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Detection of temporal trends in atmospheric deposition of inorganic nitrogen and sulphate to forests in Europe

Peter Waldner [a, *], Aldo Marchetto [b], Anne Thimonier [a], Maria Schmitt [a], Michela Rogora [b], Oliver Granke [c], Volker Mues [d], Karin Hansen [e], Gunilla Pihl Karlsson [f], Daniel Žlindra [g], Nicholas Clarke [h], Arne Verstraeten [i], Andis Lazdins [j], Claus Schimming [k], Carmen Iacoban [l], Antti-Jussi Lindroos [m], Elena Vanguelova [n], Sue Benham [n], Henning Meesenburg [o], Manuel Nicolas [p], Anna Kowalska [q], Vladislav Apuhtin [r], Ulle Napa [s], Zora Lachmanová [t], Ferdinand Kristoefel [u], Albert Bleeker [v], Morten Ingerslev [w], Lars Vesterdal [w], Juan Molina [x], Uwe Fischer [y], Walter Seidling [y], Mathieu Jonard [z], Philip O'Dea [aa], James Johnson [ab, ac], Richard Fischer [ad], Martin Lorenz [ad]

[a] WSL, Swiss Federal Institute for Forest, Snow and Landscape Research, Zürcherstrasse 111, CH-8903 Birmensdorf, Switzerland
[b] ISE-CNR, Institute of Ecosystem Study, Largo Tonolli 50, I-28922 Verbania Pallanza, Italy
[c] Digsyland, Institut für Digitale Systemanalyse & Landschaftsdiagnose, D-24975 Husby, Germany
[d] UHH, University Hamburg, Centre for Wood Sciences, Worldforestry, Leuschnerstrasse 91, D-21031 Hamburg, Germany
[e] IVL Swedish Environmental Research Institute, SE-100 31 Stockholm, Sweden
[f] IVL Swedish Environmental Research Institute, SE-400 14 Göteborg, Sweden
[g] Slovenian Forestry Institute, SI-1000 Ljubljana, Slovenia
[h] Norwegian Forest and Landscape Institute, P.O. Box 115, N-1431 Ås, Norway
[i] Research Institute for Nature and Forest, Kliniekstraat 25, B-1070 Brussels, Belgium
[j] SILAVA, Latvian State Forest Research Institute, Riga Street 111, LV-2169 Salaspils, Latvia
[k] Centre for Ecology, University of Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany
[l] Experiment Station for Spruce Silviculture, Calea Bucovinei 73, RO-5950 Campulung Moldovenesc, Suceava, Romania
[m] METLA, Finnish Forest Research Institute, PL 18, FI-01301 Vantaa, Finland
[n] Forest Research, Alice Holt Lodge, Wrecclesham, Farnham, Surrey GU10 4LH, United Kingdom
[o] NW-FVA, Nordwestdeutsche Forstliche Versuchsanstalt, Grätzelstrasse 2, D-37079 Göttingen, Germany
[p] ONF, Office National des Forêts, Département Recherche et Développement, Bâtiment B, Boulevard de Constance, F-77300 Fontainebleau, France
[q] FRI, Forest Research Institute, Sekocin Stary, PL-05-090 Raszyn, Poland
[r] Estonian Environment Agency, EE-33 Tallinn, Estonia
[s] University of Tartu, Vanemuise 46, EE-51013 Tartu, Estonia
[t] FGMRI, Forestry and Game Management Research Institute, CZ-156 04 Prague 5, Zbraslav, Czech Republic
[u] BFW, Federal Research Centre for Forests, A-1131 Vienna, Austria
[v] Energy Research Centre of the Netherlands, 1755 ZG Petten, Netherlands
[w] Department of Geosciences and Natural Resource Management, University of Copenhagen, Rolighedsvej 23, DK-1958 Frederiksberg C, Denmark
[x] TECMENA, Clara del Rey 22, ES-28000 Madrid, Spain
[y] Thünen-Institute of Forest Ecosystems, D-16225 Eberswalde, Germany
[z] UCL-ELI, Université Catholique de Louvain, Earth and Live Institute, Croix du Sud 2, B-1348 Louvain-la-Neuve, Belgium
[aa] Coillte Laboratories, Church Road, Newtownmountkennedy, Wicklow, Ireland
[ab] Trent University, 1600 West Bank Drive Peterborough, Ontario K9J 7B8, Canada
[ac] UCD School of Agriculture and Food Science, University College Dublin, Belfield, Dublin 4, Ireland
[ad] Thünen Institute for International Forestry and Forest Economics, Leuschnerstrasse 91, D-21031 Hamburg, Germany

HIGHLIGHTS

- Minimum detectable trend slopes depend on length of time series.
- Temporal variability of deposition was similar across sites for many substances.
- Despite higher noise, monthly data were better than annual data for trend analysis.
- Nitrogen and sulphate deposition decreased by 2% and 6% per year, respectively.

* Corresponding author.
E-mail address: peter.waldner@wsl.ch (P. Waldner).

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ABSTRACT

Atmospheric deposition to forests has been monitored within the International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) with sampling and analyses of bulk precipitation and throughfall at several hundred forested plots for more than 15 years. The current deposition of inorganic nitrogen (nitrate and ammonium) and sulphate is highest in central Europe as well as in some southern regions. We compared linear regression and Mann–Kendall trend analysis techniques often used to detect temporal trends in atmospheric deposition. The choice of method influenced the number of significant trends. Detection of trends was more powerful using monthly data compared to annual data. The slope of a trend needed to exceed a certain minimum in order to be detected despite the short-term variability of deposition. This variability could to a large extent be explained by meteorological processes, and the minimum slope of detectable trends was thus similar across sites and many ions. The overall decreasing trends for inorganic nitrogen and sulphate in the decade to 2010 were about 2% and 6%, respectively. Time series of about 10 and 6 years were required to detect significant trends in inorganic nitrogen and sulphate on a single plot. The strongest decreasing trends were observed in western central Europe in regions with relatively high deposition fluxes, whereas stable or slightly increasing deposition during the last 5 years was found east of the Alpine region as well as in northern Europe. Past reductions in anthropogenic emissions of both acidifying and eutrophying compounds can be confirmed due to the availability of long-term data series but further reductions are required to reduce deposition to European forests to levels below which significant harmful effects do not occur according to present knowledge.

1. Introduction

Forest ecosystems have been exposed to increased atmospheric deposition of sulphur (S) in the form of sulphate (SO_4^{2-}) and inorganic nitrogen (N) since the 1950s, resulting from anthropogenic emissions of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3). Deposition of these compounds is a major driver for various changes in forest ecosystems. It may alter nutrient limitations and lead to increased forest growth and carbon (C) sequestration (e.g. de Vries et al., 2008; Solberg et al., 2009), accelerate soil acidification (e.g. Ulrich et al., 1980) and eutrophication effects (e.g. Aber et al., 1998) as well as mobilising aluminium in soil solution to levels that are toxic for roots (Cronan et al., 1989). Eutrophication effects include loss of nutrients by leaching, elevated nitrate (NO_3^-) levels in percolation and runoff water (Dise et al., 2009), nutrient imbalances in trees, and altered susceptibility to pests and diseases (Flückiger and Braun, 1999).

Determination of temporal trends of atmospheric deposition of S and N compounds to forests is therefore of considerable interest. Measures were implemented to reduce the emissions of S and N compounds during the last three decades (Reis et al., 2012). Deposition assessments in long time series are required (i) to monitor the success of these measures in reducing deposition and (ii) to investigate the impact of deposition on the long-term stability of forest and its ecosystem services at selected intensively monitored sites (Paoletti et al., 2010).

For this purpose, temporal trend analyses based on bulk precipitation and throughfall measurements performed under the framework of the International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) are regularly carried out at the intensively monitored sites of the ICP Forests Level II network and published on pan-European level (e.g. Lorenz and Granke, 2009; Granke and Mues, 2010; Waldner et al., 2012). Further trend analyses of parts of the ICP Forests deposition data and other data have been carried out at the national, regional and European levels using various methods (Meesenburg et al., 1995; Kvaalen et al., 2002; Hůnová et al., 2004; Rogora et al., 2006; Fagerli and Aas, 2008; Vanguelova et al., 2010; Graf Pannatier et al., 2011; Oulehle et al., 2011; Pihl Karlsson et al., 2011; Staelens et al., 2012; Verstraeten et al., 2012; Johnson et al., 2013; Marchetto et al., 2013).

