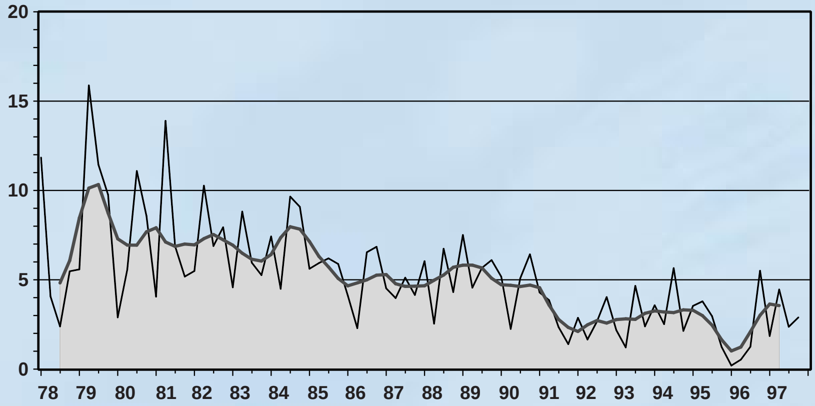
Ministry of Environment and Energy
National Environmental Research Institute

The Background Air Quality in Denmark

1978 - 1997

NERI Technical Report No. 341



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2000

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Data sheet

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Abstract: "The Background Air Quality in Denmark 1978 – 1997" presents 20 years of results from the national Background Air Quality Monitoring Programme. Data are reported for sulphur and nitrogen compounds in rural air and precipitation, a number of elements in aerosols including heavy metals, and ozone and nitrogen dioxide.

Background air pollution in Denmark is under considerable influence from the European continent. Because of atmospheric transport from Europe pollutant concentrations in both air and precipitation are larger in the southern than in the northern part of the country. During the two decades concentrations have fallen by factors of 2 – 10 times because of reduced emissions throughout Europe, and the number and severity of air pollution episodes have also decreased. But the levels of the nitrogen compounds emitted from agricultural activities and from traffic remain almost unchanged. Quite similar conclusions can be drawn for the wet depositions; also here very considerable decreases can be followed through the two decennia.

Concentrations in air and precipitation as well as depositions are shown to be approximately log-normally distributed.

The main foreign contributions to the general pollution level in Denmark originate from West Europe although concentrations are largest in winds from East Europe. A major part of the depositions of both sulphur and oxidised nitrogen have a foreign origin, domestic sources contribute only 20 %. Nevertheless Denmark is a net exporter of air pollution, but the contributions to depositions in other countries are small.

Keywords: Air quality, precipitation quality, background concentrations, depositions, monitoring, trends, deposition export, deposition import, transport, sources.

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Preface

Purpose

This report gives a general overview of the air quality in the background areas in Denmark in the last couple of decades. It is composed of selected, but typical, results from a variety of stations and aims to illustrate some main features of the development of the state of the atmospheric environment in this period. The idea of the report is primarily to present the observational view of the Danish background air quality and it is therefore based mainly on results of measurement , and model results are only used where necessary. The report does *not* aim to give a complete description of the occurrence of all air pollutants everywhere. In consequence complete data coverage has not been attempted and methods for sampling, analysis, and quality control are only treated in a cursory fashion, detailed descriptions of these subjects can be found in the references.

The term 'background air' warrants a commentary. In this report the term refers to air in rural areas that may be somewhat but not directly influenced by local sources whether industrial, agricultural or urban, *e.g.* traffic. The background air quality thus defined should therefore be considered as representative of the typical state of pollution in the lower troposphere in such a densely populated country as Denmark.

Structure

The report is organised in five main chapters and a concluding section in both English and Danish.

The first chapter presents the general context of the atmospheric monitoring activities in Denmark and gives an overview of the development of the network and the measurement programme from its early start in the late 1970's to its present extent.

The following two chapters present the results from the measurements of airborne pollutant concentrations and the precipitation contamination. These chapters include overviews of the statistical distributions of the data, typical results from selected stations and the temporal developments on both a short-term and long-term basis. Subsequently the deposition of pollutants to Danish rural areas are presented based on the precipitation results and supplemented by calculated values to obtain the total deposition.

The final chapter attempts to put the Danish background air quality into a European context. The atmospheric transport of pollution is illustrated by the pollution levels that are typical for various wind directions and estimates of the contributions from pollution sources inside and outside the country are presented and discussed.

Acknowledgements

The Background Air Quality Monitoring Programme is run by the Department of Atmospheric Environment (ATMI) of the National Environmental Research Institute (DMU) in Denmark. The results from this programme constitute the combined and dedicated efforts of a great number of people through many years. The author gratefully acknowledges the efforts of all persons, both presently and for-

merly employed, who have contributed to the success of the programme. This goes for both the local personnel that has manned the stations all over the country, the staff of the analytical laboratory and that of the PIXE laboratory that have untiringly analysed a very large number of samples year after year and controlled and corrected the results. The technical staff has also managed the exchange of exposed and unexposed samples with the stations, and the staffs at the workshop and the monitor laboratory have kept the equipment operational. The author is also greatly indebted to the Department's scientific staff that has not only ensured the quality of the results and their proper use in many scientific projects but also constantly has striven to improve and develop the programme. In particular the author wishes to thank those national and international colleagues who have actively helped to produce this report, either by giving permission to present their results or by supplying new tables and figures. The author also wishes to acknowledge the great amount of work that has gone into the establishment and maintenance of the vitally important databases where the results are stored and from where they can be retrieved. Finally he also expresses his thanks to the administrative staff that over the years somehow managed to make things hang together.

1 The Background Air Quality Monitoring Programme

1.1 Introduction

Monitoring since 1978

Surveillance of the air quality in rural areas of Denmark has been carried out since 1978 and started at a few stations as regular measurements of sulphur and nitrogen compounds in air and precipitation. Over the years the activities have grown steadily both with respect to components and geographical coverage. This growth followed from increasing demands from both national and international obligations which led to establishment of a number of separate monitoring programmes each aimed at fulfilling a specific set of requirements.

BOP - A national programme

The national Background Air Quality Monitoring Programme, which will be referred to by its Danish acronym BOP (BaggrundsOvervågningsProgrammet), has now replaced these ad hoc programmes as a national framework programme that gives a wide geographical coverage of a basic set of air pollutants. The purposes of BOP are to give as complete a description as possible of the state and of the development of the atmospheric environment over the land and sea areas of Denmark. That includes assessments of trends and geographical differences and identification of the sources and the transport routes. Also the fate of this pollution as deposition of acidifying, eutrophying or otherwise harmful substances to ecosystems in Denmark or abroad should be assessed. To meet these purposes BOP is conceived as a continuous and long-term nationwide monitoring programme that is constantly being developed in order to incorporate new and better methods for sampling and analysis. The data provided by the programme also serves as a basis for research projects in these fields.

National and International Obligations

The BOP programme is a framework programme that covers first of all the general obligations of DMU to monitor the atmosphere in Denmark and in addition also the obligations from the following set of projects

- VMOP, the Monitoring Programme of the Danish Action Plan for the Aquatic Environment;
- IONBAL, the Ion Balance programme for studies of air pollution effects in forests;
- EMEP, the European Monitoring and Evaluation Programme under the UN-ECE Convention of Transboundary Air Pollution in Europe, CLRTAP (Convention on Long Range Transport of Air Pollution);

- HELCOM, the air monitoring programme under the Helsinki Commission for the Convention on Protection of the Marine Environment in the Baltic Sea;
- OSPARCOM, the air monitoring programme under the Oslo-Paris Commission for the Conventions on Protection of the Marine Environment of the North Sea and North Atlantic.

Various parts of the results obtained in BOP have been published earlier (Ellermann *et al.* 1996; Hertel and Hovmand 1991; Heidam 1987, 1989, 1993; Hertel and Frohn 1997; Hovmand *et al.* 1994), notably in the series of annual VMOP-reports (VMOP_89 - VMOP_97). This report represents, however, the first attempt to give a comprehensive overview of the air quality in Denmark since the start of the programme.

1.2 Measurement network

A network of 6 stations

In BOP continuous and synchronous collection of data on pollutant concentrations in air and precipitation takes place at a number of representative sites. In order to ensure that data are comparable and reliable the sampling techniques are standardised and the analytical methods are all well documented and tested (EMEP Manual 1996). After analysis the data are subjected to a set of quality control procedures before they are finally stored in the database. The measurement network is composed of a set of 6 main stations with an extensive measuring programme supplemented with a number of satellite-stations for geographical coverage and territorial representativity. The locations of the stations shown on the map in Figure 1.2.1 have accordingly been chosen in various types of background areas, sufficiently remote so as to be under moderate to small influence from major anthropogenic pollution sources in the area. Of the coastal stations Husby, Anholt, Keldsnor, and Pedersker the former three are under marine influence. It should be mentioned that originally the three stations at Ulborg, Lindet, and Frederiksborg were set up in relation to the forest programme and they are therefore placed on towers in the forest. Although elevated to levels above the tree canopy some results, *e.g.* on ozone, may not be truly representative of values in the open land.

It should also be mentioned that it has not been found necessary to report results from all stations. A station at Lille Valby has been in operation in recent years, partly as a background station for the Urban Monitoring Programme and partly as an experimental station for BOP. Results from this station are not included here. Also bulk precipitation results from the satellite stations Hansted_1, Hansted_2, and Almindingen are not included.

The stations in this report, their acronyms, their locations and surroundings and potential local sources are listed in Table 1.2.1. In the figures and tables the stations will often be referred to by their acronyms. Bulk sampling at two of the main stations is, for reasons of representativity and quality of data, represented by nearby satellite stations.

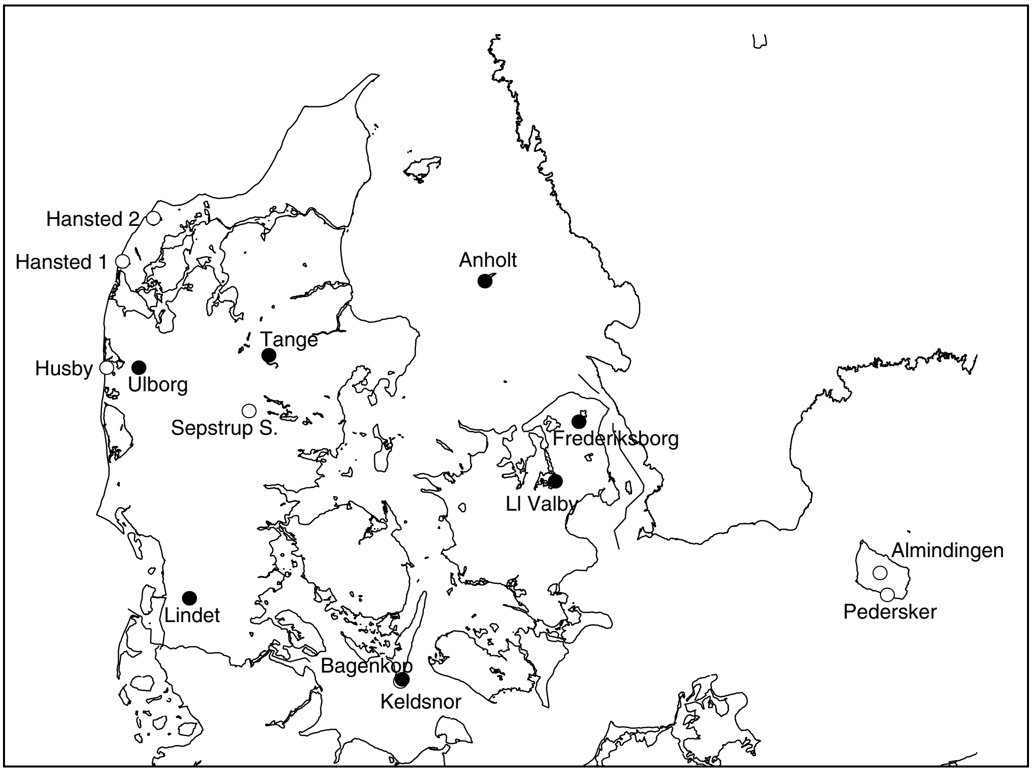

Figure 1.2.1 Map of the BOP stations in Denmark in 1996 - 1997. • Main stations with measurements of gases and aerosols and wet-only collection of precipitation. ° Substations with bulk sampling of precipitation.

Table 1.2.1 BOP network stations.

Name	Acronym	Latitude N	Longitude E	Surroundings	Sources
Ulborg	ULBG	56° 18'	8° 26'	forest	few
Husby	HUSB	56° 18'	8° 09'	coast	few
Tange	TANG	56° 21'	9° 36'	rural, lake	agriculture
Sepstrup	SEPS	56° 05'	9° 25'	forest, heath	few
Anholt	ANHO	56° 42'	11° 34'	coast	few
Frederiksborg	FRBG	55° 57'	12° 21'	forest	town
Lindet	LIND	55° 09'	8° 53'	forest	agriculture
Keldsnor	KELD	55° 44'	10° 43'	coast, forest	agriculture
Pedersker	PEDE	55° 01'	14° 57'	coast	few

Sampling frequencies

At the main stations samples of gases and aerosols are collected continuously on a diurnal basis by a filterpack-sampler. Wet-only sampling of precipitation also takes place at all main stations, generally on a ½-monthly basis, but one sampler operates on a weekly basis, and 2 collectors operate on a diurnal basis. At both the main stations and at the substations bulk precipitation samples are collected on a semi-monthly basis. After exposure all samples are returned to the laboratory for analysis. An overview of the network and its development over the years is shown in Table 1.2.2.

Network history

It is seen that the network expanded in the latter half of the 1980's from the original two stations, Tange and Keldsnor, to become a nationwide monitoring network. The results since 1978 will mainly be considered in the framework of the total period of 20 years but at times also in the context of 3 subperiods, consisting of the initial 7-year period 1978 - 1984, the middle 6 years 1985 - 1990 and the recent 7 years 1991 - 1997.

Table 1.2.2 Overview of network stations in operation.

Station	Measurement	Averaging time	Operational	Stops
ULBG	Filterpack	24 h	8505-	
	NO_2	24 h	8910-	
	Ozone	½ h	8509-	
	Wet-Only	½ month	9002-	[9104-9505]
Husb[1]	Bulk	½ month	8901-	
TANG	Filterpack [2]	24 h	7804-	
	NO_2	24 h	9002-9106	
	Wet-Only	24 h	7801-	
Seps[1]	Bulk	½ month	9001-	
ANHO	Filterpack	24 h	8810-	
	NO_2	24 h	8911-	[1992]
	Ozone	-	-	
	Wet-Only	½ month/week[3]	8903-	[9304-9504]
	Bulk	½ month	8809-	
FRBG	Filterpack	24 h	8505-	
	NO_2	24 h	8906-9109	
	Ozone	½ h	8807-	
	Wet-Only	½ month	9605-	
	Bulk	½ month	8506-	
LIND	Filterpack	24 h	8810-	[8904-8912]
	NO_2	-	-	
	Ozone	-	-	
	Wet-Only	½ month	9507-	
	Bulk	½ month	8804-	
KELD	Filterpack [2]	24 h	7804-	
	NO_2	24 h	9002-9103	
	Ozone	½ h	9501-	
	Wet-Only	24 h	7801-	[9112-9203]
	Bulk	½ month	9001-	
PEDE	Bulk	½ month	8906-	

[1] Satellite station
[2] Limited programme 1978-1988.
[3] Weekly from 1996

1.3 Measurement programme

Pollutants measured

The components measured in BOP comprise sulphur and nitrogen compounds in air and precipitation, elements in airborne aerosols, and ozone. They may all have both indigenous and foreign origins. The components have been selected so as to enable a description of the anthropogenic (man-made) impact on the background air quality in Denmark and also to be in accordance with the national and international obligations on atmospheric monitoring. A short overview of the various compounds is given below and details of the sampling programme are shown in Table 1.3.1.

