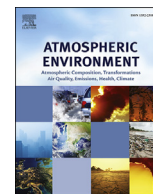


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Trends in ammonia measurements in the Netherlands over the period 1993–2014

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HIGHLIGHTS

- Trends in observed ammonia and reported emissions between 1990 and 2004 are consistent.
- Trends between 2005 and 2014 diverge: emissions further decline but concentrations rise.
- Trends in ammonium in aerosol and precipitation do not match the trends in ammonia.
- No trend in ammonia exists due to a trend in meteorological conditions.

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ABSTRACT

We present measurements of atmospheric concentrations of ammonia and ammonium in the Netherlands over the period 1993–2014 and measurements of wet deposition of ammonium for 1985–2014. The various time series have been obtained at 16 monitoring stations from the Dutch National Air Quality Monitoring Network. The monitoring stations are geographically homogeneously spread over the Netherlands and are equally distributed over regions with relatively low, moderate and high ammonia emission.

During the period covered, changes in the monitoring have occurred. To obtain consistent time series, data are revalidated or corrected when necessary, according to current validation procedures or latest technical insights. The time series of ammonia concentrations are gap filled and time series corrected for meteorological influences are constructed.

The course in the ammonia concentrations shows roughly two periods. For 1993–2004, the ammonia concentrations show a downward trend of 36%, which is statistically significant with a confidence interval (CI) of 99%. For 2005–2014, an upward trend of 19% (CI 90%) is reported. Correcting time series of ammonia concentrations for meteorological influences enhances the statistical reliability of the derived trends. This resulted in trends of –40% (CI 99%) and 24% (CI 95%) respectively. For the full period there exists no trend in ammonia concentrations due to a trend in atmospheric conditions. For 2005–2014 ammonia concentrations increased especially in springtime, while showing no change in winter months. After correcting for meteorological influences, all seasons in this period show an increase in ammonia concentrations although the increase in the spring months is still the largest.

For 1993–2014 the reported ammonia emissions in the Netherlands declined in both periods with respectively 51% and 22%. The trends in emissions and ammonia concentrations correspond in the period 1993–2004 whilst over the period 2005–2014, the trends in emissions and concentrations of ammonia diverge. This divergence is for roughly a third accounted for by processes related to changes in chemical climate (see accompanying modelling paper by Wichink Kruit et al., 2016) but it is not clear what explains the remaining difference in trends.

For 1993–2014, downward trends of wet deposition of ammonium and ammonium in aerosol are found to be 47% and 68%, respectively. A split into two periods is not found as is the case with the ammonia concentration. However, although statistically not significant, both wet deposition of ammonium and ammonium in aerosol show a leveling off in decline between 2005 and 2014.

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1. Introduction

Already in the 1990s, hourly ammonia concentrations (NH_3) were measured continuously at several monitoring stations in the Netherlands (Buijsman et al., 1998). This observation network was set up to monitor the effect of Dutch policy measures on the reduction of ammonia emissions. In the Netherlands, ammonia concentrations are among the highest in Europe due to a high density of agricultural activities. High NH_3 detriments vegetation such as lichens and leads to deposition in nature areas. Nitrogen deposition above a critical load leads to acidification and eutrophication causing a loss of biodiversity (e.g. Bobbink et al., 2010). In order to mitigate these high nitrogen deposition values, several abatement policies have been implemented over the years, of which the techniques to reduce ammonia emissions caused by housing livestock, and storing and applying of manure are best known.

As a result of the abatement policies, reported ammonia emissions show a steady decline since 1990 with the largest decline taking place in the first decade (Fig. 1). The decline is largely due to the measure of incorporating animal manure into the soil instead of broadband spreading. In the Netherlands, the total ammonia emission consists for about 85% of agricultural emissions, the latter being calculated with the National Emission Model for Agriculture (NEMA, Bruggen van et al., 2011; Velthof et al., 2012). Since 2011, the Dutch Pollutant Release and Transfer Register uses NEMA for its annual reporting of ammonia emissions from agriculture (Maas van der et al., 2011) to the European Commission (NEC Directive) and United Nations (Gothenburg protocol). The emission time series is updated every year according to the latest insights, in this article the time series as reported in 2014 are used.

The main question discussed in this paper is whether the reported decline in ammonia emissions is reflected in atmospheric concentration time series. The relation between emissions and concentration of NH_3 is not straightforward since emission characteristics and several atmospheric processes determine NH_3 in the atmosphere. After ammonia is emitted, it is subsequently mixed and transported in the atmosphere. It is chemically transformed into secondary inorganic aerosols such as ammonium nitrate and ammonium sulfate and it is removed from the atmosphere by dry and wet deposition. Finally, meteorological processes influence the

effectiveness of the previously mentioned processes. Yet, atmospheric concentration of NH_3 is the most reliable component to monitor the emission trends over the years (Jaarsveld van et al., 2000; Sutton et al., 2003; Bleeker et al., 2009).

Because ammonium in aerosol ($(\text{NH}_4^+)_{\text{air}}$) and wet deposition of ammonium ($(\text{NH}_x)_{\text{wet}}$) suffer from additional factors making them less suitable indicators than NH_3 . $(\text{NH}_4^+)_{\text{air}}$ is formed from NH_3 and as such a secondary product which is also influenced by trends in the precursors of the sulfate and nitrate parts. Especially, the rapid decline in SO_2 concentrations has an influence on the ammonium trend (see for example, Sutton et al., 2003; Horvath and Sutton, 1998). Secondly, $(\text{NH}_4^+)_{\text{air}}$ has a longer lifetime in the atmosphere than NH_3 which ensures a larger contribution of foreign emissions to its concentration in the Netherlands. Model results show 40% of $(\text{NH}_x)_{\text{wet}}$ to originate abroad (Van der Swaluw et al., 2011) while for $(\text{NH}_4^+)_{\text{air}}$ this number raises to 50%. For NH_3 this number is on average roughly 15%, though close to the German and Belgian border this number obviously may rise.

