

4. Sulphate and nitrogen deposition and trend analyses

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4.1. Introduction

The atmospheric deposition of sulphur (S) and nitrogen (N) compounds affects forest ecosystems through several processes. Deposition of acidifying compounds, inorganic nitrogen as a nutrient and base cations to forests in Europe is a major driver for many processes in forests. The development of deposition is of high interest and therefore, trend analyses of ICP forests deposition data are regularly produced and published (e.g. Lorenz & Granke, 2009). However, until recently, these trend analyses were usually carried out with data covering the last six years only. Trend analyses with longer time series using linear regression techniques have first been included in the Technical Report 2010 (Granke & Mues, 2010). Trend analyses of part of the ICP Forests deposition data have also been carried out at the national level using Mann Kendall tests or autoregressive time series modelling (e.g. Meeseburg et al., 1995; Kvaalen et al., 2002; Moffat et al., 2002; Lange et al., 2006; Rogora et al., 2006; Wu et al., 2010b; Graf Pannatier et al., 2011).

The various available techniques have their advantages and disadvantages, and the detection and magnitude of trends may to some extent depend on the test used. For example, the linear regression test cannot distinguish between trends caused by changes in precipitation volume and trends caused by changes in the ‘pollution climate’. In comparison, non-parametric tests such as Seasonal Mann Kendall tests are more robust against sporadic events, such as high calcium (Ca) peaks caused by Saharan dust events. Secondly, the minimal detectable trend may depend on the uncertainties included in the deposition measurements (ICP-Forests Manual, ICP-Forests, 2010).

When multiple tests are carried out on a large data set, the possible effect of the size of the data set needs to be considered. For example, if hundreds of tests are carried out on the basis of test having a probability threshold of 0.01, the probability of some false positive becomes relevant. On the other hand, even non-significant trends may indicate a significant change, when the trends have the same direction for most of a large number of trends.

4.2. Objectives

The main goal of this study is to detect trends in deposition at ICP Forests Level II sites (with ICP Forests and pre-ICP Forests data) and to investigate possible causes. The specific objectives are to:

- determine the bulk and throughfall deposition of sulphate and inorganic nitrogen (nitrate and ammonium) and its trends

¹ For addresses see Annex III-4

- investigate the influence of the trend analyses technique on the detection of statistically significant trends by comparing the linear regression test with the Seasonal Mann-Kendall approach.
- investigate the minimal detectable trend in case of deposition measurements made according to the ICP Forests Manual.
- investigate and discuss possible reasons for trends on a European and a regional level.

4.3. Methods

Continuous sampling of throughfall (TF) and bulk deposition (BD) is carried out on ICP Forests intensive monitoring plots (Level II) and at a nearby open field, respectively. The methods used in the countries fulfil the requirements defined in the ICP-Forest Manual (earlier versions and ICP-Forests, 2010) to a large extent (Norway: Kvaalen et al., 2002; Moffat et al., 2002; Italy: Mosello et al., 2002; Switzerland: Thimonier et al., 2005; Czech Republic: Boháčová et al., 2010; UK: Vanguelova et al., 2010; Wu et al., 2010a; Swedish Throughfall Monitoring Network (SWETHRO): Pihl Karlsson et al., 2011). Collectors (10 to 20 replicates) are placed in the forest based on a random or fixed design in order to cover the spatial variation. Tests to determine the minimal number of samplers required to cover spatial variations to gain a representative plot mean have been carried out on a number of plots (e.g. Thimonier, 1998; UK: Houston et al., 2002; Belgium: Staelens et al., 2006). Some samples are collected at least monthly, filtered, and then stored at about 4°C before chemical analyses are performed to determine the concentrations of the macronutrients. The laboratory results are checked for internal consistency based on the conductivity, the ion balance, the concentration of organic N and the Na/Cl ratio, and are repeated if suspicious. The 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 working ring tests (e.g., Marchetto et al., 2006) to check international comparability.

Data was submitted annually by countries to the Programme Coordinating Centre (PCC), checked for consistency and stored in ICP Forest database.

We selected the data used in the analysis by applying the following criteria to the deposition data from the years 1998 to 2010: (i) continuous sampling during >330 days per year, (ii) non-missing concentration values for >330 days per year. Hereby, sampling periods with mean precipitation below 0.1 mm days⁻¹ were counted as non-missing even if no chemical analyses could be performed.

Since precise dates of the sampling periods have not been submitted for data collected before 2007, the sampling dates were reconstructed based on start and end date and the number of sampling periods per year. Data of the sampling periods were interpolated to regular monthly and annual data with three steps: (i) intersection of sampling periods at end of months/years distributing precipitation quantity proportional to the duration to the new sampling periods, /split of every sampling period overlapping two consecutive months into two new sampling periods, by distributing precipitation quantity in proportion to the duration of the new sampling periods (ii) using deposition=0 for periods with missing concentrations and mean precipitation < 0.1 mm day⁻¹ (iii) calculation of the deposition fluxes qc (kg ha⁻¹ a⁻¹) of these periods by multiplying precipitation quantity q (L m⁻²) with the concentrations c (mg L⁻¹) with

$$qc = 0.01 q c$$

and summing up the fluxes of months and years.

Both bulk precipitation and throughfall deposition of sulphur were corrected for the contribution from sea salt to estimate the anthropogenic part of sulphur deposition $SO_4^{--}{}_{corr}$ (mg L^{-1}) with

$$SO_4^{--}{}_{corr} = SO_4^{--} - 0.54 \text{ Cl}^-$$

where SO_4^{--} and Cl^- (mg L^{-1}) are the concentration of sulphate and chloride.

Trend analyses were carried out with (i) linear regression (LRegr) (Granke & Mues, 2010) and (ii) Mann-Kendall (MK) test (Mann, 1945; Helsel & Hirsch, 2002) using annual deposition fluxes, and with (iii) Seasonal Mann-Kendall (SK) (Hirsch et al., 1982; Hirsch & Slack, 1984), and (iv) Partial Mann Kendall (PMK) tests (Libiseller & Grimvall, 2002) using monthly deposition data. The SAS and R software was used for the linear regression and Kendall tests, respectively (Marchetto, 2012). For the Kendall tests (MK, SK, PMK), trend slopes were estimated using Sen's (1968) equations.

We calculated a relative slope *rslope* (a^{-1}), an estimated mean relative change per year, with

$$\text{rslope} = \text{slope} / \text{mean},$$

where slope ($\text{kg ha}^{-1} \text{ a}^{-1}/\text{a}$) is the estimator for the absolute trend resulting from the trend analyses and mean ($\text{kg ha}^{-1} \text{ a}^{-1}$) is the mean value of the time series.

The relative slope was plotted against the p-value to investigate patterns that may be used to define a minimal detectable trend for deposition data.

