IDŐJÁRÁS

Quarterly Journal of the Hungarian Meteorological Service
Vol. 118, No. 2, April – June, 2014, pp. 167–191

Long-term trend of deposition of atmospheric sulfur and nitrogen compounds in Hungary

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(Manuscript received in final form April 11, 2014)

Abstract—Acidification caused serious environmental problems over Europe in the 70's and 80's. The signs of the phenomenon were observed also in Hungary. However, a comprehensive assessment of acidic deposition on long term has not been carried out yet. Therefore, the purpose of this study is to assess the degree of this process and to investigate its long-term change in Hungary based on deposition time series for oxidized sulfur, oxidized nitrogen, and reduced nitrogen compounds. To achieve our goal, we used existing results of atmospheric chemistry transport models, and precipitation chemistry as well as background air pollution measurements at the Hungarian K-puszta site. Comparing the results with national emission datasets, we also made an attempt to interpret the changes in depositions. According to our time series (oxidized sulfur: 1880–2011, oxidized nitrogen: 1982–2012, reduced nitrogen: 1981–2012), the effect of acidification was most likely to intensify before 1980. Since then, the phenomenon presumably has been weakening gradually. In the case of oxidized sulfur and nitrogen compounds, transboundary transport has to be considered while comparing them to depositions. On the other hand, the impact of Hungarian industrial recession as well as the improvement of emission abatement techniques and national emission controlling measures can be observed not just on the emissions, but depositions as well. Moreover, we found that the atmospheric concentration and subsequent deposition of ammonia is strongly affected by the atmospheric concentration of sulfur dioxide, which highlights the need for further refinement of the estimation method for yearly dry deposition of ammonia.

Keywords: acidic deposition, long-term, oxidized nitrogen, oxidized sulfur, reduced nitrogen, ammonia, atmospheric concentration, emission, emission reduction.

1. *Introduction*

The problem of acidification got wider public and scientific attention at first in the beginning of the 70's, when the reason for the serious damage of Scandinavian lakes and German forests was identified: the decreasing pH of freshwaters and soil (*Almer et al.*, 1974; *Sakamoto et al.*, 1986). It was found that the phenomena had been caused by the excessive emission and subsequent deposition of oxidized sulfur (sulfur dioxide, SO_2 and sulfate, SO_4^{2-}) and oxidized nitrogen compounds (nitric acid, HNO_3, nitrogen oxides, NO_x and nitrate, NO_3^-) (see the quoted references in *Galloway*, 1989). Since then, the problem has been considerably mitigated over Europe, owing to a series of emission control measures (*Grennfelt* and *Hov*, 2005). However, it has been a more and more serious environmental issue in the developing countries of Asia, especially in China (*Duan et al.*, 2013).

The process that leads to acidification consists of three main steps: i) emission of acidifying components or their precursors, ii) their atmospheric transport, simultaneous chemical conversion, phase transition to particles, iii) deposition to the surface. The main source for oxidized sulfur as well as nitrogen compounds is anthropogenic. Most of the oxidized sulfur compounds are emitted during the combustion of fossil fuels (*Seinfeld* and *Pandis*, 2006). These usually contain a certain amount of sulfur, which is oxidized to SO_2 during burning. The primary emission sectors of the oxidized nitrogen compounds are transportation and energy industry (see the same reference). In both cases, nitrogen content of the air is oxidized mainly to nitric oxide (NO) and in smaller amount to nitrogen dioxide (NO_2) at the high burning temperature.

In addition, reduced nitrogen compounds (ammonia, NH_3, and ammonium, NH_4^+) are considered as additional exacerbating factors for acidification. In the soil during nitrification, NH_4^+ ions are oxidized while two equivalent hydrogen-ions (H^+) are produced (*Raven*, 1985). In freshwater ecosystems, algae and macrophyte species release equivalent H^+ when NH_4^+ is consumed (*Goldman* and *Brewer*, 1980). Therefore, further sources must be considered for acidifying components. The largest emission sector of reduced nitrogen compounds is agriculture, releasing gaseous NH_3 to the atmosphere. The primarily source of NH_3 is the breakdown of urea in livestock excreta, but a similar process takes place in the case of urea- and ammonium-based fertilizers as well.

There are two ways for an atmospheric compound to get back to the surface from the atmosphere: by wet or dry deposition. Wet deposition occurs when the compound is washed out from the atmosphere by being dissolved in precipitation, whilst during dry deposition, the substance is transported to the surface by the turbulent flux.

In the atmosphere, SO_2 and NO_x compounds are further oxidized to sulfurous acid (H_2SO_3) and sulfuric acid (H_2SO_4), as well as nitrous acid

(HONO) and nitric acid (HNO_3), respectively. The produced acidic components may be neutralized by dissolved NH_3, forming aerosol particles. These usually act as condensation nuclei; therefore, they can be easily washed out of the atmosphere by precipitation. In addition, during droplet growing as well as rainfall, acidic species and gaseous SO_2 and NH_3 may also dissolve to the droplets. Dry deposition of acidifying compounds is possible as gas molecules as well as in the form of aerosol particles. Deposition of NH_3 and SO_2 in this way is closely related and largely dependent on the pH of the surface wetness (*Flechard et al.*, 1999).

The distance, from the source the atmospheric trace compounds can be transported to, besides meteorological conditions, is basically determined by their atmospheric lifetime. Calculating with a lifetime of 2 days (172 800 s) for SO_2 (*Seinfeld* and *Pandis*, 2006) and an average wind speed of 3 m s^{-1} at 2 m height, the result is more than 500 km. The lifetime of NO_x as well as NO_3^-, SO_4^{2-}, and NH_4^+ aerosols usually ranges also from a few days to weeks, which raises the problem of transboundary air pollution. On the other hand, as a result of their high solubility and reactivity, NH_3 and HNO_3, depending on the surface characteristics and micrometeorological conditions, especially at higher air temperature and lower humidity when dissociation of ammonium nitrate particles into gases is dominant (*Stelson* and *Seinfeld*, 1982), can have a lifetime of a few hours, causing local rather than regional problems.

Beside the damage of surface water and forest ecosystems, high concentration of acidic components can have a severe impact also on human health through inhaling the respirable, fine fraction of formed aerosols (*Pope et al.*, 2002). In addition, in the 70's and 80's, erosion of buildings and statues by "acid rain" was reported (*Lipfert*, 1987). Despite serious acidification caused mainly by excessive emission of SO_2 (*Johnson* and *Reuss*, 1984) has been largely mitigated over Europe, the environmental effect of reactive nitrogen compounds (N_r), such as NH_3, HNO_3, and NO_x, has been still in the focus of scientific research projects (e.g., GRAMINAE, NitroEurope, ENA, ÉCLAIRE). *Sutton et al.* (2011) identified five key threats related to excessive N_r emissions: water quality, air quality, greenhouse balance due to the aerosol particles, ecosystems and biodiversity, and soil quality.

Signs of acidification occurred also in the country: yield reduction of crops, potential forest damage, especially in synergy with other biotic factors, corrosion of historic monuments, and deformation of building ornaments made of limestone were reported (*Várallyay et al.*, 1986; *OKTH/MTA*, 1987). Since then, the impact of acidic compounds, similarly to the whole European region, has been weakening in the country.

Although *Horváth et al.* (2009) published time series of measured atmospheric concentration and wet deposition of NH_3 and NH_4^+ for the period of 1981–2005 for a Hungarian site, for the country a comprehensive assessment of acidic deposition on long term has not been carried out yet. Therefore, the purpose of this study is to assess the degree of this process and to investigate its long-term change in Hungary based on deposition time series for oxidized sulfur, oxidized nitrogen, and reduced nitrogen compounds. The data sets were compiled from existing atmospheric chemistry transport model results and air concentration as well as precipitation chemistry data measured at the Hungarian K-puszta site.

2. Methods and data

2.1. Oxidized sulfur compounds

The long-term deposition data set for oxidized sulfur compounds were compiled from existing results from different versions of the atmospheric chemistry transport model (ACTM) ran by the European Monitoring and Evaluation Programme (EMEP) under the Convention on Long-range Transboundary Air Pollution (CLRTAP). An ACTM calculates atmospheric concentration and deposition fields for a given time and grid from predefined emission fields. Driven by a meteorological model it is capable of simulating the horizontal and vertical transfer of atmospheric trace compounds, as well as the mixing of the different pollutants and the possible chemical reactions between them.

EMEP is a policy driven program for international co-operation to solve transboundary air pollution issues. The model results from their ACTM are used by policy makers Europe-wide. EMEP consists of five Centers and four Task Forces. Among them, the Meteorological Synthesizing Centre-West (MSC-W) is responsible for the modeling of acidifying and eutrophying air pollutants, photochemical oxidants, and particulate matter.