Because NH_3 is influenced by several factors as mentioned above, model calculations are necessary to account for all these processes. Wichink Kruit et al. (2016) give in an accompanying paper a detailed analysis of the trend in NH_3 using the Operational Priority Substances (OPS) model (Sauter et al., 2015), which is an atmospheric transport and deposition model. In the current article we explore what can be inferred about the reported decline in ammonia emissions from ammonia measurement analyses alone.

In this paper we will present time series of all three components NH_3 , $(\text{NH}_4^+)_{\text{air}}$ and $(\text{NH}_x)_{\text{wet}}$ and derive linear trends for various periods. The data sets were partly revalidated and re-analyzed for this study. The influence of meteorological processes on NH_3 is quantified through a multivariate regression analysis of measurements of meteorological parameters. Finally, we will discuss the trends in ammonia measurements with respect to reported emission reductions.

2. Materials and methods

The Dutch National Air Quality Monitoring Network (LML, Landelijk Meetnet Luchtkwaliteit, www.lml.rivm.nl) measures various air quality components. This article discusses all measurements related to ammonia in the period 1993–2014: ammonia concentrations (NH_3), ammonium in aerosol ($(\text{NH}_4^+)_{\text{air}}$) and the wet deposition of ammonium ($(\text{NH}_x)_{\text{wet}}$). For wet deposition a time series starting in 1985 is taken. An overview of the monitoring stations and the components measured is given in Table 1 and the configuration of the monitoring stations is presented in Fig. 2.

2.1. Air concentrations of ammonia

In the network, hourly ammonia concentrations have been measured since 1993 at eight monitoring stations and since 2014 at six locations. Continuous-flow denuders, named AMORs (Amanda for MOonitoring RIVM developed by ECN, Wyers et al., 1993) are used. AMORs have a concentration range for ammonia in air of 0.5–500 $\mu\text{g}/\text{m}^3$. The uncertainty in the observed annual mean values has been estimated to be 7% (Blank, 2001). The instrument samples air by leading the airflow through a fluid in a rotating denuder tube. Ammonia is absorbed by this fluid and electrical conductivity is determined as a measure for the ammonia concentration. AMORs are stable and accurate instruments, but expensive in maintenance and use of chemicals. At the two monitoring stations where AMOR measurements have ended, triplets of Gradko passive samplers (Lolkema et al., 2015) are used for monthly mean values; in this study the measurements for the year 2014 have been included.

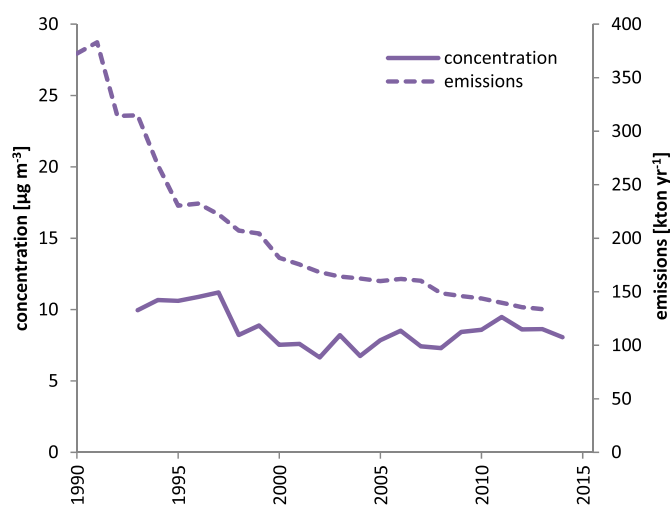


Fig. 1. Trends in reported ammonia emissions (Jimmink et al., 2015) and measured NH_3 between 1990 (emissions)/1993 (measurements) and 2014. The ammonia concentration is represented by the mean of gapfilled time series of 8 monitoring stations (see Materials and methods for more information).

Table 1
LML monitoring stations (number # and name) with ammonia related measurements. Measurement periods in brackets were not used in this study. *) Due to the short length of the time series data of Witteveen is only used in the applied gapfilling procedure. +) Since 2014 measurements obtained with passive samplers.

Monitoring station		NH ₃		(NH _x) _{wet}		(NH ₄) _{air}	
#	Name	Start date	End date	Start date	End date	Start date	End date
131	Vredepeel	1993	2014	1988	2014	1993	2014
134	Beek	–	–	1985	2012	–	–
231	Gilze Rijen	–	–	1985	2012	–	–
235	Huijbergen	1993	2014 ⁺	–	–	1993	2012
318	Philippine	–	–	1985	2014	–	–
434	Rotterdam	–	–	1985	2012	–	–
444	De Zilk	1994	2014	1995	2014	1994	2014
538	Wieringerwerf	1993	2014	1988	2014	1993	2014
540	Leiduin	(1993)	(1993)	1985	1992	–	–
627	Bilthoven	–	–	–	–	1993	2012
628	De Bilt	–	–	1985	2014	–	–
633	Zegveld	1993	2014	–	–	–	–
722	Eibergen	1993	2014 ⁺	–	–	–	–
738	Wekerom	1993	2014	–	–	–	–
928	Witteveen	(1993)*	(1999)	1985	1999	1993	1999
929	Valthermond	2000	2014	2000	2014	2000	2014
934	Kollumerwaard	–	–	1990	2012	1993	2012