Sulphur compounds

Sulphur occurs in air as SO_2, a gas that mainly derives from combustion of fossil fuels, and in aerosol particles. SO_2 is oxidised in the atmosphere to form particulate sulphur, S mainly in the form of sulphuric acid, H_2SO_4 or as various sulphate salts, $SO_4^=$ that are incorporated in aerosol particles or in water droplets. In this case the particulate sulphur is said to be a secondary pollutant in contrast to primary sulphate particles that derive from sea-spray aerosols. The oxidation time of SO_2 is of the order of one day, so the particulate sulphur may have originated as SO_2 several hundred kilometres away whereas the gas SO_2 may be of both local and remote (foreign) origin. In precipitation sulphur occurs mainly as sulphate, and it may be of anthropogenic origin or it may derive naturally from sea-spray. This sea-salt component often has a rather well defined ratio to other sea salt components such as Na, Mg, or Cl. These minor constituents can therefore be used to estimate and correct for this component, leaving a non_sea-salt component, NSS_S that is dominantly of anthropogenic origin.

Nitrogen compounds

Nitrogen occurs in air and precipitation as both oxidised and reduced compounds, and in air it is found in both gases and aerosol particles. The oxidised nitrogen gases, NO and NO_2, derive from combustion processes, notably in motor vehicles and power plants. It is mainly emitted as NO that is oxidised to NO_2, often very quickly by means of the reactive ozone. NO_2 may be further, but much more slowly oxidised to various nitrate salts, NO_3^-, that may occur both in atmospheric aerosols and in precipitation. Most of the oxidised nitrogen is therefore of a secondary nature and can be of both local and remote origin. In reduced form nitrogen is mainly released from agriculture as ammonia, NH_3, a very reactive gas that is quickly transformed into various ammonium salts, NH_4^+. These salts may contain sulphate or nitrate and can occur both in atmospheric aerosols and in precipitation. Most of the reduced nitrogen is therefore of a secondary nature and can be of both local and remote origin.

Elements in aerosols

A large number of elements occur in atmospheric aerosols. In BOP a fair number of these elements are determined, comprising usually Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Cd, and Pb. They may derive from a number of sources, either natural such as Na, Cl and S (sulphate) from sea-spray or anthropogenic sources, such as combustion or industrial processes, *e.g.* NSS_S and Pb. Several of the metals may be emitted as vapours that subsequently condense.

Table 1.3.1 Components sampled in precipitation and air.

	PRECIPITATION			AIR	
Sampling	Wet-only	Bulk	Bulk	Filterpack	Monitor
Frequency	Daily, Weekly & Semi-monthly	Semi-monthly	Monthly	Daily	½-hour
Ozone, O_3					X
Nitrogen dioxide, NO_2				X	
Ammonium, NH_4^+	X	X		X	
Ammonia, NH_3				X	
Nitrate, NO_3^-	X	X			
Nitrate + Nitric acid, $NO_3^- + HNO_3$				X	
Sulphate, SO_4^{2-}	X	X			
Sulphur dioxide, SO_2				X	
Chloride, Cl^-	X	X			
Sodium, Na^+	X	X		X	
Magnesium, Mg^{2+}	X	X		X	
Potassium, K^+	X	X		X	
Calcium, Ca^{2+}	X	X			
Hydrogen ions, H^+/pH	X	X			
Elements			Heavy Metals 1)	X 2)	

1) Heavy metals, see below, are collected in monthly bulk samples at the stations Ulborg, Tange, Anholt, Frederiksborg, Husby, and Pedersker.

2) See preceding paragraph.

Heavy metals in precipitation

The heavy metals that occur in precipitation are normally of anthropogenic origin and may be of both local and remote origin. Monthly bulk samples are collected at several stations (cf. table 1.3.1 footnote) and analysed for the heavy metals Cr, Ni, Cu, Zn, As, Cd and Pb. The samples have been analysed by AAS - and in later years by ICP-MS at RISØ National Laboratory and NILU in Norway. These results are not included here as they will be reported elsewhere (Hovmand and Kemp, 1999).

Ozone

Tropospheric ozone is a secondary pollutant that is formed by photochemical reactions involving both hydrocarbons and NO_2. The formation rate is strongly dependent on solar radiation, on the concentrations of NO and NO_2 and on the abundance of hydrocarbons that may be of both natural and anthropogenic origin. In background areas ozone may build up by photochemistry or be supplied by long range atmospheric transport, whereas in cities ozone is normally decomposed due to the high abundance of the other pollutants mentioned above. Ozone may therefore be of both local and remote origin.

1.4 Experimental methods and quality control

Gases and phase-sums

All airborne components containing sulphur and nitrogen are sampled over 24 hours on 4 sequential filters in a filterpack-sampler that automatically switches to new filters at pre-set times every day. The first filter is used for collecting particulates, and the subsequent 3 filters are specially impregnated to catch the gaseous components (Fuglsang 1986a, b; Ellermann et al. 1996). The filters are subsequently analysed in the laboratory by well-documented and reliable methods (EMEP Manual 1996). However, depending on ambient conditions some degassing from the deposit of nitrogen-containing particles on the first filter may occur during sampling, particularly for oxidised nitrogen. Whereas such gas components are not lost but collected downstream this phenomenon does mean that an accurate distinction between particulate and gaseous nitrogen is not always possible (Andersen and Hilbert, 1993). For this reason it is preferred to consider the phase sums of particles and gases rather than the separate phases, at least for oxidised nitrogen. However, for both oxidised and reduced nitrogen the particulate phase is usually the dominating one.

Elements in aerosols

A central section of the particle filter is used for analysis by PIXE (Proton Induced X-ray Emission spectroscopy) for detection of elements in aerosols, from Al and all heavier elements. These results constitute a very large amount of data but in this report the main focus will be on S and Pb.

Nitric dioxide

NO_2 is sampled for 24 hours on specially impregnated glass filters (EMEP Manual 1996) in a separate semiautomatic sampler (Ellermann et al. 1996).

Ozone

Ozone is measured continuously by an ozone monitor and the results are at regular intervals transmitted automatically to the laboratory as ½-hour mean values.

Precipitation samplings

Precipitation is collected in either single wet-only samplers or in multiple (typically 2-3) parallel bulk collectors in ½-monthly sampling periods (Ellermann et al. 1996). The wet-only samplers that operate on a basis of 24 hours, 1 week or ½-month, only allow sampling during precipitation and thus are well suited for estimation of the wet deposition. The bulk samplers are on the other hand open constantly and will therefore give an estimate of both the dry and wet deposition. It is a draw back for bulk samplers that they are easily contaminated by *e.g.* bird droppings and that the long sampling time may cause evaporation of precipitation, which in turn will lead to higher concentrations. However, in principle, the deposited amount of material is not affected.

Quality control

As noted all sampling and analysis is carried out using well-documented, proven and internationally approved methods (EMEP Manual 1996). All results from BOP are subjected to quality control procedures, including those recommended by EMEP, that involve *i.a.* comparison with historical data, comparison of results among stations, comparison of selected ratios of pollutant concentrations, and in the case of precipitation also control of the ion-balance. In addition the sampling and analytical methods are controlled annually through international intercomparisons and intercalibrations both in the field and in the laboratory (EMEP_CCC 1995; 1996). Upon approval the results are stored in relational databases.

1.5 Air quality criteria and critical levels and loads

Limit values

The air quality of a given region should be evaluated with respect to the possible detrimental effects of air pollutants on human health, materials, vegetation and ecosystems in general. To this end a number of *limit and/or guideline concentration values*, below which such effects are expected to be absent or negligible, have been defined and enforced or recommended by EU or WHO. The Danish limit values are presented in Table 1.5.1 below. In relation to BOP, where most results are obtained as 24h averages, it should be noted that the majority of the limit values refer to the normally higher concentrations averaged over 1h.

Ozone thresholds

Ozone has been found to be harmful to human beings and to many plants. The ozone limits shown in Table 1.5.1 refer to the protection of vegetation. However, effects on plants often depend on the accumulated exposure to high concentrations of ozone as well as on the plant species. Such critical levels are measured in units of ppb· hours, which denotes the sum of ozone concentrations above a certain threshold over the number of hours this threshold is exceeded in a year. The species dependent critical levels introduced by UN_ECE are shown in Table 1.5.2 (Kärenlämpi and Skärby, 1996). The critical levels are named AOT40 (Accummulation Over Threshold) where the number indicates the concentration threshold of 40 ppb (for ozone 1 ppb (v) ~ 2 $\mu g/m^3$). A different set of critical ozone levels relating to human health and named AOT60, presently used on a tentative basis in EMEP-models, may later acquire official status.

Critical loads

For deposition the criteria are expressed as critical loads with respect to either acidification or eutrophication (excess nutrient) effects. These effect-related critical loads are defined as limiting depositions of one or more pollutants to (specified elements of) an ecosystem below which no harmful effects have been observed. Critical loads are complex concepts that depend not only on the type of effect and type of ecosystem in question but also on the combination of pollutants (Posch *et al.* 1997). Some critical loads are shown in Table 1.5.3 and the units of acidic keq have been chosen so as to accommodate combinations of acidifying pollutants (Holten-Andersen et al. 1998). The critical loads are exceeded by atmospheric deposition in large parts of Europe. Because of their complexity the concepts of critical loads are most often used in conjunction with model calculations of depositions. The models perform calculations relative to a spatial system of grid elements. Since these grid elements in the period of concern to this report may be up to 150 km on the side they contain a fairly large number of ecosystems, each with its own critical load. A grid square therefore covers a range of critical loads and to avoid any harmful effects in this grid the deposition should ideally be reduced to a value lower than the minimum value in this range. In many cases, however, a few of the ecosystems have so low critical loads that it is both economically and practically impossible to attain such small depositions. Instead it is common practice to consider the lower 5%-percentile (the pentile) of this range as target depositions to be reached by emission reductions. If the pentile critical load is not exceeded then it is fair to say that at most 5% of the ecosystems in the grid element may suffer damage, the rest go free.

Table 1.5.1 Overview of Danish Limit Values for concentrations of air pollutants, measured[0)] in µg/m^3.

Compound and limit type	Median (P50)		Mean	Annual 98- percentile (P98)	Maximum
Period	Year	Winter	Year	Year	Year
Sulphur Dioxide					
Limit for 1h averages	80	130		250	
Nitrogen Dioxide					
Limit for 1h averages				200	
Guide for 1h averages	50			135	
Ozone					
Limit for 1h averages					200
Limit for 8h averages					110
Limit for 24h averages					65
Suspended Particles					
Limit for 24h averages			150	300 [1)]	
Lead					
Limit			2 [2)]		

[0)] The whole molecular mass. [1)] 95-percentile (P95). [2)] EU limit, not introduced in Denmark

Table 1.5.2 Critical AOT40 levels for O_3. Concentrations above 40 ppb are cumulated during daylight hours. The AOT40 values should be averaged over 5 years.

Vegetation and effect	AOT40	Remarks
Long term Critical Level for tree species (annual increment)	10.000 ppb ·hr	Cumulated for 6 months (April-October)
Long term Critical Level for crop species (yield) and natural vegetation	3.000 ppb ·hr	Cumulated for 3 months (May-July)
Short term Critical Level for crops (Visible injury)	500 ppb ·hr	For high vapour pressure deficit over 5 days
	200 ppb ·hr	For low vapour pressure deficit over 5 days

Table 1.5.3 Critical loads for acidification and eutrophication in various types of ecosystems. The loads are given in $keq \cdot ha^{-1} \cdot yr^{-1}$ where 1 acidic keq corresponds to 16 kg S or 14 kg N (from Holten-Andersen *et al.* 1998).

Ecosystem	Acidification	Eutrophication
Planted Oak and Beech	0.8 - 2.7	17 - 28
Coniferous forests	1.4 - 4.1	7 - 15
Fenlands		15 - 20
Raised Bogs		5
Water Meadows, poor		5 - 10
Commons	0.9 - 2.4	

1.6 Notation and units

Airborne pollutants

The units used for concentrations are mass per volume and for deposition mass per area (and time). The concentration units for the airborne components are μg/m^3 (STP), except ozone, O_3 that is given in ppb(v).

Pollutants in precipitation

For the components in precipitation the concentrations are given in mg/l (μg/ml) and deposition is measured in kg/km^2 (mg/m^2) with deposition rates or fluxes specified as deposition per day, month, or year as the case may be. For results from the multiple bulk samplers at each site a precipitation weighted average value is used as the result from that site.

Atomic mass concentrations

Except for ozone the mass entry in these units usually refers to the atom or element in question, unless specified otherwise. In the case of sulphur dioxide for instance the concentration refers to the sulphur content SO_2-S and is given in μg S/m^3, even if the reference in the text or table entry has been given as SO_2. The particulate sulphur may be referred to as SO_4, meaning SO_4-S, or just S. A similar notation also applies to the compounds in precipitation or deposition, e.g. μg N/ml for NH_4-N denoting the nitrogen content of the ammonium.

Abbreviations

The sum of gaseous and particulate phases of oxidised sulphur is sometimes of interest. It is referred to as total (oxidised) sulphur and labelled TSO_x which is defined as $TSO_x = (SO_2[g] + SO_4[p])$. The concentrations are in μg S/m^3 and refer to TSO_x-S. The sums of gaseous and particulate phases of oxidised or reduced nitrogen in air are termed total nitrate and total ammonium and labelled TNO_3 (or TNO_y) and TNH_z, respectively. They are defined as $TNO_3 = (HNO_3[g]) + NO_3[p])$ and $TNH_z = (NH_3[g] + NH_4[p])$. The concentrations are in μg N/m^3 and refer to TNO_3-N and TNH_z-N.

Non-sea-salt sulphur

In both air and precipitation sulphur usually occurs as sulphate and may be of both anthropogenic and natural origin. The natural fraction derives mainly from sea-salt and may be calculated by means of the atmospheric or precipitation concentrations of the marine tracers. In this report we use the average contribution from all three tracers $(0.084 \cdot \text{Na} + 0.702 \cdot \text{Mg} + 0.047 \cdot \text{Cl})/3$, where the coefficients are the ratios in seawater of sulphur to each tracer. When subtracted from the total sulphur in sulphate we arrive at the anthropogenic non-seasalt sulphur component, which is labelled NSS_S.

Total nitrogen in precipitation

For precipitation and deposition it is often of interest to know the total content of nitrogen because in the context of eutrophication it acts as a nutrient. For this purpose a combined variable, termed total nitrogen and labelled TOT_N is introduced. It is defined as TOT_N= (NO_3^- + NH_4^+)-N.

Simplified notation.

Please note that in some figures and tables it has been necessary to use a simplified chemical notation, such as SO2 instead of SO_2 or NH4 for NH_4^+.

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2 Air Quality

2.1 Overview and statistics

Pollutants concentrations

The air pollutants considered comprise the gases SO_2, NO_2, and O_3, the gas and particulate phases of reduced nitrogen NH_3 and NH_4^+ as well as their phasesum, total ammonium TNH_z, the phase sum of total nitrate, TNO_3 and the aerosol contents of sulphur S and lead Pb. The elements in aerosols are considered only briefly and mainly used for supplementary illustrations.

One year of data

Examples of the data to be considered are presented in Figures 2.1.1 - 2.1.2 that show one year (1996) of concentrations of selected pollutants. Daily mean values are represented by data points overlaid with smoothing curves to illustrate the general behaviour through the year. The combustion derived sulphur compounds normally have a peak in the winter whereas nutrient related nitrogen compounds have maxima in the spring and autumn. Hourly mean values of ozone are shown in Figure 2.1.3 either as directly connected datapoints or as data points overlaid with smoothing curves. The highest levels occur in the summer period where the photochemical activity is most intense. Most of the ozone derives from long range transport of air pollution (LRTAP) from the southern parts of Europe.

Statistical overview

To give a general overview of the levels in background air in Denmark Table 2.1.1 shows mean and maximum values, standard deviations and number of results at all main stations in the most recent subperiod 1991-1997. The table contains data for all major components, including particulate sulphur and lead, as well the soluble cations Na, Mg, and K. The stations are arranged with the northern stations above southern ones and otherwise listed in the order west to east. Results on NO_2 from Tange and Keldsnor have been excluded as not representative because of the low number of observations. In Table 2.1.2 the corresponding values are listed for all elements detected in the subperiod 1991 - 1997, but limited to the stations Tange and Keldsnor. These tables show that the levels across the country are fairly similar, with a few exceptions the average concentrations differ by less than 50%. There is, however, a general tendency for higher concentrations of pollutants such as SO_2, S, NO_2, TNO_3, Pb and other anthropogenic elements to occur at Keldsnor and Lindet, the stations most readily exposed to atmospheric transport from the southern directions. The concentrations are lower at the more remote and less exposed stations Ulborg and Anholt.

