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Summary of the published, historical nitrogen load data collected for ECOSUPPORT

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The data is available at the home page of the ECOSUPPORT programme for use in the project.

1. Data coverage

The location of the stations has been estimated with help of information in the publications with the data, present-day names of the sampling locations and historical documents of activity at old research stations. Not all stations have yet been located. Further analysis of the data might define the localization of the stations.

The early measurements covered only compounds in precipitation.

Fig 1. Stations with data for nitrogen in precipitation covering decades 1850, 1860 or 1870.

Concentration or deposition data at the stations cover mainly short periods, months or a couple of years. For some of the stations only one annual or typical value is given in a review article.

Fig. 2. Stations with data for nitrogen in precipitation covering decades 1880, 1890 or 1900.

Data from Rothamsted in UK is rather extensive and well documented. At the agricultural research station near Copenhagen in Denmark, the measurements covered 4 years. Other data series are shorter.

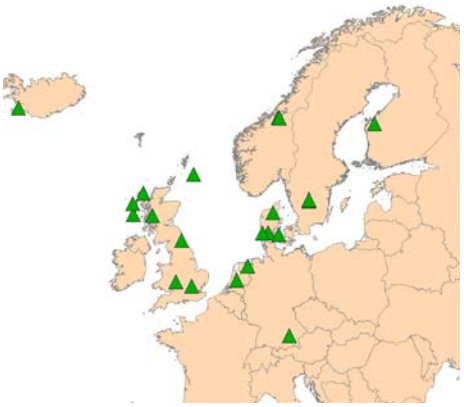

Fig. 3. Stations with data for nitrogen in precipitation covering decades 1910, 1920 or 1930.

Data from Weihenstephan, Germany, cover years 1928-35 and data from Askov, Sweden 1921-27. From Rothamsted there is data for years 1910-1916. Other stations have shorter time series or only one typical value.

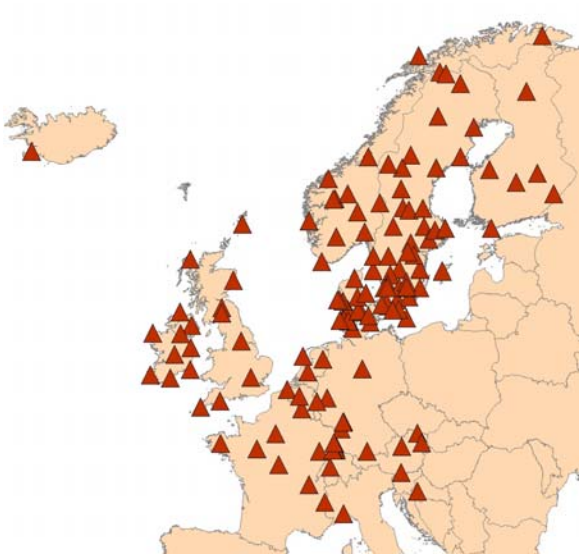

Fig. 4. Stations with data for nitrogen in precipitation or air covering decades 1950 or 1960.

Most of the stations belonged to the European Air Chemistry Network. First measurements began in the network in 1954. During the years 1956-58 most stations made measurements. Some stations continued monitoring in the 1960's. Ammonia in air was often measured at the stations besides the components in precipitation.

2. Discussion about the quality of the data

The most extensive time series at Rothamsted 1853-1966 has been analyzed carefully by Brimblecombe and Pitman (1980). The seasonal variation for monthly deposition with typical standard variance was estimated for nitrate and ammonium during the different time periods. For ammonium, the seasonal variation for the time series 1876-1916 and 1955-66 agreed fairly well, although the scatter increased. For nitrate a change was detected in the annual distribution. The authors considered that for both compounds the time series were fairly reliable.

Sutton et al. (2008) has published an extensive review of ammonia in the environment. The article estimates also the quality of the historical ammonia concentrations in the air. The 19th century atmospheric ammonia concentrations in city air were much larger than present-day values. The high values, mostly in cities, were estimated as plausible. The coal burning was the major source in cities. The article comments also about the measuring methods used. The

chemical analyses were performed by careful laboratory practice according to published analytical methods. Methods were based on gravimetric and colorimetric methods. The measurements were generally robust and the papers reported few details. According to Sutton et al. (2008), there was little doubt that the concentration in 19th century cities was locally extremely high.

Results given in tables in the review articles include in general no information about the reliability of the data. Their usefulness has to be analyzed together with the rest of the data e.g. in areal analyses.