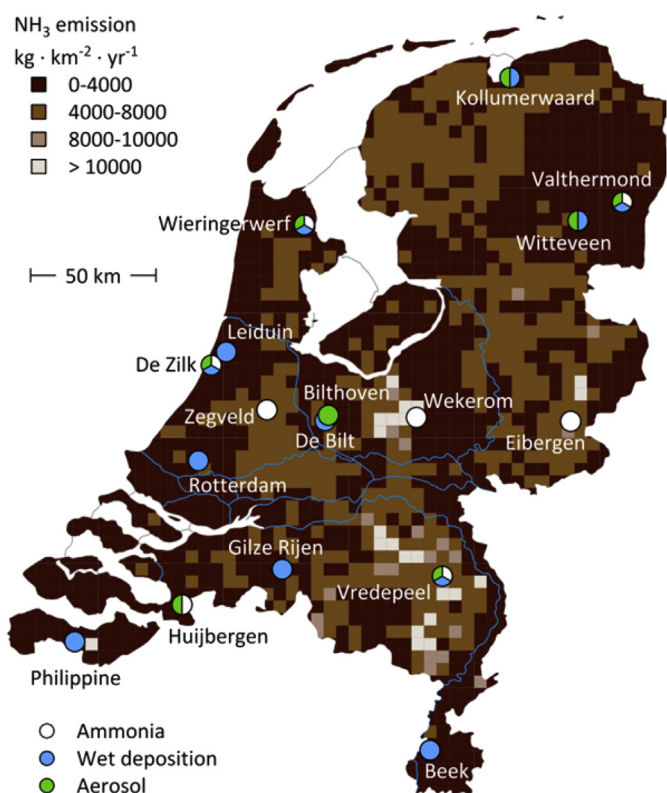


Fig. 2. The locations of the monitoring stations of the Dutch National Air Quality Monitoring Network (LML) as presented in Table 1. The map shows the total ammonia emissions on a 5 by 5 km grid for the year 2014.

NH₃ in the Netherlands displays a high spatial variability. As a consequence, a representative monitoring network to cover this variability would be very expensive. Therefore, at its set up, it has been decided to use a limited amount of measurements in combination with modelling of the ammonia concentrations for the Netherlands (Buijsman et al., 1998). The monitoring stations were carefully selected for equal distribution of regions of high, moderate and low emission densities. Pul van et al. (2004) demonstrated the eight monitoring stations (although representing somewhat

higher emission areas) to show a similar agreement with model calculations as was obtained with a vast network of 159 measurements over the Netherlands.

To reduce the effect of missing data, a method developed for gap-filling hourly NO₂ and PM₁₀ time series (Nguyen and Hoogerbrugge, 2014) was applied to the NH₃ time series. Two options for gap filling were explored. In the first option missing data at a specific monitoring station was gap filled based on the measurements at the remaining 7 monitoring stations. In the other option only data was used from monitoring stations with similar emission density characteristics. For example, Vredepeel data were used to fill the data gaps at Wekerom. The first option was selected because differences between the two options were small, indicating that differences in emission density characteristics are not crucial for gap filling. In electronic supplement Appendix A 3 tables with annual mean values at each of the eight monitoring stations can be found; i.e., not gapfilled and gapfilled with the above two options. Also a figure with the uptime of the AMOR instrument over the years is presented. After gap filling, 3% of the hourly values is still missing due to the simultaneous lack of data at all monitoring stations.

Differences between the original dataset and the gap filled data set are small for most years and most monitoring stations (Fig. 3). Some larger differences appear at the beginning of the dataset for monitoring stations in areas with high to moderate emission density. The gap filled data is more plausible because missing data regularly occur over longer periods. Missing a longer period can lead to a bias in the mean annual concentration due to seasonal variability (Erisman et al., 1998; see also Fig. 9). Note that when a time series is not gap filled, missing values are implicitly assumed to be equal to the average of the measured data.

2.2. Influence of atmospheric conditions on ammonia concentrations

Atmospheric conditions such as temperature and rainfall influence NH₃. Here we will determine the influence of meteorology on ammonia concentrations by constructing meteorological normalized time series. Here for, the most simple multivariate regression analysis which is statistically reliable and physically plausible, is used.

Both the hourly meteorological variables as measured at De Bilt by the Royal Netherlands Meteorological Institute (KNMI) as the

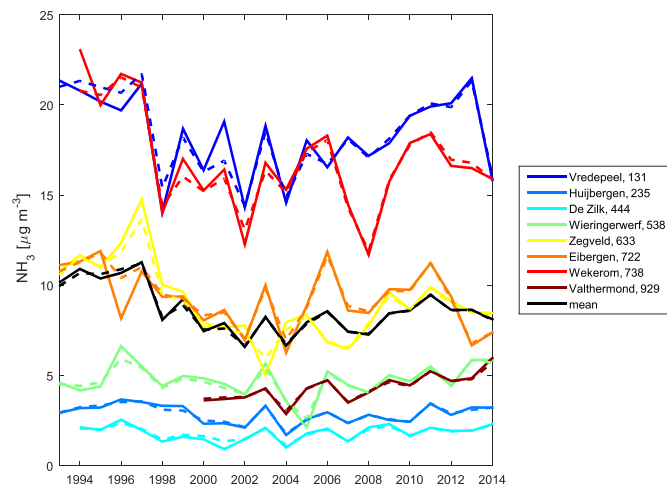


Fig. 3. Time series of the annual mean ammonia concentrations at the eight LML monitoring stations. The continuous lines denote the original dataset while the dashed lines refer to the gap filled dataset.

gap filled ammonia concentrations are downscaled to monthly averages. This is done as the preliminary meteorological normalization study was based on monthly ammonia values available from the MAN network for the period 2005–2013 and it is preferred to have one meteorological normalization procedure for both datasets.

We define the following meteorological parameters to take into account in the multivariate regression analysis:

- temperature (T) in degrees Celsius minus the mean of the time series: $T - 10$,
- pressure (P) in mbar in the following equation: $(P - 1010) * (P - 1000) - 100$,
- temperature difference of consecutive months (ΔT) in the following equation: $\Delta T * (\Delta T + 4) - 12$, with ΔT defined as $\bar{T} - \bar{T}_{t-1}$,
- rainfall duration (RD) in minutes per hour minus the mean of the time series: $RD - 4.7$

The above terms were selected by exploring the various possible meteorological parameters. The parameter which described the largest part of the variance was selected first. Then the second was selected to give the most powerful combination with the first one and so on. The equations for P and ΔT have been chosen in order to center the data around the origin. Parameter P and ΔT are included as quadratic terms in the regression analysis since the model residuals showed a strong nonlinear dependence. In the analysis, a parameter 'time' was included to take into account the change in ammonia over the years. Due to the opposite behavior in the first half of the time series compared to the second half, this variable 'time' was split into two periods: 1993 till 2004 and 2005 till 2014. Due to manure application in spring and late summer, the annual cycle of ammonia shows two distinct peaks (see Fig. 9), of which the springtime peak is the most pronounced. A 'spring' term equaling 1 for the months of February until April has been added in the analysis to take this into account.