The first part of our deposition data set, for the period 1880–1980, originates from a model experiment (*Mylona*, 1992) for 1880–1991 with an early version of the EMEP model (*Sandnes* and *Styve*, 1992). *Mylona* determined the required SO_2 emission fields based on historical energy and industry statistics. The effect of meteorological variability was disregarded in the experiment, meteorological data for 1991 were used for every year. Depositions were simulated over the 150×150 km^2 EMEP grid, for every fifth year.

From the year 1980 we obtained model results, derived from later versions of the EMEP model, from the open database of MSC-W (*EMEP/MSC-W*, 2013). The main differences compared to the version used by *Mylona* are that these operate on a higher resolution grid (50×50 km^2), and in every year the meteorological data for the given year were fed to the model (for detailed description of the different model versions see the references at *EMEP/MSC-W*, 2013). The data to the second part of our deposition time series, for the period 1980–2011, are originating from the following model versions:

- version rv4.4: for the years 1990, 2000–2011,
- version rv2.5: for the years 1995–1999,
- version rv2.1: 1980, 1985.

During personal communication, Sophia Mylona provided us her model results for the four 150×150 km^2 grid cells in which the fraction of Hungarian area are the largest (the shaded cells in *Fig. 1*). To keep the consistency of the deposition data set for the whole period (1880–2011), we downloaded the gridded version of the model results from the MSC-W database, and then selected the 36 pieces of 50×50 km^2 grid cells covered by the four grid cells provided by Sophia Mylona. All the deposition data were given as flux; therefore, to get the total deposited sulfur over the grid cells, we multiplied the fluxes by the corresponding grid area. According to *Kugler et al.* (2014), the background air pollution in Hungary can be considered homogenous. Therefore, to get country scale depositions, we up-scaled the grid depositions (for 4×150×150 = 90,000 km^2) for the area of Hungary (93,036 km^2).

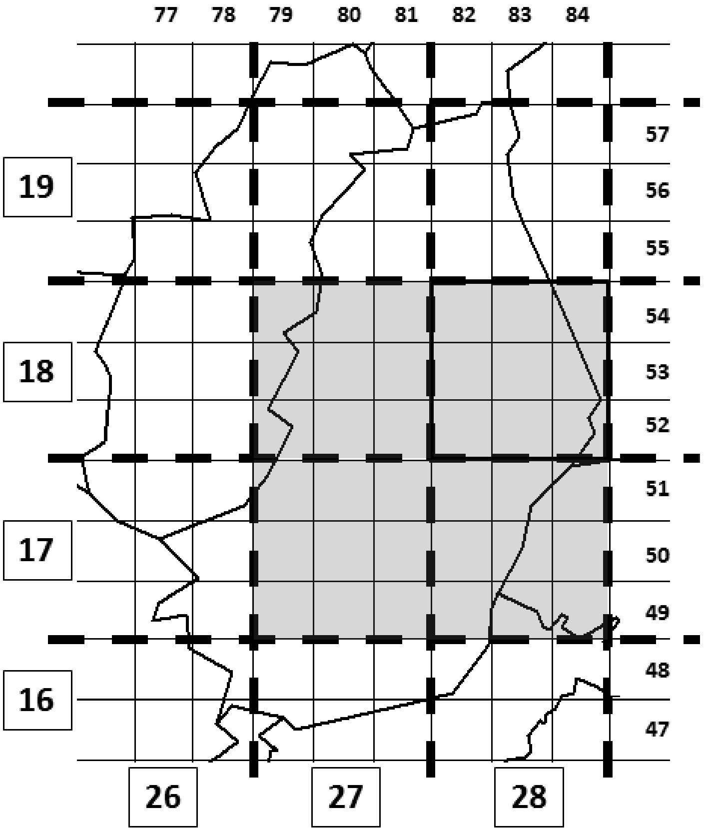

Fig. 1. Hungary on the new EMEP grid with 50×50 km^2 resolution (solid lines), and on the old EMEP grid with 150×150 km^2 resolution (dashed lines). Plain numbers and numbers in boxes indicate the EMEP coordinates for the new and the old grid, respectively. For our sulfur deposition calculations, the shaded grid cells were used from both grids.

2.2. Oxidized and reduced nitrogen compounds

The longest available Hungarian atmospheric chemistry data set for oxidized and reduced nitrogen compounds can be obtained from the measurement data base of the Hungarian precipitation chemistry and background air pollution monitoring network maintained by the Hungarian Meteorological Service (HMS). Among the stations of the network, K-puszta has the longest measurement time series; it has been operating since 1974. Therefore, we choose it as the base of our further investigations.

K-puszta (46°58’ N, 19°33’ E, 136 m a.s.l.) is situated on the Hungarian Great Plain, in the clearing of a mixed coniferous-deciduous forest, far from main anthropogenic emission sources. The site is a part of the network of the Global Atmospheric Watch (GAW) and the EMEP. The starting year of the available data sets for atmospheric concentration and rainwater chemistry (including also precipitation sums) can be seen in *Table 1.*

Table 1. Starting year of the measurements of concentration in air and in precipitation of the depositing nitrogen compounds at K-Puszta station

	Oxidized nitrogen compounds	**Reduced nitrogen compounds**
Atmospheric concentrations	NO_2 : 1974	NH_4^+: 1977
	NO_3^- : 1977	NH_3 : 1981
	HNO_3: 1982	
Concentration in the rain water	NO_3^- : 1974	NH_4^+ : 1974

As we attempted to assess the country scale deposition of nitrogen compounds on the base of a single station’s measurements, we kept the data in the form of fluxes, rather than calculating the total mass of deposited nitrogen over the country. For simplicity’s sake, in the following we will refer to only deposition without ‘flux’. We calculated the total deposition as a sum of dry and wet deposition. Calculation of dry deposition was carried out by the inferential method using Eq. (1) for both oxidized and reduced N-compounds:

$$F_{dry} = \sum_i F_{dry,i} = \sum_i c_{air,i} v_{d,i} f \,, \tag{1}$$

where

- F_{dry} – total yearly deposition flux of oxidized/reduced nitrogen compounds (g N m^{-2} $year^{-1}$),

- $F_{dry,\mathrm{i}}$ – yearly dry deposition of the oxidized/reduced compound i (g N m^{-2} $year^{-1}$),
- $c_{air,i}$ – yearly average air concentrations of the oxidized/reduced nitrogen compound i (μg N m^{-3}),
- $v_{d,i}$ – yearly average dry deposition velocity of the oxidized/reduced nitrogen compound i (cm s^{-1}), and
- f – conversion factor between the different units (3.1536×10^{-1}).

According to its definition (Eq. (2), *Seinfeld* and *Pandis*, 2006), dry deposition velocity is the reciprocal of the sum of the resistances between the atmosphere and the surface. These are the aerodynamic resistance (R_a), the resistance of the quasi-laminar layer (R_b), and the bulk canopy resistance (R_c). Whilst R_a and R_b account for the atmospheric turbulence, R_c expresses for a given trace substance the absorbing or adsorbing capacity of the canopy that covers the surface. Therefore, v_d is a function of the actual micrometeorological conditions, and it strongly depends on the surface characteristics. For our yearly estimations, however, we used constant yearly average deposition velocities, collected from the literature for selected land-cover types.

$$v_d = \frac{1}{R_a + R_b + R_c}. \qquad (2)$$

For both oxidized and reduced compounds we gave estimation for dry deposition on grass, and in the case of oxidized compounds, we calculated it also for mixed land-cover types (grass, forest, arable, urban), giving a closer approach for dry deposition on country level. The same could not been carried out for reduced nitrogen compounds due to the relatively rare occurrence of NH_3 and NH_4^+ dry deposition velocity values in the literature. All the applied dry deposition velocities can be seen in *Table 2*. Data for oxidized nitrogen compounds are originating from the deposition velocity inventory compiled by *Marner* (2003). To get the dry deposition velocities for mixed land coverage, we averaged the data for every oxidized compound using the land-cover fractions (*Table 3*) from the CORINE CLC-50 database over Hungary as weights.

The steps of calculation of yearly wet deposition are described in Eqs. (3), (4), and (5). Daily wet deposition of oxidized and reduced nitrogen compounds can be calculated as a product of the amount of daily precipitation (p_i, dm^3 m^{-2} day^{-1}) and the concentrations of NO_3^- and NH_4^+ ions measured in precipitation samples ($c_{aq,i}$, mg N dm^{-3}), respectively. Summed up these for a month (Eq. (3)), one can get the monthly wet deposition ($F_{wet,j}$, mg N m^{-2} $month^{-1}$).