Statistical distributions

The majority of the airborne components are to a good approximation distributed lognormally. That is illustrated by some of the distributions of data in the most recent subperiod 1991-1997 shown in Figures 2.1.4 - 2.1.6. In these plots the data are ordered sequentially and the circles show the 50-, 16-, and 84-percentiles, *i.e.* the median and the two fractiles removed by one standard deviation. Note that the vertical axes describe the distribution in two different ways. The left axis is linear and shows the deviation from the median in units of standard deviations whereas the corresponding cumulated percentage is shown non-linearly on the right axis. Also note that the horizontal concentration axes are logarithmic. The straight line shows the lognormal distribution as determined by the geometric mean and standard deviations, which are indicated by the vertical lines. Data that are lognormally distributed should all fall on this line, including the circled fractiles.

Log-normal distributions

The distributions of the gases NO_2-N and SO_2-S and S, the sulphur content in aerosols at a few stations are shown in Figure 2.1.4. Similarly distributions of the phase sums of reduced and oxidised nitrogen as well as lead in particles are shown in Figure 2.1.5. The figures show that the lognormal approximation is a fairly good one, especially around the median values, although only few of the pollutants are actually distributed log-normally in the strict statistical sense.

Ozone

The hourly mean concentrations of ozone appear to be distributed differently. That is shown in Figure 2.1.6 where the distributions are shown for both logarithmic and linear concentration axes. The approximation between the data and the distribution line is much better in the linear than in the logarithmic case. At all three sites these highly time resolved data therefore seem to be distributed normally rather than log-normally.

Means and percentiles

Details of the distributions of selected components are given in Tables 2.1.3 - 2.1.7 for different subperiods. For selected components these tables contain *arithmetic* as well as *geometric* means and standard deviations, 50- and 98-percentiles all in units of $\mu g \cdot m^{-3}$, and number of observations. It is also indicated whether the distribution in 1991 - 1997 can be considered to be lognormal according to a statistical test. For components that are approximately log-normally distributed the geometric mean will be close to the 50-percentile, and closer than the arithmetic mean. This actually applies for almost all components although they are not log-normally distributed in the strict sense.

Decreasing concentrations

The tables show that in several instances the concentration levels decrease from one period to the next. Where this is a true and significant decrease according to a Student’s t-test for the lognormal case it has been noted in the *History* column, where ‘D’ denotes a significant decrease from one subperiod to the next. ‘U’ similarly marks the occasional but significant upward trends. The concentrations of SO_2, S, and, to some extent, of the reduced nitrogen components have decreased considerably over these two decades whereas the concentrations of the oxidised nitrogen species NO_2 and TNO_3 either decrease very little or have actually grown. The question of trends is treated in more detail later in this report.

Autocorrelations

The measured concentrations are randomly, and approximately lognormally, distributed but they are not independent of each other. The concentrations measured do to some extent depend on previous concentrations. That is demonstrated by the autocorrelation functions in Figures 2.1.7 and 2.1.8 which are correlation's of daily mean concentrations measured some days apart as a function of this lag of separation. The autocorrelation functions span three years and are calculated for two subperiods and two stations. The shaded areas delineate the 5% significance levels.

Memory and periodicity

In most cases the influence from one sample to the subsequent ones is fairly high over the first few days but after a week or so the 'memory' fades into insignificance. However, in several instances the autocorrelation function exhibits maxima, although barely significant, at considerably larger lags. Maxima can be observed at lags corresponding to an integral number of weeks or - especially for the nitrogen compounds - an even number. That indicates a weekly or biweekly periodicity in the results with weak correlation's among concentrations separated by these periods. Since nature does not know the difference between weekdays and Sundays or workdays and holiday periods this must be an effect from weekly patterns in anthropogenic emissions. As transport times from remote sources may vary from one to several days depending on meteorological conditions these patterns are probably related to variations in emissions in the local area. However, the weekly peaks in the autocorrelations functions are barely significant so the local influence is quite weak - in accordance with the definitions of background stations given in section 1.2. The nitrogen compounds even seem to possess a semi-annual period. The autocorrelations also show that there are yearly effects in the concentrations. Whether natural or anthropogenic this reflects the average annual variation where concentrations are consistently high or low at certain times of the year. The periodicity is however not present for all compounds. It can be noted that it is more pronounced for a primary pollutant such as SO_2 compared to a secondary pollutant such as S, particulate sulphur. It can also be seen from Figure 2.1.8 that for some pollutants there is a tendency for the periodicities to change or even weaken from the 1980s to the 1990s, probably an effect of changing emission patterns and decreasing concentrations. The question of periodicity in the results is considered in more detail later.

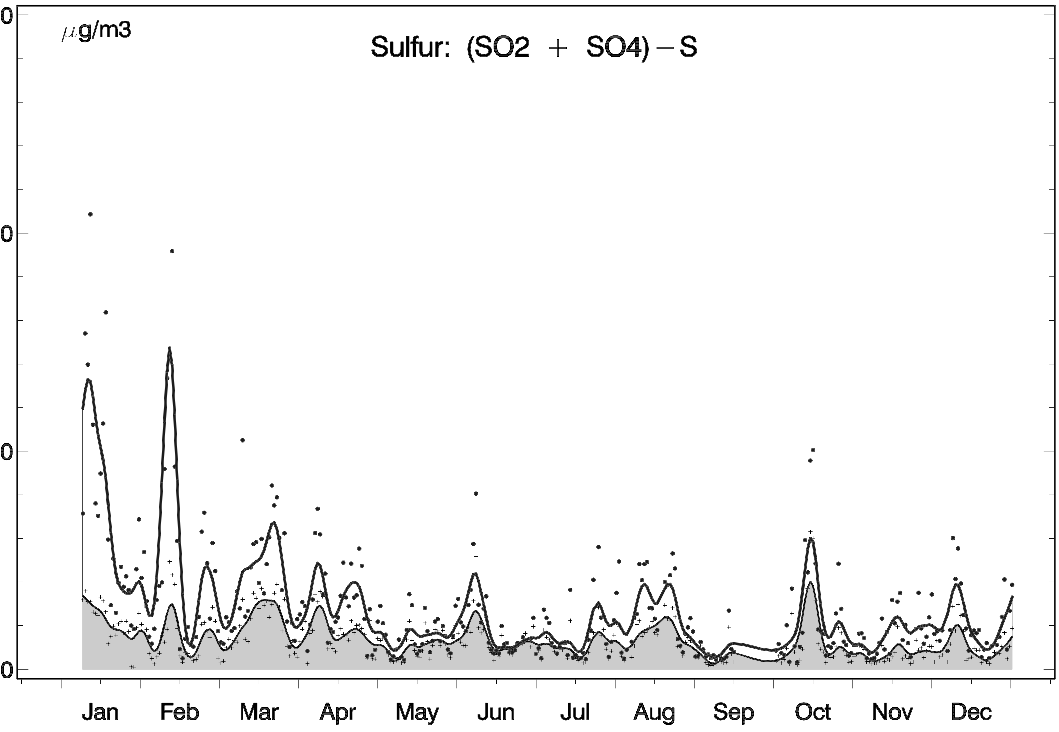
Stoichiometry

The particles in the atmospheric aerosol consist mainly of compounds containing ammonium, sulphate, and nitrate. In fact the major part of the particle mass is made up of the compounds ammonium sulphate $(NH_4)_2SO_4$ and ammonium nitrate NH_4NO_3. These compounds arise from chemical processes where ammonia NH_3 to a greater or lesser extent neutralises the particulate sulphuric and gaseous nitric acids, H_2SO_4 and HNO_3. With surplus ammonia the processes result in full neutralisation where all ammonium occurs as a stochiometric mixture of these two compounds

$$[\,NH_4^+\,] = 2\cdot[\,SO_4^=\,] + [\,NO_3^-\,]$$

Ammonia surplus

This is illustrated in Figure 2.1.9, which on a molar basis, *i.e.* with units in nMol/m^3, shows the relationships between total ammonium as well as particulate ammonium and the stochiometric sulphur/nitrate mixture compared to the line of full neutralisation. A very good agreement with the neutralisation hypothesis is clearly to be seen, even though the x-axis contains total particulate sulphur and not only sulphate. The upper panels show the concentrations of the total reduced nitrogen phase versus the stoichiometric mixture and a comparison with the line of slope 1 reveals that ammonia is indeed in surplus and that the background aerosol in Denmark is usually fully neutralised. In the four lower panels only the particulate part, the ammonium is compared to the stoichiometric mixture. The middle panels show that a 1:1 line is a good approximation whereas the lower panels, which contain results from regression analyses, show that the best regression lines have slopes that exceed 1 by about 12%. That probably reflects the presence of other compounds such as ammonium bisulphate, NH_4SO_4 not accounted for on the abscissa axis. The good agreement obtained also shows that the separation of the nitrogen phase-sums into particulate and gaseous compounds (cf. Section 1.4 above) seem to be permissible in a statistical context when a large number of samples are considered.



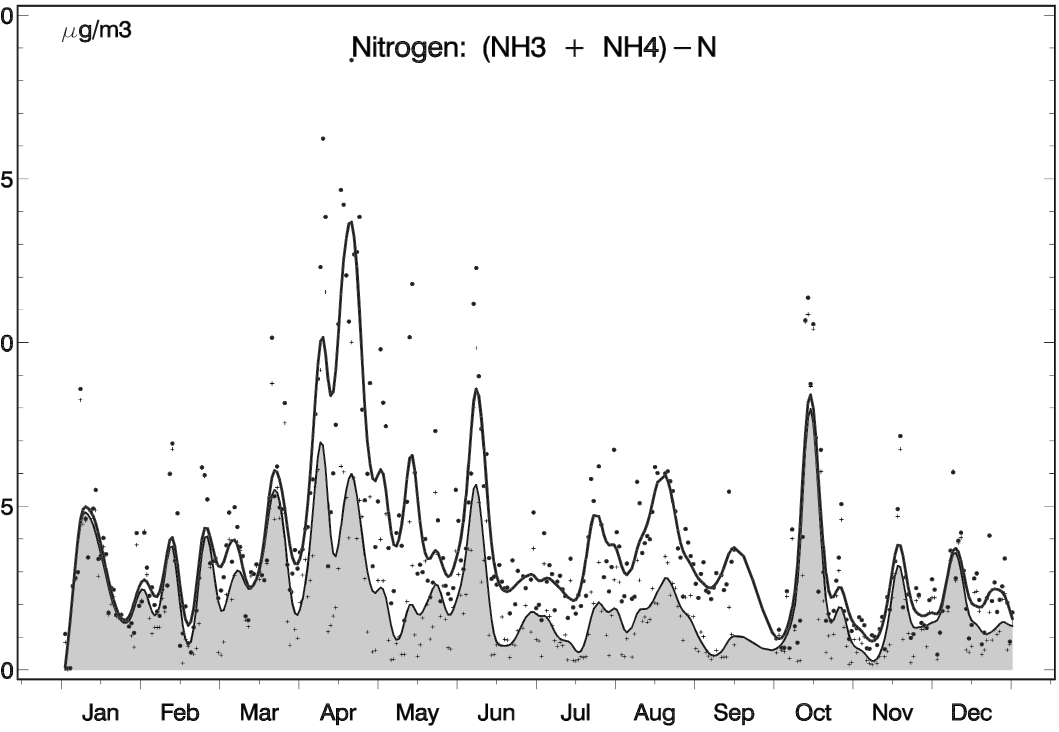
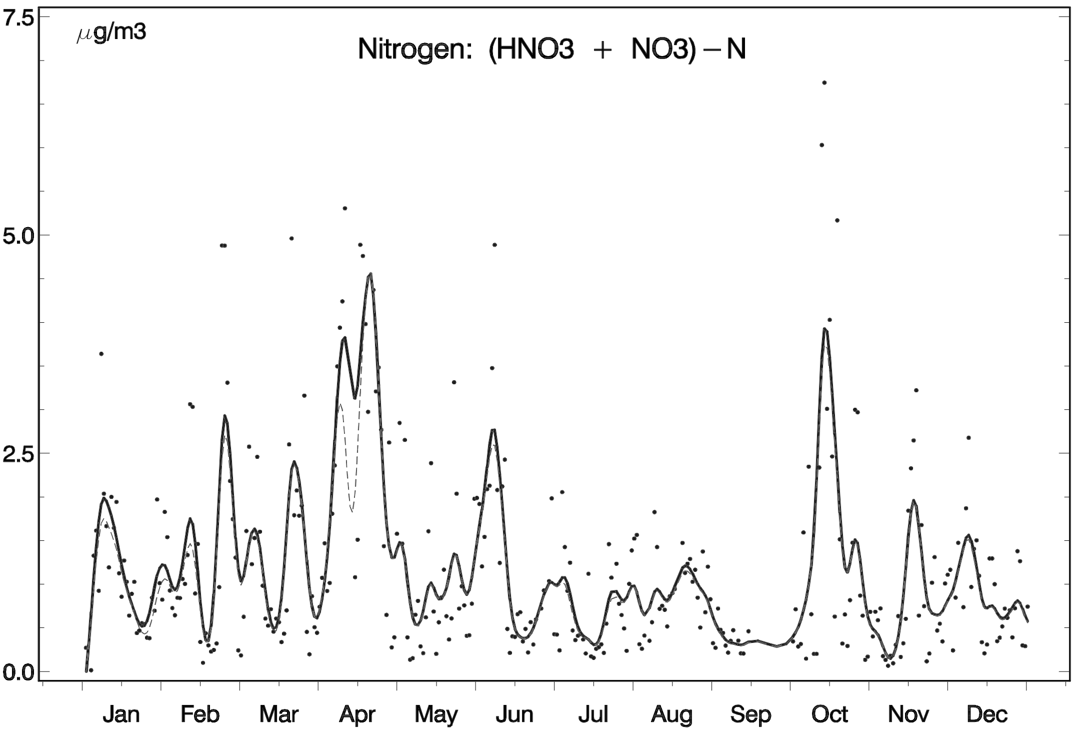


Figure 2.1.1 Daily concentrations in air (points) of sulphur and reduced nitrogen compounds at Tange in 1996, overlaid with smoothing curves. Concentrations of gaseous (dots) and particulate phases (crosses, shaded) are summed.



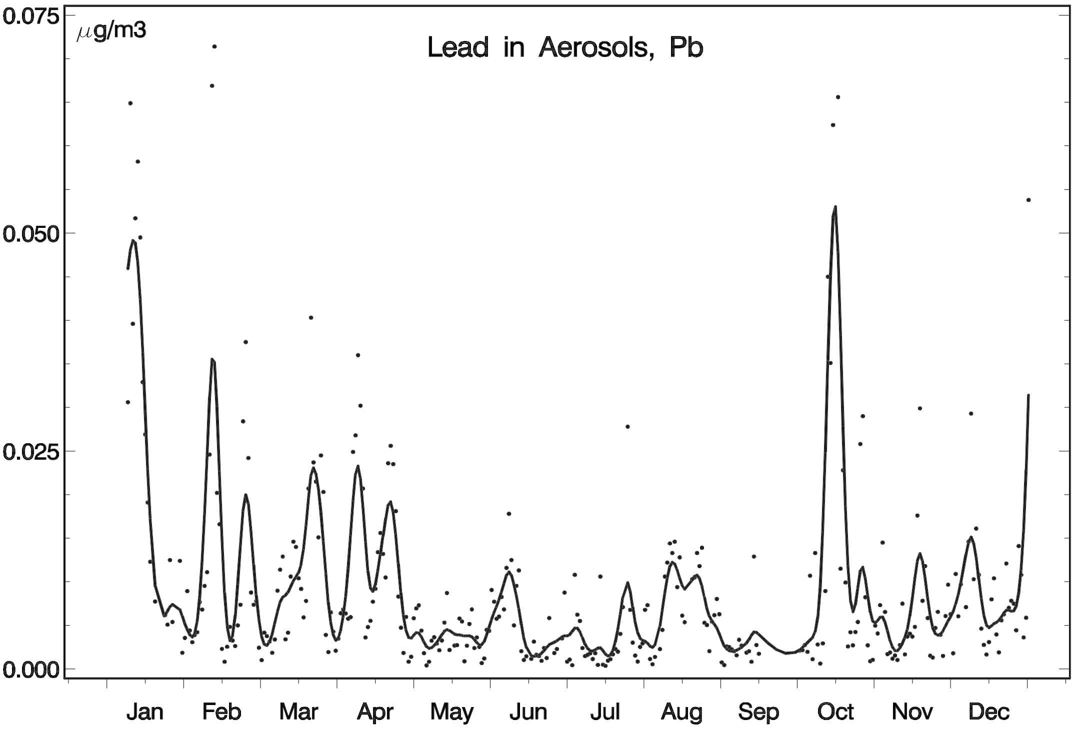


Figure 2.1.2 Daily concentrations (dots) in air of oxidised nitrogen and lead at Tange in 1996, overlaid with smoothing curves.