For the calculation of the meteorologically normalized ammonia concentrations, the two time variables and the 'spring' term were not used. Thus, the effect of these terms is taken into account in the determination of all regression coefficients, while the correction term to compute the normalized, monthly mean ammonia concentrations is solely based on meteorological parameters. The

applied correction term is often substantial on a monthly basis and the explained variance (R^2) lies between 40 and 70% for all monitoring stations. In electronic Appendix B, a table with t-stat values and regression coefficients is presented. Further two examples of meteorologically normalized, monthly time series are shown and R^2 for each monitoring station is given in a table.

2.3. Wet deposition of ammonium

Wet deposition of several components including ammonium have been measured since 1978 by the Dutch National Precipitation Chemistry Monitoring Network.¹ However, the locations of monitoring stations, equipment, and chemical analysis have changed considerably since measurements started. The current wet-only sampler replaced an older type in 2006 and before 1988 bulk deposition was measured (Van der Swaluw et al., 2011). According to Blank (2001) wet deposition measurements have an uncertainty of about 6%. The data have been corrected for the effect of replacing bulk samplers with wet-only samplers. Data before 1992 were revalidated according to the current validation rules (Somhorst et al., 1994), to obtain consistent time series. In this study data from 1985 onwards were used in order to be able to present data before abatement policies were implemented.

Mean annual concentrations per monitoring station were calculated as a precipitation-weighted mean value over all periods with valid concentration and rainfall measurement data. Annual mean values used for trend calculations were based on data availability of at least 75%. The wet deposition flux was subsequently calculated by multiplying this precipitation-weighted mean concentration by the total rain fall measured at a monitoring station. Samples for which precipitation was measured, but a concentration of NH_4^+ was lacking, were filled up with the annual precipitation-weighted mean concentration.

To determine the trend in the period 1985 to 2014, monitoring stations were selected to provide a good coverage for the whole period. Witteveen and Valthermond were combined as one monitoring station and also Leiduin and De Zilk. In both cases, the monitoring stations are located close enough (see Fig. 2) to be considered as a single time series.

2.4. Ammonium in aerosol

Ammonium aerosol ($(\text{NH}_4^+)_{\text{air}}$) have been measured since 1987 as part of the Secondary Inorganic Aerosols analysis (like ammonium nitrate and ammonium sulfate). Because of changes in the network configuration, we selected data from 1993 onwards for this study. Annual mean values have been based on at least 50% data availability. The time series for the ammonium aerosol concentration at Witteveen and Valthermond were combined for the same reason as the wet deposition time series at those two monitoring stations.

Up to 2008, particles were sampled with a dedicated Low Volume Sampler (LVS); according to Blank (2001) the observations have an estimated uncertainty of 6%. This LVS had a low flow of $1.7 \text{ [l min}^{-1}\text{]}$ and consequently no sharp cut of point like current PM_{10} or $\text{PM}_{2.5}$ samplers. From 2009 onwards, sampling of the PM_{10} fraction of ambient aerosol was applied in conformity with European Standard EN 12341. However, this method is known for losses during sampling, due to evaporation, of up to 30% (EN16913).

Comparison of these two methods showed, weighted over all components, a systematic difference of a factor of 1.6 (Hafkenscheid

¹ Since 1989 the Dutch National Precipitation Chemistry Monitoring Network is an integral part of the Dutch National Air Quality Monitoring Network (LML).

et al., 2010). This factor of 1.6 is applied as correction on the LVS data. The factor is presumably caused by a lower cut off point of the particles on the LVS. Note that a factor of 1.13 was observed for NH_4^+ specifically (Hafkenscheid et al., 2010). However, this value is considered unlikely, being much smaller than the factor for nitrate and sulfate, and would have led to a serious unbalance between the amount of anions and cations for historical data. A clear explanation for the difference in correction factor is not available. The most likely hypothesis is that using the EN 12341 sampling technique implies a much higher flow resulting in the loss of volatile components like NH_3 and HCL (Weijers et al., 2012) and an underestimation of NH_4^+ .

3. Results and discussion

3.1. Time series

NH_3 concentration exhibits a wide spatial variation depending on local emission density; annual mean values vary from 2 to 20 [$\mu\text{g m}^{-3}$] (Fig. 3). A large variability in the mean concentrations from year to year is also visible. This is most clearly for the two monitoring stations (Vredepeel and Wekerom) in high emission areas: several changes of the order of 5 [$\mu\text{g m}^{-3}$] occur from year to year. This is most likely due to changes in local emission sources, but meteorological influences can play a role as well. Despite the interannual fluctuations in the concentration all monitoring stations show a remarkable similar pattern over the whole period; indicating they are capable of catching a national trend in the ammonia concentration, despite the low number of monitoring stations. The similarity in pattern is visibly more pronounced when every time series is normalized with its individual mean over the period 1993–2014 (Fig. 4).

When meteorological influences play a role this is often visible as a difference in NH_3 between consecutive years at several monitoring stations simultaneously. The meteoronormalized time series of NH_3 in Fig. 5 show that in those years meteoronormalization helps reducing the variability in the time series. For example, the effect of the exceptionally hot and dry summer of 2003 is accounted for and also the corrections for the years 1997 and 1998 are substantial. The dry year of 1997 was followed by an exceptionally wet year: because of the effect of rainfall on the ammonia concentration this results in a sharp change in the original time series. The meteoronormalized time series show a more gradually decline, most noticeably at Vredepeel and Wekerom; but the effect is present at the other monitoring stations as well.

Fig. 6 shows the time series of the wet deposition between 1985 and 2014. Like NH_3 , wet deposition shows a dependence on the emission density in the nearby region of the monitoring station, although less pronounced since wet deposition scavenges both NH_3 as well as $(\text{NH}_4^+)_{\text{air}}$. The variability in the $(\text{NH}_x)_{\text{wet}}$ time series is a factor of two. The station with the highest amount is Vredepeel (situated in a high emission density region) while the station with the lowest amount (de Zilk) is located in a low emission region. The dependence, however, is less than by NH_3 due to the spatially more homogeneous $(\text{NH}_4^+)_{\text{air}}$ and by the fact that $(\text{NH}_x)_{\text{wet}}$ has a larger contribution from long range transport than NH_3 . All stations show a decline over the considered period. Around 2003 the variability in the time series reduces. A change in analysis method of rainwater samples in that year is the most plausible explanation, but real physical causes cannot be ruled out.

