

Comparison of atmospheric concentrations of sulphur and nitrogen compounds, chloride and base cations at Ähtäri and Hyytiälä, Finland

Tuija Ruoho-Airola

Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland

Received 7 Apr. 2011, final version received 25 July 2011, accepted 20 June 2011

Ruoho-Airola, T. 2012: Comparison of atmospheric concentrations of sulphur and nitrogen compounds, chloride and base cations at Ähtäri and Hyytiälä, Finland. *Boreal Env. Res.* 17: 128–138.

Seven-year (2003–2009) time series of atmospheric SO_2 , SO_4^{2-} , NO_3^- , NH_4^+ and Cl^- concentrations as well as four-year time series of atmospheric Na^+ , K^+ , Ca^{2+} and Mg^{2+} concentrations from Ähtäri and Hyytiälä background stations in southern Finland, located within 85 km of each other were compared. At Ähtäri the air sampler was located in a clearing within a young forest, while at Hyytiälä it was within dense forest stands. Pearson's correlations between the time series were very strong ($r_p \geq 0.9$) for SO_2 , SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- and Ca^{2+} , strong ($r_p > 0.8$) for Na^+ and Mg^{2+} and weak ($r_p = 0.65$) for K^+ . The concentrations recorded at Hyytiälä were on average 0.8–1.0 times those at Ähtäri, although for K^+ and Ca^{2+} the ratios were higher. The GLS-ARMA method used takes into account the seasonal behaviour and serial correlation in the air quality time series, which revealed similar seasonal and temporal behaviour for S and N compounds and Cl^- at both stations. As a result of the dense seasonalization of the time series, the part of the data heavily influenced by local agricultural sources could be identified. This enables elimination of the minimal part of the data affected and the use of the remaining data for further studies on a more regional level.

Introduction

A decade-long, continuous time series of air pollutants would be ideal for investigating changes in air quality patterns. However, studies typically suffer from shorter monitoring periods and a lack of continuity in the measurement procedures. Stations are often relocated because the focus of research alters or changes take place in the local emission pattern. Old monitoring activities are then terminated and new ones started in different locations. When data from a sufficiently long parallel measurement period are available,

the comparison of time series helps in deciding whether the original time series might be continued with that from the new monitoring activity.

The levels of harmful atmospheric sulphur and nitrogen compounds are currently low at the Finnish background stations as compared with those in many areas in Europe (Ruoho-Airola *et al.* 2004, Anttila and Tuovinen 2009, Hole *et al.* 2009). The main contributor to Finnish air quality in remote areas is long-range transport (LRT) from different parts of Europe (Nyíri *et al.* 2010). The fairly sparse network in the large but rather flat country can reveal the general pattern

of air quality in background areas, but regional variation might remain more uncertain. Two seven-year time series of atmospheric monitoring data collected with the same methods from the stations at Ähtäri and Hyytiälä in southern Finland, located 85 km apart, offer a possibility to examine the regional differences in this area. Since the 1970s, Ähtäri has been among the first stations with continuous air-pollution monitoring in Finland (Kulmala *et al.* 1982), whereas Hyytiälä, as a SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relations) station, currently covers a wide programme of air quality and ecosystem measurements (Kulmala *et al.* 2001). Thus, it would be beneficial if at least part of the air quality time series from these stations could be used in joint research.

The main aim of this study was to specify the comparability of the air quality time series from the background stations at Ähtäri and Hyytiälä, both situated in southern Finland but located in different environments and thus influenced by different local emissions. The seasonal behaviour and serial correlations typical in air quality time series are not always taken into account in comparisons. In this article, methods for comparison are presented that evaluate the natural seasonal and intercorrelative factors of the time series (Brockwell and Davies 2002, Anttila and Tuovinen 2009). In addition, the differences in the concentration patterns of atmospheric sulphur (S) and nitrogen (N) compounds, chloride (Cl⁻) and the base cations sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺) and magnesium (Mg²⁺) in the region around Ähtäri and Hyytiälä are discussed.

Methods

The measurement data used in this study were collected by the Finnish Meteorological Institute (FMI) from two background stations in southern Finland. Atmospheric concentration of sulphur dioxide (SO₂), sulphate (SO₄²⁻), nitrate (NO₃⁻, representing the sum of particulate NO₃⁻ and gaseous HNO₃), ammonium (NH₄⁺, the sum of particulate NH₄⁺ and gaseous NH₃), Cl⁻, Na⁺, K⁺, Ca²⁺ and Mg²⁺ were simultaneously monitored at Ähtäri and Hyytiälä between 2003 and 2009.

Sampling sites and measurement period

The Ähtäri Niemisjärvi site (62°35′N, 24°11′E, 175 m a.s.l.) is an EMEP (UN/ECE European Monitoring and Evaluation Programme) station. It is located about 85 km to the north of the Hyytiälä station (61°51′N, 24°17′E, 181 m a.s.l.). Hyytiälä is a SMEAR II Station, operated by the University of Helsinki. Both stations represent boreal forest areas. At Ähtäri, the sampler is located circa 4 m above the ground in a hillside glade within young, mainly coniferous forest. However, single trees are growing sparsely around the sampling platform, the distance to the nearest trees being in order of 10 m. At Hyytiälä, the sampler is located about 2 m above the ground, also on a hill, between homogeneous 40-year-old Scots pine (*Pinus sylvestris*) stands. The tree density is 2500 per hectare (Kulmala *et al.* 2001). The distance from the sampler to the nearest trees is between 1 to 2 m. Figure 1 illustrates the placement of the samplers in their immediate surroundings.

