.000)	-1.8 ± 3.0	-
Cobolt	01/96	168	0.0 (0.0)	-0.000 (0.000)	-1.2 ± 1.6	-
Chromium	01/96	168	0.1 (0.0)	-0.000 (0.000)	-2.1 ± 3.1	-
Copper	01/96	168	0.8 (0.1)	-0.003 (0.001)	-4.2 ± 2.5	**
Iron	01/96	168	25.8 (2.7)	-0.022 (0.027)	-1.0 ± 2.5	-
Manganese	01/96	168	0.7 (0.1)	-0.001 (0.001)	-1.7 ± 2.0	-
Nickel	01/96	168	0.6 (0.1)	-0.001 (0.001)	-2.4 ± 2.5	-
Lead	01/96	168	1.1 (0.1)	-0.002 (0.001)	-2.0 ± 3.0	-
Vanadium	01/96	168	0.5 (0.0)	+0.000 (0.000)	+0.5 ± 2.3	-
Zinc	01/96	168	1.9 (0.3)	+0.003 (0.003)	+1.8 ± 3.4	-

***; $p < 0.001$
**; $p < 0.01$
*; $p < 0.05$
-; $p > 0.05$

Sulphur dioxide had a distinctive seasonal variation (Figure 1) and also statistically significant decreasing trend -4% per year. Atmospheric concentrations of heavy metals have been monitored at Pallas since 1996 (weekly aerosol sampling, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn were analysed by ICP-MS at FMI). Trace metal concentrations typically varied a lot from year to year but only two statistically significant long term (i.e. fourteen years) trends were detected at Pallas (see Table 2); As and Cu concentrations decreased also by -4% per year between 1996 and 2009 (Figure 1). On the other hand Ni had weaker and insignificant decreasing trend.

Nevertheless, these results suggest that the sulphur and trace element load from the Kola peninsula to Pallas area has been slightly decreasing for the past fourteen years.
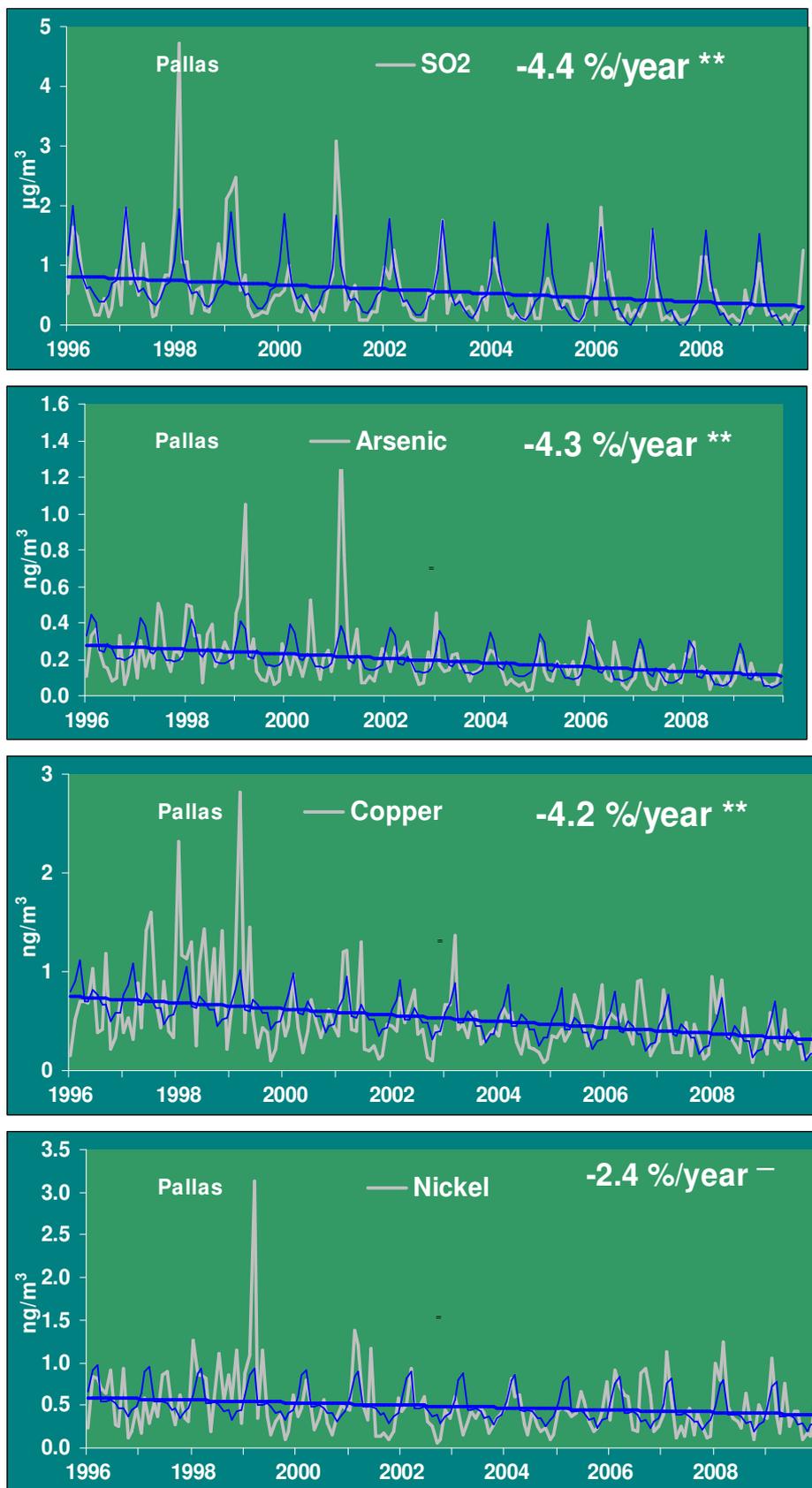
Figure 1. Monthly mean concentration (grey line) and estimated seasonal component and trend (blue lines) of SO$_2$, As, Cu and Ni at Pallas in 1996- 2009.

Highest concentrations of SO_2 detected at Pallas in 2009 were strongly associated to easterly and south-easterly air masses (Figure 2). In addition to the Kola peninsula area, the surroundings of White sea, Archangel region and Upper Volga areas west from Urals were origins of high SO_2 concentrations at Pallas in 2009.
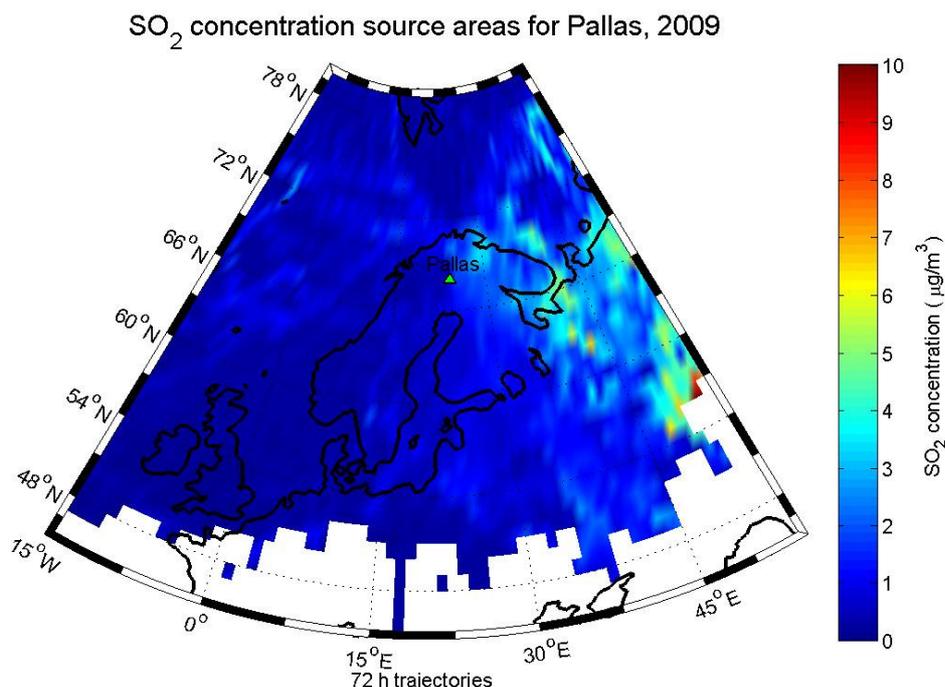

Figure 2. SO_2 concentration field for Pallas. Calculated from the hourly SO_2 concentrations in 2009. A high concentration value in a grid cell means that, on average, air masses crossing over this cell result in high concentrations at Pallas measurement site.

3.2 NO$_2$ and LRT inorganic particles

In contrast to SO_2, nitrogen dioxide NO_2 had no considerable source areas in Kola Peninsula in 2009. Instead the remote source areas in the densely populated continental Europe became highlighted (Figure 3). During the ten year measurement period at Pallas (1999-2009) the NO2 concentration have been seasonally cyclic without no long term trend (Figure 4). Of the long range transported secondary inorganic ions (SO_4, NO_3 and NH_4), only sulphate had a significantly decreasing trend (Table 3, Figure 4).