Both the air concentrations of NH_3 and $(\text{NH}_4^+)_{\text{air}}$ as well as the amount of precipitation have an influence on the amount of wet deposition. In Fig. 7 ammonium concentration $(\text{NH}_4^+)_{\text{water}}$ in precipitation samples measurements are depicted. In general, time series of $(\text{NH}_4^+)_{\text{water}}$ are smoother than time series of wet

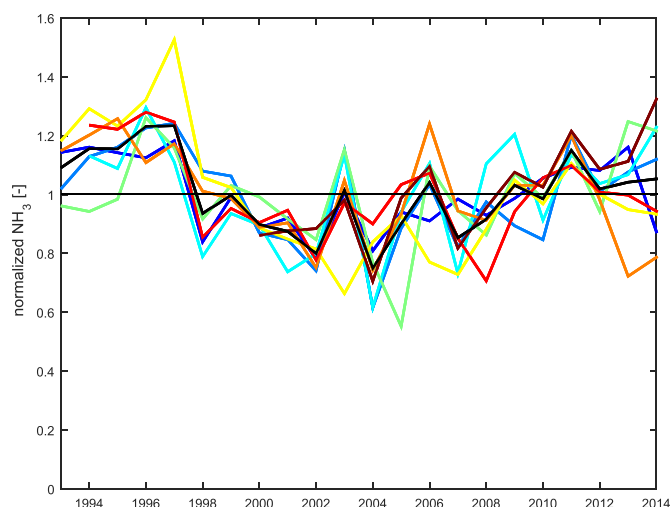


Fig. 4. NH_3 time series of eight LML monitoring stations (identical data as the gap filled set of Fig. 3), normalized with its individual mean over the period 1993–2014. For legend see Fig. 3.

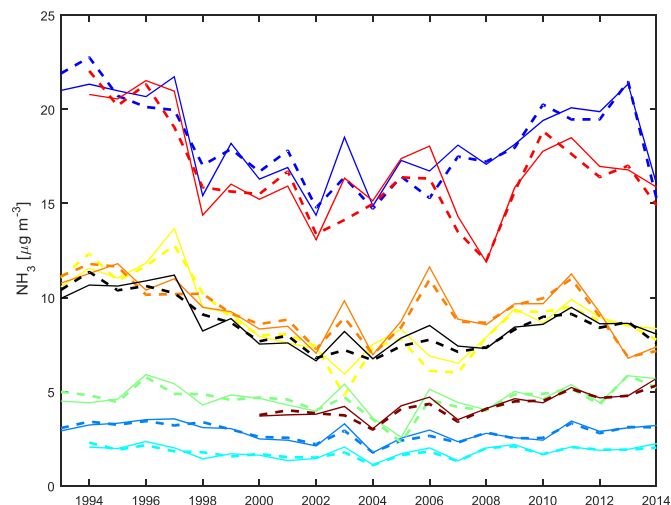


Fig. 5. Time series of the meteoronormalized ammonia concentrations at the eight LML monitoring stations. The thick dashed lines denote the meteoronormalized time series; the original, gap filled time series are added in thin continuous lines for easy comparison. For legend see Fig. 3.

deposition. They both show a similar decline. Yet, $(\text{NH}_4^+)_{\text{water}}$ and $(\text{NH}_x)_{\text{wet}}$ show opposite behavior in years with extreme rainfall. In dry years such as 1996 and 1997 (600 and 765 mm precipitation compared to 890 mm on average between 1993 and 2014) $(\text{NH}_4^+)_{\text{water}}$ peaks while $(\text{NH}_x)_{\text{wet}}$ shows a temporal minimum. In 1998, an extreme wet year (1265 mm precipitation) the opposite occurs. In recent years the decline in $(\text{NH}_4^+)_{\text{water}}$ appears to level off while in $(\text{NH}_x)_{\text{wet}}$ this signal is less visible.

The amount of ammonium in aerosol $(\text{NH}_4^+)_{\text{air}}$ over the period 1993–2014 is shown in Fig. 8; the time series of the two instruments are presented as two separate lines. Compared to NH_3 and $(\text{NH}_x)_{\text{wet}}$, ammonium in aerosol is homogeneously distributed over the Netherlands. However, the highest concentration is still found in a high emission area (Vredepeel) and the lowest in low emission areas such as De Zilk; showing that a correlation with emission density is present. However, this correlation is much smaller than for NH_3 and $(\text{NH}_x)_{\text{wet}}$ due to the larger contribution of long range transport to $(\text{NH}_4^+)_{\text{air}}$. Similarly to $(\text{NH}_x)_{\text{wet}}$ a steady

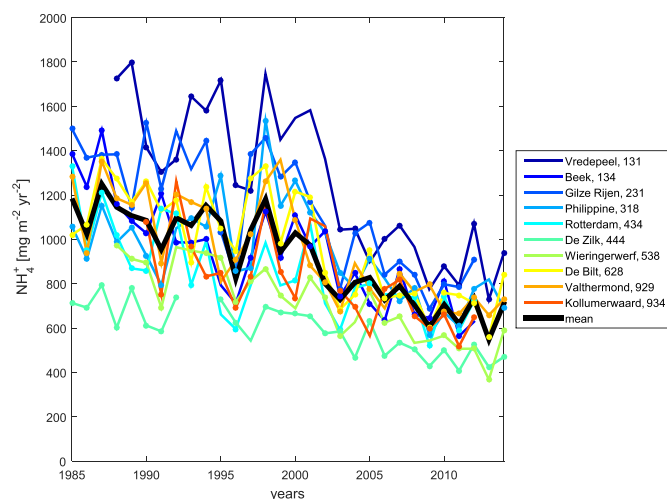


Fig. 6. Wet deposition of ammonia at 10 LML-stations over the period 1985–2014. All annual mean values are presented even when data coverage is less than 75%; annual mean values with data coverage more than 75% are marked with a dot.