At Ähtäri, the area within a 1-km radius around the sampling platform consists of forest, a lake, wetlands and arable land. The fields are located in the southwestern sector. At Hyytiälä, the 1-km radius surrounding the sampler mainly consists of forest and a lake, while a small field is located in the southern sector and the proportion of wetlands is low.

The average annual mean temperature in 2003–2009 was about 4 °C at both stations, being somewhat higher at Hyytiälä than at Ähtäri. The temperature was lower at Ähtäri throughout the year, the largest difference occurring during the winter period. Hyytiälä received more precipitation, especially during the summer. The mean annual rainfall was 650 mm in Ähtäri and 700 mm in Hyytiälä. Annual and seasonal averages of temperature and rainfall at Ähtäri and Hyytiälä measured with the standard meteorological methods of the World Meteorological Organization (WMO) are presented in Table 1. Southerly and south-westerly winds were the most frequent at Ähtäri, and easterly winds the rarest. Trajectory analysis revealed a similar prevailing westerly air flow at the Hyytiälä station (Sogasheva *et al.* 2005).

The land use in the areas surrounding the stations is mostly forestry. However, agricultural



Fig. 1. The air sampling devices at Ähtäri (left-hand-side photo) and Hyytiälä (right-hand-side photo).

activity is greater near the Ähtäri station than at Hyytiälä (Karvosenoja 2008). The background stations were located so that local influences on the monitoring would be minor. Detailed information on the Ähtäri station is available together with the information on EMEP stations ([www.emep.int/measurement network](http://www.emep.int/measurement-network)), and for Hyytiälä in e.g. Kulmala *et al.* (2001) and Pihlantie *et al.* (2007).

The period for which sampling and analyses at both stations overlapped was from 31 March 2003 to 31 December 2009 for SO_2 , SO_4^{2-} , NO_3^- , NH_4^+ and Cl^- . Parallel sampling and analysis for the base cations Na^+ , K^+ , Ca^{2+} and Mg^{2+} covered the periods 31 March–30 July 2003 and 1 January 2007–31 December 2009. At Ähtäri, daily samples were collected and analysed in 2003, after which weekly sampling was performed. At Hyytiälä during the whole period, three samples per week, covering 2, 2 and 3 days, were collected and analysed.

Sampling and analysis

The samples were collected with an open-face filter pack with an NaOH-impregnated Whatman 40 filter. Particulate SO_4^{2-} was sampled on a Whatman 40 filter installed in front of the SO_2 sampling unit. The sum of the gaseous HNO_3 and particulate NO_3^- as well as chloride and the base cations were sampled using the same filter pack as the sulphur compounds. For the sum of the gaseous NH_3 and particulate NH_4^+ , a second

filter line was used with a $(\text{COOH})_2$ -impregnated Whatman 40 filter. After the beginning of 2004, all the filters were placed in one filter pack and the front filter was changed to a Teflon® (Millipore $3 \mu\text{m}$) filter. The analysis was performed at the Air Chemistry Laboratory of the Finnish Meteorological Institute (EN ISO/IEC 17025 accredited). All compounds were analysed by ion chromatography, the particles and gases after H_2O extraction. The sampling and analysis methods used were always identical at both stations, and are described in detail in Karlsson *et al.* (2007).

Karlsson *et al.* (2007) specified the uncertainty of the methods used in the monitoring with filter-pack methods for daily and weekly samples at the Finnish background stations. Their combined expanded measurement uncertainty, U_{tot} , covered the main uncertainty sources of the filter-pack method: the analysis, the varia-

Table 1. Seven-year annual and seasonal averages of temperature and precipitation at Ähtäri and Hyytiälä, 2003–2009.

Season	Mean temperature (°C)		Precipitation (mm)	
	Ähtäri	Hyytiälä	Ähtäri	Hyytiälä
Dec–Feb	–6.3	–5.5	137	144
Mar–May	2.3	2.9	107	100
Jun–Aug	14.3	14.6	222	254
Sep–Nov	4.3	4.9	185	194
Year	3.7	4.2	651	692

tion of the field blank filters and the accuracy of the sample volume. U_{tot} were 3%–4% for higher concentration levels (Table 2).

Excellent agreement was also found between the 24-hour and the week-long samples for the sulphur and nitrogen compounds (Karlsson *et al.* 2007).

Statistical analyses

Pearson's correlations (r_p) and least square regressions (PASW Statistics 18, SPSS Inc., 2010) were performed for pairs calculated always from the shortest common mean values for both stations throughout the whole measuring period. In 2003, the mean values covered a period of two or three days, and one week thereafter during 2004–2009. Over 400 mean values were compared for the sulphur and nitrogen compounds and chloride, whereas for the base cations, the correlation analysis consisted of more than 200 pairs. Altogether, 4 pairs were excluded from the correlation analysis because of a very high mean value in the Ähtäri time series. The deleted outliers included one value for NO_3^- , two values for Na^+ and one value for K^+ .