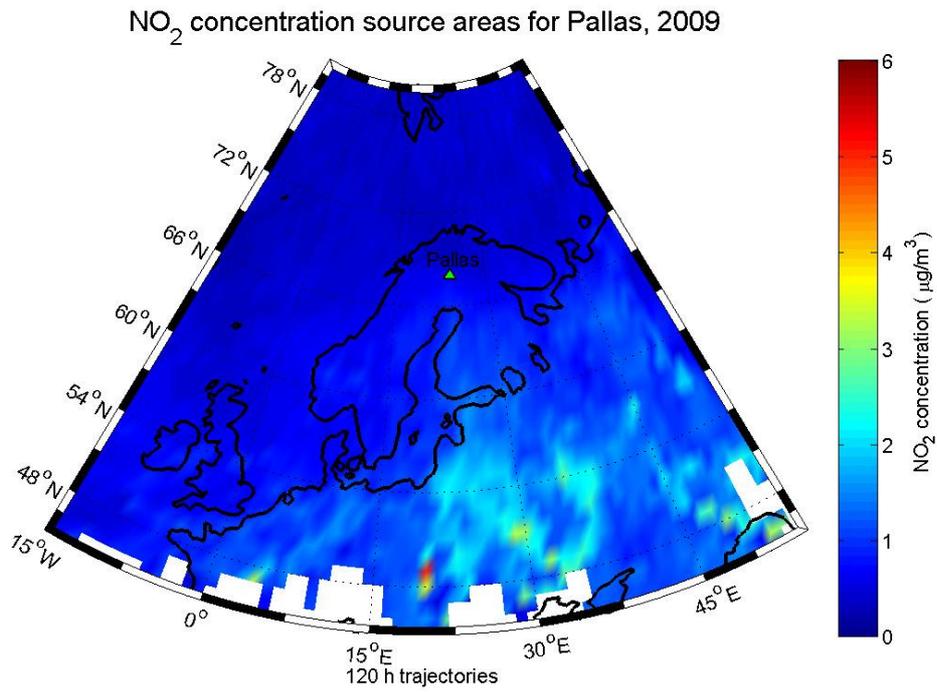NO₂ concentration source areas for Pallas, 2009

Figure 3. NO₂ concentration field for Pallas. Calculated from the hourly NO₂ concentrations in 2009. A high concentration value in a grid cell means that, on average, air masses crossing over this cell result in high concentrations at Pallas measurement site.
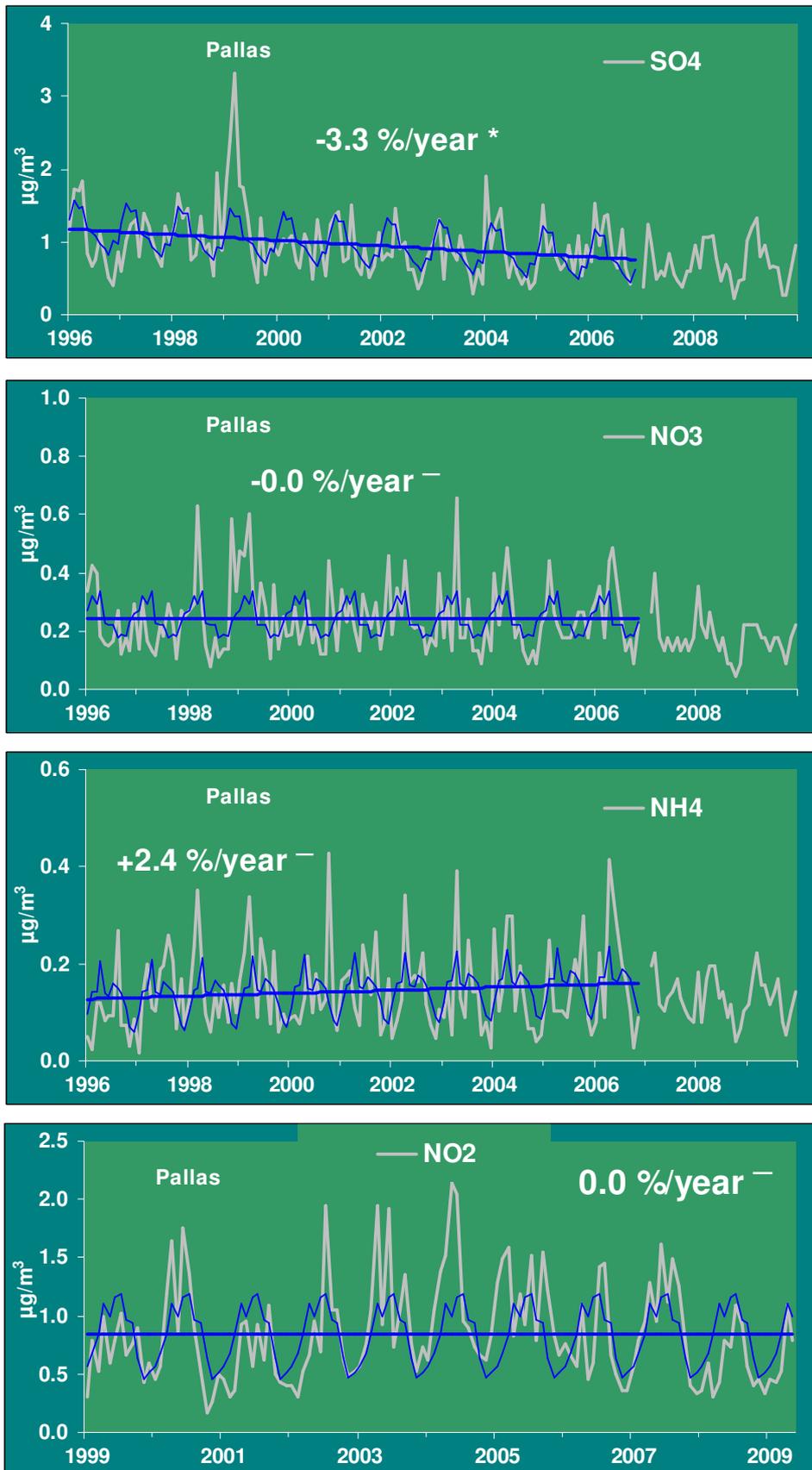
Figure 4. Monthly mean concentration (grey line) and estimated seasonal component and trend (blue lines) of SO4, NO3, NH4 in 1996- 2006 and NO2 in 1999-2009. (The sampling method of the SO4, NO3 and NH4 changed in 2007 and caused a break in the time series.)

Table 3. Results of the trend analysis of the LRT-ions SO$_4$, NO$_3$ and NH$_4$ concentrations at Pallas in 1996-2006 and NO$_2$ in 1999-2009. Standard error is shown in parentheses. The yearly change is shown with its 95% confidence intervals.

Component	Start	n	Intercept µg/m^3	Slope µg/m^3/month	Change %/year	Signific.
SO$_4$	01/96	132	1.18(0.115)	-0.003 (0.0015)	-3.3 ±3.0	*
NO$_3$	01/96	132	0.24(0.020)	+0.000 (0.0003)	+0.0 ± 2.5	-
NH$_4$	01/96	132	0.13(0.014)	+0.000 (0.0002)	+2.4 ± 3.5	-
NO$_2$	08/99	125	0.8 (0.1)	+0.000 (0.002)	+0.0 ± 4.5	-

3.3 Ozone and VOCs

Light molecular weight hydrocarbons (C$_2$-C$_6$) are common compounds in the atmosphere. The main source of light hydrocarbons is the combustion of fossil fuel. They are emitted into the air as a result of petrol exhaust and evaporation, stationary combustion, gas leaks, solvent use, etc. Some light hydrocarbons also have natural sources, for example isoprene is emitted in large quantities from several tree species (Kesselmeier et al., 1999 and the references therein).

In the atmosphere, reaction with the hydroxyl radical is the main sink reaction for all hydrocarbons and this reaction can result in ozone production when enough nitrogen oxide is present. Ozone formation takes place on various space and time scales. The fast-reacting compounds react close to their source areas, resulting in high ozone concentrations downwind, but slowly-reacting compounds can be transported far, particularly in winter when the amount of light, and hence hydroxyl radicals, is limited. The life-times of VOCs are presented in Table 4 together with the mean concentrations. During winter the VOCs accumulate in the northern latitudes, their concentration reaches a maximum during January-February and starts declining during spring when days get longer. Ozone formation can then occur in clean areas, and high ozone concentrations have been measured at high latitudes during spring (Laurila, 1999). Ozone concentrations have increased in Finland in the years 1990-2000, although a decreasing trend is observed in the other Nordic countries (Laurila et al., 2004; Solberg et al., 2005).

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Table 4. The mean winter and summer concentrations 1994-2009 (ppt) of some light hydrocarbons at Pallas together with average lifetimes in winter (Jan, Feb., Dec.)and in summer (June-Aug.) in relation to their dominant sink reaction with hydroxyl radical.

	life-times (days)		mean concentrations (ppt)	
	winter	summer	winter	summer
ethane	1097	37	2225	788
ethyne	346	12	613	81
propane	245	8	1195	122
benzene	214	7	209	28
2-methylpropane	121	4	277	20
butane	112	4	493	42
2-methylbutane	72	2	198	13
pentane	71	2	147	10
hexane	50	2	49	2

The air samples have been collected into evacuated stainless steel canisters twice a week during 1994-2009 at Pallas and the samples were sent to the laboratory for gas chromatographic analysis (Hakola et al., 2006). During the course of 16 years of VOC measurements, VOC emissions have decreased in Europe. According to the emission data reported to the Convention on Long-Range Transboundary Air Pollution (CLRTAP), non-methane hydrocarbon emissions have decreased 35% between the years 1988 and 2001 in Europe (Vestreng, 2003). A decreasing trend in the ambient concentrations would also be expected and it has been observed in many locations in Central Europe. For example at two EMEP sites, Waldhof and Košetice, the median VOC concentrations have decreased about 20-50% during the years 1993-2000 (Solberg et al., 2002). In the same report no trend was found for the Finnish sites Utö and Pallas.