Articles of measurements at a certain measuring station describe usually methods for sampling and chemical analysis. Problems for the chemical composition of precipitation with material used in ordinary rain amount samplers were recognized already in the 1800's. Scientists tried to avoid them with selection of suitable material. The chemical analyses were performed from large quantities of rain water with methods used earlier.

If the samples were taken for short periods, hours or a few days, and analyzed without storage, the largest source for error is probably the occasional sampling contamination (bird dropping etc.). If the samples were staying in the vessel for a month without a preservative which would avoid biological activity, at least losses in the ammonium content could have taken place.

The air samples were taken at least in the 1950's with a bubbler, where both gas phase ammonia and particulate ammonium were absorbed in the solution. Those concentrations represent mainly the sum of the two compounds in air (Sutton et al. 2008).

The publications of the earliest measurements give the impression that the work, including often the field work, was performed by professionals who were familiar with experimental research work and had studied the literature of others before starting own measurements. The values are compared to corresponding levels and differences discussed. So, values published in literature, mostly represent careful practical work with materials and methods best available. However, sometimes the low concentrations are outside the skills or instruments. On the contrary, in the 1950's chemical equipments enabled analysis of lower concentrations, but all the field personnel in the wide network of stations was not so experienced to handle samples without contamination.

3. Preliminary analysis of the levels and changes in the concentration/deposition levels

The changes in the nitrogen level can be studied from reliable, long time series. Figure 5 shows that the deposition of both nitrate and ammonium at Rothamsted has increase during the time period. The ammonium values in the 1850's were too high because of insufficient chemical method (Brimblecombe and Pitman 1980) and have been excluded from the figure. The variation between years is larger during the last years of measurements. However, all values after 1970 were higher than before year 1916.

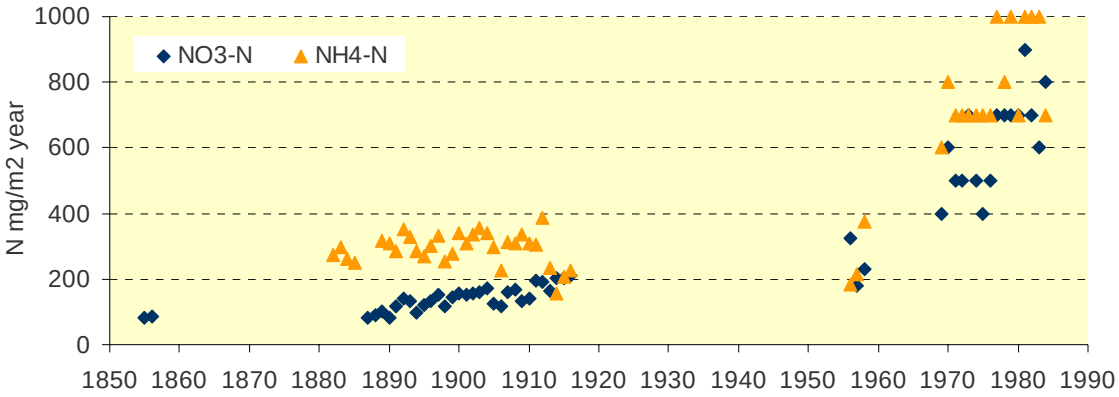

Figure 5. Annual nitrate and ammonium depositions at Rothamsted between 1852 and 1988.

Möller (2008) composed mean values for the first long term precipitation measurements in Europe. (table 1). The level of the total nitrogen in precipitation was lowest in Germany.

Tab. 3 First long-term precipitation chemistry monitoring (cited after *Warington* 1889), in ppm as nitrogen / *Die erste chemische Langzeit-Niederschlagsbeobachtung (zitiert nach Warington 1889), bezogen auf Stickstoff*

	Germany (13 yr)	Montsouris (10 yr)	Lincoln, Newzealand (3 yr)	Tokyo (2 yr)	Rothamsted, London
Nitrate	0.47	0.70	0.150	0.085	0.19
Ammonium	0.146	0.18	0.096	0.126	0.84

Table 1. Mean values of nitrogen in precipitation after Möller (2008).

At Flahult in Sweden, the development in the ammonium and nitrate deposition between 1909 and 1958 is very near that at Rothamsted (Figure 6). At Askov, in Denmark, no clear change is detectable between 1922 and 1958.