Generalized least-squares (GLS) regression with classical decomposition and autoregressive moving average (ARMA) errors used for monthly mean values was carried out using the method of Brockwell and Davies (2002) (ITSM Professional 7.3, B and D Enterprises Inc., 2005), applied by Anttila and Tuovinen (2009).

Table 2. The combined expanded measurement uncertainty U_{tot} of the 1-stage and 2-stage filter-pack method (Karlsson *et al.* 2007). p = particulate, g = gaseous.

Compound	U_{tot}	Concentration area of validity for U_{tot}
S-SO ₂	± 0.045 μg m ⁻³	< 1.0
	± 4.0%	> 1.0
S-SO ₄ ²⁻	± 0.015 μg m ⁻³	< 0.5
	± 3.0%	> 0.5
N-[NO ₃ ⁻ (p) + HNO ₃ (g)]	± 0.010 μg m ⁻³	< 0.3
	± 3.5%	> 0.3
N-[NH ₄ ⁺ (p) + NH ₃ (g)]	± 0.035 μg m ⁻³	< 0.8
	± 4.5%	> 0.8

The detailed steps used for the calculation of the seasonal components by a moving average with a 13-month window, a preliminary regression model for the trend in the deseasonalized data, the iteration of the optimal ARMA(p,q) model for the residuals and the final estimates for the trend and error structure are described in Anttila and Tuovinen (2009). Further principles of the method are presented in Brockwell and Davies (2002).

Results and discussion

Mean values and correlations

The mean values of all components for the whole period at both stations were close to each other (Table 3). For SO₂, SO₄²⁻ and NH₄⁺, the difference in the average concentrations over the whole period was within the measurement uncertainty U_{tot} given for samples with low concentrations (Karlsson *et al.* 2007), but larger differences naturally occurred in individual sample pairs. For NO₃⁻, the mean levels differed by twice the U_{tot} given for concentrations < 0.3 μg m⁻³.

The average concentration of sulphur dioxide, calculated as the mass concentration of sulphur (S-SO₂), was 0.24 μg m⁻³ at Ähtäri and 0.21 μg m⁻³ at Hyytiälä. The variation in the S-SO₂ levels was also higher at Ähtäri (SD = 0.29 μg m⁻³) than at Hyytiälä (SD = 0.25 μg m⁻³). Likewise, the average values for sulphate and the nitrogen compounds as well as chloride were slightly higher at Ähtäri. Conversely, the mean level at Hyytiälä was somewhat higher for the base cations K⁺ and Ca²⁺. The mean values for Mg²⁺ were at the same level at both stations.

The correlation between the concentrations of sulphur and nitrogen compounds at Ähtäri and Hyytiälä was high, at least 0.9 (Table 3). This high similarity between the stations 85 km apart is an indication that the air masses are mostly well mixed in this part of southern Finland, and local emission sources only have a small effect on the concentrations at these two background stations. Significantly, despite the difference in the immediate environment of the samplers, the deviation between the measurement results was very low. The location of the Hyytiälä sampler

within dense tree stands did not cause a notable filtering effect for the particulate compounds. The main contributor to the concentration of sulphur compounds and oxidized nitrate is long-range transport (LRT), with a contribution of 60%–90% in this area (Nyíri *et al.* 2010). For the reduced nitrogen concentration, local agricultural emissions might have a larger effect, but the overall correlation was also very strong ($r_p = 0.91$).

The correlations between the concentrations of chloride, sodium, calcium and magnesium at the two stations were also very strong ($r_p = 0.83$ – 0.89), showing a good correspondence between the stations. A relatively weak correlation ($r_p = 0.65$) was found for the potassium values. Most differences in the time series of K^+ were detected for samples from June, when 6 pairs differed by over 100%. Biomass combustion is a typical emission source for potassium, although not the only one (Sillanpää *et al.* 2005), and local small-scale biomass combustion might be the reason for the lower correlation of the potassium values. In Finland, wood-heated saunas are frequently used at summer houses in the sparsely populated areas, especially during summer. In addition, the sampler at Hyytiälä was located within the canopy, where the influence of the nearby vegetation was greater than at Ähtäri, where the sampler was situated in an open location. The relatively long averaging time for the values

compared, from two days to one week, prevents a more detailed analysis of the differences in the potassium concentrations.

Least square (LS) regressions were calculated for all the components for the same short-period mean values (Table 3). The slope in the regression models was approximately 0.8 for all components except potassium (0.9) and calcium (1.1). All the LS regression slopes were highly significant ($p < 0.001$). The 95% confidence interval for the slopes was moderate for the sulphur and nitrogen compounds, slightly higher for chloride and higher still for the base cations, especially for potassium. Thus, the comparability of the base cation concentrations at the two stations is more uncertain than that of the other compounds. A greater influence of regional sources of chloride, sodium and magnesium (sea salt), and local sources of potassium and calcium (vegetation, soil) may be more directly related to the larger differences in their concentrations compared to the more strongly long-range transported sulphur and nitrogen compounds. The forest canopy acts as a sink for many air pollutants (Ferm and Hultberg 1999, Mustajärvi *et al.* 2008), which partly explains the lower concentrations at Hyytiälä, where the sampler was surrounded by forest stands. However, bidirectional exchange of NH_3 has been measured with an aerodynamic gradient technique (Wyers and Erisman 1998).