4.4. Results

4.4.1. Current deposition

Mean annual throughfall (TF) and bulk deposition (BD) of sulphur and nitrogen was calculated for 289 and 357 plots with at least one of the years 2008, 2009 and 2010 meeting the mentioned completeness criteria (Figures 4.4.1-1 and 4.4.1-2).

High sulphur deposition has been measured in northern central Europe especially in a region covering Belgium/Netherlands, Central Germany, Czech Republic and Poland, as already mentioned by Granke et al. (2010), reaching up to the southern Baltic and the Central Hungarian area. Furthermore, high values have also been found in some Mediterranean regions in Spain, France, Southern Italy and Greece. Higher values in throughfall than bulk deposition confirm that sulphur is filtered from the air by the tree canopies. High sulphur depositions along the coast mostly occur with high Cl deposition, which is typical for sulphur that originates from sea salt.

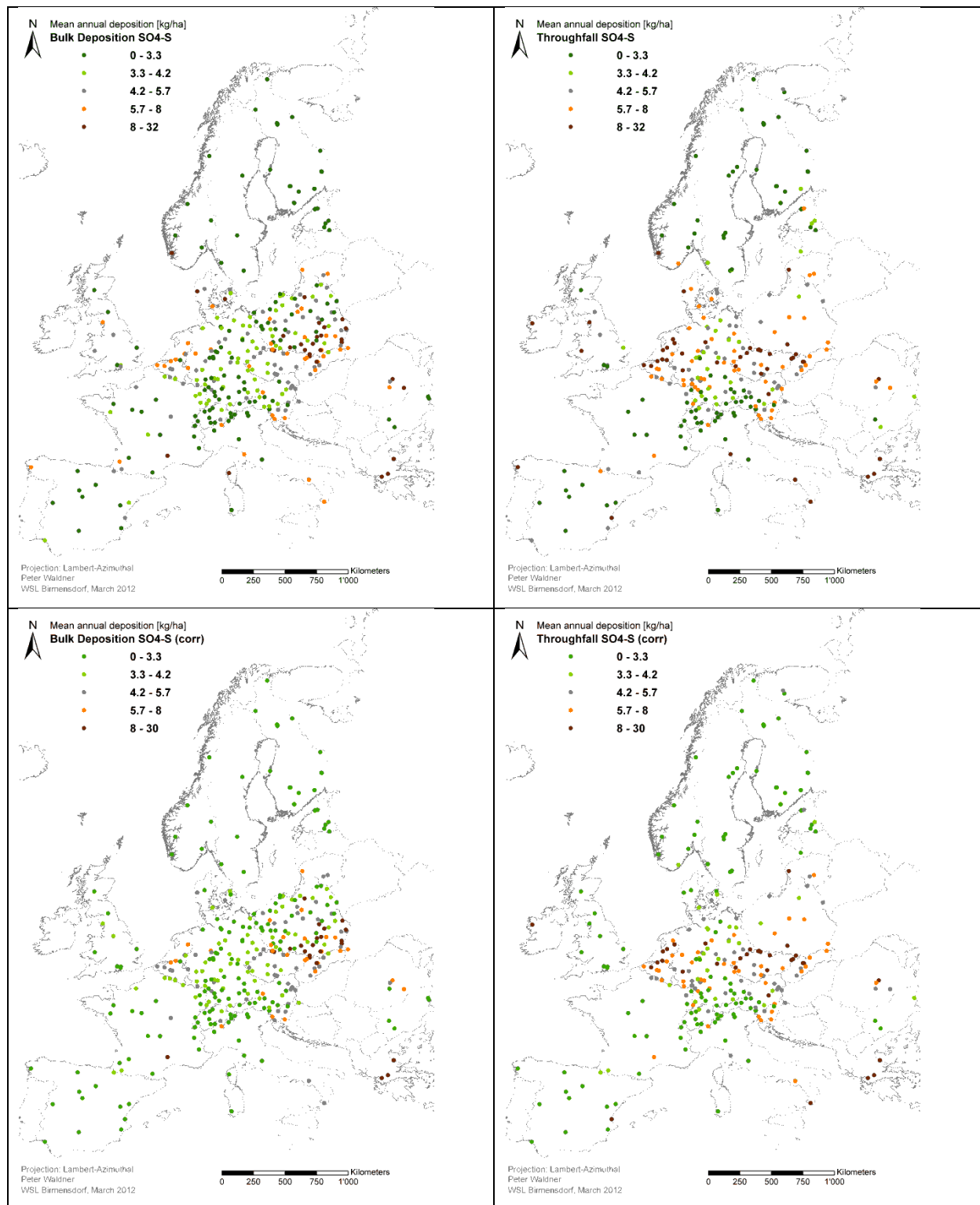


Figure 4.4.1-1 Mean annual sulphate sulphur (SO₄⁻) throughfall and bulk deposition 2008 to 2010 with and without sea salt deposition included. Corr = no sea salt included