Table 5 summarizes the trends in VOC concentrations and ozone at Pallas during 1994-2009. A downward trend of about 1%/year can be seen for most of the alkanes, benzene and ethyne, but the decreasing trend is significant for ethyne and pentane only (Table 5 and Figure 5). Ethane is the longest living compound and its concentration has not decreased. This could indicate a growth of VOC emissions in areas more distant than Europe.

Despite of VOC emission and concentration reductions in Europe, the ozone concentrations have not decreased.

Table 5. Results of the trend analysis of VOC and ozone concentrations at Pallas in 1994-2009. Standard error is shown in parentheses. The yearly change is shown with its 95% confidence intervals.

	Start	Months	Intercept ppt	Slope ppt/month	Change %/year	Significance
Ethane	01/94	192	1 543 (84)	-0.20 (0.75)	-0.2 ± 1.1	-
Propane	01/94	192	656 (25)	-0.40 (0.22)	-0.7 ± 0.8	-
Ethyne	01/94	192	386 (25)	-0.45 (0.23)	-1.4 ± 1.4	*
2-Met.-Propane	01/94	192	127 (9)	+0.01 (0.08)	+0.1 ± 1.4	-
n-Butane	01/94	192	263 (17)	-0.25 (0.15)	-1.1 ± 1.3	-
2-Methylbutane	01/94	192	92 (10)	+0.05 (0.09)	+0.6 ± 2.3	-
n-Pentane	01/94	192	74 (2)	-0.05 (0.02)	-0.8 ± 0.6	**
n-Hexane	01/94	192	24 (1)	-0.02 (0.01)	-1.0 ± 1.2	-
Benzene	01/94	192	129 (5)	-0.07 (0.05)	-0.6 ± 1.0	-
Ozone	03/94	190	72 (2)	-0.02 (0.02)	-0.4 ± 0.5	-

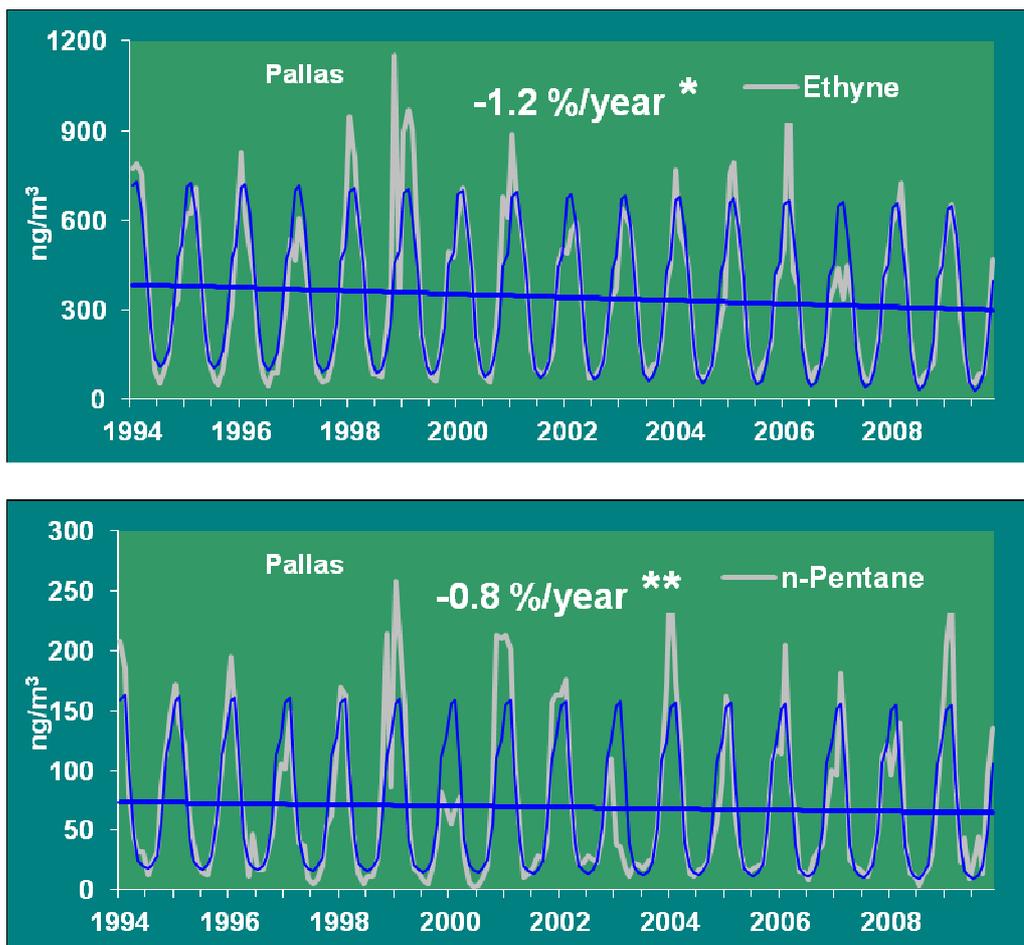***; $p < 0.001$

**; $p < 0.01$

*; $p < 0.05$

-; $p > 0.05$

Figure 5. Monthly mean concentration (grey line) and estimated seasonal component and trend (blue lines) of selected VOCs at Pallas in 1994-2009.

3.4 POPs and PAHs

Persisted organic pollutants (POPs) are man-made organic compounds, which are stable in the nature for a long time without or with only minor degradation. Consequently they have accumulated into the ecosystems, even though the use of most of these have been banned or restricted since 1970's, 80's and 90's in almost all countries. Because of their long half-lives in soil, water and in air, POPs can be transported to arctic areas from long distances.

Depending on the temperature, these species can be in a gas phase or attached into the particles. During cold winter periods, most of the POPs are in particle phase, whereas during summer most volatile of these compounds exist in gas phase. Organic pollutants are transported into the Arctic via air and also within sea currents and

migratory birds. The atmospheric transport is probably the most important transfer route for POPs (AMAP, 2004).

POPs belong to several groups which can be classified according to their use or origin. Except for the PAHs, all POP compounds in this report are halogenated, mainly with chlorine. Despite of their different chemical structures and other properties, the common characteristics for all these are low water solubility and high lipophilicity with long resistance times for degradation in air and soil. Because of these characteristics, these compounds tend to accumulate into the fat tissues of animals and eventually into humans on the top of the food chain (AMAP, 2004).

Polycyclic aromatic hydrocarbons (PAHs) are particularly harmful compounds among the anthropogenic aerosols due to their carcinogenic effect on humans. PAHs are formed during incomplete combustion of organic material, and are emitted into the atmosphere from several natural and anthropogenic emission sources. These compounds can exist in both gas and particulate phases in the atmosphere. Lighter, high-volatile PAH compounds consisting of two or three aromatic rings exist in the gas phase, whereas heavier compounds with more aromatic rings are incorporated into particles in the atmosphere. Benzo(a)pyrene (BaP) is a PAH marker for the carcinogenic risk of PAH-compounds in ambient air and the limit values are set for benzo(a)pyrene.

Natural PAH sources include emissions from volcanic activity and forest fires, whereas anthropogenic sources consist of fossil fuel and biomass burning (Ravindra et al., 2008). Wood combustion, especially in residential heating is a significant PAH source in Northern Europe (Hellen et al., 2008). Long-range transport also has a significant effect on the air quality of the Nordic countries (EMEP, 2008).

Hexachlorobenzene (HCB) was used in 1960's as fungicide. It is produced as a by-product in the production of chlorinated compounds. Other sources of HCB include waste incinerators and metallurgical industry. HCB's half-life has been estimated as 2.7-5.7 years (Howard 1991).

Polychlorinated biphenyls (PCBs) are classified as probable carcinogens and their production and use is banned in U.S. and Europe. PCBs are released to the environment from hazardous waste sites; illegal or improper disposal of industrial wastes and consumer products; leaks from old electrical transformers containing PCBs; landfills and burning of some wastes in incinerators (ATSDR, 2000). These activities occur primarily in urban areas suggesting that these areas are likely to be significant sources of PCBs (Yi et al., 2008).

Dichlorodiphenyltrichloroethane (DDT) has been widely used in agriculture to control insects on cotton, fruit, and corn. The use of DDT is banned in Western countries, but it has still limited use as insecticide in developing countries. Dichlorodiphenyldichloroethane (DDE) and Dichlorodiphenyldichloroethylene (DDD) are the breakdown products of DDT which, along with DDT, are now commonly found in the environment (ATSDR, 2002).

Polybrominated diphenyl ethers (PBDEs) are used as flame-retardants that are added to plastics and foam products. These compounds are structurally related to PCBs, but with the bromine substituents instead of chloride. Because they are mixed into plastics and foams rather than bound to them, PBDEs can leave the products that contain them and enter the environment (ATSDR, 2004).