Table 2. Applied yearly average dry deposition velocities for reduced and oxidized nitrogen compounds (latter from the inventory by *Marner* (2003)) for different surface types, their references and - where applicable – their weighted average, as used in our dry deposition calculations for mixed vegetation (for the weights see *Table 3*)

Compound	**Deposition velocity (cm s^{-1})**				
	Grass	**Arable**	**Forest**	**Urban**	**Weighted average**
NH_3	0.99 (*Horváth et al.,*2005)	–	–	–	–
NH_4^+	0.087 (*Gallagher et al.,*2002)				
NO_2	0.16 (*Nicholson et al.*, 2001)	0.16 (*Nicholson et al.*, 2001)	0.26 (*Puxbaum and Gregori*, 1998)	0.08 (*Nicholson et al.*, 2001)	0.17
HNO_3	1.39 (*Marner*, 2003)	2.06 (*Marner*, 2003)	7.33 (*Marner*, 2003)	7.33 (*Marner*, 2003)	3.81
NO_3^-	0.15 (*Slinn*, 1982)	0.26 (*Davidson et al.*, 1982)	1.78 (*Ruijgrok et al.*, 1997)	1.78 (*Ruijgrok et al.*, 1997)	0.77

Table 3. Area of the different land cover types over Hungary and their fraction in the total area of the country, used as weights in our dry deposition calculations

	Grasslands		**Forest**			**Arable**	**Urban**
	Semi-natural	**Pasture**	**Deciduous**	**Mixed**	**Coniferous**		
Area (10^{10} m^2)	0.58	0.39	1.55	0.08	0.16	5.12	1.42
Fraction	10.43%		19.25%			55.05%	15.27%

The variability of the time series derived in this way is influenced by that of the monthly precipitation amount. According to *Horváth* (1978), there is a positive, strong and significant relationship between the monthly amount of precipitation and the monthly wet deposition. Same was true for our datasets (*Fig. 2*). Based on this, we normalized the monthly wet deposition values applying Eq. (4), where a and b are the slope and the intercept of the regression line, respectively (*Fig. 2*), p_j is the monthly precipitation, and $F_{wet,ave}$ is the wet deposition with the long-term average monthly precipitation (for the values of a, b, and $F_{wet,ave}$ see *Table 4*). Finally, to get the yearly wet deposition (F_{wet}, mg N m^{-2} $year^{-1}$), we summed up the normalized monthly values ($F_{wet,j}^{norm}$ mg N m^{-2} $month^{-1}$) for a year (Eq. (5)).

$$F_{wet,j} = \sum_i c_{aq,i} p_i , \qquad (3)$$

$$F_{wet,j}^{norm} = F_{wet,ave} \frac{F_{wet,j}}{ap_j + b} , \qquad (4)$$

$$F_{wet} = \sum_{j=1}^{12} F_{wet,j}^{norm} . \qquad (5)$$

After calculating the total deposition ($F_{total}=F_{wet}+F_{dry}$) for both the oxidized and reduced nitrogen compounds, to get the total nitrogen load we summed up the two total deposition values over grass. To characterize the change in all of the resulted nitrogen time series, we fitted trends to them. The trends with the best fit were determined by applying the Akaike information criterion (AIC, *Sakamoto et al.*, 1986), as a built-in function in the statistical programming language R.

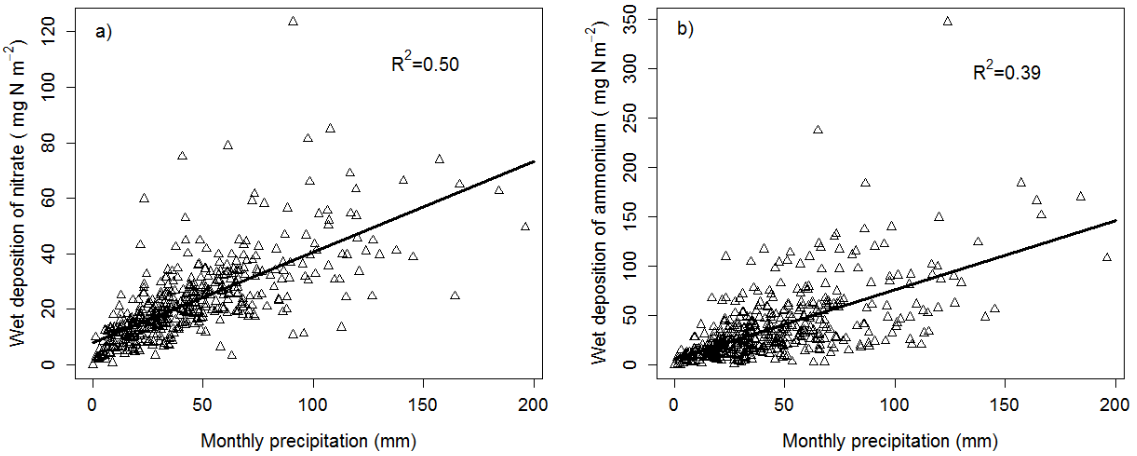

Fig. 2. Regression between monthly precipitation and wet deposition of nitrate (a) and ammonium (b) over the period 1974-2012 at K-puszta. R^2 indicates the square of correlations between the datasets.

Table 4. Parameters of the regression between the monthly precipitation and monthly wet deposition of nitrogen species, where p_{ave} (mm) is the long-term average of the monthly precipitation values, a (mg N dm^{-3} month^{-1}) is the slope, b is the intercept (mg N m^{-2} month^{-1}), and $F_{wet,ave}$ ($a \times p_{ave}+b$) is the wet deposition with the average monthly precipitation (mg N m^{-2} month^{-1})

Ions	p_{ave}	a	b	$F_{wet,ave}$
NH_4^+	44.3	0.70	5.92	36.9
NO_3^-		0.33	7.90	22.4

2.3. Further data sources

During the interpretation of our results, we used further data sources. In the case of oxidized sulfur compounds, we compared the deposition time series to a national emission time series compiled from the historical emission database of A.S.L. & Associates (*Lefohn et al.*, 1999) for the period 1880–1990 and from emissions reported to the EMEP (*CEIP*, 2013) for the period 1990–2011. The emission data obtained from the open database of A.S.L. & Associates (*A.S.L. & Associates*, 1999) are in a good agreement with the emissions published by *Mylona* (1992); however, for illustration purposes the A.S.L. data set is better, as it has a finer, yearly temporal resolution compared to the 5-year resolution of the data set by *Mylona*.

The deposition of oxidized nitrogen species were compared to the national NO_x emissions reported to EMEP that are available in the emission database of EMEP for the period of 1980–2011. In addition, we refined our comparison with data for the total number of cars in Hungary for 1974–2011, from the freely available database (*KSH*, 2013) of the Hungarian Central Statistical Office.

To interpret our results for NH_3 and NH_4^+ depositions, we compiled a national NH_3 emission dataset from *Horváth et al.* (2009) (for 1980–2005) and from the EMEP database (for 2006–2011). As deposition of SO_2 and NH_3 has a strong relationship, for further investigations we calculated also the average yearly SO_2 surface concentrations based on the daily HMS measurements at K-puszta.

3. Results

3.1. Time series of oxidized sulfur compounds

Between 1880 and 1950, deposition of oxidized sulfur compounds over Hungary showed a moderate increase (*Fig. 3*), which was interrupted only by World War II. Over this period, sulfur deposition was mainly under 100 Gg S year^{-1}, except in 1940, when it slightly exceeded this limit. From 1950, sulfur deposition was intensifying until it peaked at 381 Gg S year^{-1} in 1980. In the last three decades deposition has been decreasing. Since 2005, the values has been under 100 Gg year^{-1} again.

The emission time series (*Fig. 4*) is very similar to that of the deposition. However, also differences can be noticed between the two time series. In 1880–1950, the increase of emission was not as steady as that of the deposition. Despite it reached its maximum in 1940, there were several other substantial peaks and lows over this period, including a clear minimum after World War II. For this difference more explanations are feasible.