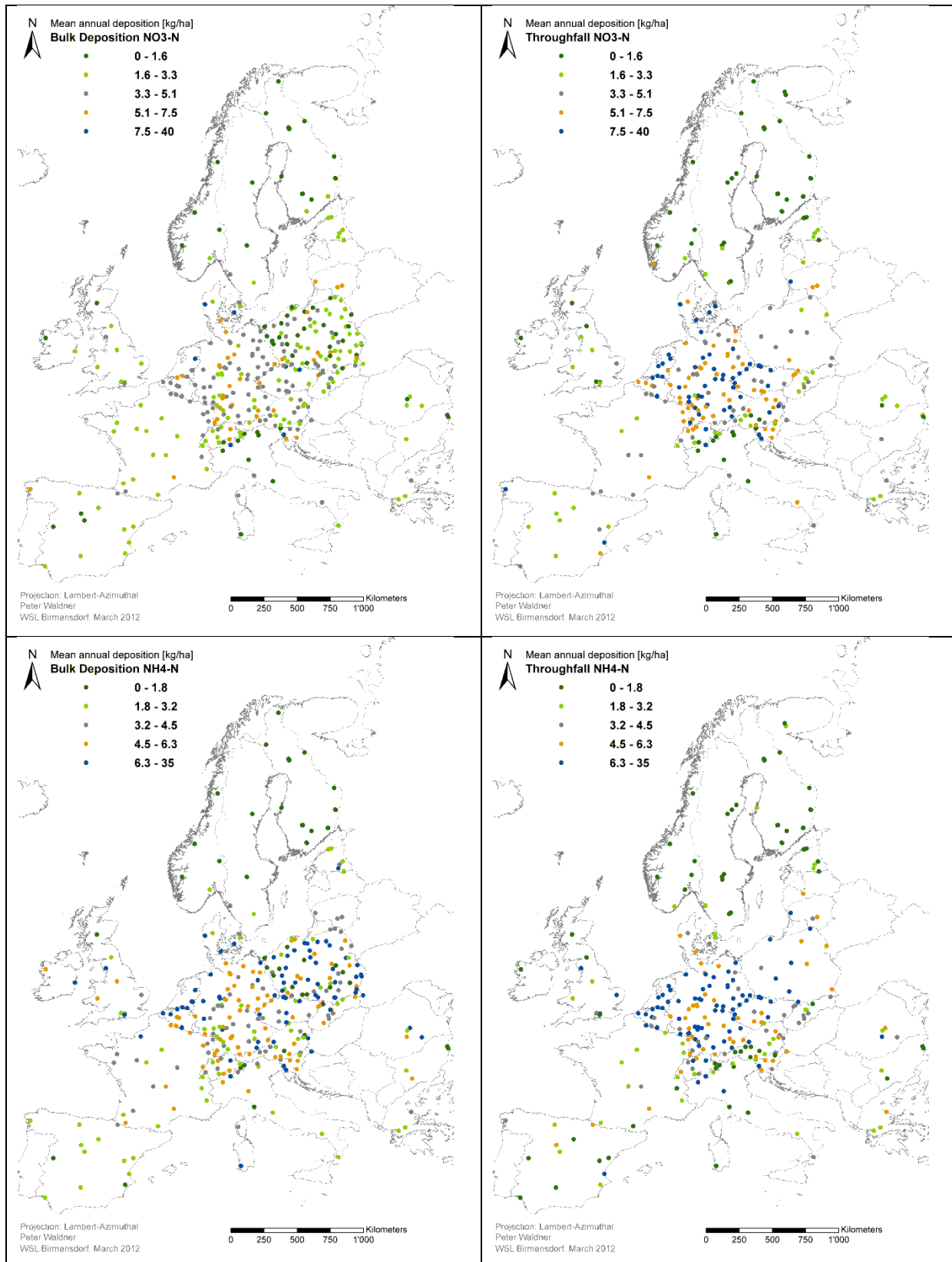


Figure 4.4.1-2 Mean annual nitrate (NO₃⁻-N) and ammonium (NH₄⁺-N) bulk and throughfall deposition during the period from 2008 to 2010.

High nitrogen deposition is also recorded in northern central Europe, as for sulphur, but extends further to the South down to southern Germany and the Swiss Plain, as observed in earlier years (Granke & Mues, 2010). Data from sites in UK and Ireland, not included in Granke et al. (2010), show that for ammonia the high deposition regions extends also further to the West, not only to northern France, but also to central UK and Ireland. In contrast to sulphur, the regions south of the Alps show relatively high bulk and throughfall deposition of nitrate and ammonium as well. In the Mediterranean area, relatively high values have been recorded at some sites in Spain and in southern France.

4.4.2. Temporal trends

For 87 and 55 sites with throughfall and bulk deposition measurements from 1998 to 2001 respectively, we calculated time series for sulphur and nitrogen. These time series include the period 1998 to 2007 for which trend analyses have been carried out by Granke et al. (2010) as well as the period from 2001 to 2010 analysed here. At some few of these sites, the correction for sea salt could not be performed because chloride data did not meet the mentioned criteria.

The sulfur deposition showed a decreasing trend for the period from 2001 to 2010 that is detected by linear regression as being significant for the majority of the sites (Figure 4.4.2-1)

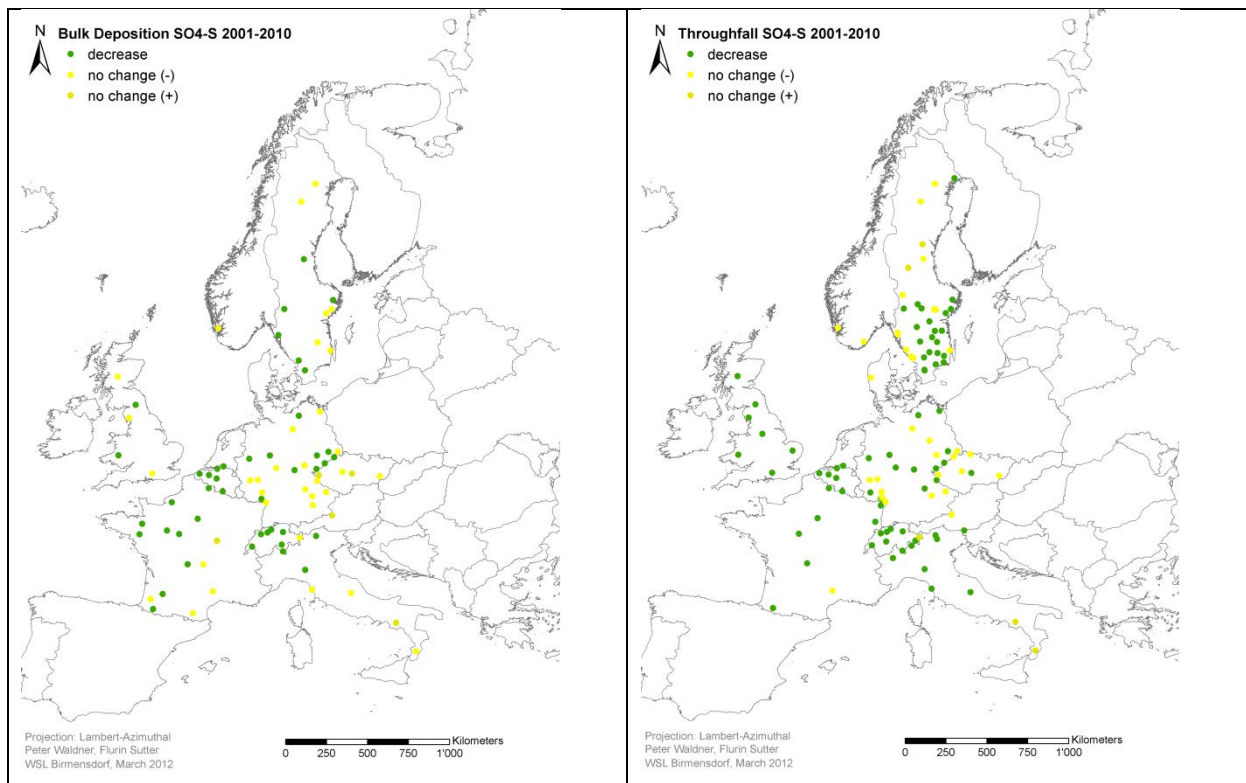


Figure 4.4.2-1 Trend of sulphate ($\text{SO}_4^{2-}\text{-S}$) bulk and throughfall deposition on plots with continuous measurements from 2001 to 2010. Non-significant positive trends are indicated with 'no change (+)' and non-significant negative trends with 'no change (-)'.

The mean of the sites with continuous measurement from 1998 to 2010 decreased from about 10 and 7 $\text{kg S ha}^{-1} \text{a}^{-1}$ to about 5 and 4 $\text{kg S ha}^{-1} \text{a}^{-1}$ (Figure 4.4.2-3) for throughfall and bulk deposition, respectively. This corresponds to a relative decrease of about 6% per year. However, for the individual sites, the mean relative decrease ranged from about 0% to 10% per year (Figure 4.4.3-1) and low relative decreases have also been estimated for some of the sites

with high sulphur deposition. In comparison, the mean precipitation volume remained quite stable except for the drier year 2003 and, to a lesser extent, 2005.