However, the commonly reported absolute trend slopes and percentage of statistically significant trends vary and seem to be partly contradicting. This may be due to the variation of methods used in these studies, e.g. different trend analysis techniques, variations in length and temporal resolution of time series, spatial variation of emission time trends or other factors influencing deposition.

The main aims of this study were to:

- determine and explain the minimum detectable trend on a single plot with deposition measurements carried out according to the ICP Forests manual
- investigate the influence of trend analysis technique, time series length and temporal resolution on the detection of statistically significant trends
- assess bulk deposition (BD) and throughfall deposition (TF) of SO_4^{2-}, nitrate (NO_3^-) and ammonium (NH_4^+) and their trends across Europe at ICP Forests sites

2. Methods

2.1. Sampling and chemical analyses

Continuous sampling of below canopy throughfall and open field bulk deposition is carried out on ICP Forests Level II forest monitoring plots and at nearby open field sites, respectively. The methods used in the various countries (France: Ulrich and Lanier, 1993; Norway: Kvaalen et al., 2002; Moffat et al., 2002; Italy: Mosello et al., 2002; Switzerland: Thimonier et al., 2005; Finland: Lindroos et al., 2006; Denmark: Gundersen et al., 2009; Czech Republic: Boháčová et al., 2010; Latvia: Lazdiņš et al., 2010; United Kingdom: Vanguelova et al., 2010; Swedish Throughfall Monitoring Network (SWETHRO): Pihl Karlsson et al., 2011; Belgium: Verstraeten et al., 2012) follow the ICP Forests manual (earlier versions and ICP Forests, 2010).

In general, collectors (3–20 replicates) are placed in the forest based on a random or fixed systematic design in order to cover the spatial variation (Switzerland: Thimonier, 1998; United Kingdom: Houston et al., 2002; Belgium: Staelens et al., 2006). Samples are

collected at least monthly (typically fortnightly or weekly), filtered, and stored below 4 °C before chemical analyses are performed to determine the concentrations of SO_4^{2-}, NO_3^-, and NH_4^+. The laboratory results are checked for internal consistency based on the conductivity, the ion balance, the concentration of total N and the sodium to chloride (Na/Cl) ratio, and analyses are repeated if suspicious values occur (Mosello et al., 2005, 2008; ICP Forests, 2010). The quality assurance and control (QA/QC) procedures further include the use of control charts for internal reference material to check long-term comparability within national laboratories, as well as participation in periodic laboratory ring tests (e.g. Marchetto et al., 2009) and field inter-comparisons (Draaijers et al., 2001; Žlindra et al., 2011a) to check the international comparability.

Data were reported annually to the pan-European data centre, checked for consistency and stored in the programme database.

2.2. Data processing

Data for the period from 1999 to 2010 were used in this analysis. Precipitation and throughfall data sampled during more than 330 days per year, and with concentration values for more than 300 days per year were included. Sampling periods with mean precipitation below 0.1 mm day^{-1} were counted even if no chemical analyses could be performed.

Data from each sampling period were interpolated to regular monthly and annual data by: (i) splitting each sampling period overlapping two consecutive months by distributing precipitation quantity in proportion to the duration of the new sampling periods; (ii) setting deposition = 0 for periods with missing concentrations and mean precipitation <0.1 mm day^{-1}; (iii) calculating TF and BD ($Q \cdot c \cdot 10^{-2}$, in kg ha^{-1}) by multiplication of the precipitation quantity (Q, in L m^{-2}), the concentrations (c, in mg L^{-1}) and the unity conversion factor 10^{-2}; (iv) summing up to fluxes by month and year, respectively.

Mean annual fluxes of SO_4^{2-}–S and the inorganic N species NO_3^-–N and NH_4^+–N for 2010 were calculated for 286, 282, and 287 TF plots and 266, 265, and 268 BD plots, respectively.

2.3. Trend analyses

We analysed the temporal trends of individual time series for sets of plots with continuous measurements from 2007 to 2010 (4 years), from 2005 to 2010 (6 years), from 2003 to 2010 (8 years), from 2001 to 2010 (10 years) as well as for 1999 to 2010 (12 years). We checked that time series were normally distributed and showed a seasonal pattern (see Annex).

Trend analyses were carried out using (i) linear regression (LR), (ii) Mann–Kendall (MK) test (Mann, 1945; Helsel and Hirsch, 2002) using annual deposition fluxes, (iii) Seasonal Mann–Kendall (SMK) (Hirsch et al., 1982; Hirsch and Slack, 1984), and (iv) Partial Mann–Kendall (PMK) tests (Libiseller and Grimvall, 2002) using monthly deposition data. The PMK test includes testing the influence of a co-variable, and we chose precipitation quantity for that. Linear regression and Kendall tests were performed using the 'rkt' package (Marchetto, 2013) in the R software (R Development Core Team, 2009). For the Kendall tests (MK, SMK, PMK), trend slopes b (kg ha^{-1} yr^{-2}) were estimated following Sen (1968).

For each time series, we calculated a relative slope *rslope* (yr^{-1}), as an estimated mean relative change per year, with

$$rslope = b/\mathrm{mean}(y), \tag{1}$$

where b (kg ha^{-1} yr^{-2}) is the estimator for the absolute trend resulting from the trend analyses and mean (y) (kg ha^{-1} yr^{-1}) the mean value of the time series.

2.4. Temporal variability (background signal)

The temporal variability of the original data (CV0), data after removing estimated temporal trend (CV1), and data after removing temporal trend and seasonality (CV2) were determined for each time series and averaged for each parameter (see equation (3) in Annex).

2.5. Minimum detectable trends

Minimum detectable trends $rslope_{min}^{emp}$ were derived empirically from the p-values and the *rslope* results of the individual trend analyses for each combination of parameter, time series length and trend analysis technique. The $rslope_{min}^{emp}$ value above which the majority of tests identify a trend as significant, with $p < 0.05$ (at significance level 95%), was determined by fitting a Gauss shaped function through the band of p- to *rslope* values of the test results (see Annex).

Secondly, minimum detectable trends were modelled based on the temporal variability of the overall dataset with

$$rslope_{min}^{mod} = c_7\, 2\, \frac{\mathrm{CV}}{n_{\mathrm{years}}} \frac{T_{\mathrm{crit}}\left(\frac{n}{2}\right)}{\sqrt{\frac{n}{2}}} \tag{2}$$

where n_{years} is the duration of time series in years, n is the number of observations ($n = n_{\mathrm{years}}$ for annual and $n = 12 \cdot n_{\mathrm{years}}$ for monthly data), CV the coefficient of variation of the temporal variability (see Table 1) and T_{crit} the test statistic of the T-test (e.g. $T_{\mathrm{crit}} = 2.45$ for $n/2 = 6$, $T_{\mathrm{crit}} = 2.23$ for $n/2 = 10$, $T_{\mathrm{crit}} = 1.98$ for $n/2 = 100$) and c_7 an adjustment parameter (see Results and Annex).

3. Results and discussion

3.1. Current deposition

Clear regional variation was observed in the depositions. Highest SO_4^{2-} BD (not shown) and TF deposition was recorded in forest plots in northern central Europe and Poland reaching up to the southern Baltic and the central Hungarian area, and in some Mediterranean regions in Spain, France, southern Italy and Greece (Fig. 1). Highest inorganic N BD (not shown) and TF deposition was recorded in northern central Europe, as for SO_4^{2-}, but also in southern Germany and the Swiss Plateau and further to the west, in northern France, the central UK and Ireland. The regions bordering the Alps in the south and some sites in Spain and in southern France also showed relatively high N deposition.