Hexachlorocyclohexanes α-HCH, β-HCH and γ-HCH (lindane) have been used as insecticides on hardwood logs and lumbers, seeds, vegetables and fruits. Other isomers than lindane have been banned in the U.S. and Europe since 1970's and production of lindane was banned as late as in 2009 in Stockholm convention (UNEP, 2009). Lindane has a half-life of 2.3 to 13 days in air and two years in soil (UNEP, 2005). HCH's , due to their low Henry's law constants, tend to accumulate into the aquatic environment (Li et al., 2002).

Chlordane has been used as a pesticide to control termites and as a broad-spectrum insecticide on a range of agricultural crops. Chlordane remains in the soil for a long time and has a reported half-life of one to four years. Chlordanes are more volatile compared to other chlorinated pesticides and therefore they are easily evaporated from

water and soil. Chlordane was banned in 1980's except the use of termite control (ATSDR, 1994).

3.4.1 Source apportionment with PMF

Weekly samples

Long term monitoring of POPs and PAHs at Pallas has been carried out in co-operation with Swedish Environmental Research Institute, IVL (Brorstöm-Lunden et al., 2010; Hung et al. 2010). FMI is responsible for the maintenance of the sampling site and IVL processes and analyses the samples. Weekly POP and PAH samples (one week/month) from 1996 to 2009 were collected using quartz filters following polyurethane foam filter (PUF) collection in high volume sampler. In this way, both gas and particle phases were collected. Both filters and plugs were processed and analyzed in IVL's laboratory using soxhlet extraction and gas- and liquid chromatographs with mass spectrometers (Brorstöm-Lunden et al., 2010).

Measurement data of inorganic gases and major ions, trace elements and PM_{10} are used here as supportive material. Filter packs were used on a daily basis for sampling of SO_4-S, SO_2-S, Na, K, Ca, Mg, (NH_3+NH_4)-N and (HNO_3+NO_3)-N in air according to the EMEP manual (EMEP, 1996). These samples were analysed by ion chromatography. Trace elements were collected weekly on teflon filters and analyzed by ICP-MS. SO_2 was monitored with a UV fluorescence analyser (TEI43CTL), NO/NO_2 with a chemiluminescence NO-NO_2-NO_x analyser (TEI42CTL) and O_3 with a UV absorption analyser (TEI49C). Particulate matter mass (PM_{10}, diameter <10 µm and $PM_{2.5}$, diameter <2.5µm) was monitored with a beta attenuation analyser (Thermo-ESM-Andersen FH62I-R).

Positive matrix factorization was applied to the complete weekly dataset between 1996-2009 so that analogous weekly time series were compiled from the supportive inorganic components.

PMF-analysis of weekly samples yielded five potential source factors. Factor 1 is presented in Figure 6. F1 contained large amounts of trace elements; 71% of As, 72%

Ni, 67% Cu, 66% Pb, 67% V, 59% Zn and also 87% of gaseous SO_2, i.e., pollutants which are characteristic to the industries in Kola peninsula (see also Table 1). According to the trajectory sector analysis air masses in high contribution weeks for this factor came most often from east (Figure 6). So during the study period 1996-2009 at Pallas the trace element and SO_2 pollution load have been strongly connected to each other and the source profile and the air mass trajectory analysis suggest that the industry in Kola peninsula was the major source. Also some of the heavier PAHs (e.g. benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene; 30-40%) could be related to this source, but no remarkable amount of organochlorines. The relatively high contribution of DDD (30%), compared to DDT and DDE, in this factor remains unclear.
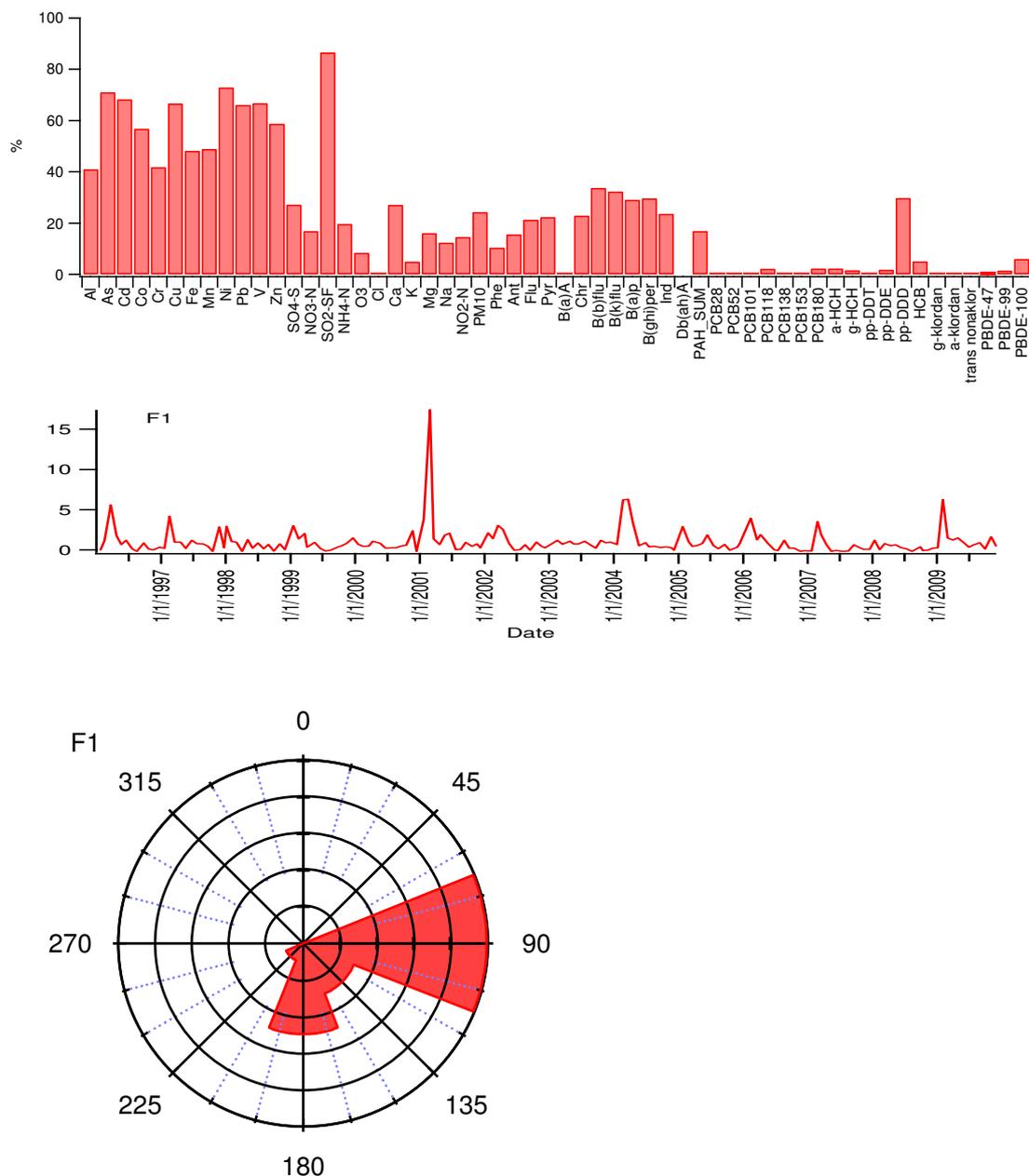
Figure 6. Factor profile, source contribution time series and trajectory sector distribution plot for weekly factor 1.