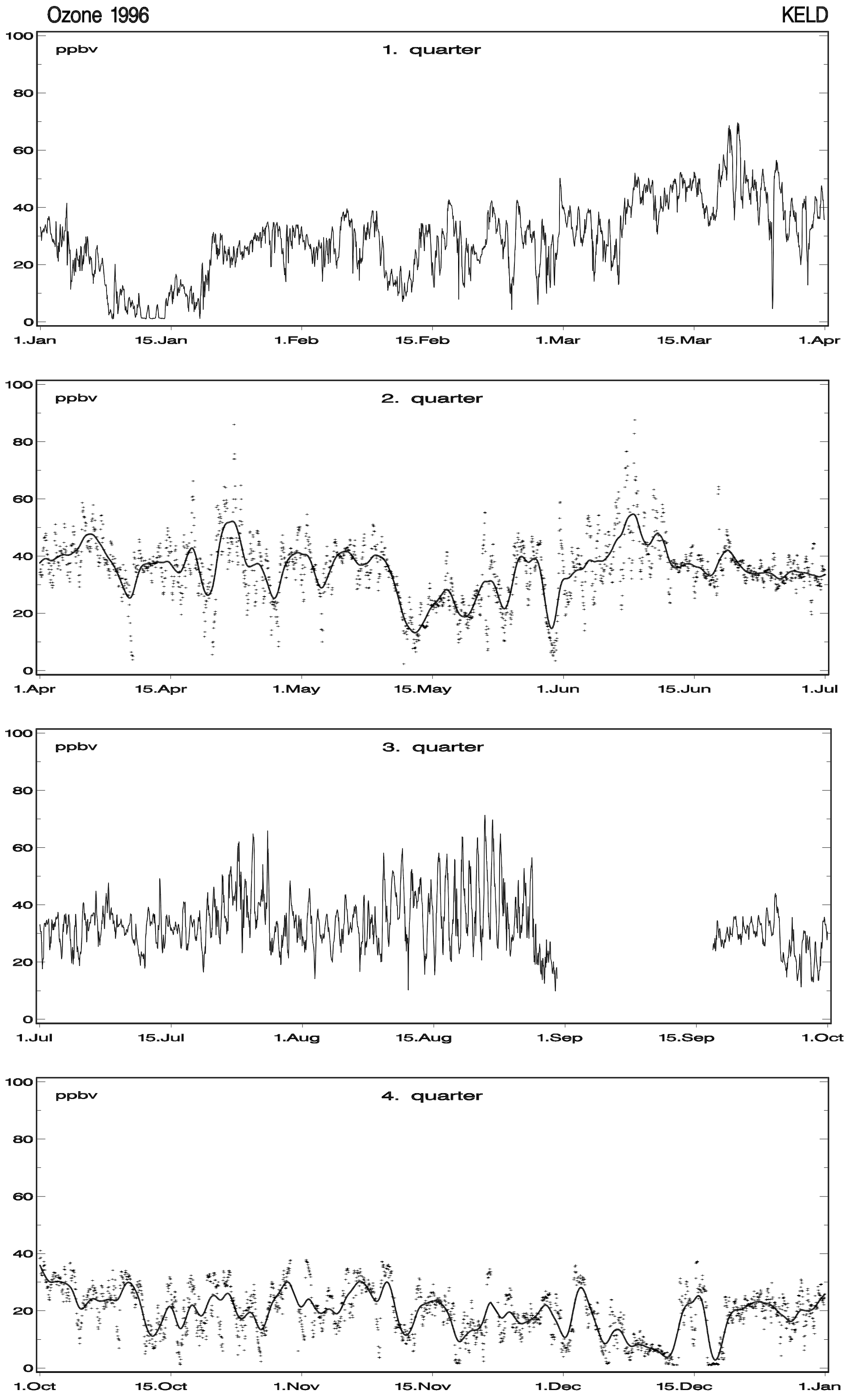


Figure 2.1.3 Hourly mean concentrations of ozone at Keldsnor in the 4 quarters of 1996, shown either as connected data points or as data points (dots) overlaid with smoothing curves.

Table 2.1.1 Mean values of air pollutant concentrations 1991-1997 in μg/m^3.

Site	Arit. Mean	Std. dev	Max	Number
NO_2 -N				
ULBG	1.73	1.71	22.78	2226
TANG	-	-	-	166
ANHO	2.26	2.13	19.58	1602
FRBG	3.24	2.40	13.56	229
KELD	-	-	-	75
SO_2 -S				
ULBG	1.06	2.11	26.14	2473
TANG	1.29	2.23	31.47	2432
ANHO	1.52	2.41	27.74	2484
FRBG	1.61	2.98	36.47	2438
LIND	1.42	3.04	42.84	2481
KELD	2.11	3.69	57.21	2424
S				
ULBG	1.41	1.21	11.40	2469
TANG	1.39	1.09	9.05	2423
ANHO	1.42	1.12	10.00	2475
FRBG	1.50	1.24	10.20	2450
LIND	1.60	1.33	12.70	2481
KELD	1.75	1.34	12.40	2428
THNz-N				
ULBG	2.52	2.32	18.07	2418
TANG	3.61	2.44	20.78	2378
ANHO	1.74	1.87	26.39	2466
FRBG	2.07	1.89	17.52	2421
LIND	3.90	3.70	27.64	2483
KELD	3.65	2.91	35.95	2404
TNOy-N				
ULBG	0.98	1.09	12.97	2457
TANG	1.08	1.11	11.59	2412
ANHO	0.97	1.10	16.75	2472
FRBG	0.95	1.01	11.80	2443
LIND	1.22	1.29	14.52	2487
KELD	1.38	1.40	17.92	2422
Na				
ULBG	1.52	1.39	10.30	2481
TANG	1.16	1.01	7.91	2444
ANHO	1.68	1.41	24.94	2488
FRBG	0.90	1.25	44.59	2456
LIND	1.31	1.38	30.59	2492
KELD	1.97	1.53	21.43	2427
Mg				
ULBG	0.17	0.16	1.33	2482
TANG	0.13	0.12	0.82	2443
ANHO	0.19	0.16	3.09	2477
FRBG	0.10	0.10	0.90	2457
LIND	0.16	0.20	7.11	2496
KELD	0.23	0.17	2.07	2427
K				
ULBG	0.16	0.11	1.27	2302
TANG	0.20	0.15	2.56	2283
ANHO	0.15	0.12	1.75	2318
FRBG	0.17	0.25	10.23	2278
LIND	0.18	0.15	1.99	2312
KELD	0.22	0.64	29.68	2249
Pb				
ULBG	0.011	0.015	0.146	2197
TANG	0.012	0.016	0.233	2389
ANHO	0.010	0.013	0.160	2231
FRBG	0.015	0.019	0.181	2349
LIND	0.015	0.020	0.192	2247
KELD	0.016	0.022	0.252	2398

Table 2.1.2 Mean values of air concentrations of elements at Tange and Keldsnor 1991 - 1997 in ng/m^3.

	KELDSNOR				**TANGE**			
Element	Arit. Mean	Std. dev	Max	Number	Arit. Mean	Std. dev	Max	Number
Al	178	218	2380	1727	221	347	6170	1645
Si	393	558	4760	2161	713	1539	44800	2075
P	47	53	881	408	74	248	4710	555
S	1755	1336	12400	2428	1387	1093	9050	2423
Cl	2214	2787	35000	2083	1625	2065	18000	1841
K	191	131	1280	2427	207	188	3720	2419
Ca	176	195	3270	2423	165	273	7770	2419
Ti	10.6	13.6	142	2220	14.2	23.2	498	2218
V	6.92	6.22	54.5	2239	3.89	3.32	58.7	2011
Cr	4.90	71.7	1810	636	2.01	2.42	27.8	602
Mn	5.06	5.85	66.2	2262	7.42	13.2	437	2346
Fe	140	223	7160	2424	208	921	42900	2418
Ni	3.12	20.1	918	2100	1.77	1.37	11.6	1777
Cu	3.35	40.5	1850	2093	2.22	2.82	80.3	2205
Zn	27.1	42.8	1320	2302	24.4	72.0	2480	2319
Ga	0.74	0.58	3.27	274	0.55	0.46	4.24	230
Ge	0.51	0.35	1.74	183	0.40	0.33	2.94	130
As	2.08	3.61	35.5	1338	1.67	2.29	29.8	1562
Se	0.94	0.78	9.44	2295	0.68	0.56	5.40	2238
Br	7.09	5.40	50.2	2421	4.88	3.41	28.3	2378
Rb	0.82	0.91	10.9	1232	0.85	0.93	13.0	1276
Sr	2.48	2.03	37.4	2359	1.99	2.06	55.1	2351
Y	0.44	0.35	4.77	220	0.48	0.36	4.51	251
Zr	0.88	0.75	7.64	1308	1.27	1.87	41.2	1285
Nb	0.38	0.09	0.54	5	0.43	0.28	1.92	54
Mo	0.84	2.67	67.5	651	0.62	0.35	2.77	430
Ag	1.71	2.91	17.5	32	0.94	0.18	1.31	31
Cd	1.73	0.68	5.04	105	1.50	0.55	3.74	67
Sn	3.38	1.85	13.6	387	2.90	1.37	11.2	230
Sb	3.71	1.67	14.9	163	3.17	1.68	17.1	149
I	5.17	1.34	8.93	72	4.91	1.19	8.24	66
Ba	14.6	6.13	46.7	200	14.9	11.0	94.1	234
Pb	16.3	22.1	252	2398	12.2	15.8	233	2389

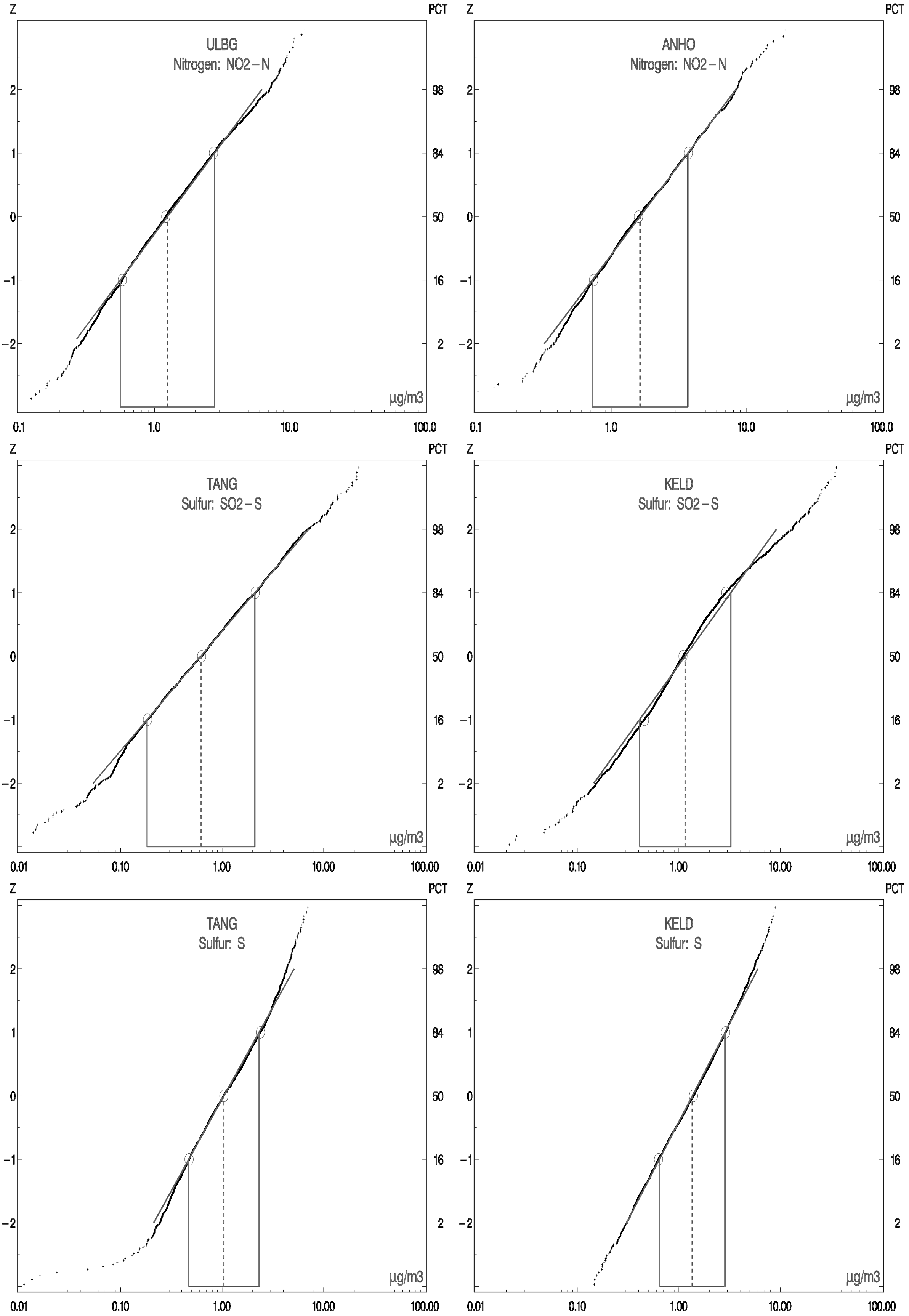


Figure 2.1.4 Statistical distributions of log-concentrations on the horizontal axis for selected pollutants and stations in 1991-1997. Circles denote the 16-, 50-, and 84-percentiles and the straight line is the log-normal fit through the indicated geometric mean and standard deviations. See also text.