Considerable parts of the regionally higher inorganic N and SO_4^{2-} deposition are attributable to anthropogenic emission of NO_x, SO_2 and NH_3 (Reis et al., 2012). Other contributions are of natural origin.

Table 1
Temporal variability of annual and monthly deposition of NH_4^+–N, NO_3^-–N, SO_4^{2-}–S (kg ha^{-1} yr^{-1}) and precipitation quantity Q (L m^{-2} yr^{-1}) time series from plots with continuous data from 2001 to 2010 (10 years).

Flux	Variable	Annual	Monthly	Monthly
		CV1	CV1	CV2
BD	NH_4^+–N	0.26 (±0.11)	0.75 (±0.30)	0.67 (±0.28)
	NO_3^-–N	0.18 (±0.07)	0.48 (±0.11)	0.44 (±0.11)
	SO_4^{2-}–S	0.19 (±0.07)	0.48 (±0.08)	0.44 (±0.07)
	Q	0.18 (±0.05)	0.48 (±0.08)	0.49 (±0.07)
TF	NH_4^+–N	0.30 (±0.20)	0.98 (±0.93)	0.86 (±0.87)
	NO_3^-–N	0.20 (±0.09)	0.63 (±0.31)	0.53 (±0.26)
	SO_4^{2-}–S	0.16 (±0.07)	0.52 (±0.15)	0.46 (±0.13)
	Q	0.17 (±0.07)	0.52 (±0.15)	0.50 (±0.10)

CV1: coefficient of variation after correction for linear trend, CV2: coefficient of variation after correction for linear trend and seasonality.

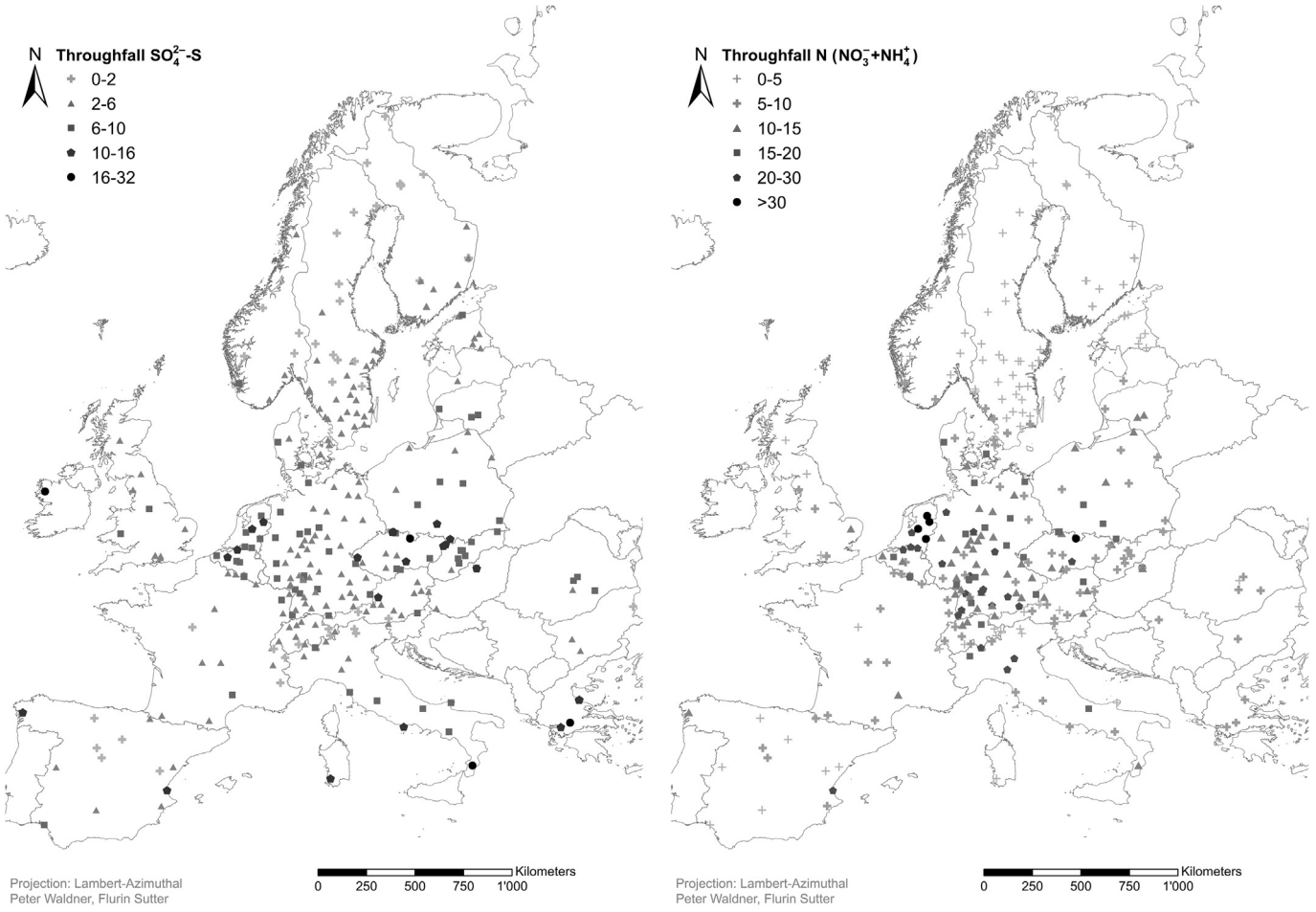

Fig. 1. Mean annual SO_4^{2-}–S (kg S ha^{-1} yr^{-1}) and inorganic nitrogen (NH_4^+–N + NO_3^-–N) (kg N ha^{-1} yr^{-1}) throughfall deposition in the year 2010.

For example, parts of the high SO_4^{2-} deposition along the coast occur together with high Cl^- deposition (e.g. at some Norwegian coastal sites), which is typical for SO_4^{2-} originating from sea salt (Granke and Mues, 2010).

The measurements support the findings of modelling and mapping approaches (e.g. Posch et al., 2012) according to which atmospheric deposition of SO_4^{2-} and N compounds still exceeds critical loads in parts of Europe. Critical loads apply to total deposition (TD), i.e. the sum of wet and dry deposition. In forests, TD of N is typically a factor of 1–2 higher than TF, due to uptake by plant tissue and through stomata in the canopy (Draaijers and Erisman, 1995). For SO_4^{2-}, TD is generally assumed to be equal to TF (Draaijers and Erisman, 1995). For N, the ranges from 5 to 15 and from 10 to 20 kg ha^{-1} yr^{-1} have been proposed as empirical critical loads for coniferous and broadleaved deciduous woodland, respectively (Bobbink and Hettelingh, 2011).

3.2. Trend analyses and derivation of minimum detectable trends

The slope estimates resulting from the trend analysis techniques LR, MK, SMK and PMK agreed well. The agreement between trend techniques increased with length of the time series, and with increasing *rslope* (Fig. 2, left-hand side). There was less agreement between trend analysis techniques in terms of identifying a trend as being significant or not (Fig. 2, right hand side).

The minimum detectable trend $rslope_{min}^{emp}$ decreased with increasing length of the time series and was typically smaller for methods applied to monthly data (SMK, PMK) compared to tests applied to annual data (MK, LR), as shown in Fig. 3 for SO_4^{2-}, NO_3^- and NH_4^+ in TF.

3.3. Temporal variability

The temporal variability of deposition varied little from plot to plot or from ion to ion (Table 1). The temporal variability was on average about 20–60% higher for monthly data than for the annual sums. The corrections for linear trends, and for seasonality, reduced the temporal variation on average by about 5–10%.

The temporal variability was quite similar for all ions and not much higher than that of precipitation quantity Q (L m^{-2} yr^{-1}), which might be surprising at first glance (Table 1). Andersson et al. (2006) used a chemistry transport model (CTM) and estimated that the average European land-area inter-annual variability of SO_4^{2-} and inorganic N deposition, due to meteorological variability, ranged from 11 to 14% for TD and to about 20% for wet deposition. Kryza et al. (2012) confirmed that meteorology can lead to an inter-annual variation of 20% and stated that precipitation quantity is generally the more important factor, except for regions such as the UK, where the circulation pattern might become more important.