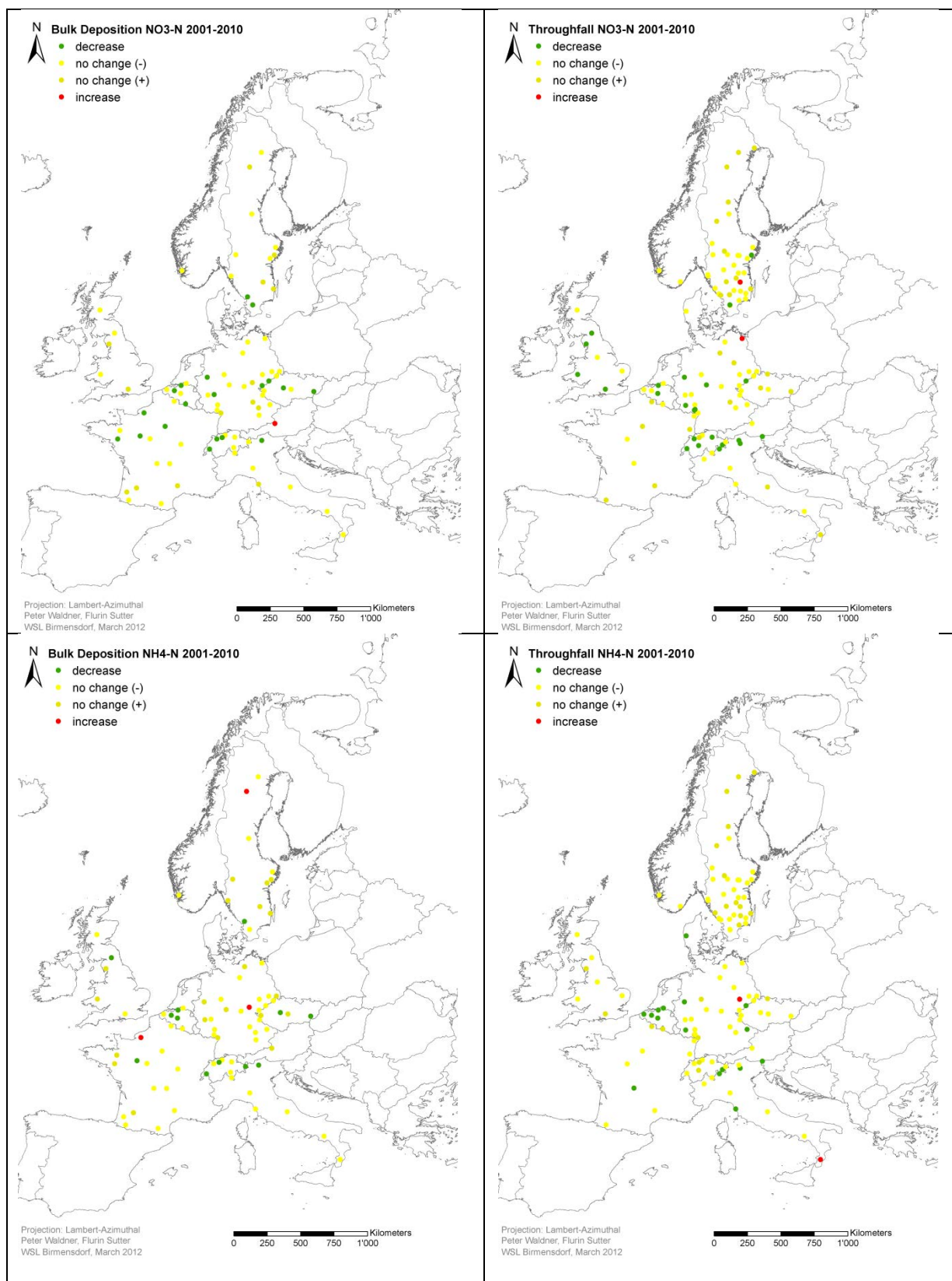


Figure 4.4.2-2: Trend of nitrate (NO₃⁻-N) and ammonium (NH₄⁺-N) bulk and throughfall deposition of plots with continuous measurements from 2001 to 2010. Non-significant positive trends are indicated with 'no change (+)' and non-significant negative trends with 'no change (-)'.

For the plots with continuous inorganic nitrogen deposition measurement in bulk and throughfall from 2001 to 2010, trends that were significant have been detected for less plots than for sulphate (Figure 4.4.2-2). The mean throughfall deposition of inorganic nitrogen on sites with continuous measurements from 1998 to 2010 decreased from about 11 to about 9 kg N ha⁻¹ a⁻¹ i.e. circa 20%, corresponding to a mean decrease of about 1 to 2% per year (Figure 4.4.2-4).

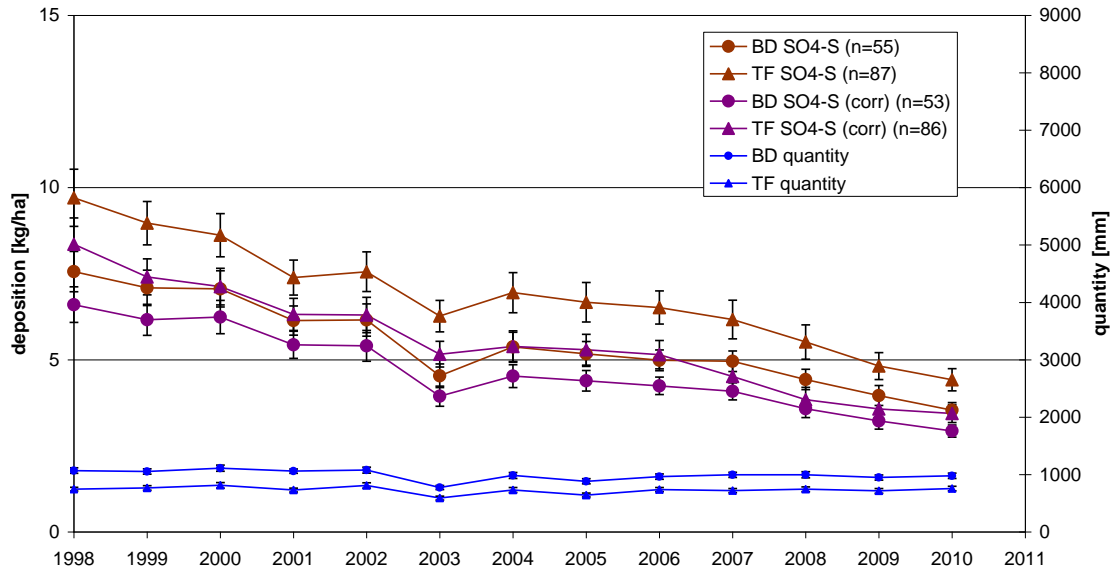


Figure 4.4.2-3: Mean sulphate ($\text{SO}_4\text{-S}$) bulk and throughfall deposition and precipitation volume (quantity) on plots with continuous measurements from 1998 to 2010, with and without correction for sea salt deposition. Corr = no sea salt included. Error bars show the standard error of the mean.