Table 3. Average values (\pm SD) for the total measurement period as well as the correlations (r) and least square regressions calculated from the shortest common-mean values of the air concentrations at Ähtäri and Hyytiälä. For the S and N compounds, the mass concentration of sulphur and nitrogen has been calculated. The periods for common sampling were 31 March 2003–31 December 2009 for S and N compounds and Cl^- , and 31 March 2003–30 July 2003 and 1 January 2007–31 December 2009 for the base cations. n = number of values. All Pearson correlation values (r_p) significant at $p < 0.01$. LS regression: (Hyytiälä) = constant + slope(Ähtäri).

Comp.	n	Mean \pm SD ($\mu g\ m^{-3}$)		r_p	LS regression	
		Ähtäri	Hyytiälä		Constant (95% conf. interval)	Slope (95% conf. interval)
S-SO ₂	424	0.24 \pm 0.29	0.21 \pm 0.25	0.92	0.02 (0.01–0.03), $p < 0.01$	0.82 (0.79–0.85), $p < 0.001$
S-SO ₄ ²⁻	427	0.40 \pm 0.26	0.39 \pm 0.25	0.93	0.04 (0.02–0.05), $p < 0.001$	0.88 (0.85–0.92), $p < 0.001$
N-NO ₃ ⁻	426	0.14 \pm 0.10	0.12 \pm 0.09	0.90	0.00 (0.00–0.01), $p > 0.3$	0.82 (0.79–0.86), $p < 0.001$
N-NH ₄ ⁺	402	0.33 \pm 0.22	0.31 \pm 0.20	0.91	0.03 (0.01–0.04), $p < 0.001$	0.83 (0.80–0.87), $p < 0.001$
Cl ⁻	428	0.12 \pm 0.13	0.10 \pm 0.12	0.88	0.01 (0.00–0.01), $p > 0.1$	0.81 (0.77–0.86), $p < 0.001$
Na ⁺	206	0.13 \pm 0.09	0.12 \pm 0.08	0.84	0.02 (0.01–0.03), $p < 0.001$	0.75 (0.68–0.81), $p < 0.001$
K ⁺	208	0.04 \pm 0.03	0.05 \pm 0.04	0.65	0.02 (0.01–0.02), $p < 0.001$	0.92 (0.77–1.07), $p < 0.001$
Ca ²⁺	210	0.03 \pm 0.04	0.04 \pm 0.05	0.89	0.01 (0.00–0.01), $p < 0.05$	1.08 (1.01–1.16), $p < 0.001$
Mg ²⁺	208	0.02 \pm 0.01	0.02 \pm 0.01	0.83	0.01 (0.00–0.01), $p < 0.001$	0.75 (0.67–0.82), $p < 0.001$

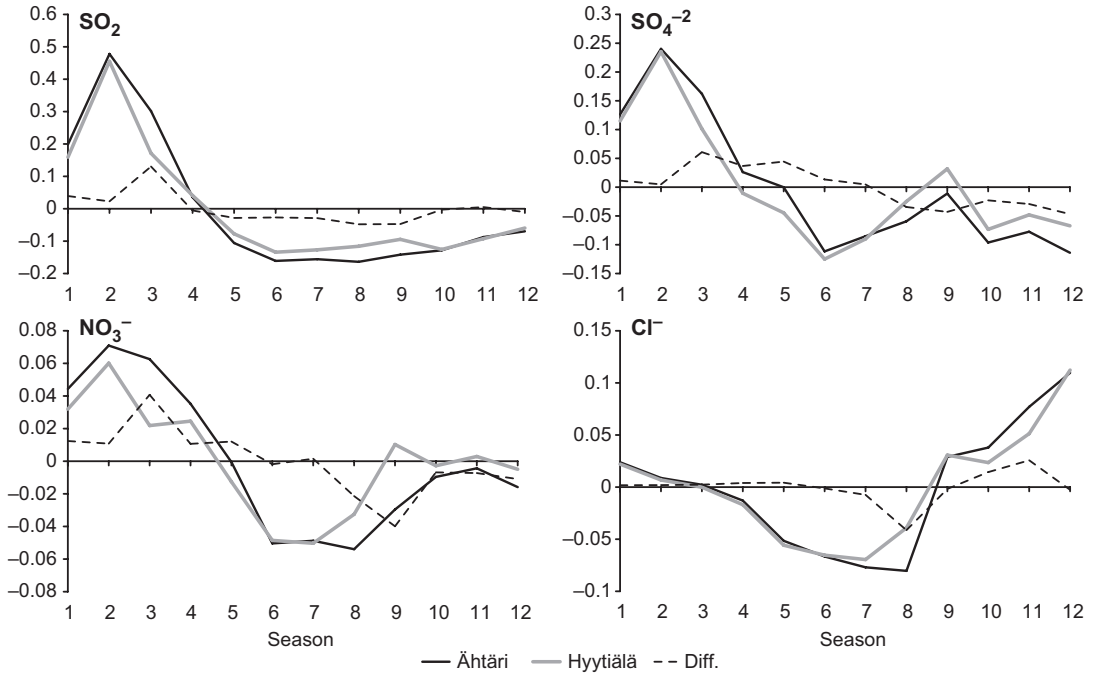


Fig. 2. Seasonal components for 12 seasons in a year derived with the GLS-ARMA procedure from the time series at Ähtäri and Hyttiälä. The seasons run from the beginning of the year.