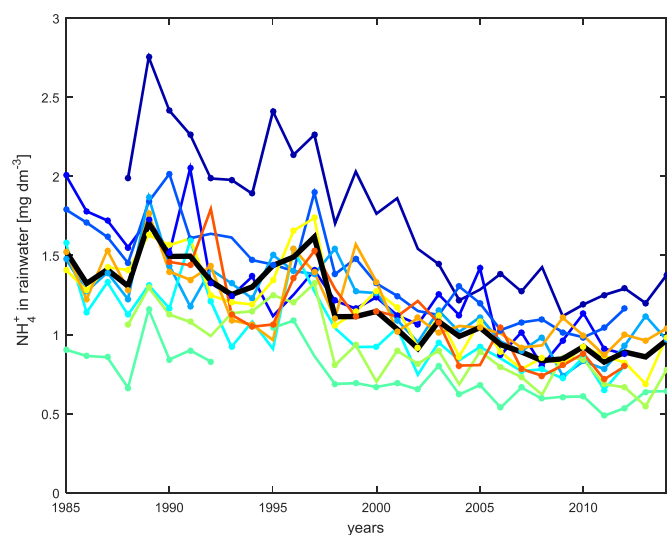


Fig. 7. Ammonium concentration in precipitation samples at 10 LML-stations over the period 1985–2014. All annual mean values are presented even when data coverage is less than 75%; annual mean values with data coverage more than 75% are marked with a dot. For legend see Fig. 6.

decline over the whole period is visible.

3.2. Calculation of trends

Linear trends have been determined for the time series shown in Figs. 3–8 for various periods. The trends are presented as percentages change of the component, relative to the value of the component in the first year of the period over which the trend is determined. In order to remove an undesirable sensitivity of the presented trends to the measured value of the component in the first year, a value for the first year is derived from the corresponding linear regression.

The gap filled NH_3 time series are used to calculate linear trends over the full period of 1993–2014 and also over two intermediate periods in which roughly speaking the trends are reversed, i.e. 1993–2004 and 2005–2014 (Table 2). The exact year where the split into the two periods occurs is somewhat arbitrary. The year

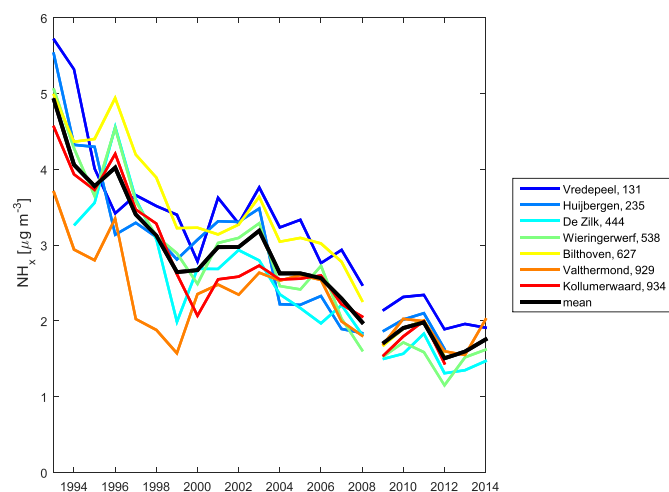


Fig. 8. Ammonium concentration in aerosol at 7 LML-stations over the period 1993–2014. The time series of the two instruments are presented as two separate lines. Note that the time series of Biltoven is present in the latter period, however, invisible under the mean.

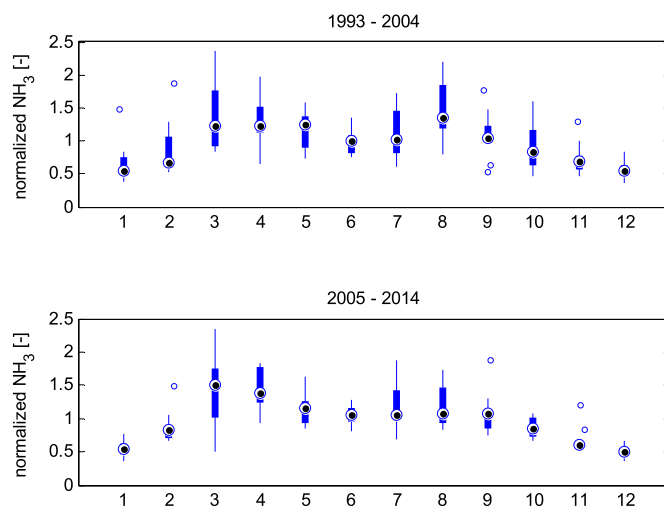


Fig. 9. Monthly ammonia concentration values averaged over 8 LML monitoring stations and the period 1993–2004 (upper panel) and 2005–2014 (lower panel). The values of the monitoring stations have been normalized with their individual mean of the depicted period before further averaging. Data are presented in a box-and-whisker plot: the 25th, median and 75th quantiles are given and the upper and lower whiskers denote plus or minus $1.5 \times (25^{\text{th}} - 75^{\text{th}}) + \text{median}$. The open circles denote outliers.

2005 is chosen as it is the starting year of the Measuring Ammonia in Nature areas (MAN) network (Lolkema et al., 2015), thus marking the starting point of a period in which more measurements are available for determining a trend based on NH_3 , see Stolk et al. (2016). In order to show the sensitivity for the choice of the year 2005, trends between 1993 and 2000 are also presented since in this period the largest emission decline is reported.

All individual monitoring stations except one show a significant ($p < 0.01$) decrease in NH_3 in the period 1993–2004, with an averaged normalized trend for all LML monitoring stations of -36% . In the next period all individual monitoring stations except one show an increase in NH_3 , yet with higher p values than for the downward trend in the first period. The normalized trend for all monitoring stations of 19% is almost significant on a 95% CI as the p value of 0.07 shows. Despite the lower confidence intervals, it is unlikely that the observed concentrations are declining in reality

Table 2

Linear trend of ammonia concentration in percentage over the denoted period; relative to the calculated ammonia concentration in the starting year of the period. For each trend the p value is given. Bold numbers denote trends with $p \leq 0.05$ (CI 95%). With respect to 'LML normalized', the annual mean ammonia values for each individual monitoring station are first normalized with their individual mean over the whole period before determining the trend in the LML mean.