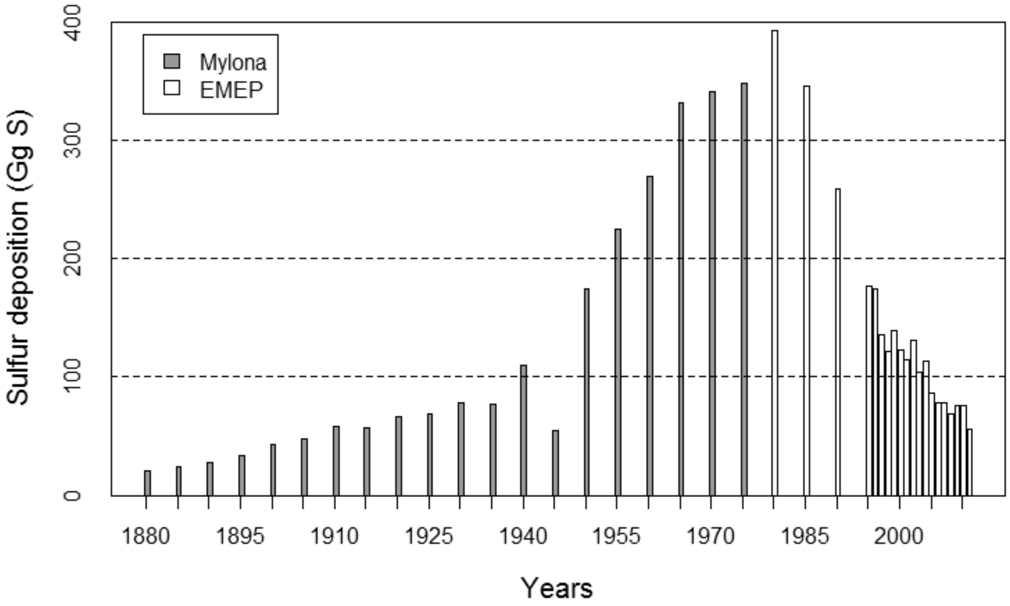

Fig. 3. Sulfur deposition over Hungary between 1880 and 2011 compiled from the two data source: *Mylona* (1992) and the EMEP database (*EMEP/MSC-W*, 2013).

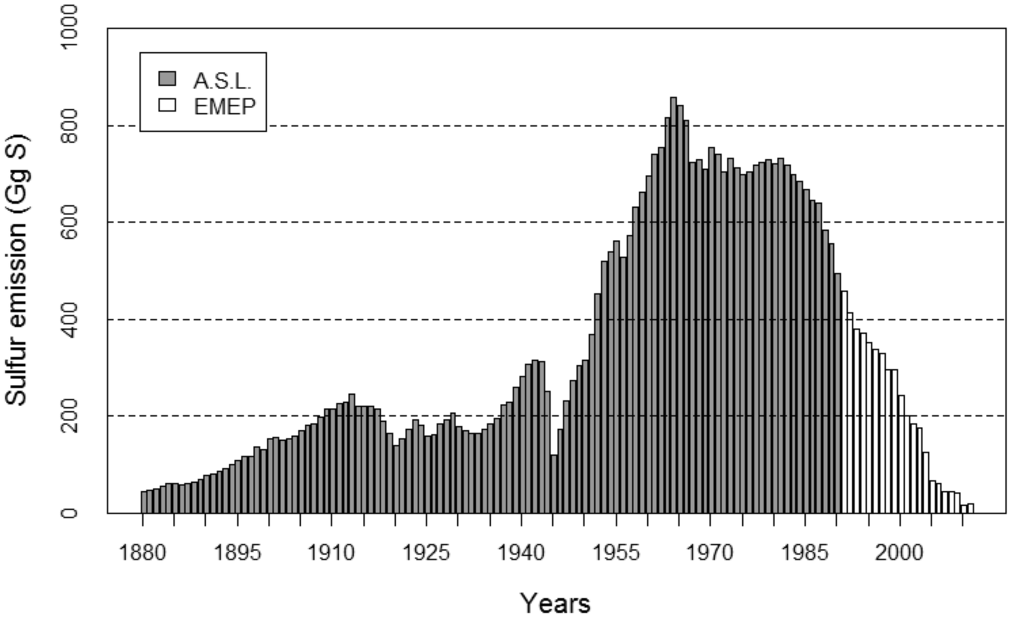

Fig. 4. Sulfur emission in Hungary between 1880 and 2011 compiled from the two data source: *A.S.L. & Associates* (1999) and the EMEP emission database (*CEIP*, 2013).

Firstly, over this period for deposition modeling another emission data set was used. On the other hand, the relationship between emission and deposition of oxidized sulfur compounds on country scale is not linear, as due to their long atmospheric lifetime, their atmospheric transport is transboundary. Consequently, not all of the sulfur emitted in Hungary deposits over the country, and similarly, a part of the deposited sulfur originates from the neighboring countries. As a consequence, even an intense increase in national emission can lead to a more moderate change in national depositions.

Emission reached its absolute maximum in 1964, 16 years earlier than deposition. Same is true for the emission dataset published and used in the model runs by *Mylona* (1992) (not presented here): the most sulfur was emitted in 1960. This could imply that the later maximum in deposition is a result of the imperfect match of the two deposition data sets. However, in the whole deposition time series derived by *Mylona* for 1880–1991, the highest value occurred also in 1980. The difference can be explained only by the above described phenomena of transboundary air-pollution, i.e., the emission tendencies on a larger scale in Europe suppressed the local emission trends. This is supported by the European total emission time series by *Mylona*, that shows an absolute maximum in 1980, at the same time with the highest deposition in Hungary.

It is difficult to qualify the strength of acidification, because it depends, among others, on the buffering capacity of the surface. However, based on the observations – the higher deposition, the stronger the effect of acidification – it can be concluded that during 1950–1980, Hungary was the most exposed to the harmful effects of acidification triggered by the deposition of oxidized sulfur compounds. In the last 3 decades, sulfur emissions has been reducing presumably due to the recession of Hungarian industry as well as the more conscious handling of European industrial emissions as a result of – among other international conventions on air pollution – the 1979 Geneva Convention on Long-range Transboundary Air Pollution. Consequently, the oxidized sulfur deposition has been also decreasing over the last 30 years, possibly leading to gradually weakening acidification.

3.2. Oxidized nitrogen compounds

The wet deposition of oxidized nitrogen compounds (*Fig. 5*) in the period of 1974–2012 ranged between 150 and 350 mg N m^{-2}, except in 1975, when it reached an extreme high value of 446 mg N m^{-2}. Two waves of the tendency can be distinguished: one in 1974–1998 with the highest values during the middle of the 80’s, and another from 1998 to 2012 with the largest values in the middle of the last decade. However, the fitted 2nd order polynomial trend shows a steady decline over the whole period (for a summary of our results for nitrogen species see *Table 5*).

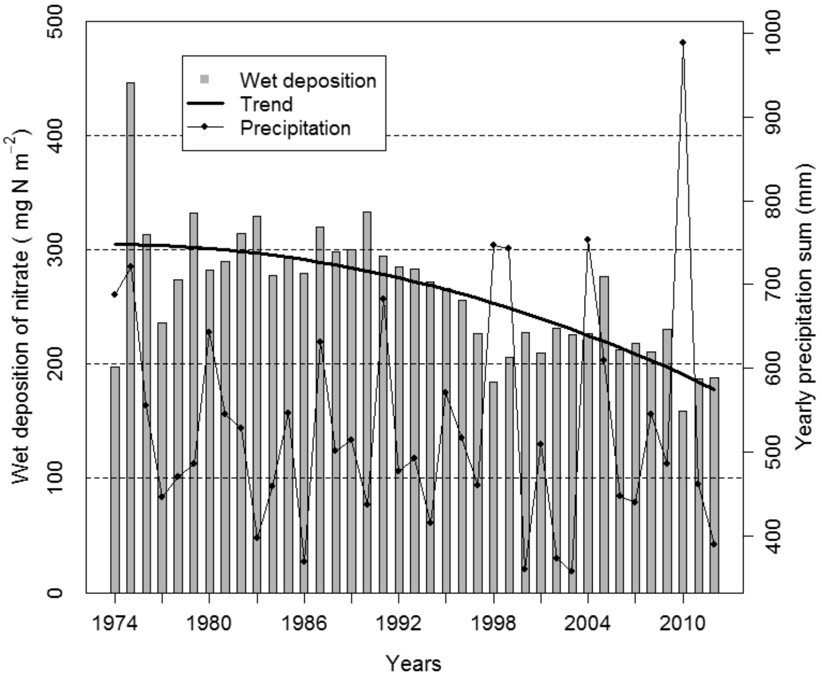

Fig. 5. Wet deposition of oxidized nitrogen compounds between 1974 and 2012 at K-puszta, the best fit line, and the yearly precipitation sum.