Comparison of seasonal components for sulphur and nitrogen compounds and chloride

For sulphur and nitrogen compounds and chloride, the period monitored was long enough for trend analysis. The calculations were applied to monthly mean values. Here, we first discuss the results for the seasonal components in the classical time series analysis carried out with the GLS-ARMA model.

The GLS-ARMA method requires definition of the number of seasons to calculate the seasonal cycle. In this case, the 12 seasons used represented 12 months and covered one year. High seasonal variation was very distinct for the sulphur dioxide and sulphate time series (Fig. 2). The seasonal component peaked in February at both stations, more strongly for sulphur dioxide than for SO_4^{2-} . This annual pattern is typical for atmospheric sulphur concentrations in Finland (Lyubovtseva 2005, Anttila and Tuovinen 2009). In the seasonal pattern for total nitrate concentrations, the maximum value in Febru-

ary (Hyttiälä) and February–March (Ähtäri) was followed by an almost as deep minimum during the summer months of June–July (Hyttiälä) and June–August (Ähtäri). The seasonal variation in the emissions of air pollutants transported by LRT to the stations is assumed to mainly explain the patterns in the seasonal components of SO_2 , SO_4^{2-} and NO_3^- . The differences between the stations might originate from different land use patterns around the samplers and the sampler locations (height, interaction with foliage).

Unlike the other compounds, the seasonal pattern for ammonium with 12 seasons fluctuated during the year. At Ähtäri, the seasonal component peaked in May and had a minimum in December, whereas at Hyttiälä values higher than zero occurred at the beginning of the year and in September, and negative values in the summer and December. The values for the seasonal components in the ammonium time series are probably a product of both LRT and local ammonia emissions. The seasonal behaviour of NH_4^+ was further studied by estimating the seasonal components for 52 periods, each one-week long and

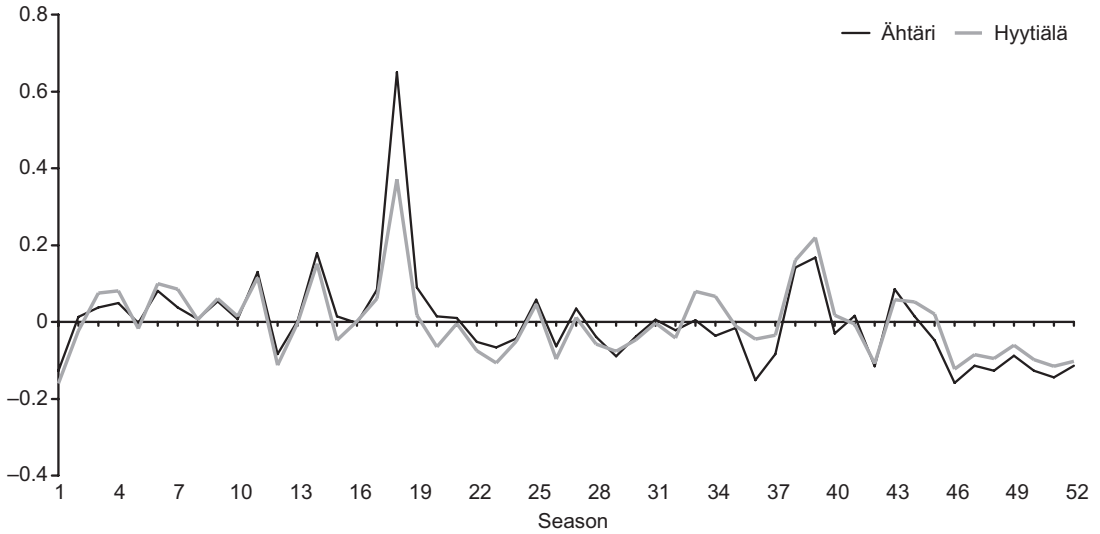


Fig. 3. Seasonal components for 52 seasons in a year for NH_4^+ at Ähtäri and Hyytiälä. The seasons run from the beginning of the year.

covering one year (Fig. 3). Weekly mean values of ammonium were therefore calculated. In the seasonal cycle, the largest difference between the stations was apparent in week 18, which occurred between late April and early May, depending on the year. In Finland, this is a time of high agricultural activity. Fertilizers are a major source of atmospheric ammonia (Galloway 1995, Erisman *et al.* 2007). According to the Finnish Government Decree on agricultural nitrates, the spreading of manure is permitted after 15 April on snow-free soil (Government Decree 931/2000). During 2003–2009, the snow melted on 4 April at the earliest and 27 April at the latest at Ähtäri, and on 28 March and 20 April, respectively, at Hyytiälä (FMI, Climate Service). The emission estimate for NH_3 in 2000 at a $1 \text{ km} \times 1 \text{ km}$ scale was higher near Ähtäri than in the vicinity of Hyytiälä (Karnosenoja 2000). The general pattern of the 52 seasonal components can thus be considered a result of LRT, and is rather similar at the two stations. However, the brief difference during the spring is a result of different land-use patterns in the vicinity of the stations.