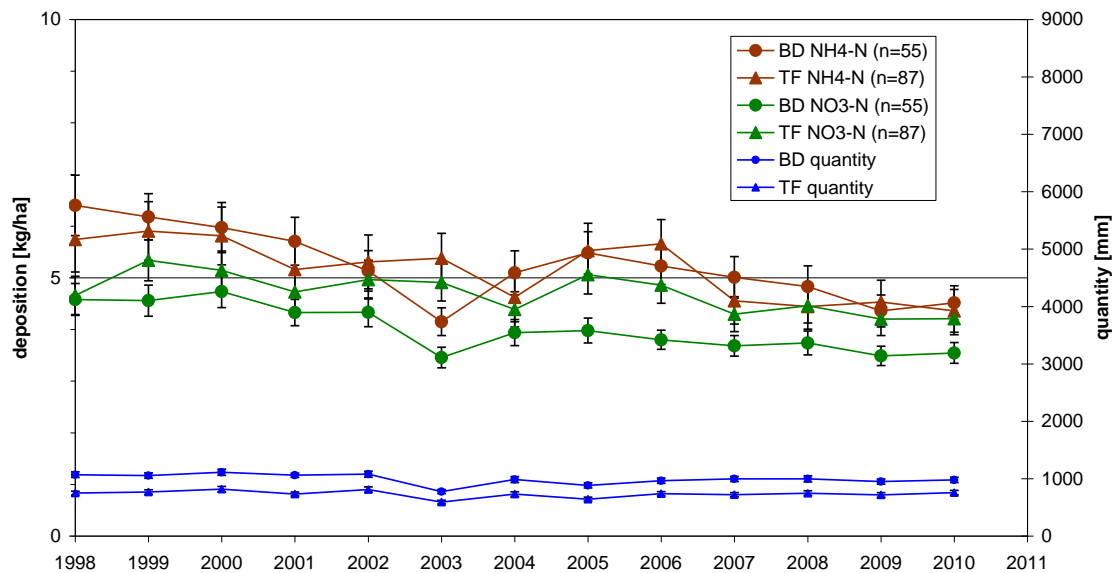


Figure 4.4.2-4: Trend of nitrate ($\text{NO}_3\text{-N}$) and ammonia ($\text{NH}_4\text{-N}$) bulk and throughfall deposition and precipitation volume (quantity) of plots with continuous measurements from 1998 to 2010. Error bars show the standard error of the mean.

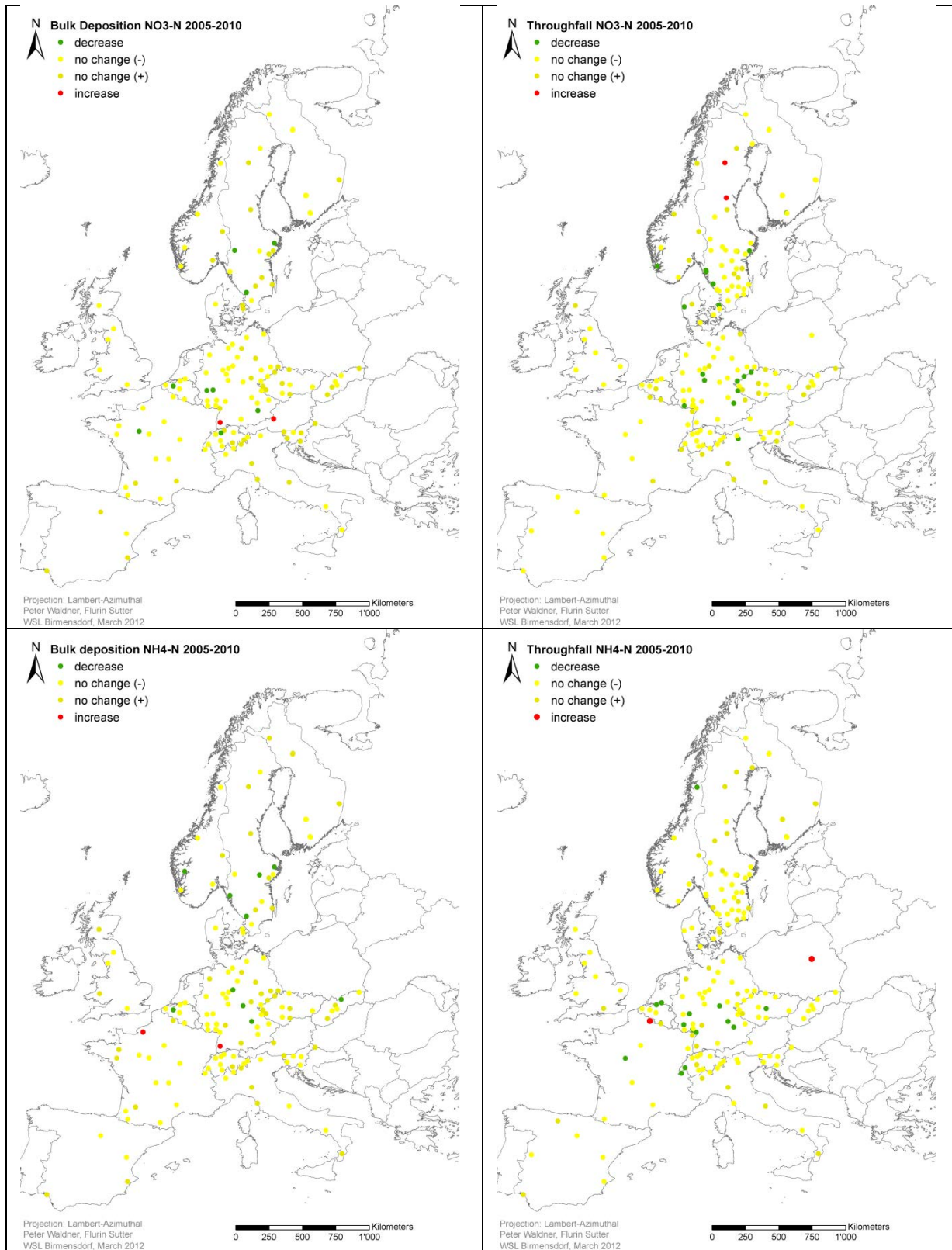


Figure 4.4.2-5: Recent trend of nitrate nitrogen (NO₃⁻-N) and ammonia nitrogen (NH₄⁺-N) bulk and throughfall deposition of plots with continuous measurements from 2005 to 2010.