Factor 2 contained 62% and 69% of the insecticides a-HCH and g-HCH (lindane), respectively (Figure 7). Interestingly, the factor also contained 33% of potassium which may be an indication of a biogenic source. Also the systematically high summer contribution of the factor (see Figure 7) and the lack of any specific source direction could refer to a biogenic related source. This factor had a decreasing trend, which probably was due to the reduction of the production and use of these compounds in many countries (Li et al., 2004) and the slow extinction of these pollutants from the ecosystems.
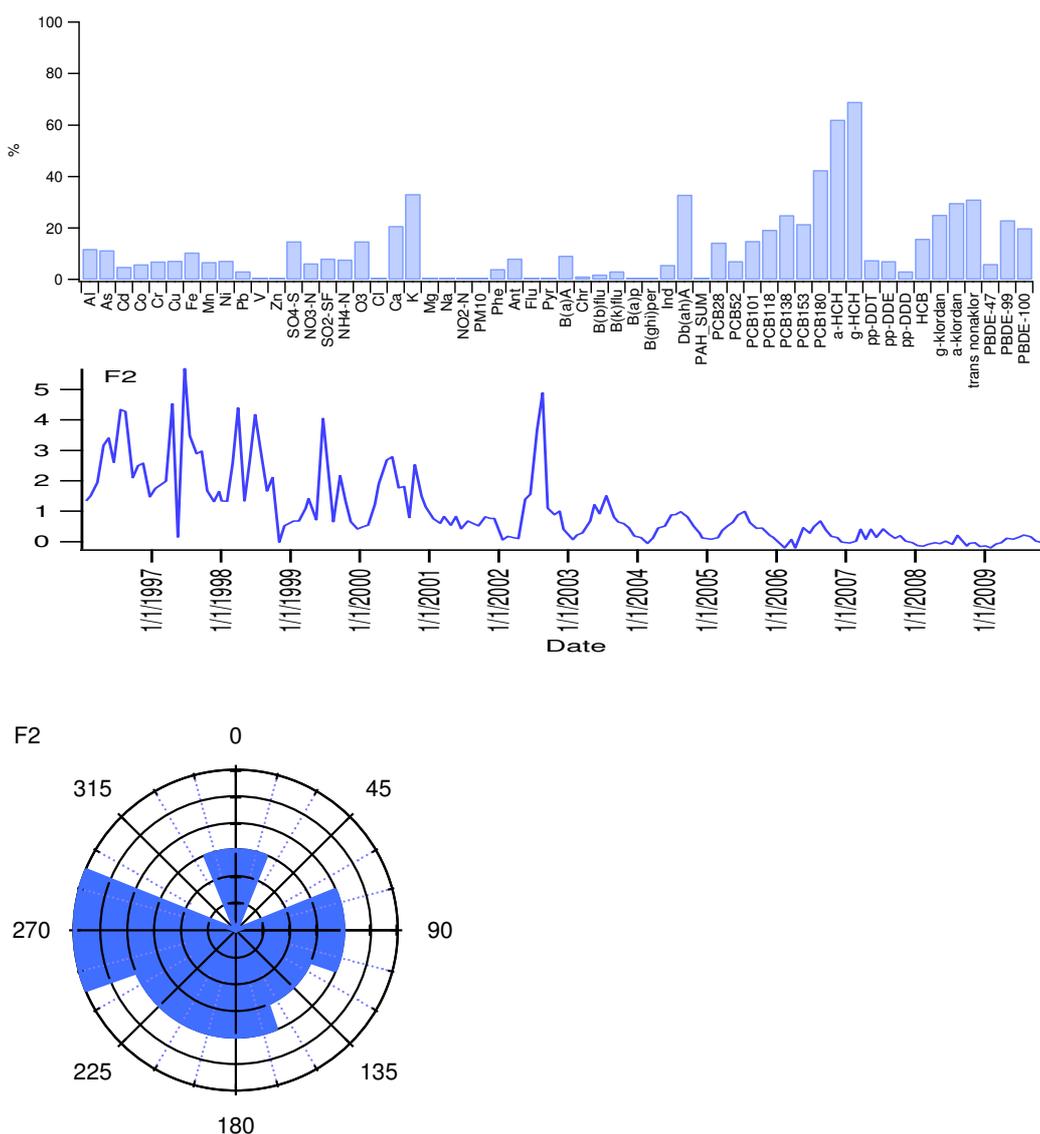
Figure 7. Factor profile, source contribution time series and trajectory sector distribution plot for weekly factor 2.

Factor 3 contained 100% of Cl with 88% of Na and 85% of Mg which made it a clear sea spray factor (Figure 8). Interestingly, also 62% of the mass of PM_{10} was associated to this factor, i.e., on average during the study period 1996-2009 a major fraction of PM_{10} detected at Pallas was related to maritime air masses and sea salt particles. This factor had no clear seasonal variation and the source direction was the Arctic and the Northern Atlantic sea. However, 73% of HCB as well as majority of other organochlorine compounds were associated with this factor as well as about 30% of the high-volatile light PAH components.
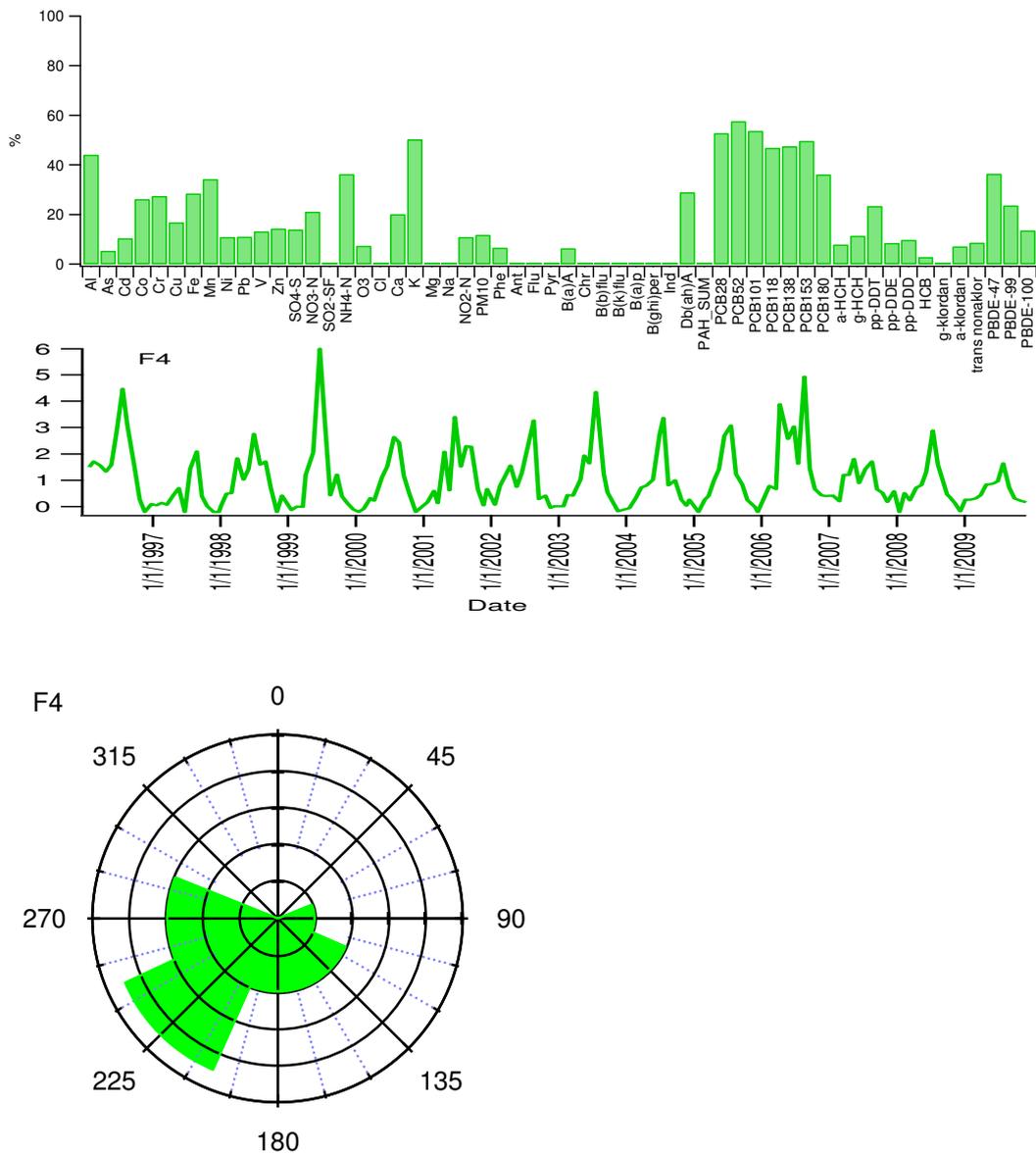
Figure 8. Factor profile, source contribution time serie and trajectory sector distribution plot for weekly factor 3.

The fourth factor collected 44% of aluminium and 28% of manganese as well as 36% of total ammonium and half of potassium, and the factor had a systematic summer maximum (Figure 9). Thus it can be concluded to be a combination of soil and biogenic sources. Also, approximately half of the PCBs fell to this factor, evidently due to contaminated soil and biogenic particles and/or evaporation from the soil (Yi et al., 2008). According to the trajectory sector distribution plot the air masses related to this factor originated mainly from south and west.

Figure 9. Factor profile, source contribution time serie and trajectory sector distribution plot for weekly factor 4.

The next factor (Figure 10) included half of all PAHs and as much as 47% of NO_2. The factor contribution was highest in winter and the dominating source direction was south and southwest. The high loading of NO_2 and long range transported nitrate and ammonium particles (47% and 33%, respectively) may refer to reasonably remote traffic sources.