Table 5. Summary of our results for the deposition time series of the nitrogen compounds, with their starting year (the last year was 2012 in every case) and the order of the best fit trends

Compounds	**Deposition**	**Beginning of the time series**	**Order of the fitted trend**
Oxidized nitrogen compounds	Wet	1974	2
	Dry^g	1982	4
	Dry^m	1982	1
	Total^g	1982	4
	Total^m	1982	1
Reduced nitrogen compounds	Wet	1974	3
	Dry^g	1981	4
	Total^g	1981	1
Total nitrogen load^g		1982	1

^{g} calculated for grass, ^{m} calculated for mixed vegetation

For grass the dry deposition ranged from 200 to 500 mg N m^{-2}, whilst for mixed vegetation it varied mostly between 400 mg and 800 N m^{-2}, except in four years (1982, 1983, 1993, and 1994), when deposition was around or over 1,000 N m^{-2} (*Fig. 6*). Despite that the atmospheric concentration of NO_2 (*Fig. 7*) was the highest over the whole period, dry deposition of HNO_3 particles was predominant for both surface types. This is a result of the high reactivity and solubility of HNO_3 and consequently its deposition velocity, that is larger by one order of magnitude compared to those of the other two compounds. This led also to the above mentioned four peak values in dry deposition for mixed vegetation, as HNO_3 concentrations were relatively high in these years. The higher dry deposition for mixed vegetation compared to grass was caused mostly by the almost three times larger average HNO_3 deposition velocity applied for this surface type.

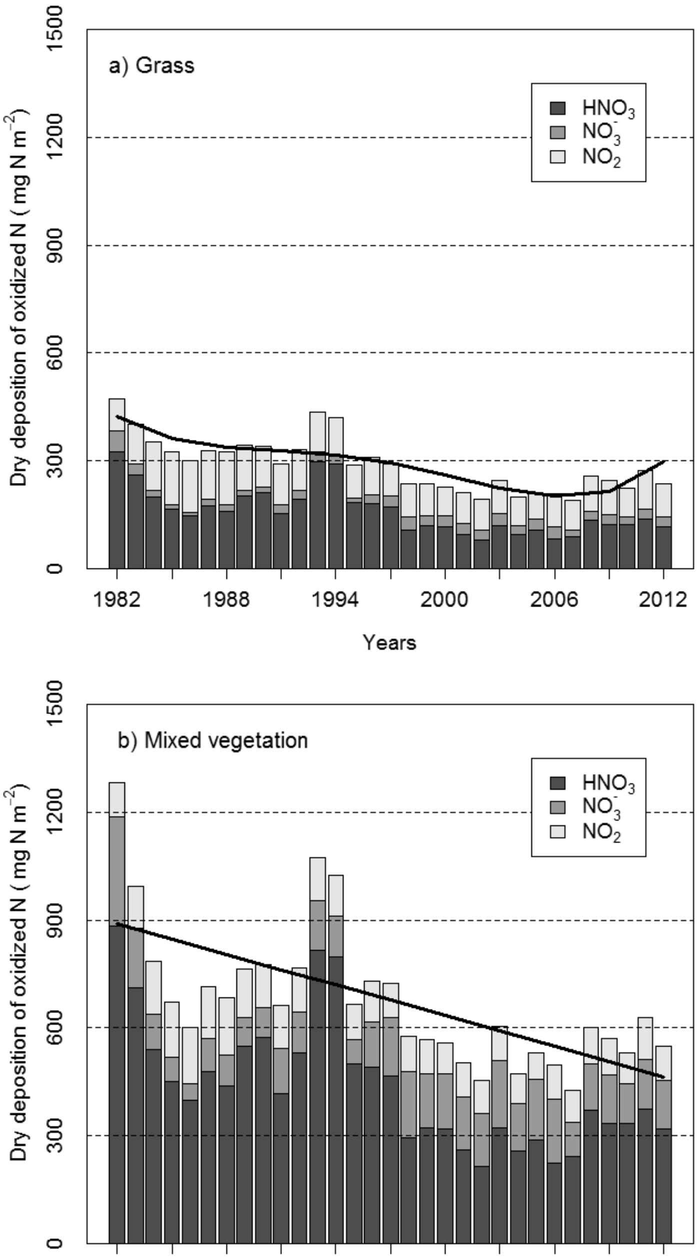

Fig. 6. Dry deposition of oxidized nitrogen compounds over grass (a) and mixed vegetation (b) between 1982 and 2012 at K-puszta, and the best fit lines to the total dry depositions.

In the case of grass, the year-to-year variability was smaller than for mixed vegetation. The fitted 4th order polynomial trend shows a moderate decrease over most of the period with an increase over the last four years. However, the significance of this rise can be considered low, regarding that the length of the period is quite short and the depositions over the four year do not change consistently. For mixed vegetation the decreasing is much clearer, the best fit trend is linear with a slope of 14 mg N m^{-2} year^{-1}.

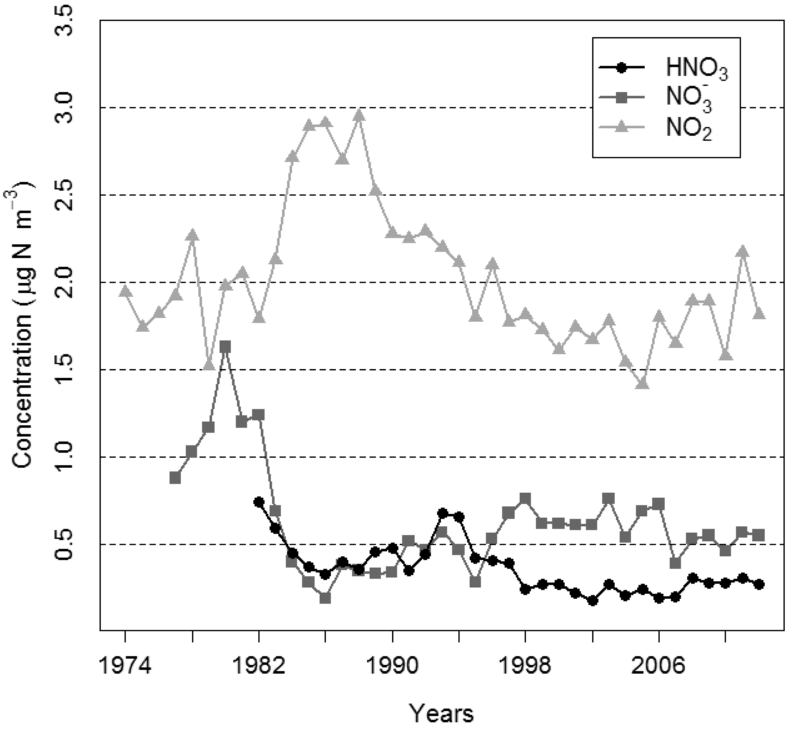

Fig. 7. Atmospheric concentration of oxidized nitrogen species between 1974 and 2012, measured at K-puszta.

Since the variability in wet deposition was smaller, the tendency of total deposition followed that of the dry deposition for both surface types (*Fig. 8*). The ranges of total deposition were 200 mg N m^{-2} higher than for dry deposition for both grass and mixed vegetations. The fitted trends are of the same order like the trends of dry depositions: 1st for mixed vegetation with a yearly reduction of 18 mg N m^{-2} year^{-1}, and 4th for grass with a slightly stronger decrease than in dry deposition.

Apparently, the relationship between national NO_x emissions (*Fig. 9*) and depositions is not as clear as in the case of oxidized sulfur compounds. A possible reason for that could be that we are comparing national emissions to depositions calculated from the data of a single station. On the other hand, due to the relatively long atmospheric lifetime of oxidized nitrogen compounds, transboundary transport of pollutants also has a strong influence on depositions. Finally, *Fowler et al.* (2007) suggested, that such non-linearity between emissions and depositions for oxidized nitrogen compounds grows with distance from the main European source region of the highly populated northern Europe, stretching from the Czech Republic to South East England.