4.4.3. Comparison of trend analyses techniques

The slope estimates of the Kendall trend analyses techniques showed a quite high agreement to those of linear regression in Figure 4.4.3-1 (left side) for SO_4^{2-}S fluxes in throughfall. The agreement of slopes was highest for Mann-Kendall (MK) that was performed with annual data as well. It was a bit less high for Seasonal Mann-Kendall (SK) and Partial Mann-Kendall (PMK) tests that were carried out with monthly data and aim on taking into account seasonal variation and the co-variable precipitation quantity. Significance of a statistical test is given, if the p-value is lower than a certain value, e.g. $p < 0.05$ in case of a 95% significance level. In Fig. 4.4.3-1 (right side) the p-values of the Kendall tests are plotted against those of the linear regression (LR) than the slopes test. In general, the differences were lower for longer time series. The relation between the p-values of MK and p-values of LR is not very strong, the points scatter. The p-values of SK and especially PMK however, tend to be lower than those of LR.

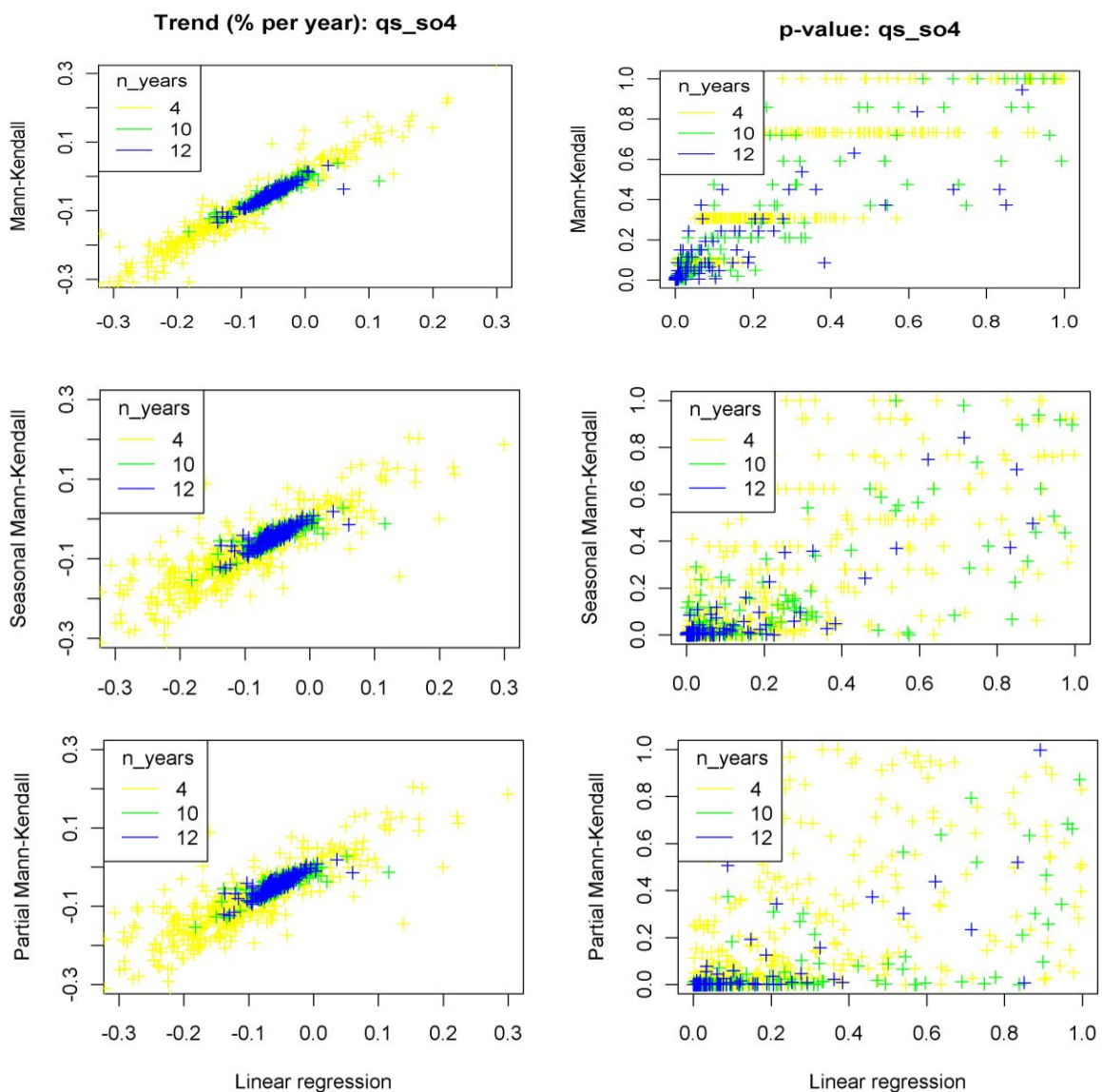


Figure 4.4.3-1: Relative slope (rslope) and p-value of Kendall trends tests MK, SMK and PMK versus linear regression trend test for SO_4^{2-}S throughfall deposition from 1998 to 2010 (12 years), 2001 to 2010 (10 years), and 2007 to 2010 (4 years).

The compared trend analyses techniques resulted thus in similar trend slope estimates, but detection with statistical significance was more frequent for PMK and SK than for MK and LReg.

4.4.4. Estimation of minimal detectable trend

The minimal relative slope of a monotonic trend that is required to identify this trend with statistical significance was investigated by plotting the p -value of the trend test versus the relative slope estimate ($rslope$).

Fig.4.4.4-1 shows the p -values are plotted against the relative slope $rslope$ for trend tests of throughfall deposition of SO_4^{2-} -S time series with 4, 6, 9, 10 and 12 years of continuous measurement until 2010.