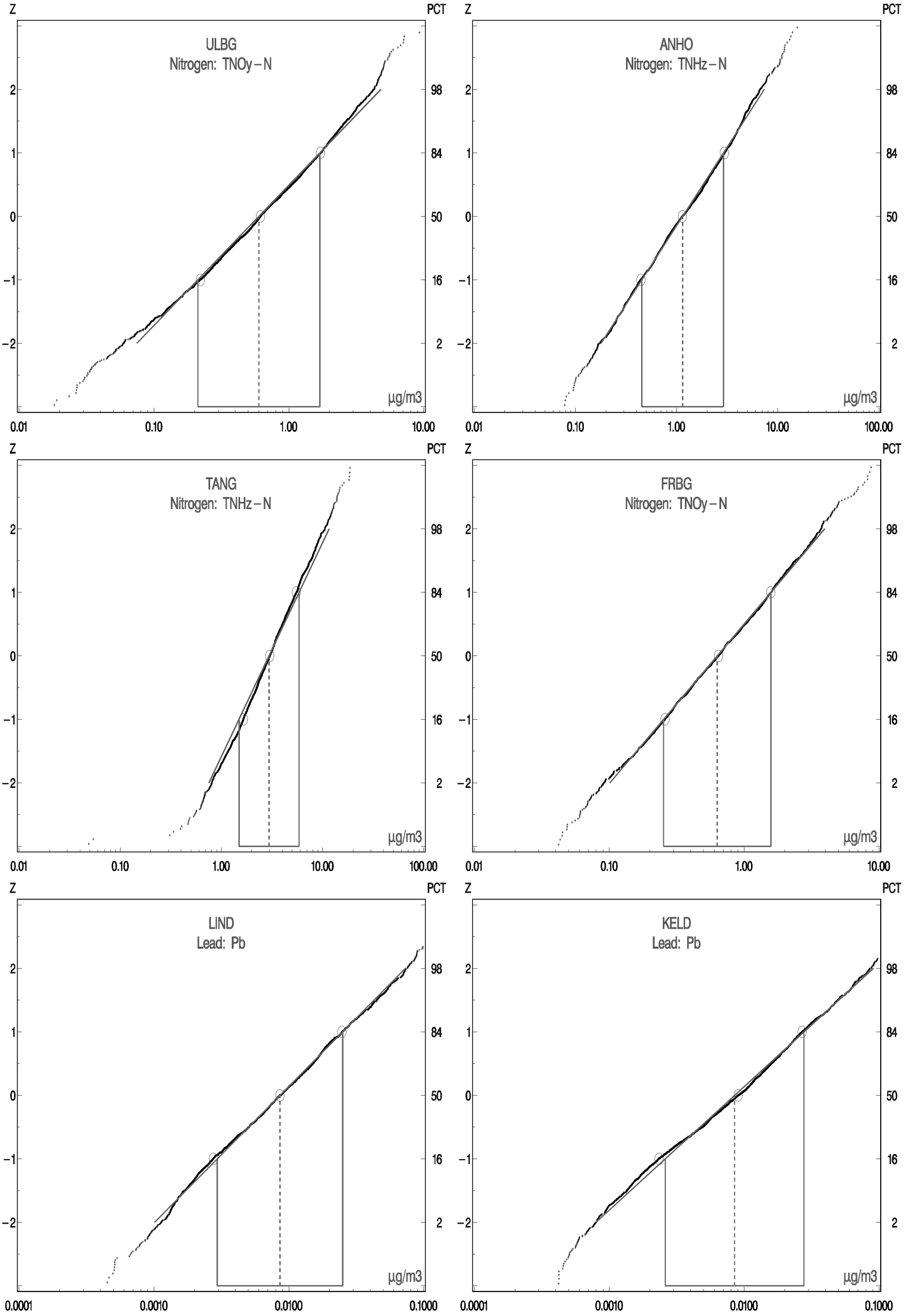


Figure 2.1.5 Statistical distributions of log-concentrations on the horizontal axis for selected pollutants and stations in 1991-1997. Circles denote the 16-, 50-, and 84-percentiles and the straight line is the log-normal fit through the indicated geometric mean and standard deviations. See also text.

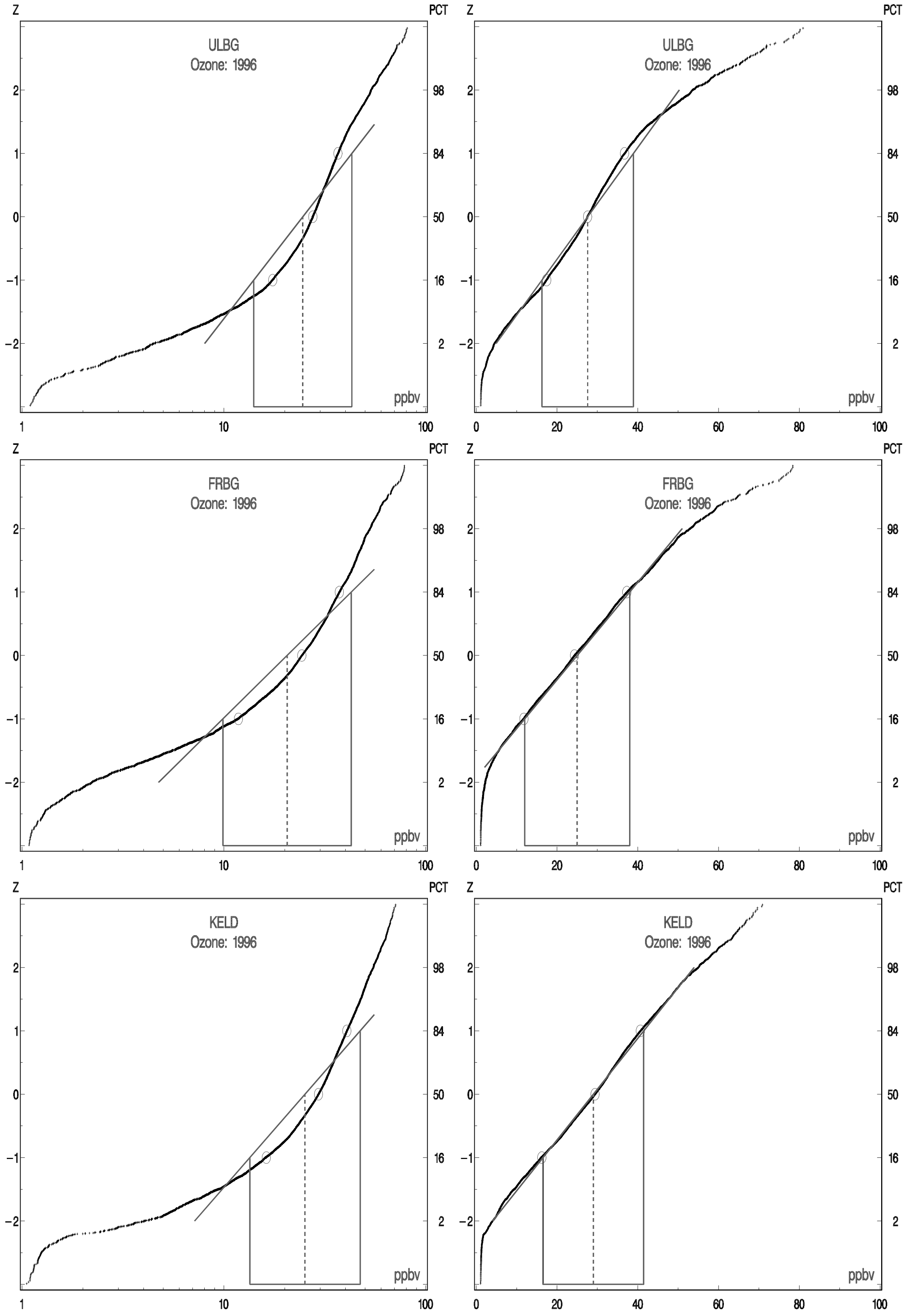


Figure 2.1.6 Statistical distributions of hourly mean concentrations of ozone, shown on the horizontal axes. Logarithmic concentration axes to the left and linear axes to the right. See also text.

Table 2.1.3 Statistics of SO_2-S data in 3 subperiods. Significant decreases from one subperiod to the next are denoted by D, increases by U. An "X" in the column Log_N 9197 indicates that data in the period 1991-1997 fit a log-normal distribution at a significance level of 5%.

Quantity	Log_N 9197	7884	8590	9197	History	Log_N 9197	7884	8590	9197	History
			ULBORG					**ANHOLT**		
Mean Aritm.			1.33	1.06				2.06	1.52	
Std. Dev			2.57	2.11				2.65	2.41	
Mean_geom	X		0.53	0.40				1.20	0.84	Db
Std_geom			4.02	4.09				2.80	2.90	
P50			0.51	0.38				1.20	0.83	
P98			9.28	7.44				11.41	8.65	
N			1232	2473				809	2484	
			TANGE					**FREDERIKSBORG**		
Mean Aritm.		4.44	2.42	1.29				2.82	1.61	
Std. Dev		5.88	3.84	2.23				4.33	2.98	
Mean_geom		2.48	1.15	0.62	Da, Db	X		1.40	0.74	Db
Std_geom		3.01	3.65	3.39				3.27	3.43	
P50		2.50	1.22	0.62				1.44	0.74	
P98		23.20	13.70	7.65				16.82	10.47	
N		2358	2105	2432				1254	2438	
			LINDET					**KELDSNOR**		
Mean Aritm.			2.06	1.42			5.60	3.51	2.11	
Std. Dev			3.93	3.04			8.14	5.63	3.69	
Mean_geom			0.92	0.51	Db		3.25	1.82	1.15	Da, Db
Std_geom			3.43	4.34			2.83	3.30	2.82	
P50			0.94	0.53			3.20	1.83	1.09	
P98			15.14	10.46			28.80	19.60	13.59	
N			486	2481			2204	2021	2424	

Table 2.1.4 Statistics of S data in 3 subperiods. For other details see caption of Table 2.1.3.

Quantity	Log_N 9197	7884	8590	9197	History	Log_N 9197	7884	8590	9197	History
			ULBORG					**ANHOLT**		
Mean Aritm.			1.54	1.41				1.50	1.42	
Std.dev			1.40	1.21				1.18	1.12	
Mean_geom			1.14	1.04	Db			1.16	1.09	Db
Std_geom			2.15	2.16				2.02	2.07	
P50			1.07	0.98				1.03	1.05	
P98			5.99	4.90				4.73	4.58	
N			1248	2469				814	2475	
			TANGE					**FREDERIKSBORG**		
Mean Aritm.		2.37	1.66	1.39				1.77	1.50	
Std.dev		2.24	1.49	1.09				1.52	1.24	
Mean_geom		1.64	1.20	1.04	Da, Db			1.28	1.11	Db
Std_geom		2.38	2.26	2.22				2.29	2.25	
P50		1.64	1.21	1.04				1.27	1.13	
P98		8.90	6.16	4.41				6.19	5.03	
N		2358	2092	2423				1281	2450	
			LINDET					**KELDSNOR**		
Mean Aritm.			1.60	1.60			2.90	2.10	1.75	
Std.dev			1.42	1.33			2.76	1.92	1.34	
Mean_geom	X		1.18	1.19			2.07	1.53	1.35	Da, Db
Std_geom			2.19	2.20			2.28	2.25	2.11	
P50			1.11	1.17			2.07	1.50	1.39	
P98			6.57	5.51			10.91	8.02	5.62	
N			490	2481			2204	2018	2428	

Table 2.1.5 Statistics of TNHz-N data in 2 subperiods. For other details see caption of Table 2.1.3.

Quantity	Log_N 9197	8590	9197	History	Log_N 9197	8590	9197	History
		ULBORG				**ANHOLT**		
Mean Aritm.		2.56	2.52			1.96	1.74	
Std.dev		2.65	2.32			2.05	1.87	
Mean_geom		1.69	1.70			1.29	1.15	D
Std_geom		2.54	2.53			2.54	2.53	
P50		1.74	1.82			1.26	1.14	
P98		10.12	9.19			7.42	7.06	
N		1367	2418			789	2466	
		TANGE				**FREDERIKSBORG**		
Mean Aritm.		4.05	3.61			2.48	2.07	
Std.dev		2.49	2.44			2.36	1.89	
Mean_geom		3.44	2.96	D		1.70	1.48	D
Std_geom		1.78	1.98			2.50	2.32	
P50		3.57	3.00			1.79	1.53	
P98		10.69	11.01			9.36	7.94	
N		646	2378			1440	2421	
		LINDET				**KELDSNOR**		
Mean Aritm.		3.94	3.90			3.89	3.65	
Std.dev		4.05	3.70			2.82	2.91	
Mean_geom		2.50	2.55		X	3.08	2.86	D
Std_geom		2.62	2.64			2.01	2.02	
P50		2.30	2.74			3.13	2.93	
P98		16.62	14.27			12.05	12.39	
N		486	2483			674	2404	

Table 2.1.6. Statistics of TNO_3-N data in 2 subperiods. For other details see caption of Table 2.1.3.

Quantity	Log_N 9197	8590	9197	History	Log_N 9197	8590	9197	History
		ULBORG				**ANHOLT**		
Mean Aritm.		0.97	0.98			1.01	0.97	
Std.dev		1.22	1.09			1.19	1.10	
Mean_geom		0.54	0.60	U		0.64	0.63	
Std_geom		3.22	2.83			2.63	2.54	
P50		0.60	0.62			0.64	0.62	
P98		4.73	4.34			3.64	4.03	
N		1366	2457			795	2472	
		TANGE				**FREDERIKSBORG**		
Mean Aritm.		1.12	1.08			1.00	0.95	
Std.dev		1.15	1.11			1.00	1.01	
Mean_geom		0.72	0.71		X	0.66	0.63	
Std_geom		2.70	2.63			2.66	2.50	
P50		0.77	0.72			0.70	0.65	
P98		4.34	4.48			3.91	3.78	
N		652	2412			1425	2443	
		LINDET				**KELDSNOR**		
Mean Aritm.		1.26	1.22			1.55	1.38	
Std.dev		1.39	1.29			1.43	1.40	
Mean_geom		0.73	0.76			1.07	0.97	D
Std_geom		3.18	2.92			2.47	2.35	
P50		0.83	0.83			1.18	1.02	
P98		5.21	4.91			6.01	5.10	
N		487	2487			675	2422	

Table 2.1.7 Statistics for NO_2-N in 2 sub-periods. For other details see caption of Table 2.1.3.

Quantity	Log_N 9197	8590	9197	History	Log_N 9197	8590	9197	History
		ULBORG				**ANHOLT**		
Mean Aritm.		1.56	1.73			2.01	2.26	
Std.dev		1.50	1.71			1.96	2.13	
Mean_geom		1.02	1.25	U		1.46	1.63	
Std_geom		2.63	2.23			2.23	2.26	
P50		1.11	1.21			1.41	1.59	
P98		5.85	7.28			8.59	8.63	
N		370	2226			371	1602	
		TANGE				**FREDERIKSBORG**		
Mean Aritm.		2.20	2.50			3.68	3.24	
Std.dev		1.58	1.94			2.27	2.40	
Mean_geom		1.78	1.96	U		2.92	2.65	D
Std_geom		1.96	2.10			2.20	1.84	
P50		1.85	1.85			3.19	2.46	
P98		6.46	8.73			9.90	11.48	
N		278	166			541	229	
						KELDSNOR		
Mean Aritm.						2.68	4.42	
Std.dev						2.15	2.95	
Mean_geom					X	2.00	3.70	U
Std_geom						2.20	1.79	
P50						2.07	3.70	
P98						9.46	15.37	
N						226	75	

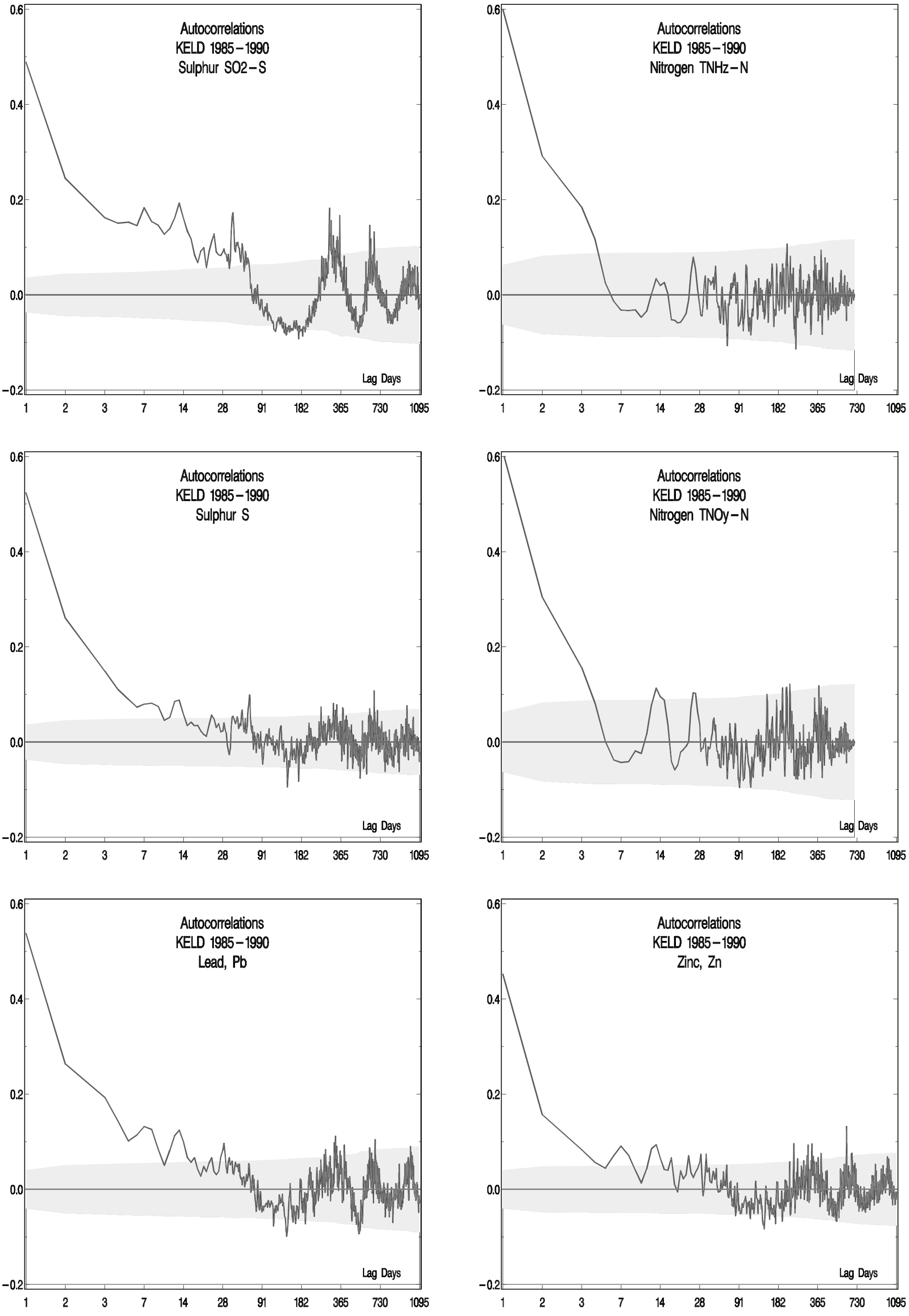


Figure 2.1.7 Autocorrelation functions over 3 years for concentrations of selected pollutants at Keldsnor 1985-1990. Values outside the shaded area are significant at the 5%-level.