Therefore, it is likely that most of the temporal variability is explained by the variability of air circulation, i.e. the source region and pollution level of the air masses, and the precipitation, i.e. the scavenging of the gaseous and particulate compounds transported in the atmosphere. For most compounds, the temporal signals of the emissions in a region, e.g. from fossil fuel burning, are probably much smoother than those of deposition. However, NH_4^+ shows a

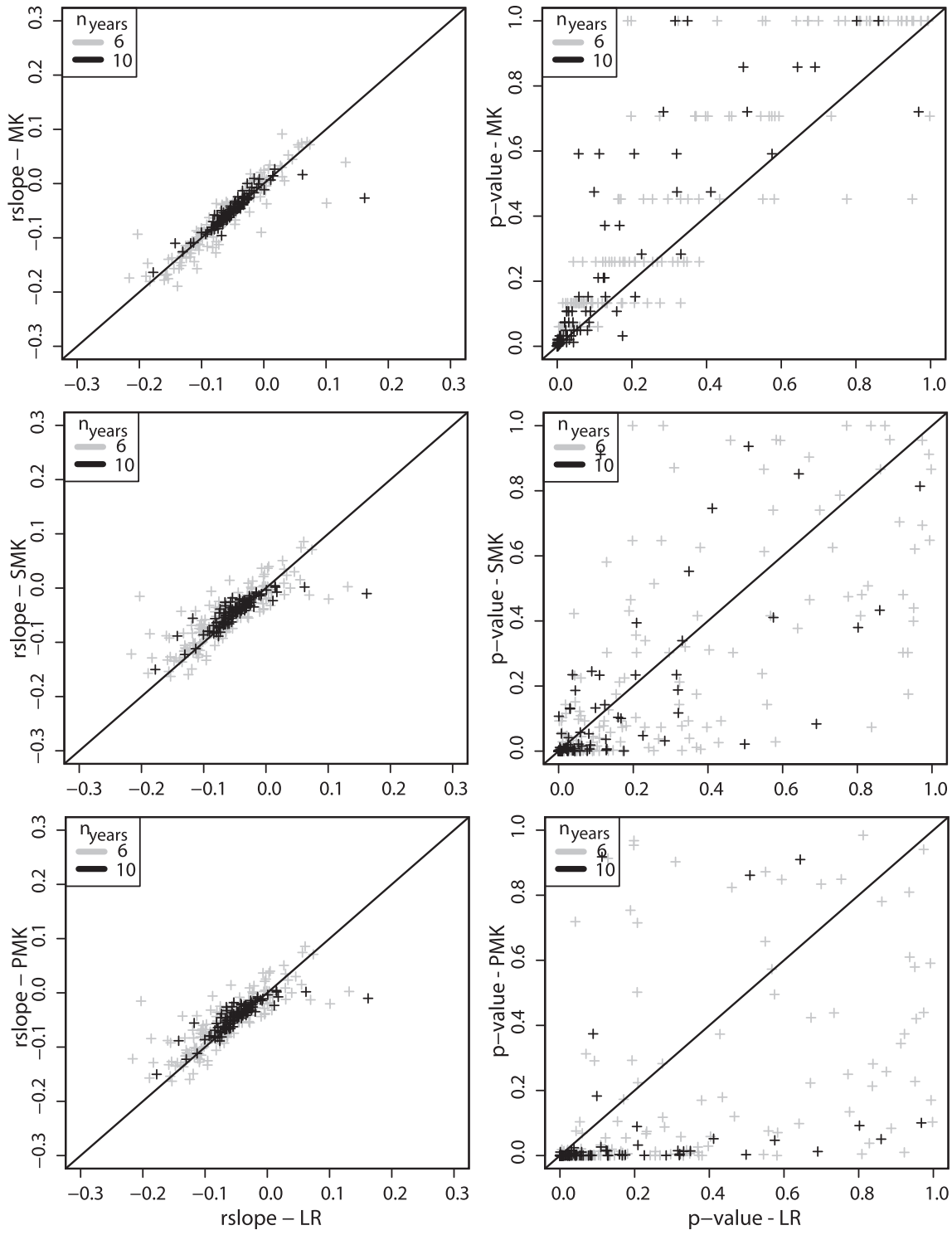

Fig. 2. Relative slope (*rslope*) (left-hand side) and *p*-value (right-hand side) of MK, SMK and PMK versus LR for SO_4^{2-}–S TF deposition from 2001 to 2010 ($n_{years} = 10$), and 2005 to 2010 ($n_{years} = 6$).

slightly higher overall variability than NO_3^- and SO_4^{2-} which may be caused by spatially and temporally more variable emission sources. The emissions from agricultural land in the form of NH_3 are a major source of NH_4^+ in precipitation and throughfall, and the emissions are themselves strongly influenced by local weather conditions (Wichink Kruit et al., 2012).

The temporal variability found here is likely to be valid for other substances transported over similar pathways. It seems that the method to estimate $rslope_{min}$ presented here is generally applicable for most of the major compounds in BD and TF, even when using just the temporal variability values shown in Table 1.

3.4. Estimated minimum detectable trends

The minimum detectable trend $rslope_{min}^{emp}$ determined empirically from the trend test results can to a large extent be explained

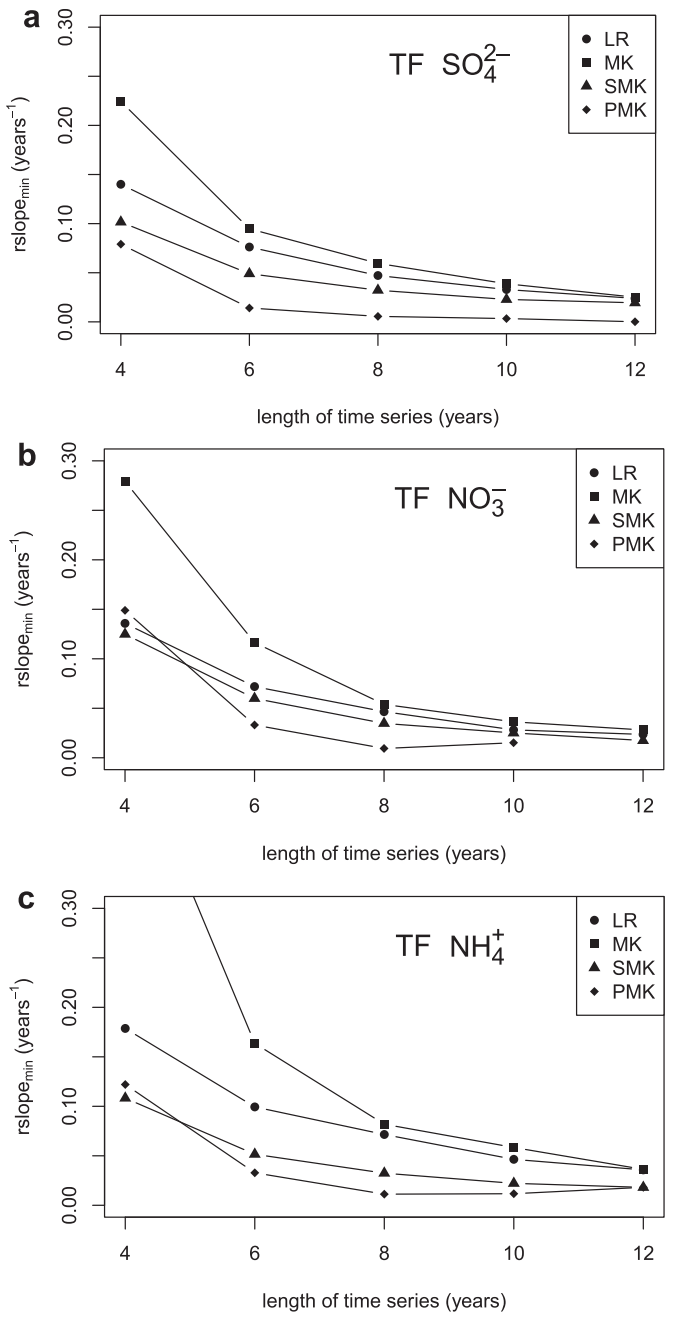

Fig. 3. Minimum detectable trends derived from the *p*-value to *rslope* plots of trend analyses with LR, and MK of annual, SMK and PMK of monthly SO_4^{2-}, NO_3^- and NH_4^+ TF deposition time series with continuous data from 2007 to 2010 (4 years), from 2005 to 2010 (6 years), from 2003 to 2010 (8 years), from 2001 to 2010 (10 years), and from 1999 to 2010 (12 years).