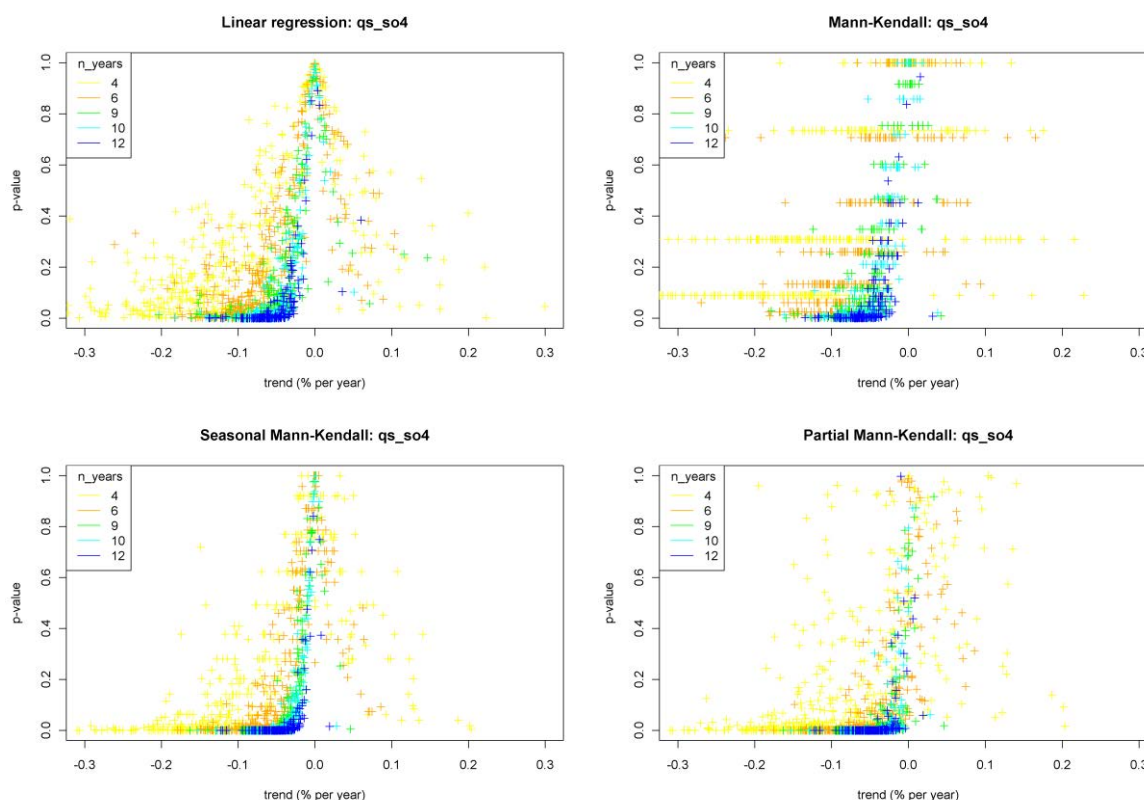


Figure 4.4.4-1: P-value plotted against relative slope estimates of trend analyses with linear regression (LReg), Mann-Kendall (MK) of annual means, Seasonal Mann-Kendall (SK) and Partial Mann-Kendall (PMK) of SO_4^{2-} -S throughfall (TF) deposition fluxes time series with 4, 6, 9, 10 and 12 years of continuous data until 2010.

On this p -value vs. $rslope$ graph, most dots, i.e. trend estimates, are within a quite narrow band with the shape of a Gaussian curve. This band and its Gaussian curve shape is narrower for longer the time series and slightly differ from trend test to trend test. For linear regression (LReg) of times series with 12 years of SO_4^{2-} -S throughfall data, most trends with $rslope$ above 3% to 5% per year have $p < 0.05$ (significant) and while most of trends with $rslope$ below 3 to 5% have $p > 0.05$ (not significant). We may conclude that an $rslope$ of at least 3% to 5% per year is required to detect a trend with statistical significance in this case. For shorter time series the required relative trend slopes $rslopes$ seem to be higher while it seem to be lower for the Seasonal Mann-Kendall (SK) and the Partial Mann-Kendall (PMK) test. The patterns were similar for the major macro nutrients ammonia, nitrate, calcium and magnesia as shown in

Fig. 4.4.4-2 the minimal detectable trends seem to be slightly higher for elements with higher temporal variability due to e.g. sporadic events such as Saharan dust deposition for calcium.

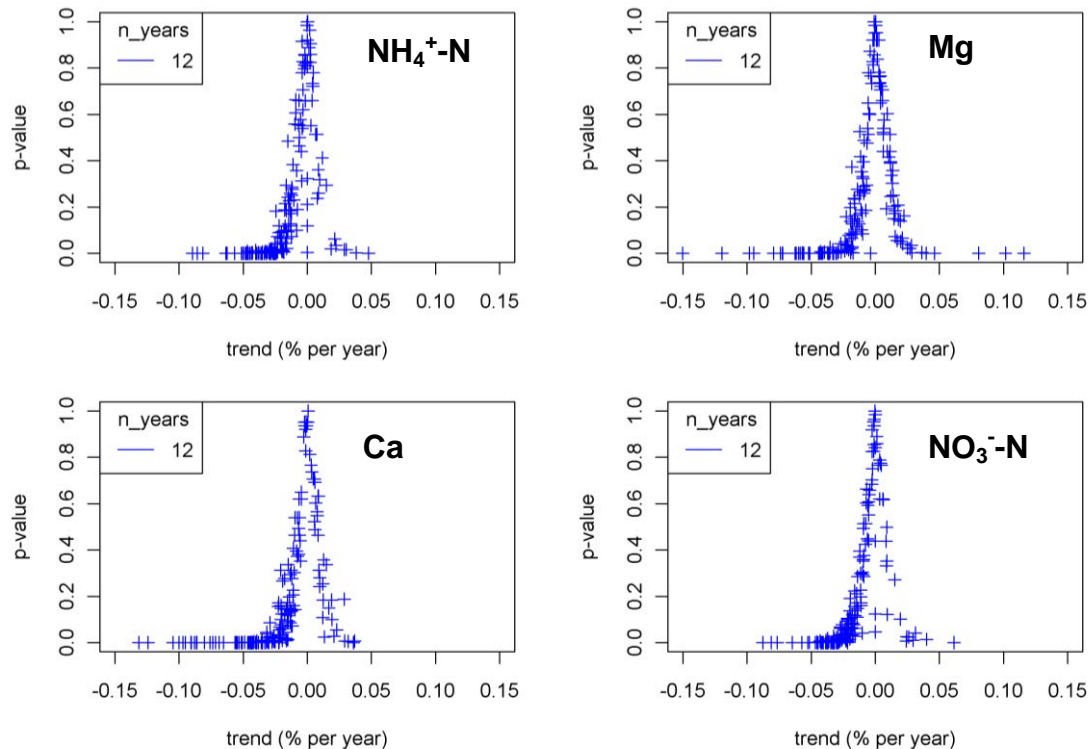


Figure 4.4.4-2: p-value plotted against relative slope estimates of trend analyses with Seasonal Mann-Kendall (SK) for ammonium, magnesium, calcium and nitrate throughfall (TF) deposition fluxes time series with continuous data from 1998 to 2010 (12 years).

4.5. Discussion

This joint evaluation that involved numerous national experts responsible for the deposition measurements in their countries opened the opportunity (i) to reconstruct the sampling periods for older datasets, (ii) to complete the dataset in case of missing years, (iii) to include corrections made on national level as well as to integrate arguments for the interpretation of the results.

The comparison of the trend analyses techniques confirmed that the choice of a specific method has an influence on the number of trends identified as being significant. Seasonal Mann-Kendall and Partial Mann-Kendall tests applied to monthly data identified more significant trends than linear regression techniques. However, there was a quite high agreement between the slope estimates of the trend analyses techniques.