Also 37% of DDT and 69% of DDE, which is the DDT's degradation product, entered into this factor. High contribution of DDT and DDE the most likely consequence of long-distance transfer of air masses from the southern areas, where DDT is still in use (ATSDR, 2002).
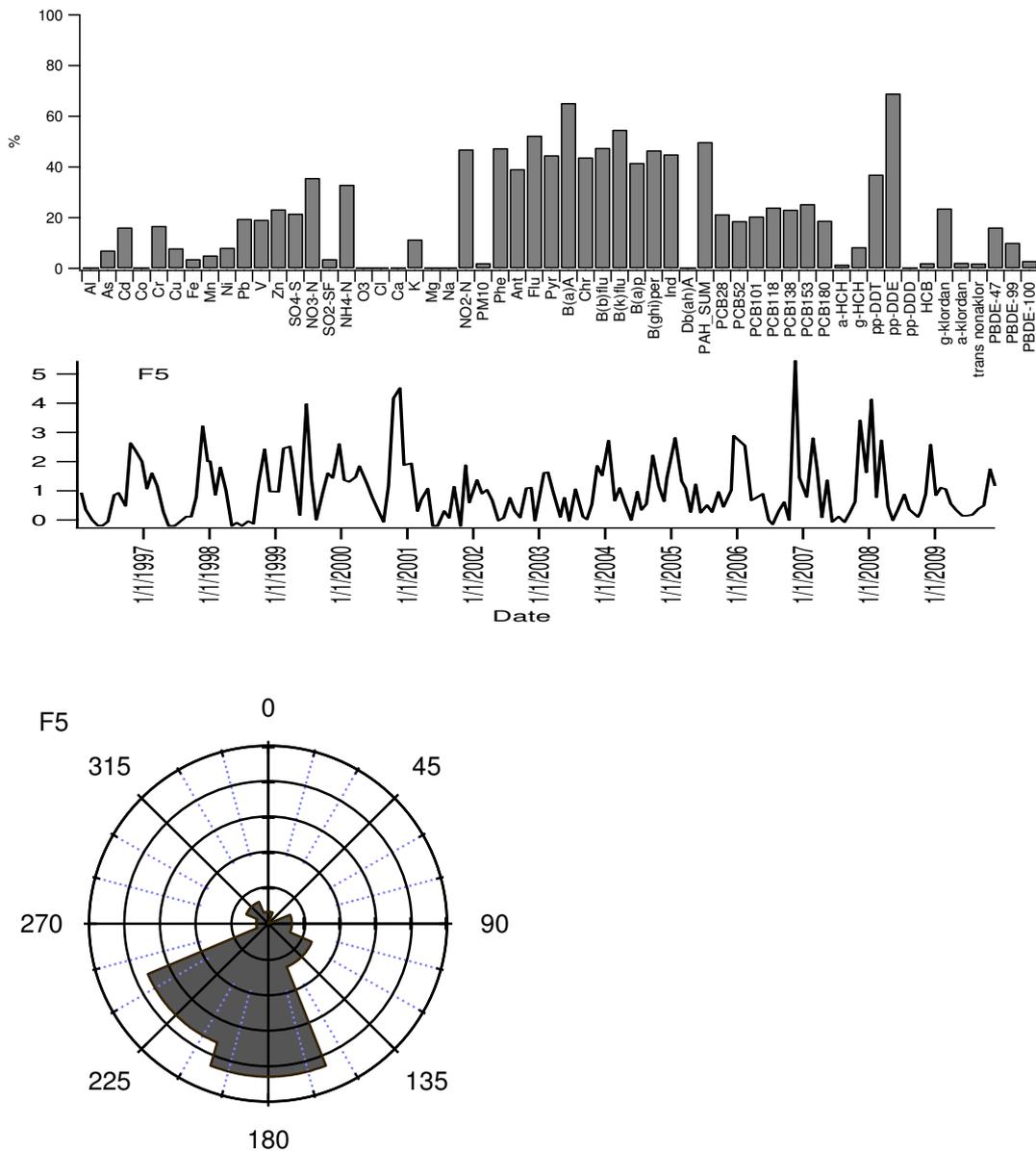
Figure 10. Factor profile, source contribution time serie and the trajectory sector distribution plot for weekly factor 5.

Daily data

FMI carried out daily PM_{10} PAH-collection for every third day between 1 January and 12 June 2010 at Pallas station. Daily PAH samples from PM_{10} teflon filters were processed and analyzed at FMI's air chemistry laboratory using soxhlet extraction and gas chromatograph-mass spectrometric analysis method. Online gas data and inorganic data were incorporated into the daily PAH dataset in order to resolve emission sources. Using daily data, three potential source factors were identified.

Factor 1 contained the majority (90%) of total PAHs and 54% of black carbon (Figure 11). As much as 59% of K was also associated to this factor, so compared to the long term weekly data (see factor 5 in Figure 10), this daily data suggests stronger association between K and PAHs. The source direction (south) and reasonably high contribution of nitrate and ammonium were analogous to the weekly factor 5. This suggests that in addition to the traffic sources, wood combustion may also have effect on the PAH concentrations detected at Pallas.
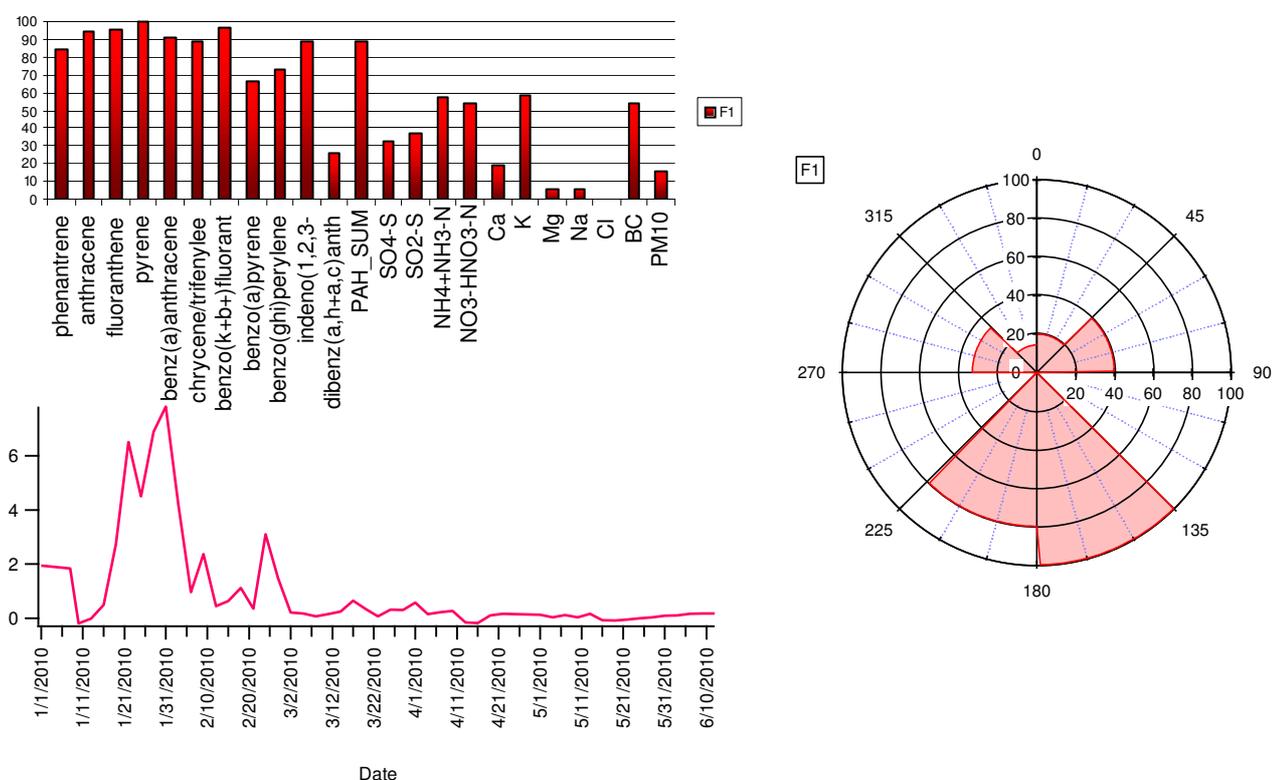

Figure 11. Factor profile, CPF plot and source contribution for daily factor 1.

The second factor (Figure 12) represents the easterly sulphur source (contains 62% of SO_2) which was detected in the weekly long term analysis too (see factor 1 in Figure 6). This factor has also high contribution of LRT particles SO_4, NO_3 and NH_4 (63%, 36% and 41%, respectively) so this short term daily data with limited component matrix fails to discern as clearly the fresh emissions from Kola peninsula. In this analysis most (76%) of PM_{10} mass is related to this factor which suggests that LRT major ions were a significant contributor to PM_{10} during this short study period.
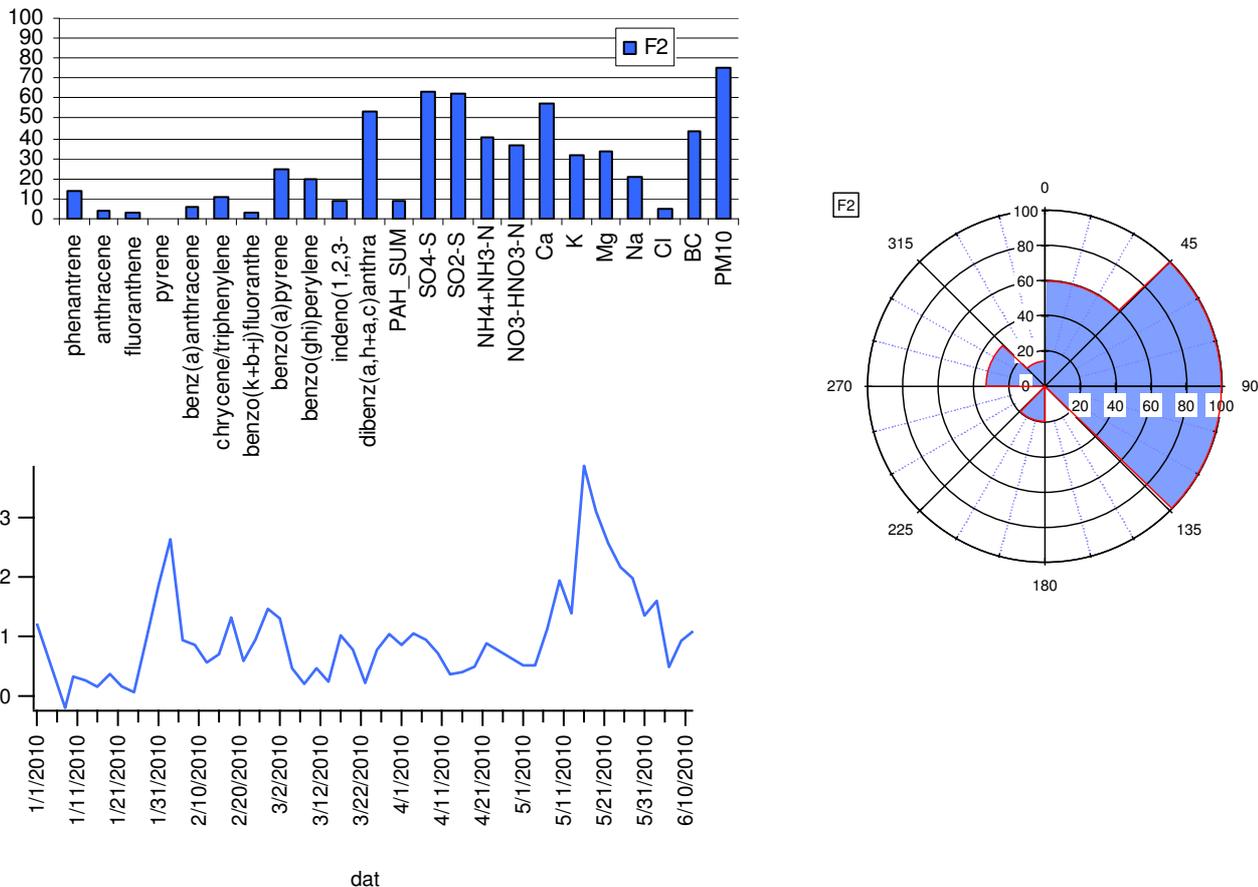
Figure 12. Factor profile, CPF plot and source contribution for daily factor 2.