by the mean short-term temporal variability. The $rslope_{min}^{emp}$ (equation (5), Annex) correlated well to the $rslope_{min}^{mod}$ (equation (2)) estimated from CV1 and CV2 values in Table 3. The PMK test showed the highest scatter. The co-variable not considered in equation (2) but used in this PMK test may be a reason for this higher scatter. For the parameter c_7 in equation (2) ($rslope_{min}^{emp}/rslope_{min}^{mod}$) we found values between 1 and 2.5 that have little dependence on the trend technique applied, the parameter or the time series length (Table 3).

Monthly data involve more data points than annual data, which seems to be favourable for detecting trends despite (i) the uncertainty of monthly data interpolation and (ii) their generally higher temporal variability.

3.5. Comparison of minimum detectable trend to sources of uncertainty of the measurements

This study suggests that the data quality objective to 'detect a change of 30% in 10 years' which is defined in the ICP Forests manual (ICP Forests, 2010) seems realistic. It has to be mentioned that this study only investigated the uncertainty related to the statistical methods. However, uncertainties related to the steps prior to the trend analyses (Thimonier, 1998; Houston et al., 2002; Bleeker et al., 2003; Erisman et al., 2003; Staelens et al., 2006; Marchetto et al., 2011; Žlindra et al., 2011b) were on average lower in magnitude than the uncertainty resulting from the temporal variability of the deposition.

3.6. Deposition trends

The results on minimum detectable trends are reflected in the stronger agreement of slopes between trend techniques and the smaller scattering of slope among plots for longer time series and for PMK and SMK compared to LR and MK (Table 2).

The trends (Table 2) agree well with the findings of earlier studies (Table 3), which is more obvious when comparing *rslope* values. The low percentages of significant trends found in several studies are to a large extent due to the expected trends being low compared to minimum detectable trend. No mean *rslope* is given in Table 3 because the slope values of non-significant changes are often omitted in literature.

Between the peak emission in the 1980s and the turn of the millennium as well as for the decade around the millennium, *rslope* values for SO_4^{2-} were typically between −5% and −10% in central Europe and between −12 and +3% in northern and western Europe (Table 3). The percentage of plots with significant trends was especially high in central Europe. In comparison, the *rslope* values of significant and non-significant changes of N deposition were lower, typically between +1 and −5%, and the percentage of plots with significant trends was also lower, especially when the time series were short.

For the 10 year period, typical *rslope* values for N compounds were around −2% per year (Table 2). Hence, typically about 10 years of data were required to detect such a trend on a plot with statistical significance with PMK (Fig. 4). For SO_4^{2-} with typical *rslope* values of 4–6%, the corresponding requirement was about 6 years of data.

The strongest decreasing trends during the 10 year period were found in northern central Europe from Belgium and the Netherlands to Germany and for N compounds the region of strongest trends (0.2 to −0.15 kg ha^{-1} yr^{-2}) extended further to Switzerland, France, Italy, Czech Republic, Slovakia and Denmark.

Sites with non-significant changes in deposition were distributed all over Europe (Fig. 5). In the 6 year period, stable or slightly increasing SO_4^{2-} deposition was reported mainly for plots in eastern central Europe and for N deposition for southern Germany, Switzerland, Austria, Italy and the Franco-Belgian border region as well as in northern Europe.

The generally decreasing trends of SO_4^{2-} and inorganic N deposition coincide and can be explained by the emission reductions achieved between 1990 and 2001 (Table 1, Reis et al., 2012). Fagerli and Aas (2008) compared NO_3^- and NH_4^+ concentrations in wet precipitation modelled by the European Monitoring and Evaluation Programme (EMEP) based on the emission inventories with measurements for the period from 1980 or later to 2003 at various sites in Europe. They stated that most of the reductions took place in the years between 1985 and 1995. Verstraeten et al. (2012) pointed out that the effect of technical

Table 2
Relative trend (*rslope* in % yr^{-1}) and standard deviation of *rslope* and percentage of plots with significant positive trends (+), significant negative trends (−) or non-significant (n.s.) changes for trend analyses of NH_4^+, NO_3^-, SO_4^{2-} bulk (BD) and throughfall (TF) deposition plots with continuous data from 2005 to 2010 (6 years) and 2001 to 2010 (10 years).

Ion	Period	Flux	*n*	*rslope*	−	n.s.	+	*rslope*	−	n.s.	+
				LR				**MK**			
SO_4^{2-}	2001–2010	BD	78	−4.1 (±3.5)	49	50	1	−4.1 (±3.4)	42	56	1
		TF	105	−4.9 (±3.9)	65	35	0	−4.9 (±3.2)	60	40	0
	2005–2010	BD	143	−5.2 (±6.1)	21	78	1	−5.1 (±6.9)	9	91	0
		TF	171	−6.3 (±7.0)	33	67	0	−6.6 (±6.1)	16	84	0
NO_3^-	2001–2010	BD	78	−1.6 (±2.8)	22	77	1	−1.7 (±2.6)	17	81	3
		TF	105	−1.5 (±3.6)	20	75	5	−1.5 (±3.5)	20	78	2
	2005–2010	BD	143	−0.9 (±5.5)	6	93	1	−0.9 (±5.7)	3	97	0
		TF	171	−3.1 (±6.3)	8	92	0	−2.8 (±6.3)	6	94	0
NH_4^+	2001–2010	BD	78	−0.7 (±4.8)	15	82	3	−0.9 (±4.2)	8	90	3
		TF	105	−1.6 (±4.8)	15	83	2	−1.8 (±4.0)	14	84	2
	2005–2010	BD	143	−2.8 (±9.9)	4	93	3	−2.6 (±8.6)	2	97	1
		TF	171	−4.9 (±9.5)	7	92	1	−4.2 (±8.0)	2	97	1
				SMK				**PMK**			
SO_4^{2-}	2001–2010	BD	78	−3.9 (±2.8)	79	19	1	−3.9 (±2.8)	62	38	0
		TF	105	−4.5 (±2.6)	91	9	0	−4.5 (±2.6)	71	29	0
	2005–2010	BD	143	−4.4 (±4.8)	60	38	1	−4.4 (±4.8)	45	54	1
		TF	171	−5.5 (±5.0)	63	37	0	−5.5 (±5.0)	46	54	0
NO_3^-	2001–2010	BD	78	−1.4 (±2.1)	37	59	4	−1.4 (±2.1)	24	73	3
		TF	105	−1.4 (±2.8)	35	61	4	−1.4 (±2.8)	24	70	6
	2005–2010	BD	143	−0.1 (±4.9)	6	92	1	−0.1 (±4.9)	6	90	3
		TF	171	−2.6 (±4.5)	23	76	1	−2.6 (±4.5)	13	85	2
NH_4^+	2001–2010	BD	78	−0.9 (±2.4)	26	67	8	−0.9 (±2.4)	22	72	6
		TF	105	−1.3 (±2.5)	31	65	4	−1.3 (±2.5)	33	62	5
	2005–2010	BD	143	−1.8 (±5.3)	22	76	2	−1.8 (±5.3)	15	82	3
		TF	171	−3.2 (±4.5)	30	69	1	−3.2 (±4.5)	23	75	2

Legend: LR = Linear regression, MK = Mann–Kendall, SMK = Seasonal Mann–Kendall, PMK = Partial Mann–Kendall.

measures taken by industry, traffic and agriculture in the 1980s and 1990s, which resulted in a clear decrease of SO_4^{2-} and NH_4^+, has become marginal in recent years, while increasing traffic counteracts the effect of stricter emission norms for vehicles.