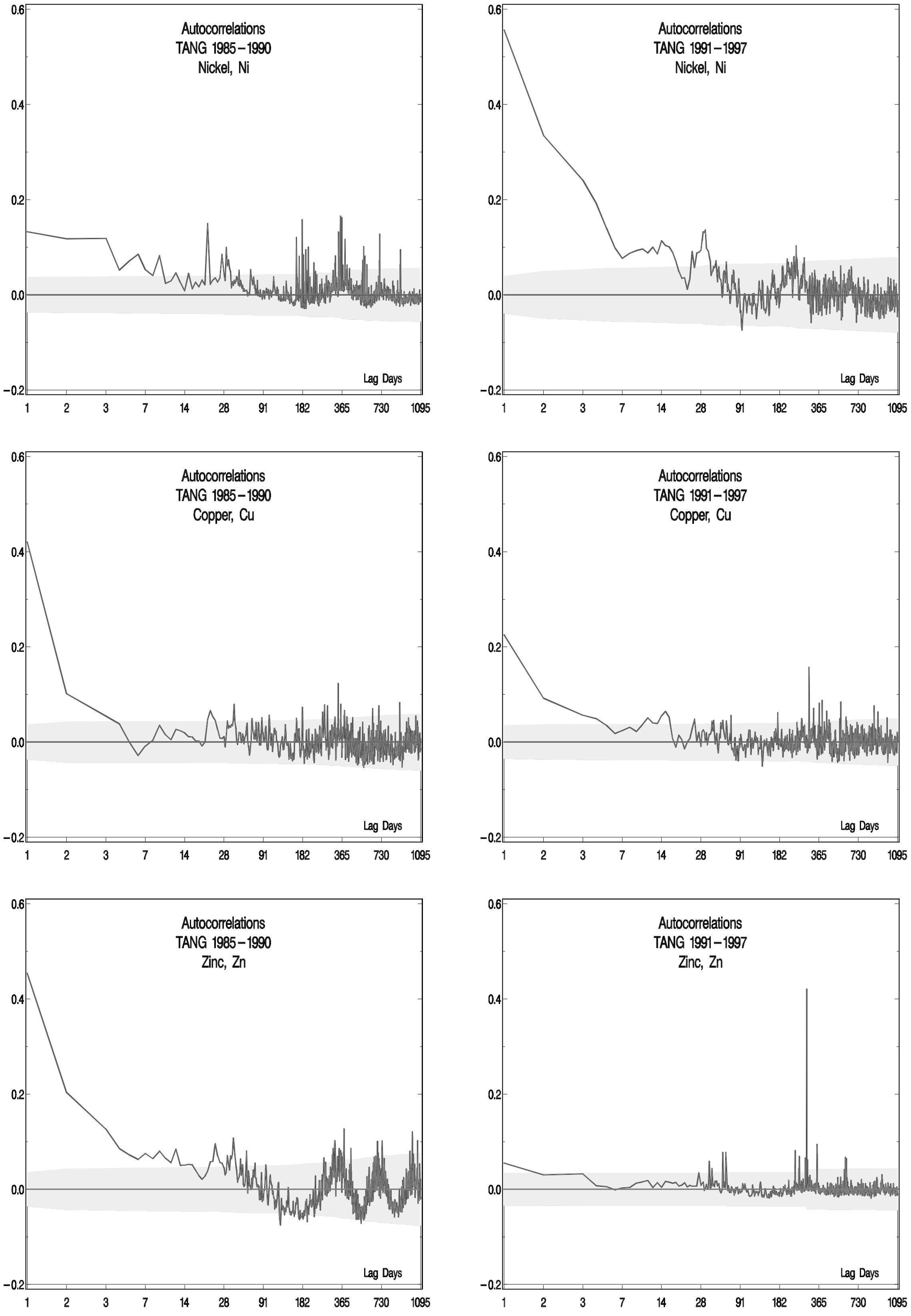


Figure 2.1.8 Autocorrelation functions over 3 years for some heavy metal concentrations at Tange in 1985-1990 and 1991-1997. Values outside the shaded area are significant at the 5%-level.

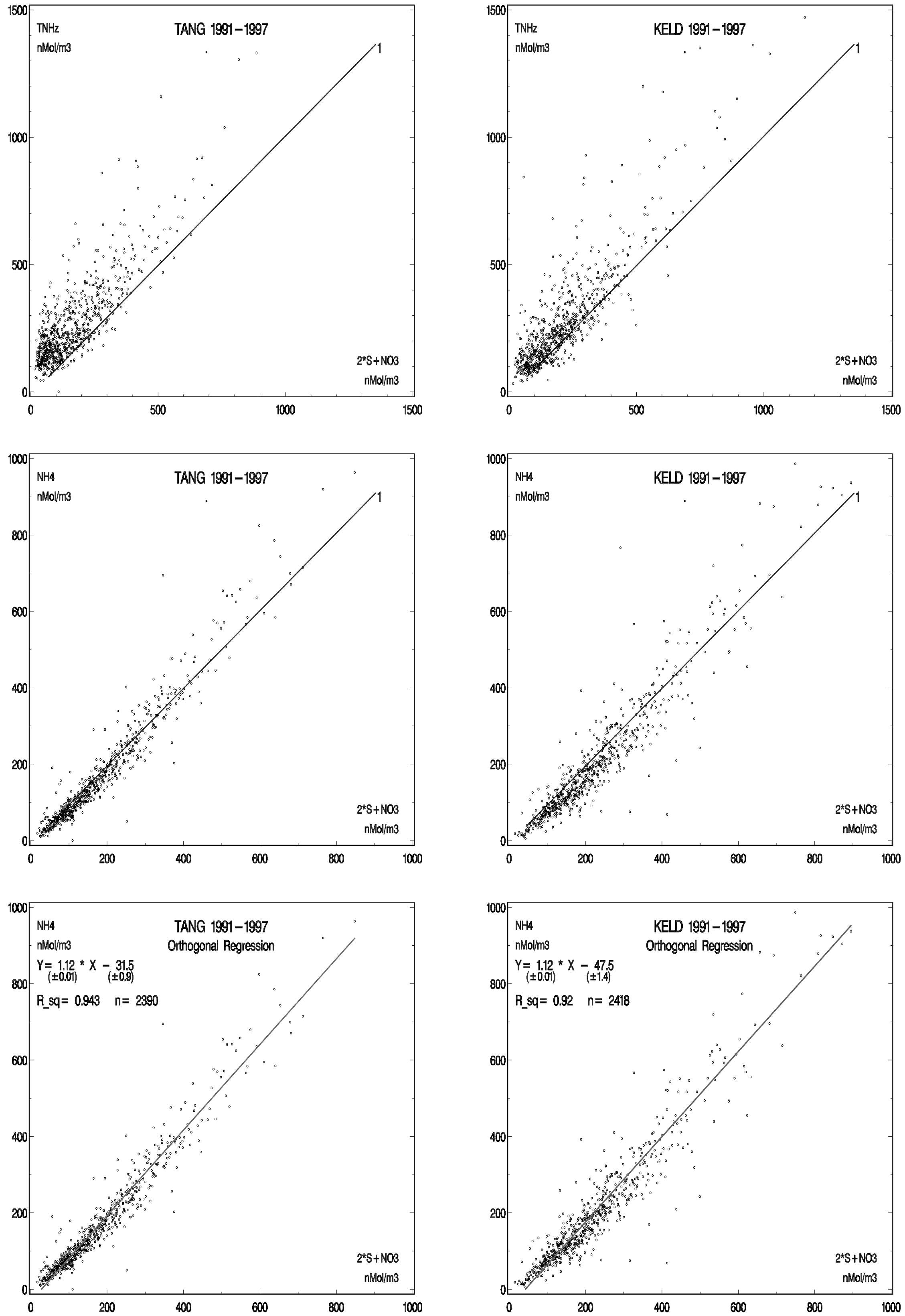


Figure 2.1.9 Stochiometric relations for reduced nitrogen. Note that units are in nMol/m^3.

2.2 Geography

Median concentrations

Variations among sites are illustrated by the examples shown in Figures 2.2.1 - 2.2.2. Here annual median concentrations of sulphur and reduced nitrogen compounds are shown at various stations. Because of the lognormal approximation medians have been chosen as more representative of the data than the mean values.

Variations in primary and secondary pollutants

The geographic variations among the sites have diminished over the years with the decreasing concentrations but some differences are still noticeable. Generally concentrations seem to increase towards the south (cf. also Tables 2.1.1 – 2.1.7) but modified by the particular component and the site characteristics. For the primary pollutant SO_2 it is evident that the lowest concentrations occur at the rather remote station Ulborg compared to other stations more exposed to pollution plumes from urban or industrial source areas at a distance of a few hundred kilometres, inside or outside Denmark. Similarly the concentrations of NH_3 at the non-agricultural sites Anholt, Frederiksborg and Ulborg (not shown), are considerably less than at the other three stations. For the secondary pollutants of $SO_4^=$ and NH_4^+ the geographic distribution is quite even with minimum concentrations at the coastal stations Ulborg and Anholt, respectively.
For NO_2, which derives from traffic emissions, it can be seen from Table 2.1.7 that concentrations at Keldsnor and Frederiksborg are the highest in the country. The station at Keldsnor is undoubtedly influenced by transport from the south, and Frederiksborg is affected by the relative proximity of Copenhagen and the general urbanisation of this region. However, the network density is insufficient for a closer study of urban influences in the open countryside.

Variations against a national average

The geographic differences between local variations can also be illustrated as in Figures 2.2.3-6. In these figures the monthly median concentrations at various sites are shown against the corresponding values averaged over all stations. These grand national averages are used as a set of common reference data. The lines are orthogonal regression lines that are the best least-squares fit to the data. In almost all cases the intercept with the vertical axis is of no significance, it is either not statistically different from zero or much smaller than typical concentration values. The slopes depend on the correlations and the standard deviations, which for the station means do not depend on the site. Therefore much of the information on geographic differences resides in the slopes of the regression lines. An overview of all the regression parameters is given in Table 2.2.1 and 2.2.2.

North-South sulphur gradient

The results for sulphur compounds shown in Figure 2.2.3 reveal a concentration gradient from north to south that probably is caused by LRTAP from the European continent. Although not shown in the figures, the concentrations for both components, sulphur dioxide and sulphur in aerosol, also tend to be a little larger at the eastern than at the western stations, see Table 2.2.1. This may also be caused by LRTAP combined with a higher proximity to sources in East Europe. A quite similar behaviour is seen for lead in aerosols in Figure 2.2.4, although the north-south gradient is not quite so pronounced at the western sites. A similar conclusion can be drawn for zinc, shown at Tange and Keldsnor in the lower panels of Figure 2.2.5. For TNO_3

Table 2.2.2 shows that the behaviour is similar at the station-pairs Anholt-Frederiksberg (low range), Ulborg-Tange (middle-range), and Lindet-Keldsnor (high range). Examples of these typical variations are shown in the four upper panels in Figure 2.2.5. These geographic differences probably reflect a combination of LRTAP and the degree of local traffic influence in various parts of the country. For total ammonium, TNHz the geographic variations are shown in Figure 2.2.6. A north-south gradient is clearly seen, pointing to LRTAP as an important influence but there is also an east-west gradient, which may tentatively be attributed to the more prominent role cattle breeding is playing in the western part of the country.

Small geographic differences

The regression parameters are all listed in Tables 2.2.1 and 2.2.2 where it is also indicated whether the slopes, by their 95% confidence limits, are significantly different from 1. By the same criterion (*i.e.* ± 2·std_dev) about half of the slopes, mainly in the middle ranges, do not differ from each other and for a majority of cases the correlations to the national averages are also quite similar across the country. It can therefore be concluded that air pollution concentrations in background areas in Denmark exhibit only small geographic differences, except that source influences and land use are of importance in some cases.

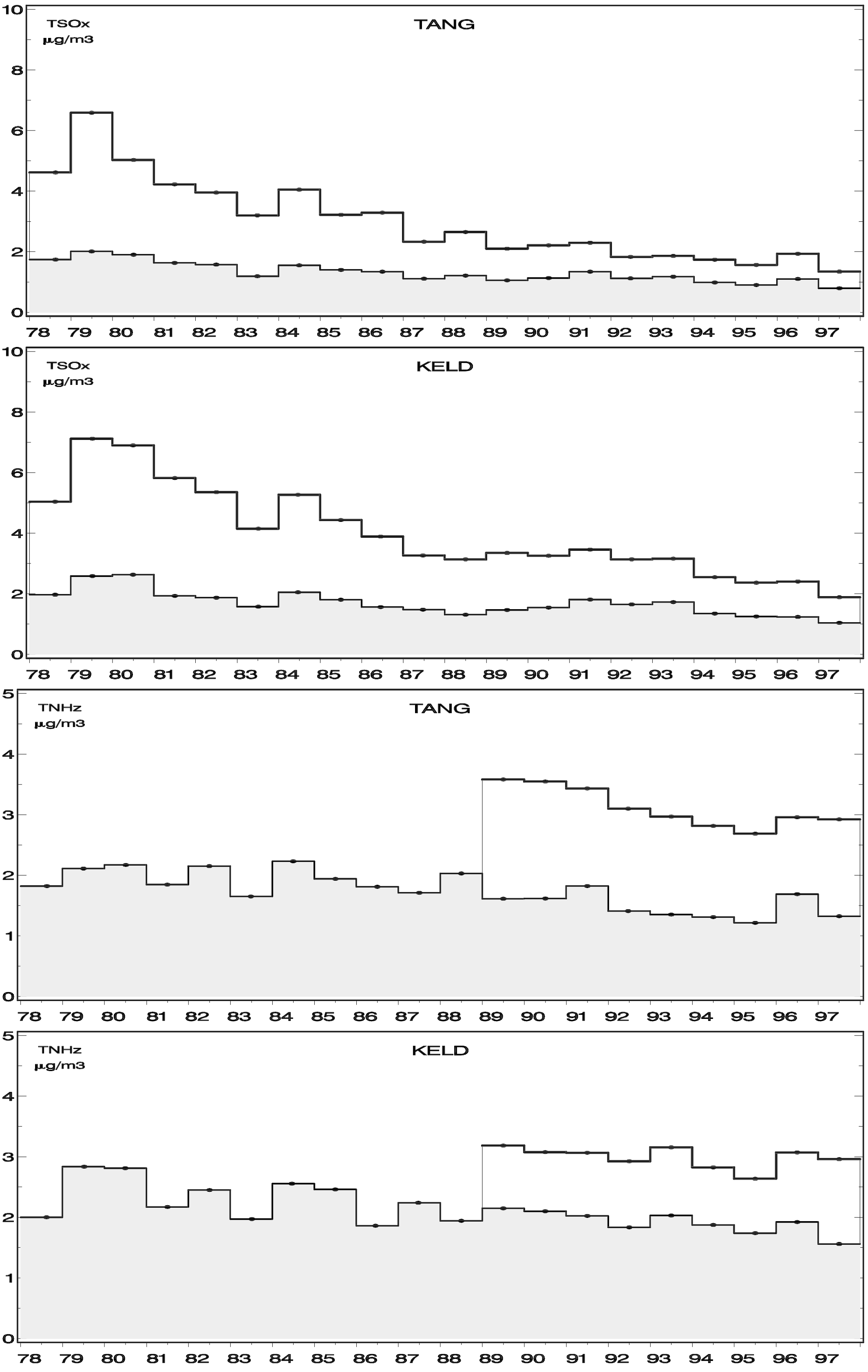


Figure 2.2.1 Annual medians of 24h concentrations of compounds of sulphur (upper) and reduced nitrogen (lower), split into gaseous phases SO_2 -S and NH_3 -N (blank) and particulate phases S, including $SO_4^=$ –S, and NH_4^+-N (shaded).