Minimal detectable trends were derived from a quite strong relation between trend significance and relative trend slope seen in the deposition fluxes time series of the same length. The results were relatively consistent in terms of the minimal relative slope required for a trend to be detected as significant for a certain length of time series. The minimal detectable trend (mdT) seem to be a bit smaller for Partial Mann-Kendall tests than for the other tests. The mdT was a bit higher for calcium (Ca) than for the other investigated nutrients. This

might be explained by a higher temporal variability. For Ca often reported that a high part of the annual deposition is due to relatively few peak events (e.g. Rogora et al., 2004).

For time series with 10 years the 'minimal detectable trend' estimated from the p-value vs. rslope diagram is in the same order of magnitude as the data quality objective (DQO) for the determination of the annual deposition defined in the ICP-Forests Manual (ICP-Forests, 2010). Working ring-tests for laboratory inter-comparison (Marchetto et al., 2011) as well as the field inter-comparison exercise with (i) a common (harmonized) sampler on national plots (Zlindra et al., 2011) as well as with (ii) national samplers in a common plot (Bleeker et al., 2003; Erisman et al., 2003) showed that these data quality objectives are realistic and that it can be assumed that they are met for the majority of the ions, laboratories and plots.

The trends found in this study for S and N compounds are in agreement with most other studies (Vanguelova et al., 2010; Graf Pannatier et al., 2011). Meesenburg et al. (1995) carried out trend analyses of annual deposition data from 1981 to 1994 of 4 plots in Germany with linear regression techniques. They also found significant decrease of SO_4^{2-} with rslope between -5 and -9% a⁻¹ for all plots but only a slight decreasing tendency for NO_3^- (between 0 and -3% a⁻¹) that was significant only at one plot. Kvaalen et al. (2002) also found a significant decreasing trend (rslope between +2 and -15%) in monthly SO_4^{2-} bulk and throughfall deposition from 1986 to 1997 that was significant for 11 out of 13 plots in Norway. Moffat et al. (2002) noted that the small but significant decrease of almost all ions in throughfall deposition from 1987 to 1997 of these plots was in line with earlier findings of Likens et al. (1996) and Stoddard et al. (1999) for stream water chemistry in North America and Europe.

When Rogora et al. (2006) compiled an overview of trend of bulk and throughfall deposition in the Alps for the two periods 1985-2002 and 1990-2002 they found that the decreasing trends of N deposition were still significant at the minority of sites (about 25% of the sites for NO_3^- and 50% of the sites for NH_4^+) while SO_4^{2-} trends were clearly significant at all sites with the Seasonal Mann-Kendall that is more conservative than linear regression used for the maps here. Hence, for the 2001 to 2010 period, decreasing trends seem to flatten for SO_4^{2-} as well as for NH_4^+ and NO_3^- .

Moreover, Vanguelova et al. (2010) found SO_4^{2-} decrease that were significant at only 4 out of 10 plots for bulk deposition but at 8 out of 10 plots for throughfall deposition in the monthly 1995 to 2006 deposition data in UK. In bulk deposition the background level of sea salt sulphur deposition might be relatively high at some of the coastal plots in UK. Same magnitudes of absolute decreasing trends might thus result in lower relative slopes of the trends at these sites, especially for bulk deposition.

Fagerli et al. (2008) compared NO_3^- and NH_4^+ concentration in wet precipitation modelled by EMEP based on the emissions inventories with measurements for the period from 1980 or later to 2003 and various sites in Europe. They also found decreasing trends being significant for about half of the sites for both modelled and measured data. The significant decreases ranged from about 20% to 60% in 20 years, corresponding thus to relative slope of about 1% to 6% a⁻¹. However, most of the reductions seem to have taken place in the years between 1985 and 1995. Other reasons for decreasing deposition are changes in the tree stand structure, such as the reduction of the number of trees due to a bark beetle attack that occurred on a Czech plot (2161).

However, atmospheric deposition values presented here are restricted to bulk and throughfall deposition fluxes of inorganic compounds. Total deposition to forests also includes organic compounds, stemflow, as well as canopy uptake. Especially for nitrogen, total deposition typically is significantly higher than the throughfall fluxes.

4.6. Conclusions

In about half of the sites a decrease of N and S was observed in the periods 2001 to 2010 and 2005 to 2010 that was strong enough to be identified with statistical significance.

It could be confirmed that the selection of the trend analyses techniques has an effect on trend detection. There was a quite high agreement in estimated trend slopes. However, Seasonal and Partial Mann-Kendall tests applied to monthly data tend to detect smaller trends with statistical significance than linear regression techniques applied to annual data.

There was a quite consistent relation between the relative slope and p-value of the trend tests for a given length of time series independent of the trend analyses technique used. These patterns also varied surprisingly little between ions. It seems likely that the minimal detectable trend depends mainly on the length of the time series. For time series with a length of 10 years, the minimal detectable trends for N and S compounds seem to be around 3% change per year for linear regression techniques applied to annual data, and around 1% to 2% for Partial Mann-Kendall tests applied to monthly data.

For N compounds, the trends in atmospheric deposition expected to result from the emission reductions in Europe typically are in this range and are unlikely to be detected with statistical significance in time series with a length of much less than 10 years of measurement. For S compounds, typical trends were often higher especially in the 90ties favouring a trend detection with statistical significance.

The deposition trends found in this evaluation are thus quite comparable to those estimated by the European Monitoring and Evaluation Programme from emission inventories. However, it is worth noting that the bulk and throughfall fluxes presented here cannot directly be compared to the total atmospheric deposition as estimated by EMEP.

4.7. Acknowledgements

The method for determination of atmospheric deposition fluxes applied in ICP-Forests has been further developed and harmonized by numerous scientists within the Expert Panel on Deposition that has subsequently been chaired by Erwin Ulrich, Nicolas Clarke and Karin Hansen during the years this investigation is focused on. Application of the methods involved numerous field technicians to install about 4000 samplers, local forest services and field observers to collect more than about a million individual samples, chemical analyses of about 200'000 pooled samples and on-going supervision by about 40 responsible scientists. Data transmission involved national focal centres and the data centre of ICP Forests that was subsequently at FIMCI in the Netherlands, at the Joint Research Centre in Ispra and is today at the Programme Coordination Centre in Hamburg. Data transmission included sophisticated conformity and plausibility checks developed by the involved data base specialists. The comparability of the laboratory analyses has been improved by the activities of the Working Group on QA/QC in labs (standardisation of lab methods, exchange of experience and working ring-tests) initiated and supported by Rosario Mosello, Nils König, Erwin Ulrich, Kirsti Derome, Anna Kowalska, Aldo Marchetto and others. Similarly activities for the field installations were organised by Albert Bleeker, Jan Erisman, Erwin Ulrich, Daniel Zlindra and others. Data quality objectives used here and other methodical improvement were the result by the activities of the QA/QC committee chaired by Marco Ferretti. The atmospheric deposition measurement was established in the frame of the ICP-Forests Programme and was enabled through various ways. Typically this involved access granted by public or private land owners, financial support from the participating countries and the EU, as well as support from

subordinated governmental organisations such as districts, communities or even local forest services.

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