The last factor (Figure 13) was clearly the sea salt factor with 95%, 74% and 61% contribution of Cl, Na and Mg. Compared to the long term weekly analysis (see Figure 8) this study period may represent a period of clear maritime air masses as contributions of e.g. PAHs in this factor are lower.
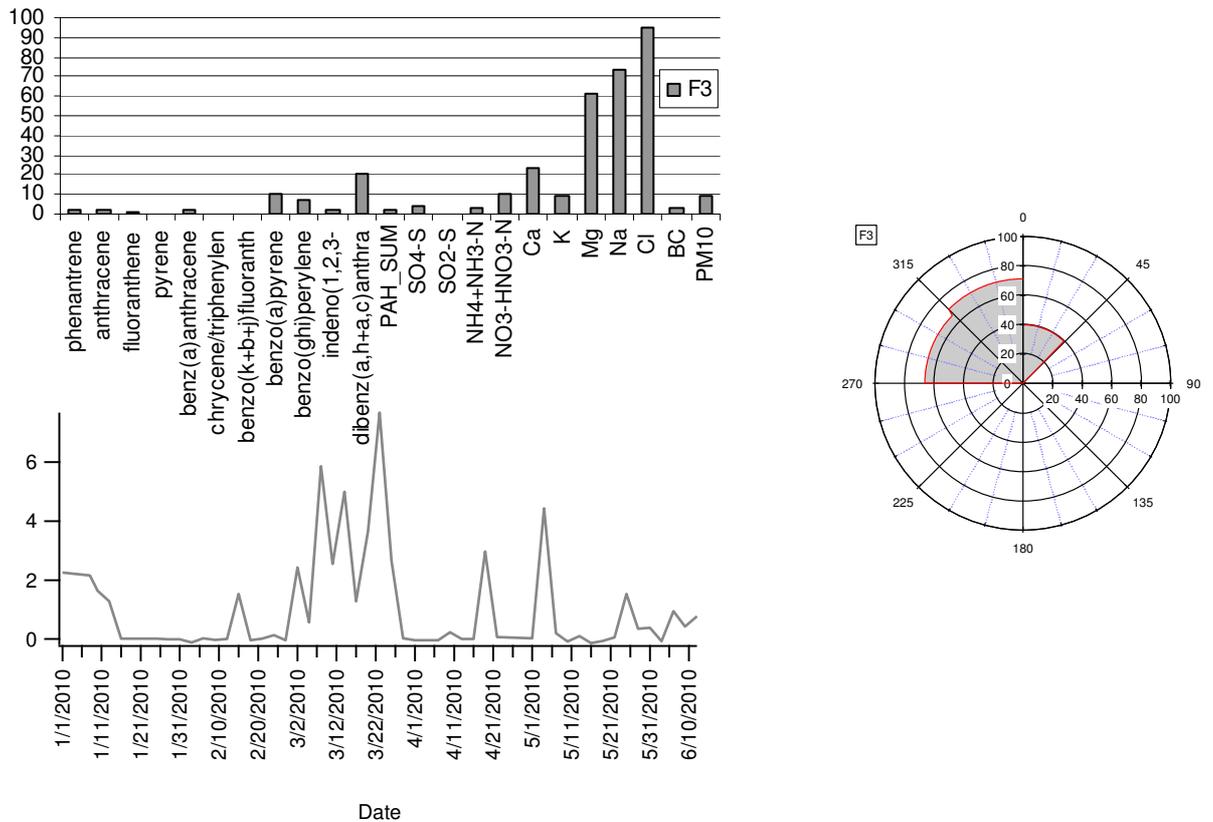
Figure 13. Factor profile, CPF plot and source contribution for daily factor 3.

3.4.2 Trend analysis

POPs

Results of the POP trends analyses from 1996 to 2009 are shown in Table 6. The majority of the POP compounds have been on decrease (significant or in-significant) during the past 14 years. However, some unfavourable exceptions from this mainstream were also detected.

Table 6. Results of the trend analysis of POP concentrations at Pallas in 1996-2009. Standard error is shown in parentheses. The yearly change is shown with its 95% confidence intervals.

POP	Start	Months	Intercept pg/m^3	Slope pg/m^3/month	Change %/year	Sign.
PCB28	01/1996	168	2.43 (0.28)	-0.0054 (0.0028)	-2.7 ± 2.7	-
PCB52	01/1996	168	2.05 (0.18)	-0.0020 (0.0018)	-1.2 ± 2.1	-
PCB101	01/1996	168	1.18 (0.10)	-0.0031 (0.0011)	-3.1 ± 2.1	**
PCB118	01/1996	168	0.43 (0.05)	-0.0015 (0.0005)	-4.2 ± 2.6	**
PCB138	01/1997	156	0.39 (0.03)	-0.0012 (0.0004)	-3.6 ± 2.1	**
PCB153	01/1997	156	0.43 (0.03)	-0.0012 (0.0004)	-3.3 ± 1.9	**
PCB180	01/1997	156	0.14 (0.01)	-0.0006 (0.0001)	-5.6 ± 1.4	***
a-HCH 1996-2000	01/1996	60	26.64 (2.92)	-0.1963 (0.0809)	-8.8 ± 7.1	*
a-HCH 2002-2009	01/2002	96	14.65 (0.56)	-0.1198 (0.0112)	-9.8 ± 1.8	***
g-HCH 1996-2000	01/1996	60	11.54 (0.56)	-0.0347 (0.0176)	-3.6 ± 3.6	*
g-HCH 2002-2009	01/2002	96	5.68 (0.50)	-0.0571 (0.0090)	-12.1 ± 3.7	***
pp-DDT 1996-2000	01/1996	60	0.24 (0.05)	+0.0005 (0.0015)	+2.6 ± 14.9	-
pp-DDT 2002-2009	01/2002	96	0.16 (0.04)	+0.0003 (0.0008)	+2.6 ± 11.6	-
pp-DDE 1996-2000	01/1996	60	0.46 (0.15)	+0.0080 (0.0043)	+20.9 ± 22.3	-
pp-DDE 2002-2009	01/2002	96	0.54 (0.05)	+0.0002 (0.0009)	+0.4 ± 4.0	-
pp-DDD 1996-2000	01/1996	60	0.48 (0.13)	-0.0101 (0.0038)	-25.5 ± 18.6	*
pp-DDD 2002-2009	01/2002	96	0.03 (0.04)	+0.0019 (0.0008)	+74.2 ± 60.8	*
g-chlordan 1996-2000	01/1996	60	0.39 (0.04)	-0.0015 (0.0011)	-4.7 ± 6.4	*
g-chlordan 2002-2009	01/2002	96	0.35 (0.01)	-0.0019 (0.0002)	-6.4 ± 1.4	***
a-chlordan 1996-2000	01/1996	60	0.77 (0.08)	+0.0021 (0.0022)	+3.2 ± 6.7	-
a-chlordan 2002-2009	01/2002	96	1.13 (0.04)	-0.0075 (0.0008)	-8.0 ± 1.6	***
trans nonachlor 96-00	01/1996	60	0.72 (0.04)	-0.0031 (0.0010)	-5.2 ± 3.3	**
trans nonachlor 02-09	01/2002	96	0.68 (0.07)	-0.0034 (0.0013)	-6.0 ± 4.5	**
PBDE-47	01/2004	72	0.63 (0.08)	-0.0039 (0.0019)	-7.4 ± 7.0	*
PBDE-99	01/2004	72	0.90 (0.15)	-0.0097 (0.0036)	-12.9 ± 9.4	**
PBDE-100	01/2004	72	0.13 (0.02)	-0.0011 (0.0005)	-10.3 ± 9.2	*

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For all PCB compounds, trend analysis showed decreasing trends through the whole 14 years period. The annual decreases of PCB concentrations varied between -1% to -6% per year (Table 6, Figure 14). This may be due to the fact that the production and use of PCB compounds is prohibited in Europe. In the source apportionment (see factor 4 in Figure 9) PCBs were associated to the contaminated soil, biogenic particles and/or evaporation from the soil, thus the decreasing trends may also reflect the slow degradation of these contaminants from the reservoirs of the ecosystems.