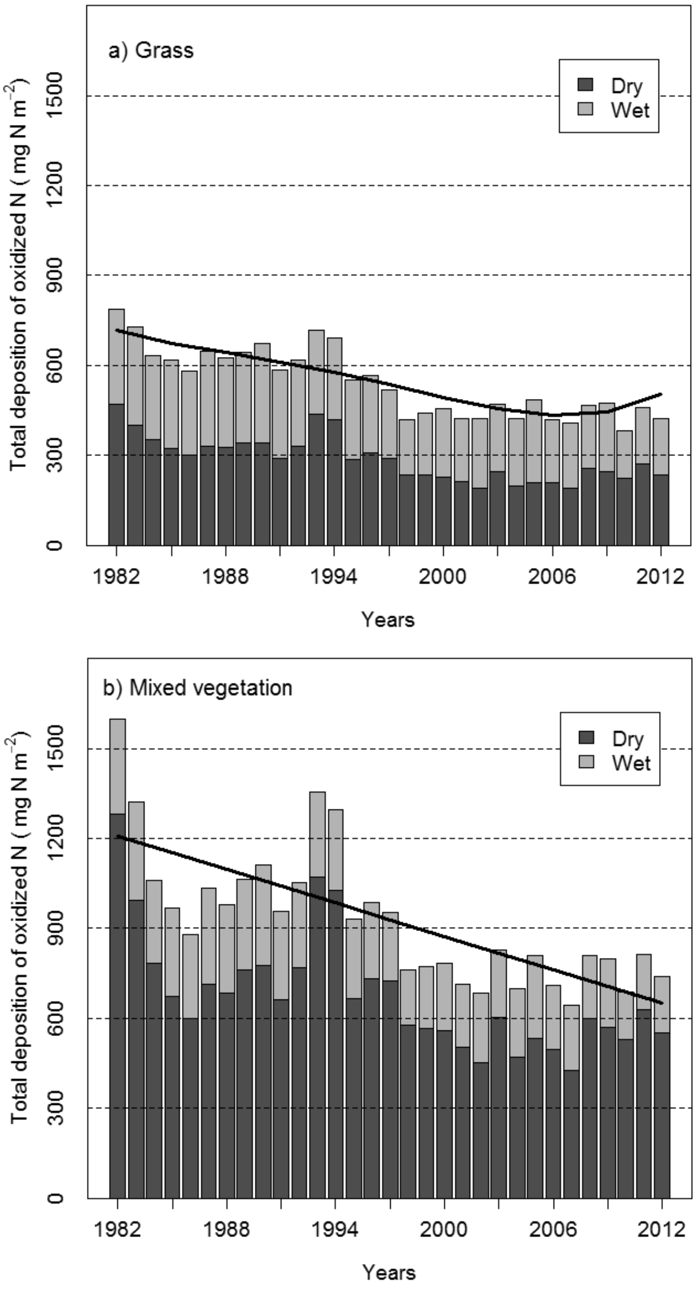

Fig. 8. Total deposition (dry + wet) of oxidized nitrogen species over grass (a) and mixed vegetation (b) between 1982 and 2012 at K-puszta, and the best fit lines to the total depositions.

The approximately 25% decrease in NO_x emission since the beginning of 90's is due to the breakdown of heavy industry after political changes. However, the steadily growing number of cars over the whole period (*Fig. 9*) comparing to the decreasing trend both of emission and total deposition may suggest the impact of technical improvements and national measures in abatement of oxidized nitrogen emission and resulting deposition – from 1990 the usage of catalyst in cars is ordered by the Hungarian law for newly sold vehicles.

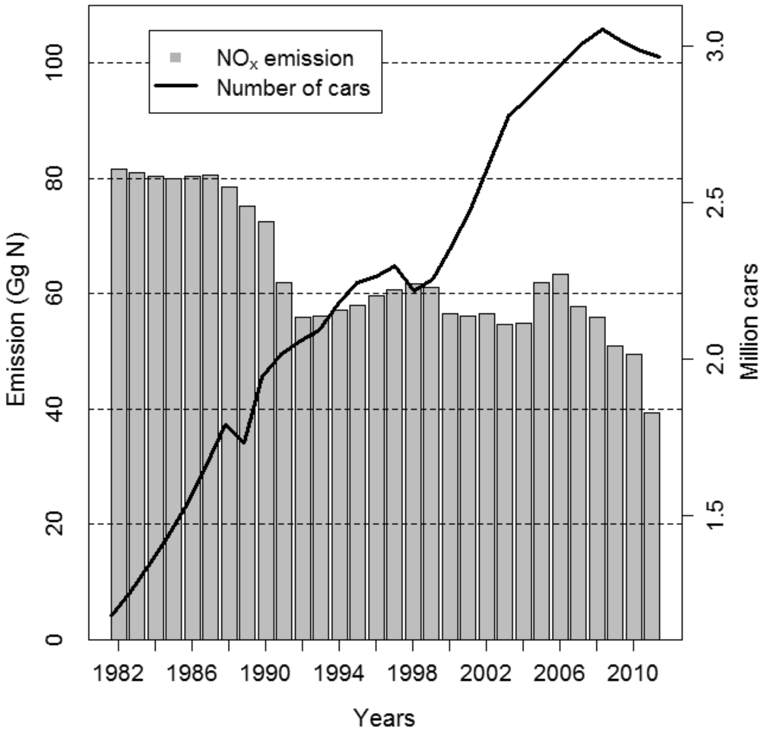

Fig. 9. National emission of NO_x and the number of cars in Hungary between 1982 and 2011.

3.3. *Reduced nitrogen compounds*

Yearly wet deposition of NH_4^+ ion between 1974 and 1982 (*Fig. 10*) varied from 800 to 1,600 mg N m^{-2}, then the values were under 800 mg N m^{-2}. The best fit trend was a 3rd order polynomial, showing a strong decrease in the first 20 years, and then a moderate further reduction until the end of the period.

Yearly dry deposition (*Fig. 11*) ranged mostly between the values of 200 and 400 mg N m^{-2} before 1996, then the great majority of deposition ranged between 300 and 500 mg N m^{-2}. The fitted 4th order polynomial trend shows a wave-like tendency, with a period of decrease before 1986, followed by a 20-year long increasing period and then a subsequent reduction until 2012. Despite that atmospheric concentration of NH_4^+ was higher in the first 20 years (*Fig. 12*), dry deposition was dominated by NH_3 deposition over the whole period. The cause of that is that NH_3 is highly soluble, resulting in a one order of magnitude higher dry deposition velocity than that of NH_4^+. Moreover, majority of ammonium are in the range of fine particles ($PM_{2.5}$) (*Horváth*, 2003), where deposition velocity has smaller rate than that of ammonia gas.

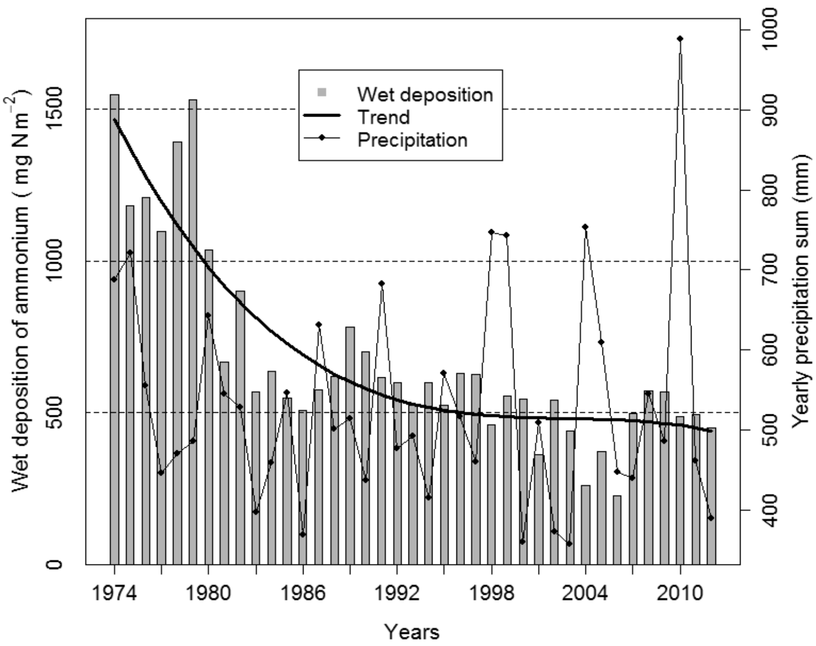

Fig. 10. Wet deposition of reduced nitrogen compounds between 1974 and 2012 at K-puszta, the best fit line, and the yearly precipitation sum.

Total deposition (*Fig. 13*) is mainly dominated by wet deposition, especially in the first half of the period. As the difference between wet and dry deposition is not too large, the opposite tendencies compensated each other, resulting in a balanced total deposition. The best fit, linear trend shows a weak decline of 1.7 mg N year^{-1}.