	1993–2014		1993–2004		2005–2014		1993–2000	
	trend	p	trend	p	trend	p	trend	p
131 Vredepeel	-8	0.37	-33	<0.01	14	0.21	-28	0.03
235 Huijbergen	-11	0.36	-35	0.02	28	0.08	-13	0.34
444 De Zilk	6	0.68	-38	0.03	23	0.19	-30	0.09
538 Wieringerwerf	8	0.56	-13	0.35	59	0.02	3	0.84
633 Zegveld	-30	0.02	-51	<0.01	23	0.13	-26	0.16
722 Eibergen	-22	0.04	-38	<0.01	-22	0.20	-27	0.01
738 Wekerom	-18	0.08	-37	<0.01	5	0.75	-35	0.03
929 Valthermond	-	-	-	-	34	0.03	-	-
LML mean	-22	0.02	-42	<0.01	12	0.21	-28	0.05
LML normalized	-10	0.27	-36	<0.01	19	0.07	-22	0.10

because of the similar behavior the time series display.

In Table 3 we present linear trends in the meteoronormalized time series. Correcting the time series of NH_3 for meteorological influences mainly enhances the statistical reliability of the trends by substantially reducing the p values. Most of the trends are 4–5% points steeper than the trends presented in Table 2; this is a moderate effect. Furthermore, the effect is not systematic since the influence is opposite in the first period of the time series compared to the second period. This suggests that meteorological effects are random for the length of the current time series and that there exists no trend in the ammonia concentration due to a trend in the meteorological variables. The latter is confirmed by the absence of a statistically significant trend in the applied meteoronormalization correction term (the regression coefficient is -0.02 with $p = 0.23$).

For $(\text{NH}_4^+)_{\text{air}}$ and $(\text{NH}_x)_{\text{wet}}$ linear trends are calculated for a normalized LML mean only. $(\text{NH}_4^+)_{\text{air}}$ declined with 68% between 1993 and 2014 ($p < 0.01$) while $(\text{NH}_x)_{\text{wet}}$ declined with 47% in the same period ($p < 0.01$) and with 48% from 1985 till 2014 ($p < 0.01$). The 95% confidence intervals for the 1993–2004 trend overlap with the value of the trend for 1985–2004; confirming that $(\text{NH}_x)_{\text{wet}}$ is not a sensitive enough indicator to catch a change in ammonia emissions due to the implementation of abatement measures in 1990. Trends in $(\text{NH}_4^+)_{\text{water}}$ differ little from the trend in $(\text{NH}_x)_{\text{wet}}$ itself. Although the time series of both components do not show, unlike NH_3 , a reversal in the direction of the trend in the last ten

Table 3

Meteoronormalized linear trend of ammonia concentration in percentage over the denoted period, relative to the calculated ammonia concentration in the starting year of the denoted period. For each trend the p value is given. Bold numbers denote trends which are significantly (at least 95% CI) different from no trend. With respect to 'LML normalized', the annual mean ammonia values for each individual monitoring station are first normalized with their individual mean over the whole period before determining the trend in the LML mean.

	1993–2014		1993–2004		2005–2014		1993–2000	
	trend	p	trend	p	trend	p	trend	p
131 Vredepeel	-12	0.18	-37	<0.01	19	0.19	-30	<0.01
235 Huijbergen	-15	0.18	-39	<0.01	34	0.01	-15	0.17
444 De Zilk	0	0.97	-41	<0.01	25	0.12	-31	0.01
538 Wieringerwerf	-0	0.98	-22	0.03	69	0.01	-6	0.61
633 Zegveld	-35	0.01	-55	<0.01	30	0.12	-30	0.05
722 Eibergen	-25	0.01	-41	<0.01	-19	0.24	-28	<0.01
738 Wekerom	-22	0.04	-40	<0.01	11	0.50	-37	<0.01
929 Valthermond	-	-	-	-	37	0.01	-	-
LML mean	-26	0.01	-46	<0.01	17	0.12	-31	<0.01
LML normalized	-15	0.09	-40	<0.01	24	0.02	-25	<0.01

years, there appears to be a slowing down in the decline. This is especially visible in the time series of $(\text{NH}_4^+)_{\text{water}}$ where the linear trend over the period 2005–2014 minimizes to -8% ($p = 0.34$). This trend, however, is statistically not significant different from the trend in the 1985–2004 period.

3.3. A comparison between trends in observations and emissions

Reported ammonia emissions have been declining steadily since 1990 with the largest decline taking place in the first decade. Here, numbers of the trends for the full period, 1993–2004 and 2005–2014 are used. These trends in emissions have been calculated consistently with the applied method for the trend in the observed ammonia concentrations. Note that the emissions represent a national total while the observations are based on a limited number of stations. Fig. 4 shows the changes in ammonia concentrations at the 8 LML monitoring stations to be similar in time, indicating that the representativeness of the observations is fairly good, albeit with a large variability. Gijlswijk van et al. (2004) have estimated the uncertainty in the Dutch ammonia emissions to be approximately 17%.

The decline in the reported ammonia emissions (Fig. 1) is 58% over the full period for which NH_3 concentration observations are available (1993–2014). Over the same period, NH_3 concentration shows a linear decrease of only 10%, ($p = 0.27$). Corrected for meteorological influences the decline in NH_3 is 15% ($p = 0.09$). The large gap between trends in measurements and emissions is mainly due to a difference in trend in the latter half of the 1993–2014 period.

Over the period 1993–2004 the decline in the reported emissions equals 51% while the declining trend in the ammonia concentrations is estimated to be 36% ($p < 0.01$). The difference between these two trends is relatively small and we may conclude that in this period the concentrations largely follow the reduction in emissions. Corrections for meteorological influences explain part of the difference between the two trends since the decline in NH_3 becomes slightly steeper when corrected for these influences. For a further explanation, model results are necessary. For example, the reduced sulphur dioxide emissions in Europe have affected the dry deposition rate of NH_3 by influencing the process of codeposition; leading to more NH_3 to remain in the atmosphere. Wichink Kruit et al. (2016), have studied such interaction of processes in the accompanying modelling article. They show that the changes in chemical climate affecting conversion rates of NH_3 into $(\text{NH}_4^+)_{\text{air}}$ as well as the dry deposition rate largely explain the rest of the difference in the two trends in the 1993–2004 period.