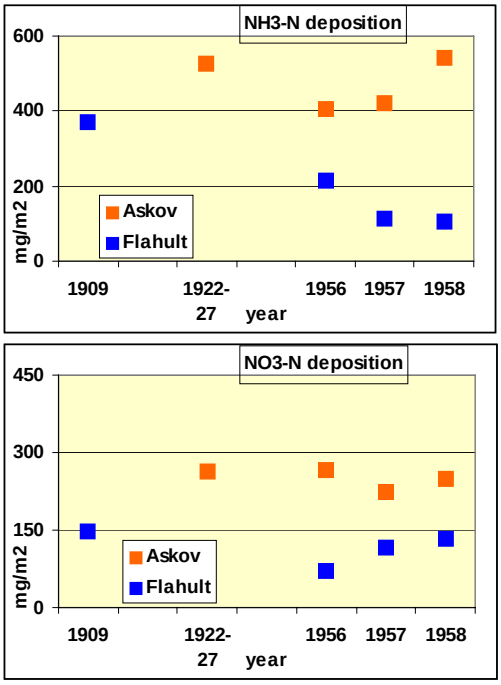

Figure 6. Annual deposition of ammonium (upper panel) and nitrate (lower panel) with precipitation at Askov, Denmark and Flahult, Sweden according to a review of Erikson (1952) and Anonymous (1956, 1957 and 1958).

Finally, the dense network of deposition values in the 1950's enables areal analysis of levels. In the 1950's, the nitrate deposition was highest in the western parts of the Central Europe and lowest in the North and in the westernmost areas. However, missing values in the Baltic countries, Russia and Poland bring extra uncertainty in the analysis.

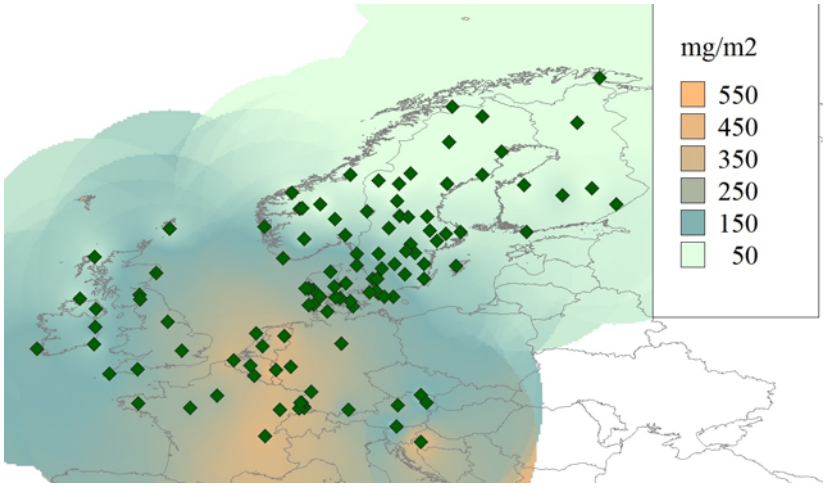

Figure 6. Areal analysis of the annual deposition of nitrate nitrogen in the 1950's. IDW interpolation of median values.

Literature

Anonymous (1956, 1957, 1958 and 1959) Current Data on the Chemical Composition of Air and Precipitation. Note. Tellus, vol. 8-11.
Brimblecombe P and Pitman J (1980) Long-term deposit at Rothamsted, Southern England. Tellus 32, 261-267.
Eriksson E (1952) Composition of Atmospheric Precipitation. I Nitrogen compounds. Tellus 4, 215-232.
Goulding KWT, Poulton PR, Thomas VH and Williams RJB (1986) Atmospheric deposition at Rothamsted, Saxmundham and Woburn experimental stations, England, 1969-1984. Water, Air, and Soil Pollution 29, 27-49.
Miller NHJ (1905) The amounts of nitrogen as ammonia and as nitric acid, and of chlorine in the rainwater collected at Rothamsted. J. Agr. Sci. 1, 280-303.
Möller D (2008) On the history of the scientific exploration of fog, dew, rain and other atmospheric water. Die Erde 139, 11-44.
Russel EJ and Richards EH (1919) The amount and composition of rain falling at Rothamsted. J. Agr. Sci. 9, 309-337.
Scharrer K and Schropp W (1940) Ueber den Stickstoffgehalt der Niederschläge. Forschungsdienst, 5, 469-472.
Sutton MA, Erisman JW, Dentener F and Möller D (2008) Ammonia in the environment: From ancient times to the present. Environmental Pollution 156:583-604.
Warington RA (1889) The amount of nitric acid in the rain-water at Rothamsted, with notes on the analysis of rain-water. Journal of the Chemical Society, Transactions 55, 537-545.

For further literature see document articles-19032010.txt in the ECOSUPPORT home page.