Finally, for chloride, the characteristic seasonal component pattern showed similar low values in summer and high values in November–December (Fig. 2). The high seasonal component in November and especially in December

is probably caused by sea salt spray carried by strong winds (Weast 1971, Ruoho-Airola *et al.* 2003). Later during the winter, the sea is usually covered by ice. According to the FMI Climate Service, in Ähtäri the proportion of southwesterly and westerly winds was higher in November and December 2003–2009 than on average around the year. At the meteorological stations located in the coastal area, high winds (over 10 m s^{-1}) were most frequent between October and January. In addition, all the days with a wind speed of over 21 m s^{-1} at Kristiinankaupunki, a coastal city 150 km west of Ähtäri, occurred in November or December. Thus, sea salt spray carried by wind could explain the high values at the end of the year.

In order to test the sensitivity of the seasonal components to coincidental changes in the monitoring data, they were all recalculated by excluding the first or the last year of the time series. No large changes were detected; Fig. 4 illustrates a typical example of the deviation in the numerical values.

Trends and ARMA model

A significant, decreasing trend was found for all the sulphur and nitrogen components and

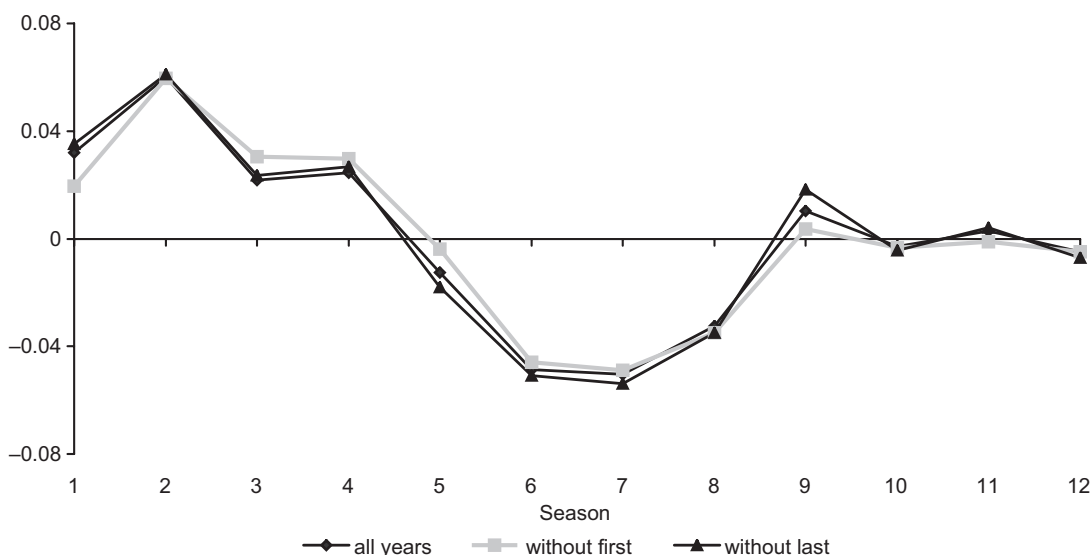


Fig. 4. Sensitivity analysis of the seasonal components of NO_3^- at Hyttiälä derived with the GLS-ARMA procedure for the time series covering the whole measuring period and periods without the first or the last year. The seasons run from the beginning of the year.

chloride at both stations, with the only exception being SO_2 at Ähtäri, where the trend was not significant (Table 4). Within the 95% confidence intervals, the significant trends were the same at both sites. SO_4^{2-} decreased annually by 3%–5%, NO_3^- , NH_4^+ by 4%–6%, and Cl^- more steeply by 12%–13%. For the SO_2 concentration at Hyttiälä, the annual reduction was 7.2%, with a rather large 95% confidence interval of $\pm 6.2\%$.

Anttila and Tuovinen (2009) demonstrated that the GLS-ARMA method, with handling of

the serially-correlated data using the ARMA processes, improved the analysis of monthly values. In addition, the use of monthly rather than annual data also revealed the weakest trends. Thus, in our calculations, the differences in weak trends could also be estimated.

Recent estimates of the SO_2 trend in 1994–2007 by Anttila and Tuovinen (2009) yielded an annual decrease between 3.4% (Ähtäri) and 8.0% (Pori) for the 5 sites in the same region as Hyttiälä and Ähtäri. Within the 95% confidence

Table 4. Results of the trend analysis of the deseasonalized monthly mean values based on the GSL-ARMA method. Statistically significant ($P < 0.05$) trends (%/year) are indicated with boldface. The annual changes are presented with their 95% confidence intervals. p and q are the order of AR and MA processes for the optimal model.