Taking all these effects into account it can be understood that the trend in the measured ammonia concentration is less steep than in the reported emissions over the period 1993–2004. Moreover, it has been suggested recently that the amount of the reported emission in the early years of the 1990s is slightly overestimated (Gerard Velthof, personal communication); the exact overestimation is still subject of debate. Note that the implementation of emission reduction measures began a few years earlier than the NH_3 measurements; the largest reported reduction in emission is thus not covered.

However, in the period 2005–2014 the reported emissions declined with a further 22% while NH_3 showed a reversed trend with an increase of 19% or even 24% when corrected for meteorological influences. For these two trends no overlapping 95% confidence intervals were found so this difference in trend is statistically significant. The above mentioned changes in chemical climate still play a role, but as is argued in Wichink Kruit et al. (2016) this only explains roughly one third of the current difference between the reported decline in emission and the observed rise in ammonia

concentration.

Further analysis of NH_3 measurements shows seasonal differences in the trend in the period 2005–2014. First in Fig. 9 the annual cycle of NH_3 in the Netherlands is presented for the period 1993–2004 and 2005–2014. The annual cycle shows a bimodal distribution due to manure spreading in springtime and late summer. Lowest concentrations are found in the months of October till January when manure spreading is not allowed; in these months emissions due to animal housing dominate. In recent years (lower panel) a shift has occurred towards a more pronounced peak in the concentration in March and April and a reduction in the peak value in August.

This is reflected in Fig. 10 where time series of three four-months-periods are shown. In the upper panel the concentrations in the winter months of October till January show a flat time series after 1998, while the concentrations display a statistically significant ($p = 0.03$) increase in February till May for the period 2005–2014. This increase is a factor two steeper than the annual trend. When the time series are meteoronormalized this picture changes: the trend in the spring months reduces with roughly a third and a trend is visible in October till January for the period 2005–2014 ($p = 0.08$). The trends in the three four-months-periods become roughly similar to the annual trend although the spring one is still the largest. In none of the four-months-periods a statistically significant trend exists in the meteorological normalization term indicating that meteorological influences are still fluctuations and not an explanation for the upward trend in NH_3 .

Finally, it is good to note that, due to the large variability in NH_3 (as reflected by the large uncertainties of the trends in certain cases) and the limited number of monitoring stations, long time series are needed to draw firm conclusions. Erisman et al. (1998) argued, based on NH_3 time series of a few years, emission abatement policies to be less effective than expected. However, the longer time series presented here show reduction in concentration although not directly after the official implementation of the abatement policies in the early 1990s. Bleeker et al., 2009 (their Fig. 11.10) also concluded that for an extended period the reported deviation between the two trends as reported in Erisman et al.

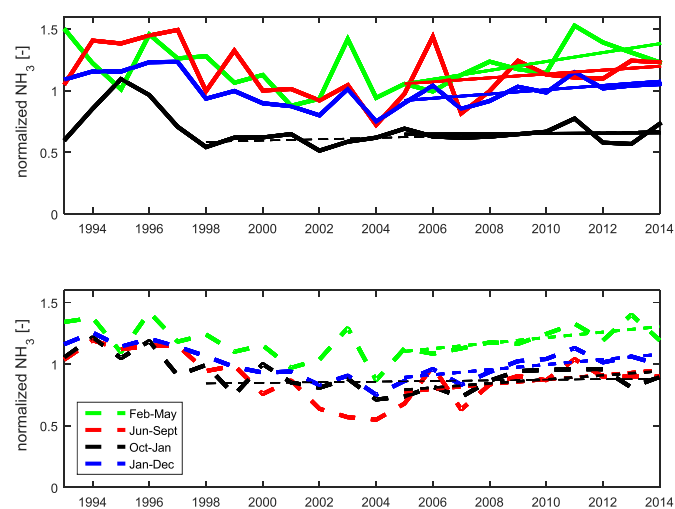


Fig. 10. Time series of the ammonia concentrations for three four month periods ('seasons') and the annual mean (upper panel, continuous lines); in the lower panel the meteoronormalized version of the time series (dashed lines). The time series are normalized with the individual mean of the monitoring station before averaging in space (over 8 LML monitoring stations) and time (the various periods defined). The lines depict the trends over the period 2005–2014. The trend for the months Oct–Jan for the period 1998–2014 is added for comparison with a dotted black line.

(1998) seemed to be solved.

4. Conclusions

The observed trend in NH_3 between 1993 and 2004 largely complies with the reported decline in ammonia emission in the same period, especially when corrected for meteorological influences. However, in the period 2005–2014 the two trends significantly diverge. The effects of process changes related to the change in chemical climate sufficiently explain the small remaining gap between the observed trend in NH_3 and the reported emissions in the period 1993–2004 (Wichink Kruit et al., 2016).

However, these effects only explain roughly one third of the gap in later years. Longer time series of observations might help in determining whether this divergence is temporarily or due to a mismatch between reported ammonia emissions and observations of ammonia in air. Attempts to associate increasing NH_3 with an unexpected increase in a specific type of ammonia emission were not successful, it is therefore not clear what explains the difference in trends.

Monthly concentrations show a large variability that can be significantly reduced using meteorological normalization. The variability also requires a careful procedure for treating gaps in the data set. For the presented time series meteorological normalization reduces the uncertainty in the trend but hardly changes the value since the meteorological normalization term displays no trend over the period 1993–2014.

The observed trends in the wet deposition of NH_x and the concentration of ammonium in aerosol are not in contradiction with the trend in NH_3 concentration. After a steady decline in the 1990s and the years directly thereafter there appears to be a leveling off in the trend since 2005. However, a distinct split into two periods was not found as was the case with the ammonia concentrations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.11.007>.

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