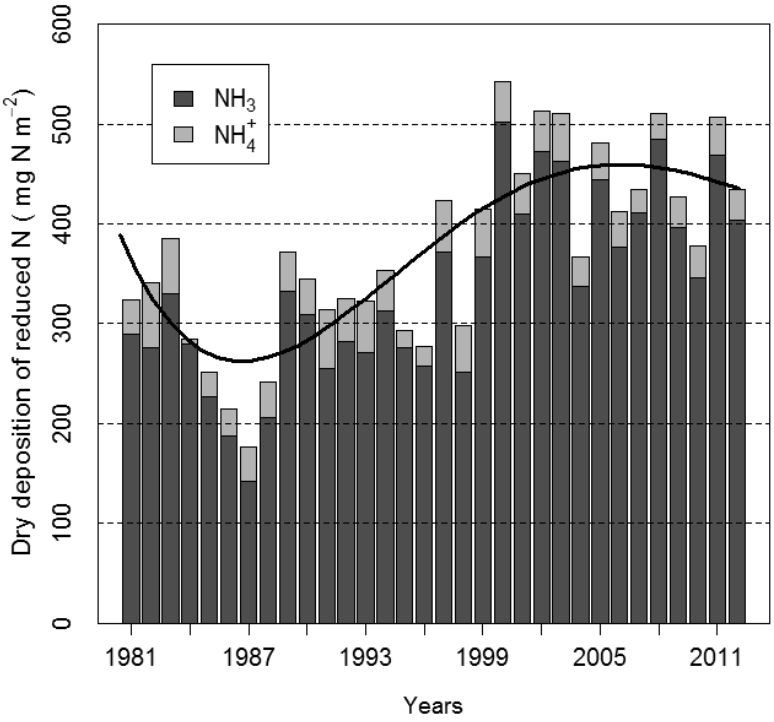

Fig. 11. Dry deposition of reduced nitrogen species between 1981 and 2012 at K-puszta, and the best fit line to the total dry deposition.

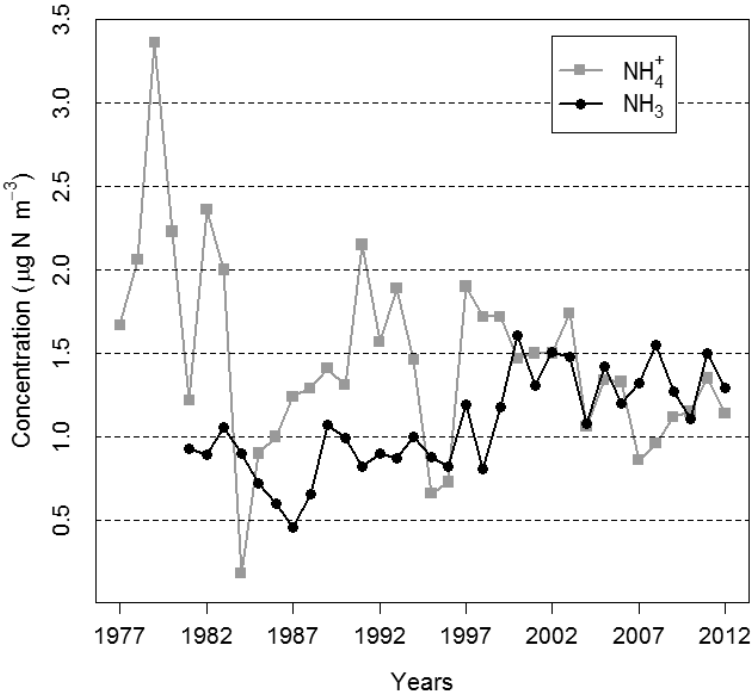

Fig. 12. Atmospheric concentration of reduced nitrogen species between 1974 and 2012, measured at K-puszta.

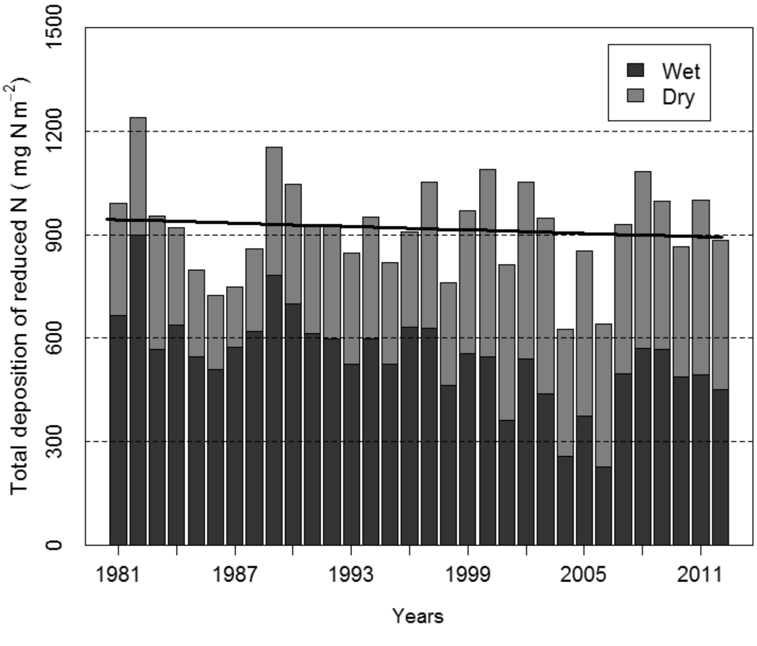

Fig. 13. Total deposition (dry + wet deposition) of reduced nitrogen species between 1981 and 2012 at K-puszta, and the best fit line to the total deposition.

In the national NH_3 emissions (*Fig. 14*), a rapid decrease can be seen between 1989 and 1994, with a close-to-constant emission before and after it. This is mainly parallel with the tendency of wet deposition, but apparently it is the opposite of the trend in dry deposition. This raises the obvious question: how can the dry deposition grow if emission is reducing? Considering that in our approach the atmospheric concentration and deposition of NH_3 differ only in a constant multiplying factor, the question is the same for concentrations and emissions. Since gaseous NH_3 after emission dissolves quickly on the surface, in this case the influence of long-range transport is presumably weak.

As an alkaline compound, dry deposition of NH_3 is largely dependent on the acidity of the surface water (water film on the surface). Therefore, its deposition is influenced by the deposition of atmospheric acidic components (*Flechard et al.*, 1999). According to *Erisman et al.* (2001) and *Fowler et al.* (2001), the lower the ratio of atmospheric concentration of SO_2 to NH_3 (i.e., SO_2 concentration is relatively low or NH_3 concentration is relatively high), the higher the surface resistance to NH_3 deposition. Consequently, even if the atmospheric input of ammonia decreases with a decreasing SO_2 concentration, it cannot be removed from the atmosphere as the higher pH of the surface water film, caused by the less dissolved SO_2, hampers NH_3 dissolution. As a result, the emitted NH_3 remains in the atmosphere raising its atmospheric concentration, as it was observed earlier by *Horváth et al.* (2009).

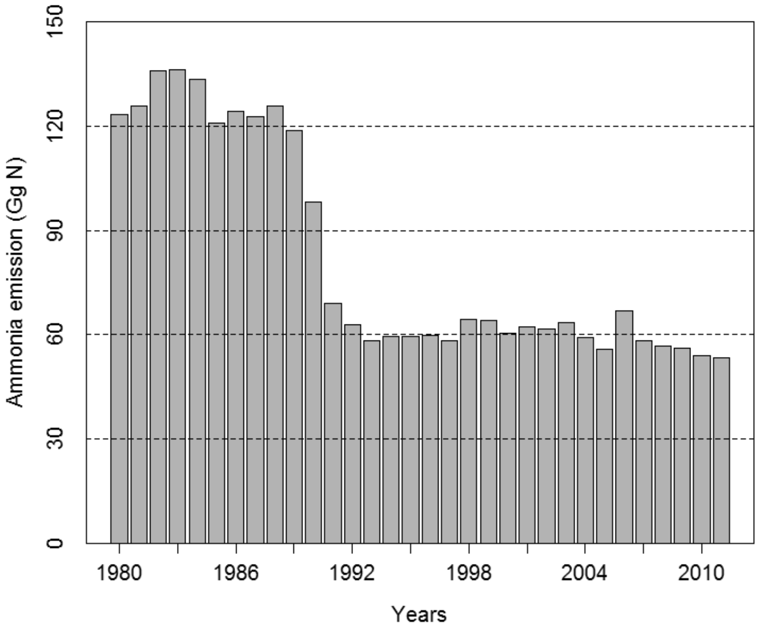

Fig. 14. National emission of ammonia in Hungary between 1980 and 2011.

According to *Fig. 15*, the above described process, referred as the co-deposition of NH_3 and SO_2, was most likely the key process in Hungary as well. On the other hand, this founding highlights the weakness of our simple estimation approach for dry deposition of NH_3, as the process, preventing NH_3

removal from the atmosphere, could lead to lower deposition than our calculations. Therefore, the estimation of NH_3 dry deposition requires further investigation.