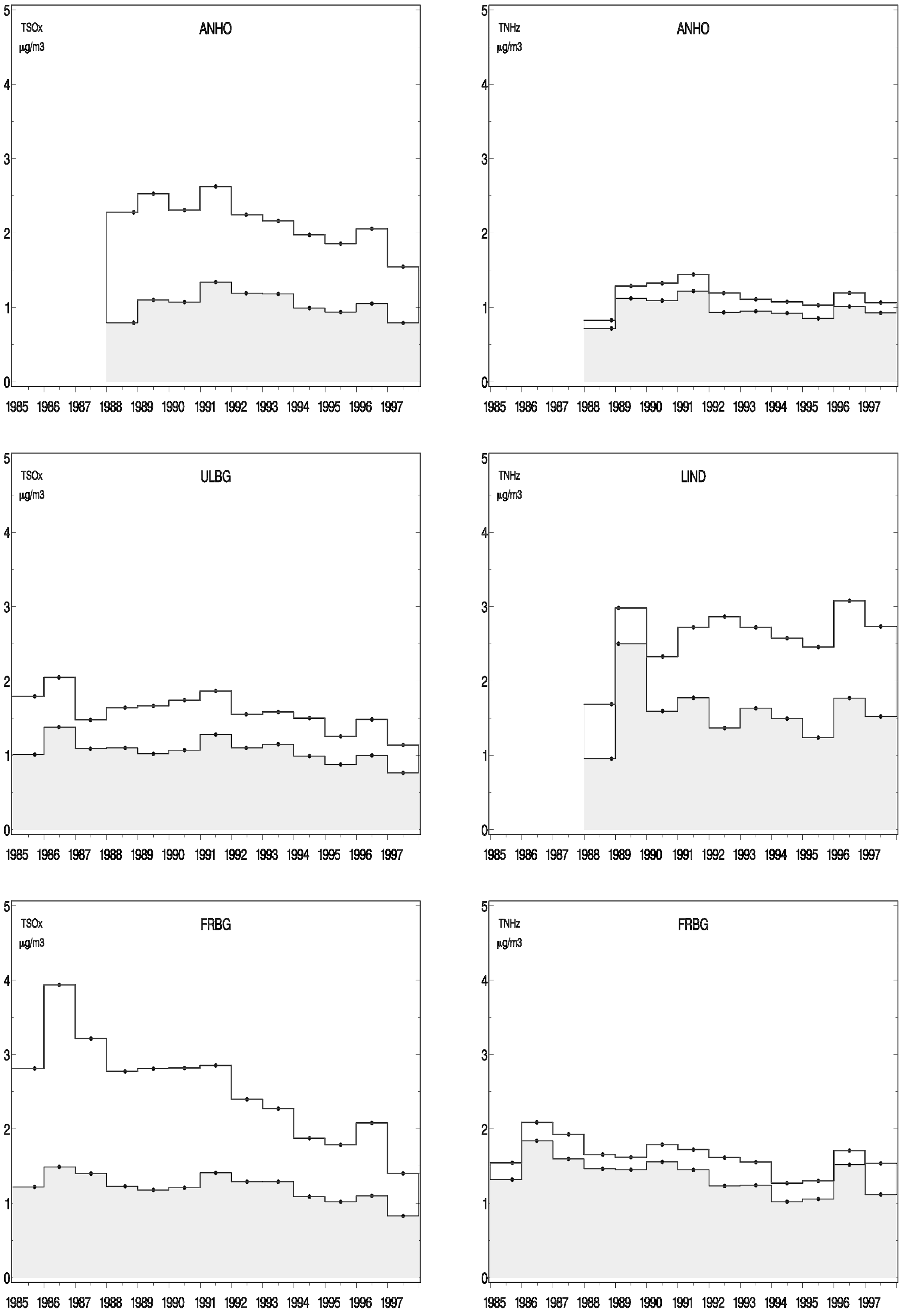


Figure 2.2.2 Annual medians of 24h concentrations of compounds of sulphur (left) and reduced nitrogen (right), split into gaseous phases SO_2 -S and NH_3 -N (blank) and particulate phases S, including $SO_4^=$ –S, and NH_4^+-N (shaded).

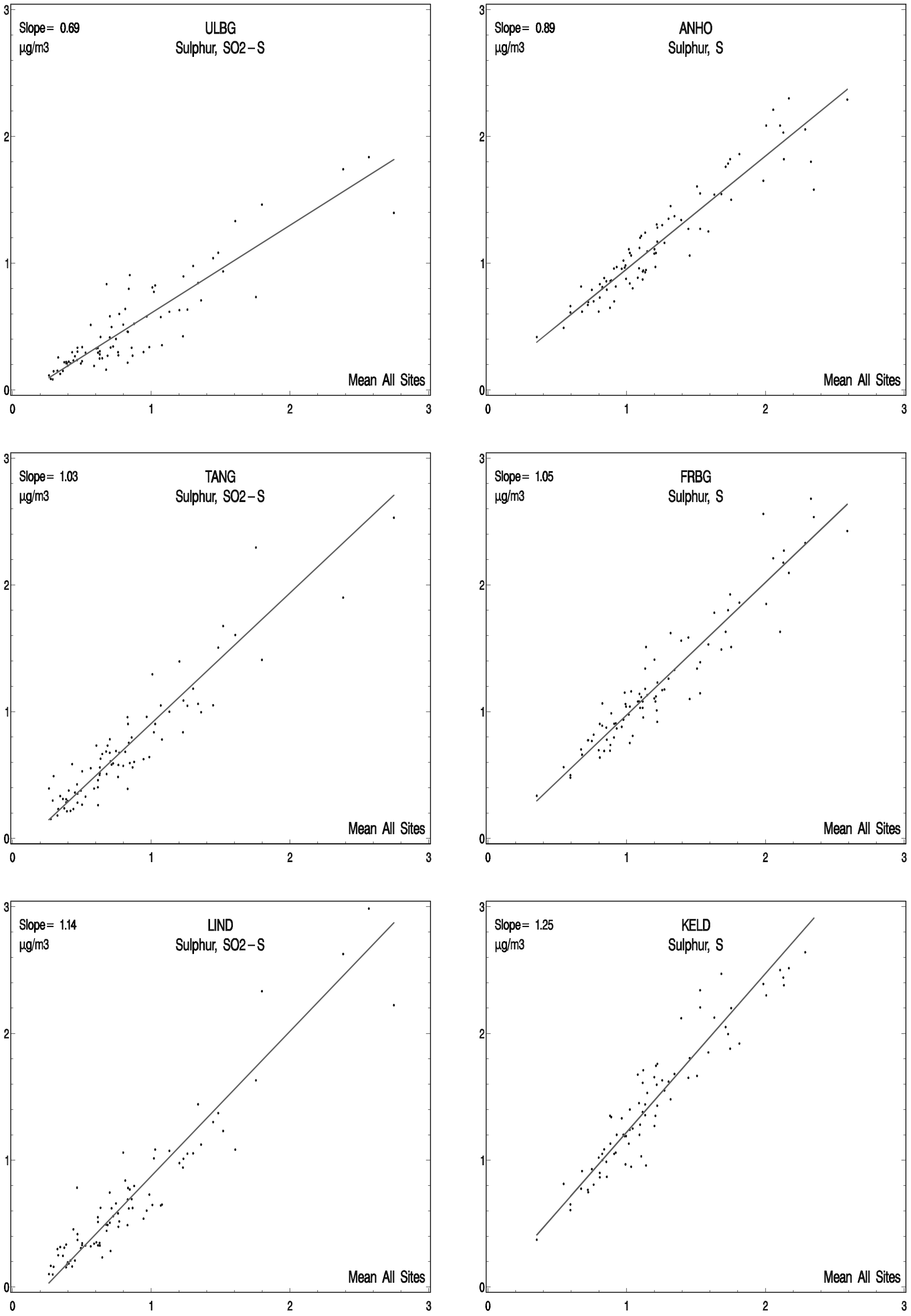


Figure 2.2.3 Monthly medians of sulphur compounds against means of monthly medians at all sites, 1991-1997, and orthogonal regressions lines.

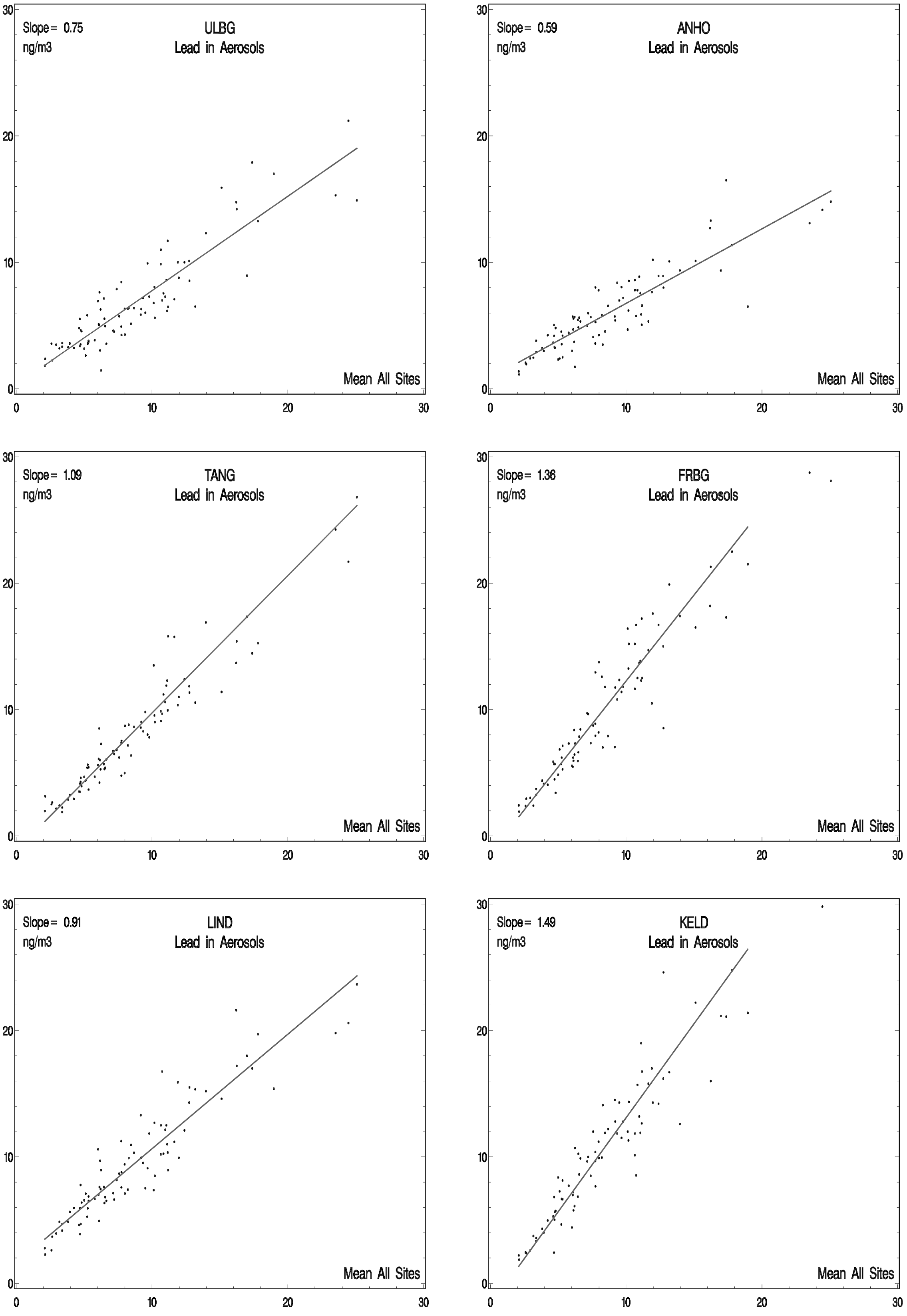


Figure 2.2.4 Monthly medians of lead in aerosols against means of monthly medians at all sites, 1991-1997, and orthogonal regressions lines.

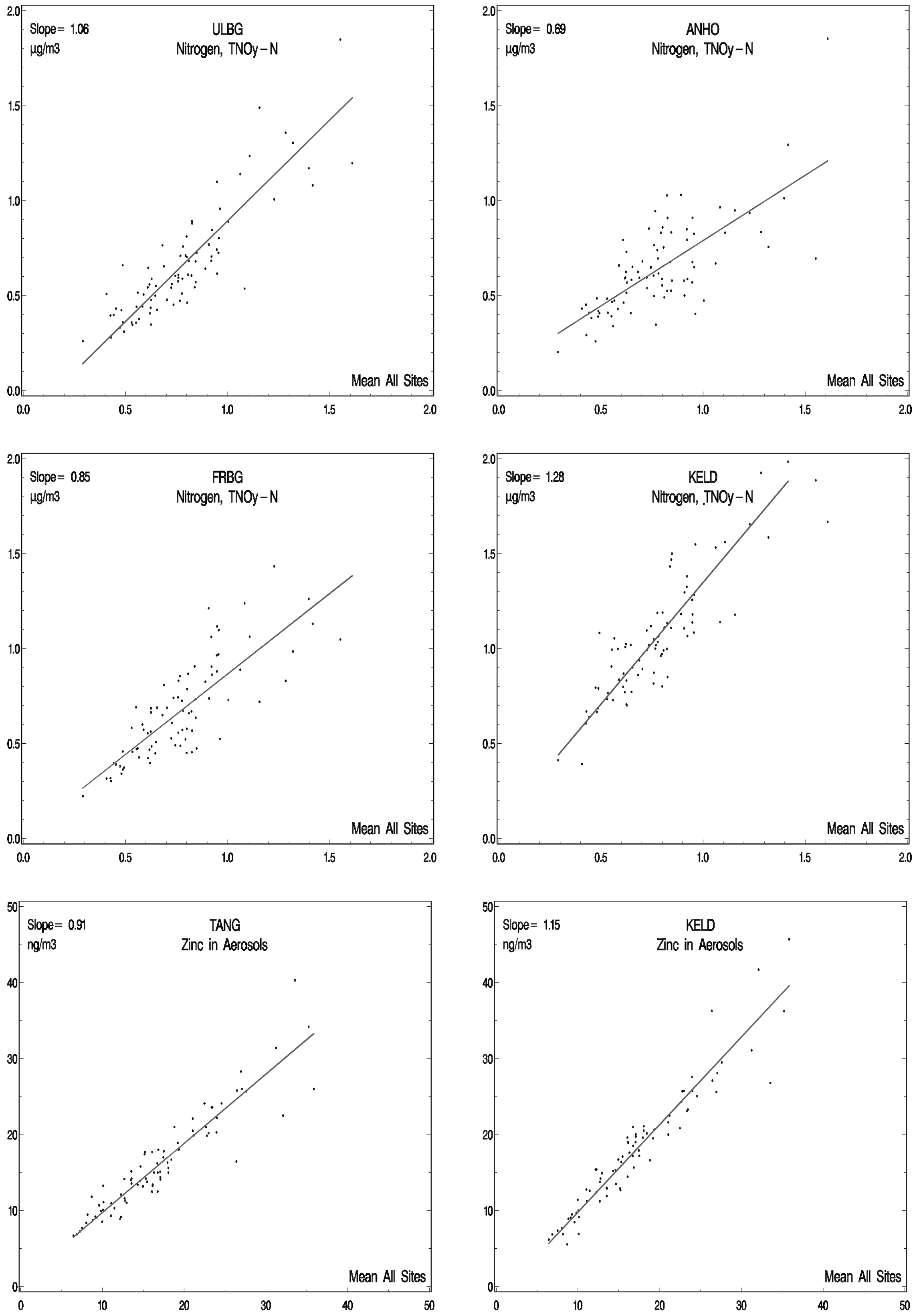


Figure 2.2.5 Monthly medians of total nitrate and of zinc in aerosols against means of monthly medians at all sites, 1991-1997, and orthogonal regressions lines.