Component	Station	ARMA p, q	Intercept ($\mu\text{g m}^{-3}$)	Slope (\pm SE) ($\mu\text{g m}^{-3}$ month)	Change (%/year)
S- SO_2	Ähtäri	0,1	0.3	-0.0016 (\pm 0.0009)	-5.9 \pm 6.2
	Hyttiälä	1,0	0.3	-0.0018 (\pm 0.0008)	-7.2 \pm 6.2
S- SO_4^{2-}	Ähtäri	4,2	0.5	-0.0013 (\pm 0.0004)	-3.4 \pm 2.4
	Hyttiälä	1,1	0.5	-0.0019 (\pm 0.0002)	-4.8 \pm 1.2
N- NO_3^-	Ähtäri	0,1	0.2	-0.0005 (\pm 0.0002)	-3.7 \pm 2.9
	Hyttiälä	0,0	0.1	-0.0007 (\pm 0.0001)	-5.8 \pm 2.3
N- NH_4^+	Ähtäri	0,1	0.4	-0.0011 (\pm 0.0005)	-3.6 \pm 3.4
	Hyttiälä	0,0	0.4	-0.0018 (\pm 0.0004)	-5.8 \pm 2.6
Cl^-	Ähtäri	0,1	0.2	-0.0020 (\pm 0.0003)	-12.6 \pm 4.1
	Hyttiälä	2,0	0.2	-0.0016 (\pm 0.0003)	-11.6 \pm 4.0

intervals, the trend at Ähtäri reported by Anttila and Tuovinen (2009) and our trend at Hyytiälä overlap.

During the 1990s, the SO_4^{2-} concentration at Ähtäri decreased annually by 4% and NH_4^+ by 5%, while for NO_3^- no significant trend was detected in the annual data by the non-parametric Mann-Kendall test (Ruoho-Airola *et al.* 2004). Thus in this region, a rather even decline appears to have taken place from 1990 to 2009 for SO_4^{2-} and NH_4^+ .

The reason for the steep decline in Cl^- by more than 10% annually is not clear. The coincidental annual variation in the wind distribution might be one reason. On the coast of the Gulf of Bothnia, west of the monitoring stations, the annual mean wind velocity can increase or decrease by 25% as compared with the average during years with high or low windiness (*see* <http://www.tuuliatlas.fi/en/index.html>). Few time series of chloride concentrations in air could be found for comparison with our results. At the Finnish Pallas station in the far north, the temporal change calculated with the GLS-ARMA method was significant, but the trend slightly lower than at Hyytiälä and Ähtäri. At Pallas, an annual decline of $7.6\% \pm 6.8\%$ was calculated for 2003–2008. However, no significant trend was found in the EMEP data from 2003–2009 (www.EMEP.int) for the two comparable Norwegian background stations, Tustervatn and Karasjok, which are not situated on the coast.

The seasonal and the trend components of the GSL-ARMA model explained well the shape of the measured time series for the sulphur compounds and moderately that for nitrate and chloride (Fig. 5). The winter maximum varied in magnitude so much that it was not always captured well. However, for ammonium, the seasonal variation within and between years was higher and the seasonal components and the trend could not as well explain the flow in the measured time series when deseasonized with either 12 or 52 seasons. The timing of the maximum in spring was captured better with a GLS-ARMA model with 52 seasons, but there was considerable irregular variation that could not be modelled by the methods used.

The preliminary autoregressive (AR) and moving average (MA) processes were estimated

from the deseasonalized time series after an ordinary least square (OLS) regression was fitted. Thereafter, the optimal ARMA(p,q) model to represent the residuals was selected (Anttila and Tuovinen 2009). The proportion not captured by the trend and seasonal components of the GLS-ARMA model is the part of the measured time series that is covered by the random component (p,q equations) in the GLS-ARMA model. The order of the p and q components is presented in Table 4, while numerical values of p and q in the equations are not given. Different processes explain the residuals at the two stations, e.g. for SO_2 the ARMA model includes one autoregressive term at Ähtäri, whereas at Hyytiälä the ARMA model includes one moving average term. It is assumed that the ARMA models are influenced by local factors.

Conclusions

Seven years (2003–2009) of parallel measurements of atmospheric sulphur, nitrogen and chloride concentrations at Ähtäri and Hyytiälä stations in southern Finland, 85 km apart, were enough for a detailed study of the seasonal factors and trends in the time series. The use of the GSL-ARMA classical time series analysis method in the study of the S, N and Cl^- data revealed the similarities and the principal differences in the concentration patterns. The shorter time series (2003 and 2007–2009) of the base cations enabled a more general comparison of the concentrations. Although the LRT is the most significant contributing factor in the time series, the methods used were able to distinguish the possible local contributions and establish their exact timing.

The correlation between the time series was very strong ($r_p \geq 0.9$) for SO_2 , SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- and Ca^{2+} , strong ($r_p > 0.8$) for Na^+ and Mg and relatively weak ($r_p = 0.65$) for K^+ . The concentrations at Hyytiälä were on average 83%–98% of those at Ähtäri for S and N compounds and Cl^- , 92%–100% for Na^+ and Mg^{2+} and 125%–133% for K^+ and Ca^{2+} . For all the base cations, the confidence interval for the slope in the regression was wider, indicating a more uncertain comparability.