Other reasons for changes in deposition to forest areas are changes in the tree stand structure, such as the reduction of the number of trees due to bark beetle attacks as reported for a Czech forest (Boháčová et al., 2010), forest age, or high levels of nitrate in insect frass falling from the canopy as reported for sites in the UK (Pitman et al., 2010).

For inorganic N especially, the decreasing trends seem too slight to avoid exceedance of the critical loads for acidification and eutrophication in different parts of European forests in the near future (Reis et al., 2012). Further reduction of N emissions is needed to prevent air pollution effects on forests.

4. Conclusions

The selection of the trend analysis technique had an effect on trend detection. There was a strong agreement between estimated

Table 3
Ranges of relative trends of S and N deposition (max|min *rslope* in % yr^{-1}) in Europe and percentage of plots with significant trends found by other studies.

Reference	Region	Period	Meth	N	*	S	N
Meesenburg et al. (1995)	NW-Germany	1981–1994	LR	4/7	1	SO_4^{2-}: BD −5|−7 (100), TF −5|−9 (100)	NO_3^-: BD 0|−3 (100), TF 1|−5 (100)
Rogora et al. (2006)	Alps	1985–2002	SMK	7		SO_4^{2-}: BD (100)	NO_3^-: BD (29), NH_4^+: BD (86)
		1990–2002	SMK	3/20	2	SO_4^{2-}: BD −3|−6 (95)	NO_3^-: BD −1|−2 (35), NH_4^+: BD −2|−5 (50)
Staelens et al. (2012)	Flanders	2002–2010	K	9		SO_4^{2-}: TD −2|−14 (100)	N: TD 0|−6 (78)
Pihl Karlsson et al. (2011)	Sweden	1996–1999 2005–2008	ratio, MK	14/52	3	SO_4^{2-}: BD −8|−4 (57), TF −7|−2 (90)	NO_3^-: BD (0), NH_4^+: BD (11), N: BD (14)
Kvaalen et al. (2002)	Norway	1986–1997	SMK	13		SO_4^{2-}: BD 3|−12 (46), TF 3|−13 (54)	
Vanguelova et al. (2010)	UK	1995–2006	SMK	10		SO_4^{2-}: BD (40), TF (80)	NO_3^-: BD (40), TF (30), NH_4^+: BD (20),TF (0)
Graf Pannatier et al. (2011)	Switzer-land	1994–2007	SMK, PMK	9		SO_4^{2-}: TF −2|−7 (100)	N: TF (11)
Marchetto et al. (2013)	Italy	1998–2010	SMK	9		SO_4^{2-}: BD −5|−12 (89)	NO_3^-: BD −11|−1 (77), NH_4^+: BD −12|−1 (66)
Verstraeten et al. (2012)	Flanders	1994–2010	SMK	5		SO_4^{2-}: TF −5|−6 (100)	NO_3^-: TF −1|−2 (60), NH_4^+: TF −3|−5 (100)
Johnson et al. (2013)	Ireland	1991–2010 (−2003)	SMK, PMK	2	4	SO_4^{2-}: BD −3|−4, TF −4|−12 (100)	NO_3^-: BD (50), TF (0), NH_4^+: BD (0) TF (0)
Hunova et al. (2004)	Czech Republic (CZ)	1985–2000	mod	mod	5	SO_4^{2-}: EM:−6	NO_3^-: TD −3, NH_4^+: TD −3
		1985–2000	mod	mod	5	SO_4^{2-}: TD −10	NO_3^-: TD −2, NH_4^+: TD −3
Oulehle et al. (2011)	Nacetin, CZ	1995–1998 2004–2009	ratio	1		SO_4^{2-}: BD −7, TF −10	N: BD −1,TF −2
Fagerli and Aas (2008)	Europe	1980–2003	EMEP	mod + sites			NO_3^- and NH_4^+: WD −1|−3 (50)

Legend: Meth = trend analysis technique: LR = Linear regression, SMK = Seasonal Mann–Kendall, K = Kendall, PMK = Partial Mann–Kendall, mod = Mapping model results, ratio = comparison of means of the two periods; *n*: number of sites; *: 1) $n = 4$ for BD and $n = 7$ for TF, 2) $n = 3$ for *rslope* ranges and $n = 20$ for percentage of plots with significant trends, 3) $n = 52$ for TF and $n = 14$ for BD, 4) generally 1991 to 2010, but 1991–2003 for TF at one site, 5) modelled; S, N: BD = bulk deposition, WD = wet deposition, TF = throughfall, TD = total deposition, EM = emissions.

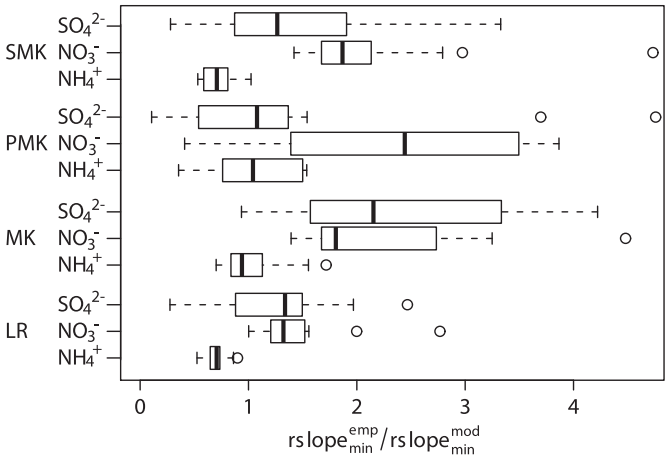

Fig. 4. Ratio of minimum detectable trend derived from trend tests ($rslope_{min}^{emp}$) to minimum detectable trend derived from mean temporal variability ($rslope_{min}^{mod}$) (c_7) for trend analyses with LR and MK of annual, SMK and PMK of monthly SO_4^{2-}, NO_3^-, NH_4^+ TF deposition time series with continuous data from 2007 to 2010 (4 years), from 2005 to 2010 (6 years), from 2003 to 2010 (8 years), from 2001 to 2010 (10 years), and from 1999 to 2010 (12 years).

trend slopes from the different techniques, but SMK and PMK tests applied to monthly data tended to detect smaller trends with statistical significance than LR or simple MK techniques applied to annual data and these tests are therefore recommended for trend analysis.

A consistent relationship between the *rslope* and *p*-value of the trend tests was obvious for a given length of time series. The choice of the trend analysis technique, the investigated fluxes and the specific element or ion had less influence on the minimum detectable trend slope $rslope_{min}$. It seems likely that the minimum detectable trend $rslope_{min}$ can be derived from the mean temporal variability caused mainly by meteorological phenomena.

For time series with a length of 10 years, the $rslope_{min}$ for inorganic N compounds and SO_4^{2-} seemed to be a change of around 3–4% per year for tests applied to the monthly data in this study.

In more than half of the sites a decrease in SO_4^{2-} deposition was strong enough to be identified as statistically significant at the plot level in the periods 2001–2010 and 2005–2010. For deposition of inorganic N compounds, relative changes were smaller and significant decreasing trends were only found for about a quarter of the plots.

Overall, decreasing trends for SO_4^{2-} and inorganic N compounds of about −6% and −2% per year respectively were typical for the 10 year period up to 2010. Trend estimates of individual sites however ranged from −15% to 7% per year. The strongest decreasing trends were found for sites in western central Europe in regions with relatively high deposition fluxes whereas stable or slightly increasing deposition during the last 5 years were found in and east of the Alpine region as well as in northern Europe.

For inorganic N compounds, the trends in atmospheric deposition (BD and TF) as a result of emission reductions in Europe are unlikely to be detected with statistical significance in time series shorter than 10 years. For SO_4^{2-}, typical trends were stronger, especially in the 1990s, and could be detected even in shorter time series.