In addition, the transfer of ammonia between atmosphere and surface is bi-directional, i.e., not just deposition but also emission can occur depending on the difference between the atmospheric NH_3 concentration and above the surface (*Farquhar et al.*, 1980). Further influencing factors on the magnitude of NH_3 exchange are, among others, temperature, wind speed, and relative humidity, which were all neglected during our approach.

However, considering bi-directional exchange would require a much complex estimation, which has not been applied either in operational ACTMs (*Sutton et al.*, 2013). ACTMs nowadays calculate dry depositions based on the same formula we used, that – even if the calculations are more detailed in an ACTM – supports the relevance of our simple approach.

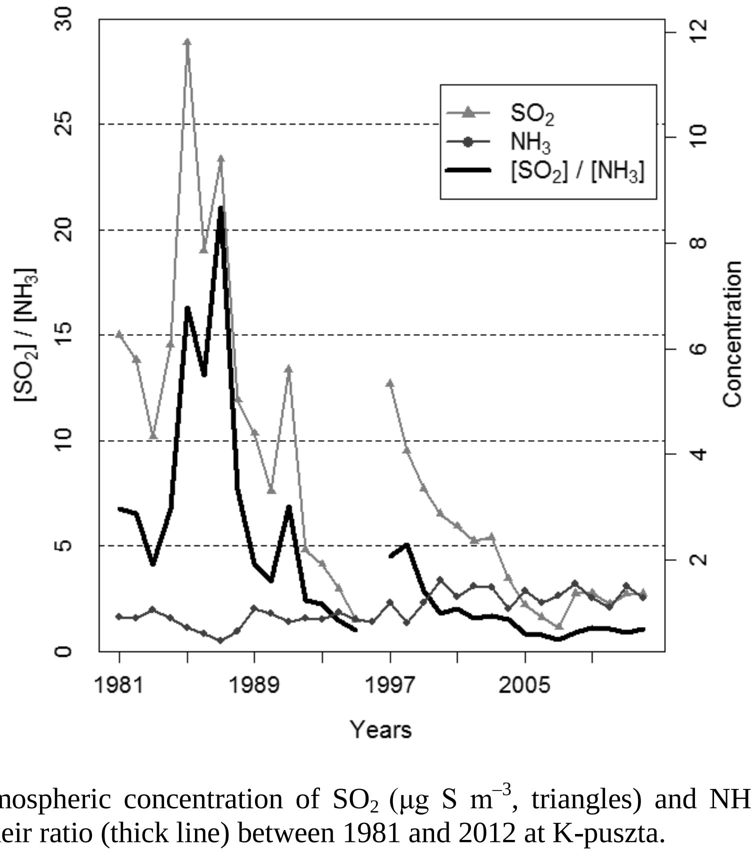

Fig. 15. Atmospheric concentration of SO_2 (µg S m^{-3}, triangles) and NH_3 (µg N m^{-3}, dots), and their ratio (thick line) between 1981 and 2012 at K-puszta.

3.4. Total nitrogen load

Summing up the total depositions of oxidized and reduced nitrogen compounds for grass, we got the total nitrogen load over grass-covered surface (*Fig. 16*). In the period of 1982 and 2012, it varied mainly between 1,000 and

1,600 mg N m^{-2}. According to the measurement practice of air concentration and dry deposition velocity, we estimated the uncertainty of the total nitrogen load ±10% shown as error bars in *Fig. 16*. This uncertainty covers much possibly the year-to-year variability of yearly dry deposition velocities. Compared to the oxidized compounds, deposition of reduced nitrogen compounds had a larger fraction in the total load. As we showed it, both of them had a slow decreasing trend, resulting in a moderate decrease in the total load as well. The fitted trend is linear, with a slope of 12 mg N m^{-2} year^{-1}.

Likewise in the case of oxidized sulfur compounds, it is difficult to quantify the acidifying effect of the nitrogen compounds examined above. In addition, in this case the neutralizing effect of dissolving gaseous NH_3 has to be also considered. However, even if dry deposition of reduced nitrogen compounds is highly dominated by NH_3 deposition, in the total load the other components overcame it. Overall, the declining trend of the total nitrogen load implies a mitigating tendency of acidification.

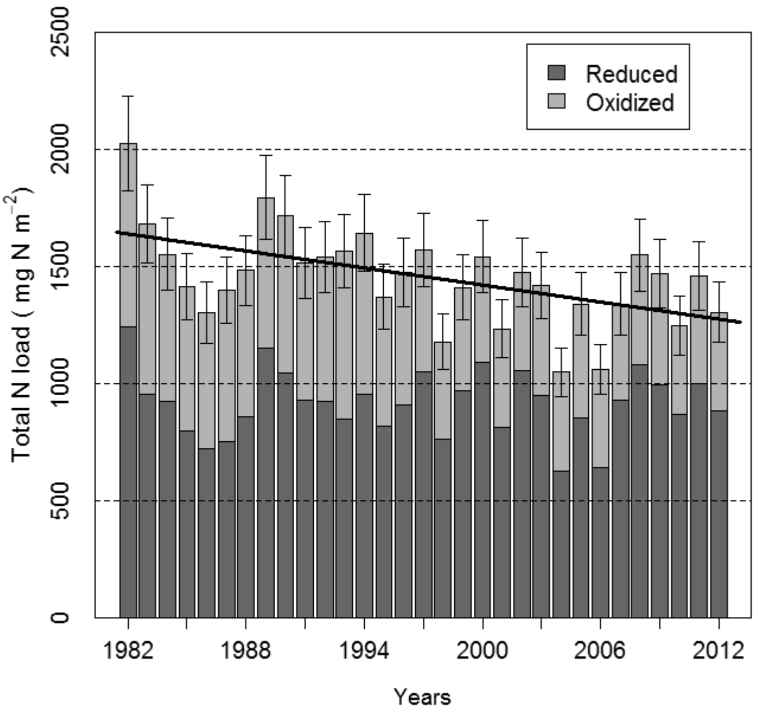

Fig. 16. Total nitrogen load (as a sum of the total deposition of reduced and oxidized nitrogen compounds) over grass between 1982 and 2012 at K-puszta.

4. Conclusions

The purpose of this work was to compile long-term deposition time series for Hungary for acidifying compounds, such as oxidized sulfur, as well as oxidized and reduced nitrogen compounds. To achieve our goal, we used existing results from ACTMs and precipitation chemistry as well as background air pollution measurements. Comparing the results with national emission datasets, we also made an attempt to interpret the changes in depositions. Finally, we gave a qualitative estimation for the strength of acidification on long term.

In the case of oxidized sulfur compounds, according to the 132-year long deposition time series, 1980 was a changing point: until this year, deposition was steadily increasing, and since then it has been decreasing rapidly. For deposition of oxidized nitrogen compounds, we got declining trend between 1982 and 2012; however, in the case of grass, a non-significant increase occurred in the last four years of the period. We found that the deposition of reduced nitrogen compounds has been also decreasing since 1982. Consequently, our calculation showed that also the total nitrogen load followed a slowly declining tendency.

Despite that the transboundary transport of both oxidized sulfur and nitrogen compounds, influences the national depositions, in the case of the oxidized sulfur compounds the relationship between the emissions and depositions was clearer than for the oxidized nitrogen compounds. On the other hand, we found that the decrease of total deposition of oxidized nitrogen compounds is most likely a sign of the improvement of emission abatement techniques and national emission controlling measures. Same is true for the total deposition of oxidized sulfur species; however, in this case, also the Hungarian industrial recession could be a substantial influencing factor. The total deposition of reduced nitrogen compounds showed only a weak declining tendency in contrast with drastically weakening NH_3 emissions. Moreover, atmospheric NH_3 concentration is nearly constant in spite of emission reduction. We showed that this trend in atmospheric concentration and – in our approach – dry deposition of NH_3 is possibly a result of the declining surface concentration of SO_2. Considering this effect, estimation of dry deposition of NH_3 requires further investigation.

Based on our results, only qualitative conclusions can be drawn regarding the progress of acidification in Hungary: the effect of acidification was most likely to intensify before 1980, since then the phenomenon presumably has been weakening gradually. On the other hand, if atmospheric concentration of NH_3 continuously grows in Hungary, in spite of its potential neutralizing effect in the atmosphere, it may raise new environmental issues in the future due to its key role in the cycle of reactive nitrogen compounds (*Galloway et al.,* 2008).

Acknowledgement – The authors are grateful to Sophia Mylona for providing her model results and to László Haszpra, who contacted her. In addition, we would like to express our appreciation to Ben Marner for sending us his PhD thesis.

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