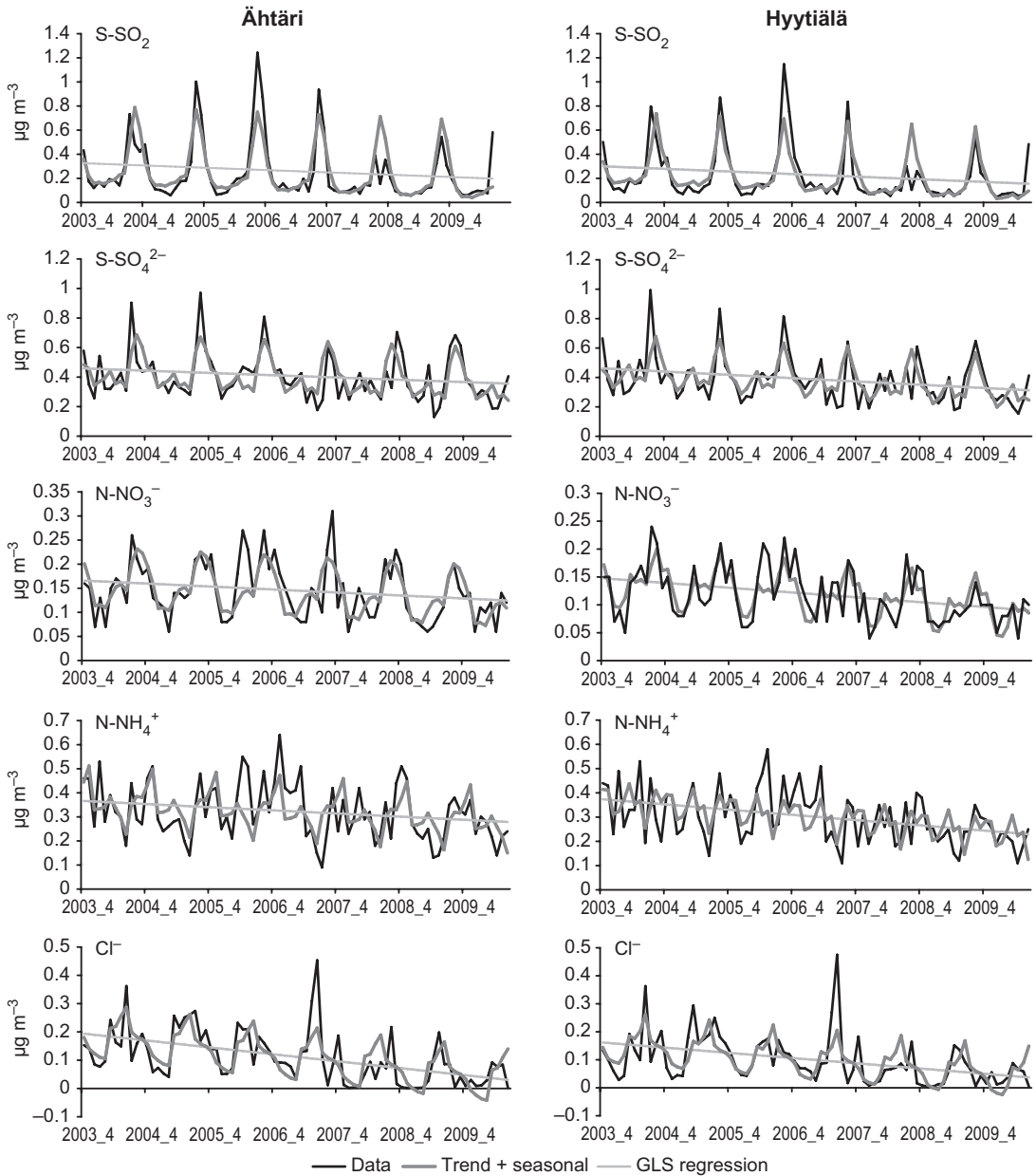


Fig. 5. Goodness of fit of the data of trend + seasonal components. Measured monthly mean concentrations, and the estimated monthly time series of the seasonal component (12 seasons) + trend and the estimated trend.

For the SO_4^{2-} , NO_3^- and Cl^- time series, the GLS-ARMA modelling results indicated similar seasonal behaviour and decreasing trends at both stations, indicating that the concentrations were mainly controlled by changes in the well-mixed air masses over southern Finland, which both stations registered similarly. For the SO_2 time

series, the seasonal pattern was also similar, but the trend was only significant at Hyytiälä. Finally, for the NH_4^+ time series, similar seasonal components with 52 seasons and trends were estimated with the GLS-ARMA method, but the variation in the data could not be represented by the seasonal and trend terms alone.

Although one of the stations was located in open surroundings and the other within dense forest, the correlation of the sulphur and nitrogen data was good. Despite the difference in the immediate environment of the samplers, there was no marked deviation between the measurement results. The location of the Hyytiälä sampler within dense tree stands did not cause a notable filtering effect for the particulate compounds compared to the more open location at Ähtäri. In contrast, distinctions in the base cation data might result from a greater influence of local sources, such as small-scale biomass combustion, vegetation and soil, but also from a smaller amount of data for comparison.

Methods that take into account the seasonal behaviour and serial correlation in air quality time series can help to estimate the unwanted local influence in the data. At both sites, the high agricultural activity in spring is evident in the NH_4^+ data. With help of the dense seasonalization of the time series, the minimal part of the data affected can be removed and the remaining data used for further studies on a more regional level.

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