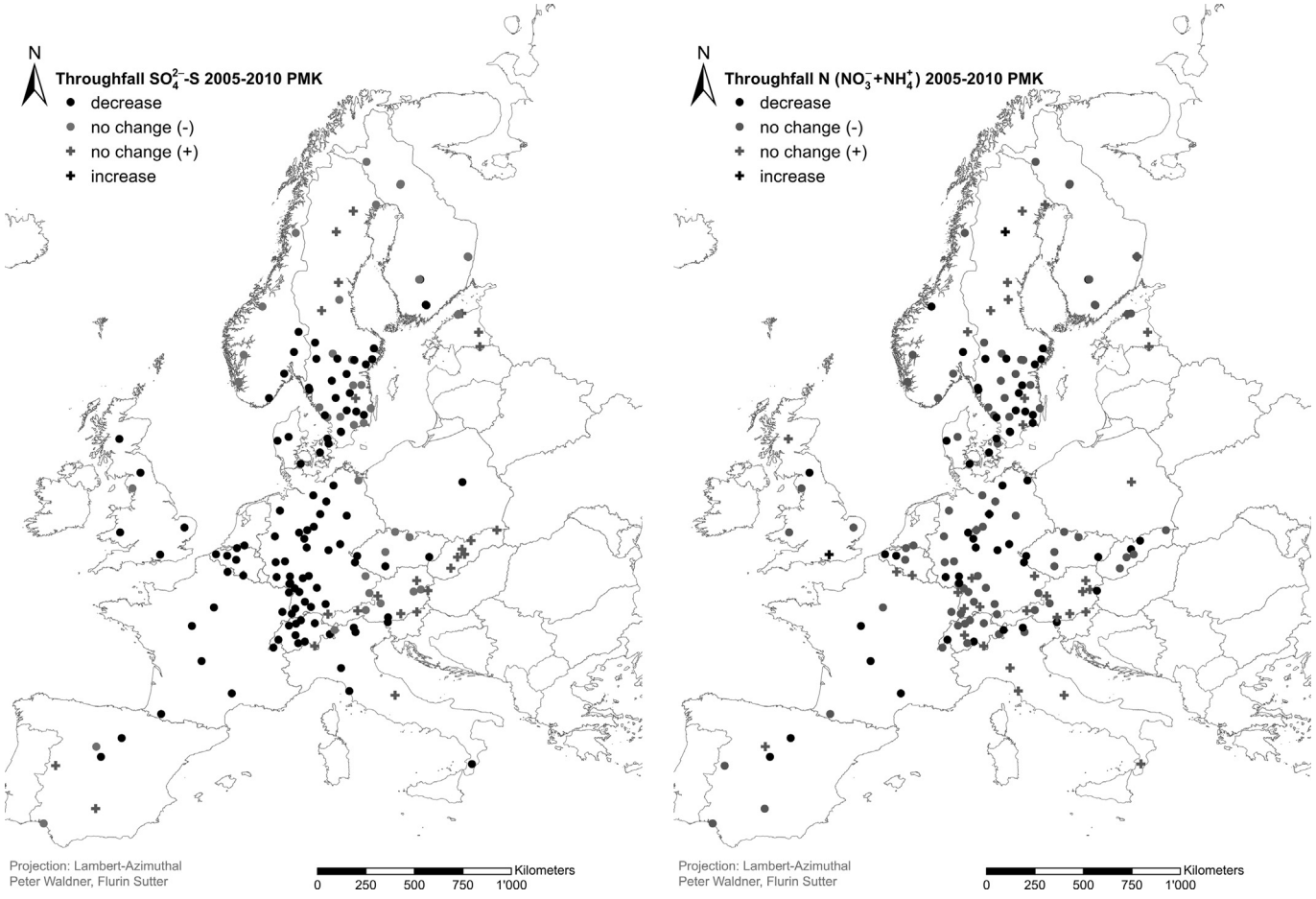

Fig. 5. Trend of sulphate sulphur (SO_4^{2-}–S) and inorganic nitrogen (NO_3^-–N + NH_4^+–N) TF deposition determined with PMK on plots with continuous measurements from 2005 to 2010. Non-significant positive and negative changes are indicated with 'no change (+)' and 'no change (−)', respectively.

The deposition trends can to a large extent be attributed to the reductions of the emissions of air pollutants achieved between 1990 and 2010. Despite decreasing trends at numerous plots, total deposition of inorganic N compounds and SO_4^{2-} to forests still exceeds critical loads in parts of Europe.

Continued long-term deposition monitoring will be necessary to demonstrate the effectiveness of emission reduction measures and to investigate observed effects on the ecosystems caused by deposition.

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The applied methods for determination of atmospheric deposition fluxes have been further developed and harmonized by numerous scientists in the Expert Panel on Deposition of ICP Forests subsequently chaired by G. Lövblad, E. Ulrich, N. Clarke and K. Hansen. Applying these methods involved numerous technicians for the installation and maintenance of about 4000 samplers, collection of roughly a million samples, and chemical analyses of approximately 200,000 pooled samples, as well as on-going supervision by some 40+ scientists. Data transmission involved national focal centres and the data centre of ICP Forests that was subsequently at Alterra, Wageningen (FIMCI), at the Joint Research Centre in Ispra and at the Programme Coordination Centre of ICP Forests in Hamburg. Data transmission included sophisticated conformity and plausibility checks developed by the involved database specialists. The comparability of the laboratory analyses has been improved by the activities of the Working Group on QA/QC in laboratories initiated and supported by R. Mosello, N. König, K. Derome, the late John Derome, A. Kowalska, A. Marchetto and others. For field installations, similar activities were coordinated by G. Draaijers, A. Bleeker, J. Erisman, E. Ulrich, and D. Žlindra. Data quality objectives and other methodological improvements were the results of activities initiated by the QA/QC committee of ICP Forests chaired by M. Ferretti. The atmospheric deposition measurements typically involved access being granted by the land owners, financial support from the participating countries and the EU, as well as support from subordinated governmental organisations such as communal or forest services. The EU partially funded the deposition network under the Council Regulation (EEC) 3528/86 on the 'Protection of Forests against Atmospheric Pollution' and the Regulation (EC) No 2152/2003 concerning monitoring of forests and environmental interactions in the community (Forest Focus) and by the project LIFE 07 ENV/D/000218 "Further Development and Implementation of an EU-level Forest Monitoring System (FutMon)".

The presented evaluation involved national representatives responsible for the deposition measurements. Thanks to all who contributed.

Annex

Checking normal distribution and seasonality

The Shapiro–Wilk test (R function 'shapiro.test', c.f. Royston, 1982) was applied to each data series to check whether deposition values were normally distributed. To test for seasonality, we further carried out a linear regression (R function 'lm') for the monthly data (y) with a model of two superposed harmonic waves with wavelengths of one and half a year, respectively, i.e.

$$y = a + b\ t_{\text{years}} + c_1 \sin(t) + c_2 \cos(t) + c_3 \sin(2t) + c_4 \cos(2t) + \varepsilon, \quad (3)$$

where y (kg ha^{-1} yr^{-1}) is the deposition, t_{years} (years, as a continuous number) the time, $t = 2\ \pi\ t_{\text{years}}$, ε the remainder and the intercept a (kg ha^{-1} yr^{-1}), the slope b (kg ha^{-1} yr^{-2}), and c_1 to c_4 (kg ha^{-1} yr^{-1}) are parameters. Seasonality was assumed if at least one of the seasonality terms (c_1 to c_4) was identified as being significant (p-value < 0.05).

The seasonality test confirmed seasonality for 85% of the time series. The remaining time series often had one of the seasonality terms (c_1–c_4) almost reaching the $p < 0.05$ threshold for significance (97% of p-values <0.2). Therefore, seasonality was assumed and SMK and PMK were applied to all time series.