α- and γ-HCH's also had substantial decreasing trends, -10% and -12%, respectively, (Table 6). Also trends of α- and γ-chlordans and nonachlor were decreasing. PBDEs were decreasing substantially, even though the usage of flame retardants has not been banned, and if anything, the usage has more likely been growing. The concentrations of PBDE's at Pallas had decreasing trends from -7% to -13% per year.
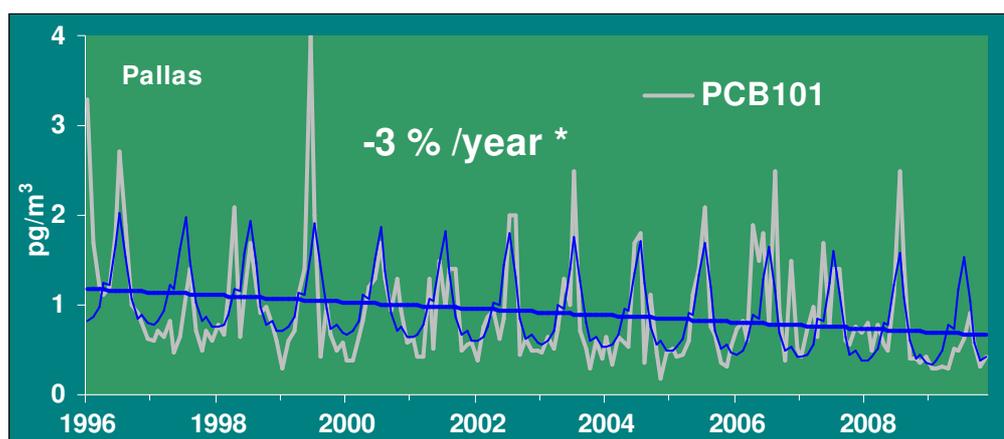

Figure 14. Monthly mean concentration (grey line) and estimated seasonal component and trend (blue lines) of PCB101 at Pallas in 1996-2009.

However, the concentrations of DDT and its breakdown products DDD and DDE behaved differently from the rest of the POPs; their concentrations were rather on increase. Trends for DDE varied from +21% for years 1996-2000 to +0.4% for 2002-2009, but these trends were insignificant. DDD has even more variability with significant trends from -26% in 1996-2000 to +74% in years 2002-2009.

PAHs

All PAH compounds had decreasing trends (majority though insignificant) from 1996 to 2009 (Table 7). As a result the sum of all measured PAH-compounds in air was

decreasing with -1,8% per year (in-significant) (Figure 15). Fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene and indeno(cd)pyrene had significant decreasing concentration trends between -2% and -4%. In the source apportionment these latter PAH components had reasonably high loadings in the Kola Peninsula factor with SO_2 and trace elements (see Figure 6), so the stronger decreasing trends of these compounds may be related to the emission changes in the Kola peninsula industries.
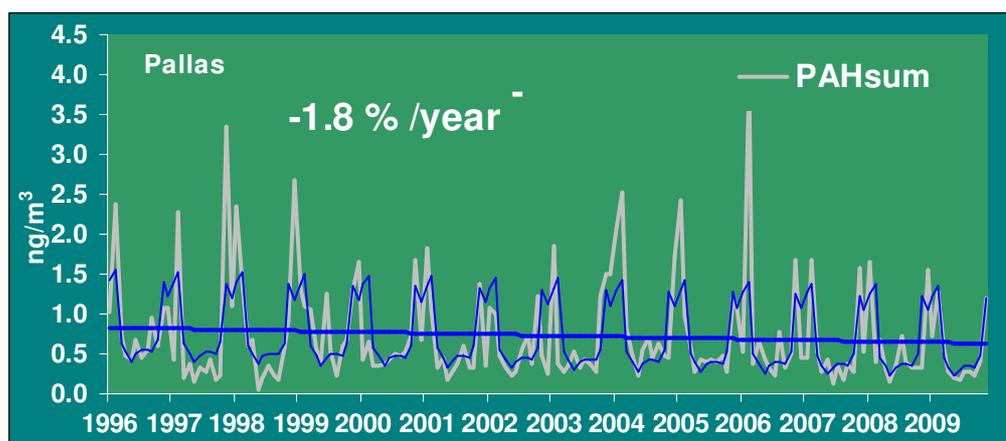

Figure 15. Monthly mean concentration (grey line) and estimated seasonal component and trend (blue lines) of PAHsum at Pallas in 1996-2009.

Table 7. Results of the trend analysis of PAH concentrations at Pallas in 1996-2009. Standard error is shown in parentheses. The yearly change is shown with its 95% confidence intervals.

PAH	Start	Months	Intercept ng/m^3	Slope ng/m^3/month	Change %/year	Signific.
Phenanthrene	01/1996	168	0.37 (0.03)	-0.00005 (0.00030)	-0.2 ± 1.9	-
Anthracene	01/1996	168	0.01 (0.00)	-0.00002 (0.00002)	-3.8 ± 6.1	-
Fluoranthene	01/1996	168	0.15 (0.01)	-0.00028 (0.00014)	-2.2 ± 2.1	*
Pyrene	01/1996	168	0.08 (0.01)	-0.00012 (0.00009)	-1.8 ± 2.5	-
Benzo(a)anthracene	01/1996	168	0.04 (0.01)	-0.00014 (0.00010)	-4.2 ± 5.7	-
Chrysene	01/1996	168	0.05 (0.01)	-0.00005 (0.00007)	-1.3 ± 3.5	-
Benzo(b)fluoranthene	01/1996	168	0.04 (0.01)	-0.00015 (0.00005)	-4.2 ± 3.0	**
Benzo(k)fluoranthene	01/1996	168	0.02 (0.00)	-0.00005 (0.00002)	-3.9 ± 3.4	*
Benzo(a)pyrene	01/1996	168	0.02 (0.00)	-0.00002 (0.00005)	-1.2 ± 6.0	-
Benzo(ghi)perylene	01/1996	168	0.02 (0.00)	-0.00005 (0.00003)	-2.9 ± 3.5	-
Indeno(cd)pyrene	01/1996	168	0.02 (0.00)	-0.00008 (0.00003)	-3.8 ± 3.2	*
Dibenzo(a,h)anthracene	01/1999	132	0.00 (0.00)	-0.00000 (0.00001)	-0.6 ± 6.7	-
PAHsum	01/1996	168	0.83 (0.07)	-0.0012 (0.0007)	-1.8 ± 2.1	-

4 Summary

This report summarizes the developments and major sources of the atmospheric pollution load detected at the Pallas measurement station since the middle of the 1990's. This site represents well the remote and pristine boreal and sub-arctic Eurasian environments. However, the signals of regional and global pollution were detectable in this study.

The Russian copper-nickel industry on Kola peninsula is an important anthropogenic source of sulphur dioxide and heavy metal emissions to the atmosphere within the Arctic and still has influence on the ambient concentrations at Pallas, too. However, these results suggest that the sulphur and trace element load from the Kola peninsula to Pallas area has been slightly decreasing for the past fourteen years. Also the long-range transported sulphate has been decreasing during the study period. For nitrogen compounds the situation is not as good, no trends were detected for the nitrogen dioxide, nitrate and ammonium. For NO$_2$ the densely populated continental Europe was identified to be the dominating source area.

Consequently, related to the traditional pollutants this remote site mirrors the development of the pollution management in Europe. The sulphur related pollution

has been successfully turned to decreasing development path while the major efforts to reduce nitrogen dioxides' emission has not resulted the desired decrease in the regional NO_2 or NO_3 . However, it is worth to note that the present sulphur load at Pallas is dominated by eastern source areas (both reasonably close and more remote) and the site will be influenced by all potential changes in the emissions of these source regions.

Ozone is an example of regional, or rather global, pollution; the ozone concentrations detected at Pallas have remained at the high level typical to these high latitudes in the northern hemisphere. In spite of effective VOC emission reductions in Europe, at Pallas, only the concentrations of the faster reacting compounds have decreased.

The concentrations of PAH compounds have been stable or weakly decreasing since the mid 1990's at Pallas. Some of the heavier PAHs were partly associated to the Kola peninsula industrial sources, these were also the ones with significant decreasing trends. However, majority of the PAHs arrived at Pallas with southern or south western air masses associated with NO_2 and NO_3, and thus suggesting that traffic exhaust is the dominating source.

Regarding the other POP compounds the global trend has been to reduce the production and use of these harmful compounds. This has resulted also an eligible development in the concentrations detected at Pallas; the majority of POP concentrations were decreasing. These compounds were strongly related to soil, biota and water sources so it is evident that the slow extinction of these pollutants from the ecosystems is underway. However, there was one exception in this positive development; the concentrations of DDT and its breakdown products DDD and DDE behaved differently from the rest of the POPs; their concentrations were rather on increase.

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