Determining minimum detectable trend from individual trend results

The relative slope values (*rslope*) were plotted against the p-values (p) for each combination of trend analysis techniques, flux, ion and period, to investigate patterns that may be used to define a minimum detectable trend for deposition data. As shown in Fig. 6 for the example of NO_3^- TF series analysed with LR, we found most p-values to be within a narrow band with the shape of a Gaussian curve when plotted against the *rslope*. This band was narrower for longer time series and wider for shorter time series. In the 10 years time series of NO_3^- in TF tested with LR, most plots with absolute values of *rslope* above about 5% per year have significant trends ($p < 0.05$), whilst plots with *rslope* below 5% have trends that are not significant ($p > 0.05$) for many plots. Hence, we can assign a minimum detectable trend $rslope_{min}$ of about 5% for the 10 years time series.

With a non-linear regression (R function 'nls'), we fitted a Gaussian shaped curve to the points on the *rslope* vs. p-value diagram for trend test results of bulk and throughfall deposition series of the same variable, the same length, and trend analysis technique. The curve was described by

$$p = c_5 \cdot e^{-\frac{1}{2}\left(\frac{rslope-\mu}{\sigma}\right)^2}, \quad (4)$$

where $c_5 = 0.8$ is the amplitude that in contrast to the normal distribution was fixed, μ the *rslope* value of the peak and σ a measure of the horizontal aperture of the Gaussian curve, which was used to derive the minimum detectable trend.

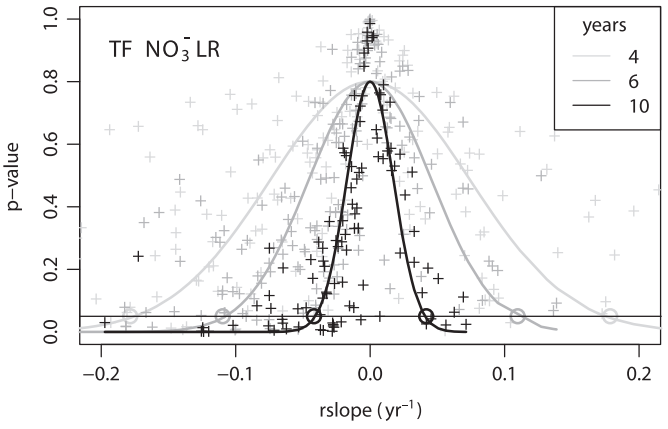

Fig. 6. Relative slope (*rslope*) and p-value of linear regression (LR) trend test for annual NO_3^- throughfall deposition time series groups from 2007 to 2010 (4 years), from 2005 to 2010 (6 years), and from 2001 to 2010 (10 years) with a Gaussian shaped curve fitted to each group using non-linear regression techniques. Trend tests with p-value <0.05 (black horizontal line) are significant (at 95% significance level). The intersections of the curves with the horizontal line (circles) were used as empirical values for the minimum detectable trend ($rslope_{min}$), i.e. the *rslope* range outside which the majority of the trends are significant.

We defined the minimum detectable trend $rslope_{min}^{emp}$ as the value above which the majority of tests identify a trend as significant, with $p < 0.05$ (at significance level 95%).

In a visual assessment of the Gauss shaped curves fitted through the points on the *p–rslope*-diagram, we found, that $rslope_{min}$ corresponds well to

$$rslope_{\min}^{emp} = c_6 \sigma_{fit}^{up}, \quad (5)$$

where σ_{fit}^{up} is the upper value of the confidence interval for σ that resulted from fitting the equation (4) to the data points, and $c_6 = 2$ a parameter.

Temporal variability (background signal)

The temporal variability was explored for the (i) original data (y), (ii) the data after removing estimated temporal trend ($y1$) and (iii) the data after removing temporal trend and seasonality ($y2$). Trends and seasonality were removed with,

$$y1 = y - b \ t_{\text{years}} + \text{mean}(y), \quad (6)$$

$$y2 = y - \text{mean}_{\text{month}}(y) + \text{mean}(y), \quad (7)$$

where mean(y) is the overall mean, and $\text{mean}_{\text{month}}(y)$ the mean over one month in all years. Hereafter we estimated the coefficients of variation CV0, CV1 and CV2 for y, $y1$ and $y2$, respectively.

The resulting temporal variability values are summarised in Table 1 and illustrated in Figs. 7 and 8.

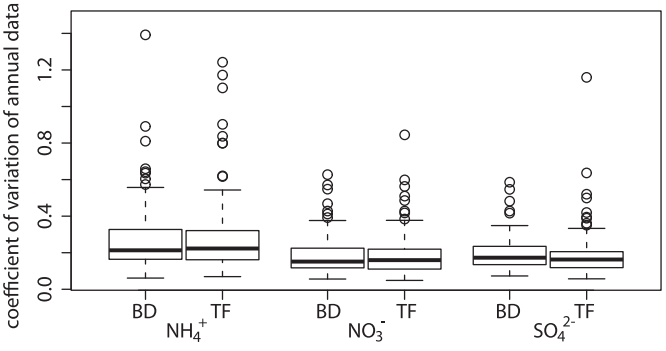

Fig. 7. Temporal variability: Coefficient of variation (CV1) of trend corrected annual NH_4^+, NO_3^- and SO_4^{2-} bulk (BD) and throughfall (TF) deposition for ICP Forests plots with measurements from 2001 to 2010 (10 years). The boxplot shows the median (thick line), 25% and 75% quantiles (box), minim and 1.5 times the interquartile range (whiskers) and higher values (circles).

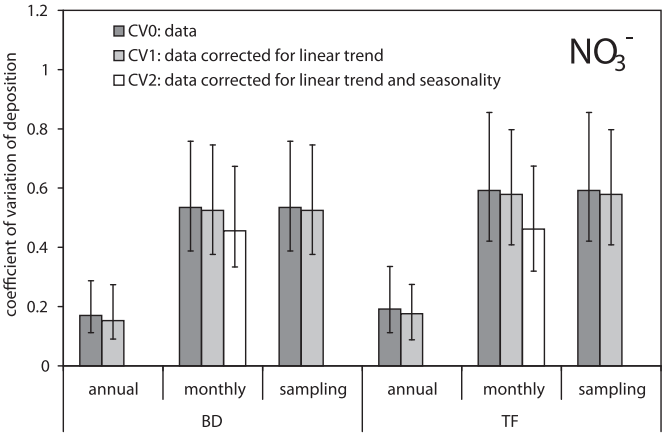

Fig. 8. Temporal variability: Coefficient of variation of (i) raw (CV0), (ii) trend corrected (CV0) and (iii) trend and seasonality corrected (CV2) annual NO_3^- bulk (BD) and throughfall (TF) deposition for ICP Forests plots with measurements from 2001 to 2010 (10 years). (Sampling = sampling period, not aggregation to monthly or annual data) (medians and error bars showing the 10% and 90% quantiles).

Relation between background signal and minimum detectable trend

In order to estimate the effect of the temporal variability on the value of the minimum detectable trend, we applied a Student's *t*-test to a two step stair approximation of a linear trend. As a working hypothesis, we assumed that (i) the time series of n_{years} (years) length is split into two halves, (ii) the mean of the values of the second half differs by $\Delta\mu$ from the mean of values of the first half, with

$$\Delta\mu = 1/2 \ n_{\text{years}} \ rslope \ \mu \quad (8)$$

where μ is the mean of all values, and (iii) the temporal variability results in a normal distribution around the mean with σ given with

$$\sigma = \text{CV}\mu \quad (9)$$

where CV can be approximated with CV1 for annual and CV2 for monthly data.

In this case, the minimum detectable trend $rslope_{min}$ can be modelled based on the temporal variability when inserting equations (8) and (9) into the test equation of the Student's t-test, which is

$$\Delta\mu > 2\sigma \frac{T_{\text{crit}}\left(\frac{n}{2}\right)}{\sqrt{\frac{n}{2}}}, \quad (10)$$

and for *rslope* we get the equation (2). Note that in eq (2), c_7 in theory is assumed to be $c_7 = 1$. We used CV = CV1 of annual data for LK and MK, and CV = CV2 of monthly data for SMK and PMK. We then compared these modelled $rslope_{min}^{mod}$ estimates (equation (2)) with the $rslope_{min}^{emp}$ values derived from trend test results (equation (5)) and derived empirical c_7 values.

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