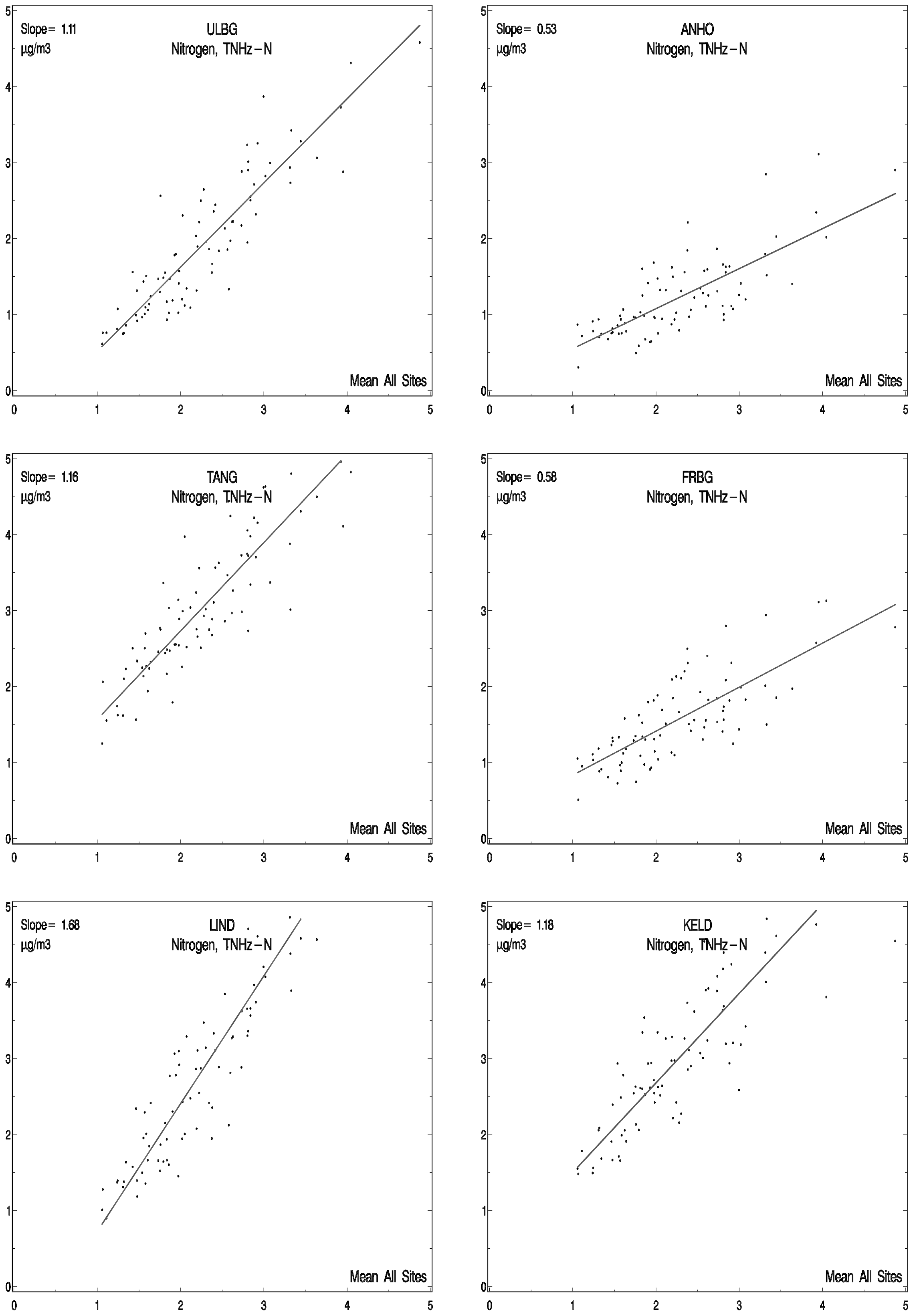


Figure 2.2.6 Monthly medians of total ammonium against means of monthly medians at all sites, 1991-1997, and orthogonal regressions lines.

Table 2.2.1 Orthogonal regression parameters for monthly median concentrations in air.

Site	Slope	Std_ Slope	Intercep	Std_ Intcep	Rsq	Slope # 1
			SO2-S			
ULBG	0.69	0.03	-0.09	0.03	0.85	-1
TANG	1.03	0.04	-0.12	0.04	0.89	
ANHO	0.75	0.04	0.31	0.03	0.84	-1
FRBG	1.05	0.04	-0.01	0.04	0.87	
LIND	1.14	0.04	-0.27	0.03	0.92	1
KELD	1.51	0.08	0.03	0.07	0.82	1
			S			
ULBG	0.94	0.05	-0.07	0.06	0.82	
TANG	0.91	0.03	0.01	0.04	0.91	-1
ANHO	0.89	0.03	0.06	0.04	0.89	-1
FRBG	1.05	0.04	-0.07	0.05	0.90	
LIND	1.09	0.04	-0.06	0.05	0.90	1
KELD	1.25	0.04	-0.03	0.06	0.91	1
			Pb			
ULBG	0.75	0.04	0.30	0.36	0.81	-1
TANG	1.09	0.05	-1.13	0.42	0.87	
ANHO	0.59	0.03	0.86	0.30	0.79	-1
FRBG	1.36	0.05	-1.32	0.46	0.89	1
LIND	0.91	0.04	1.60	0.36	0.86	-1
KELD	1.49	0.06	-1.76	0.52	0.89	1
			Zn			
TANG	0.91	0.03	0.62	0.61	0.89	-1
KELD	1.15	0.04	-1.75	0.62	0.93	1

Table 2.2.2 Orthogonal regression parameters for monthly median concentrations in air.

Site	Slope	Std_ Slope	Intercep	Std_ Intcep	Rsq	Slope # 1
			NH4-N			
ULBG	1.03	0.05	-0.24	0.08	0.83	
TANG	1.06	0.04	-0.04	0.05	0.91	
ANHO	0.68	0.05	0.05	0.08	0.68	-1
FRBG	0.87	0.04	0.04	0.06	0.84	-1
LIND	1.27	0.05	-0.21	0.07	0.89	1
KELD	1.29	0.07	0.10	0.10	0.82	1
			TNHz-N			
ULBG	1.11	0.05	-0.59	0.11	0.86	1
TANG	1.16	0.06	0.41	0.13	0.84	1
ANHO	0.53	0.04	0.02	0.10	0.65	-1
FRBG	0.58	0.05	0.25	0.11	0.66	-1
LIND	1.68	0.07	-0.96	0.16	0.88	1
KELD	1.18	0.07	0.32	0.16	0.78	1
			TNOy-N			
ULBG	1.06	0.05	-0.17	0.04	0.84	
TANG	1.04	0.05	-0.07	0.04	0.87	
ANHO	0.69	0.06	0.10	0.05	0.63	-1
FRBG	0.85	0.06	0.02	0.05	0.71	-1
LIND	1.33	0.07	-0.15	0.05	0.83	1
KELD	1.28	0.06	0.07	0.05	0.84	1

2.3 Trends

Decreasing median concentrations

The development in air concentrations on the national level since measurements started is illustrated by the annual medians at main stations in Denmark for sulphur and nitrogen compounds, for selected elements in particles, and for ozone. For reasons of representativity medians are again preferred over the mean values. The previously considered Figures 2.2.1 - 2 also illustrate the development with time. The figures confirm the indications in the preceding section (tables 2.1.3 -2.1.5) that there has been a definite decrease in median concentrations of these air pollutants in Denmark over the last two decades, with the exception of ammonia.

Turning point in late 1970s for sulphur

As seen in Figure 2.2.1 the late 1970s were a turning point where the growth in sulphur concentrations was halted and concentrations started to fall steadily in the following years. The decrease for both gaseous and particulate sulphur since around 1980 must be seen as the result of a widespread effort to curb emissions through introduction of stack exhaust cleaning technologies. That was a consequence of an increased awareness of the acidification problems and the demonstrations that air pollution can travel considerable distances from the sources (OECD 1977). The ambient concentrations continued to decrease as restrictions on the sulphur content in fossil fuel were implemented internationally according to the Sulphur Protocol of 1985 within the UN-ECE Convention on Transboundary Air Pollution (CLRTAP, Geneva 1979, 1996). The Protocol called for a reduction in sulphur emissions before 1993 by at least 30 % relative to 1980 - and was in fact almost fully implemented by 1993. It can be seen that the reductions in the concentrations of the sulphur compounds are more pronounced in the primary component SO_2 than in the secondary SO_4 (S). This may be caused by stricter regulations in Denmark than in the neighbouring countries. But the division among the gaseous and particulate phases depends on many external parameters such as meteorological conditions for atmospheric transport from abroad or the existence in the atmosphere of oxidants that have also been under restriction for some years. A new Sulphur protocol that demands further reductions by 2000 and onwards was signed in 1994 and it has been in force since August 1998 (CLRTAP 1996). In passing it should be mentioned that additional protocols on Persistent Organic Pollutants and Heavy Metals have been signed in 1998 but they are not yet in force (CLRTAP 1999).

Little or no trend for reduced nitrogen

For the reduced nitrogen species, ammonia and ammonium in Figure 2.2.2, the decrease is only apparent for ammonium although less pronounced than for sulphur. The indications in the preceding section (Table 2.1.5) were that TNHz has decreased at all stations except Ulborg (not shown) and Lindet where no trends can be discerned. The considerable influence of local agriculture at Lindet thus appears to have been unchanged. The behaviour of reduced nitrogen at Ulborg is considered below.

Development of medians and percentiles

The annual statistics are shown in more detail for individual compounds in the subsequent figures. These figures contain not only the medians but also the 25-, 75- and 90- percentiles for the period since 1985. The shaded area between the two quartiles show the range covered by the central half of the data.

Sulphur percentiles

The percentiles for gaseous and particulate sulphur, shown in Figure 2.3.1, all exhibit definite decreases, most clearly seen in the 90-percentiles. So not only have the levels fallen generally but so have the ranges. The gaps between the upper and lower quartiles have also narrowed over these 13 years.

Reduced nitrogen

The percentiles for reduced nitrogen compounds are shown in Figure 2.3.2. The behaviour of NH_3 is shown in the upper two panels. The levels of this primary and gaseous pollutant at the two selected non-agricultural stations are very low and the range of variation is very small at the marine site Anholt. There is no significant development of the median concentrations with time but the upper percentiles have an increasing tendency. The percentiles for particulate ammonium, NH_4^+, decrease however at all the four sites shown. So not only have the levels of this secondary pollutant which to a considerable degree is of foreign origin fallen generally but so have the ranges. For Ulborg in particular it seems that the temporal developments of the ammonia and ammonium compounds neutralise each other and that may be a stoichiometric effect, see below.

Oxidised nitrogen

Total oxidised nitrogen shown in Figure 2.3.3 derives mainly from combustion processes in power plants and in motor vehicles. The medians are quite similar across the country and that points to a major LRTAP -contribution from sources in Europe. For all percentiles the development with time is either absent or very small. A rather similar observation of no decrease can be made for NO_2 that is shown in the upper panels of Figure 2.3.4. The major source for NO_2 is the emission of NO from combustion processes similar to TNO_3. Emission restrictions of NO_x were internationally agreed upon in the first NO_x-protocol, which was introduced in 1988 under CLRTAP and entered into force in 1991 (CLRTAP 1996). The protocol calls for a stabilisation or reduction of emissions by 1994 to levels valid for the mid-1980s. Together with 11 other European countries Denmark signed an additional declaration according to which emissions by 1998 were to be reduced by further 30%. The protocol has advanced the process of installation of catalytic converters in petrol cars all over Europe. So emissions of NO have undoubtedly gone down, although concentrations in cities may still be several hundred ppb and the absence of a similar development for NO_2 indicates that some offsetting phenomena have affected this secondary pollutant. The culprit may be the growth in road traffic but since O_3 concentrations in background areas usually are less than 100 ppb ozone-limited oxidation of NO to NO_2 is certainly also a possibility for the lack of decreases in NO_2 concentrations. The only exception seems to be the results from Keldsnor (Figure 2.3.3) and that is confirmed by the results shown earlier in Table 2.1.6. This station, where incidentally the highest concentrations occur, is under quite pronounced influence from sources on the European continent, indicating that the NO_x -protocol has had some effect.

Ozone

Ozone behaves in a similar manner as seen in the lower panels of Figure 2.3.4. This is a consequence of the fact that ozone is closely linked to the traffic emissions and the NO_x chemistry. Much of the ozone is of remote origin that is also indicated by the similarity of levels at the two widely separated sampling sites. Note that these results are based on 1h-averages and that the upper curve in this particular instance represents the 98-percentile.

Trends over 20 years

The development with time of the monthly medians for a number of selected pollutants are shown in more detail in Figures 2.3.5 - 2.3.9 and. Each figure contains 3 curves that are, respectively, the monthly medians (jagged line), a moving 12-month average (delineating the shaded area), and a trend curve (straight line) which can be used for quantitative estimates of trends. Almost all the trends shown in the figures are negative and non-zero at a 5%-level of significance. The complete set of numerical trend values are presented in Table 2.3.1 as annual changes in percent of the grand mean median for the various components. The trends are only presented if considered significant, *i.e.* if the relative uncertainties are less than 0.5.

Major decreases

It should be noted that almost all trends are negative but that no trend can be seen for NH_3 and that total nitrate does not seem to decrease in western Denmark, in contrast to the development in the eastern part of the country. However, for the majority of the pollutants these developments have led to such considerable decreases in ambient concentrations that many of them no longer constitute an environmental problem. The most notable decreases are seen for SO_2, Pb, and As which have fallen by about 10% each year so that present levels are lower by factors 4 - 10 than they were two decades ago.

No trends for NO_2 and O_3

The long-term developments of NO_2 and O_3 are shown in Figure 2.3.9 that confirm the absence of trends pointed out earlier except for the quite considerable increase in nitrogen dioxide seen at Ulborg. This increase should, however, be considered with caution, since the measurements take place at or just above the canopy level in a forest and may be influenced by that fact. For instance, degassing of NO from the forest ground followed by rapid oxidation might influence the results. In addition, it should be noted that these time series span only 10 years or less.

Ozone

The ozone situation in Denmark has been treated extensively by Hertel and Hovmand 1991, Hovmand *et al.* 1994, Granby *et al* 1997 where it is shown that the greater part of tropospheric ozone in Danish background areas is caused by long range atmospheric transport from source areas in Mid- and Southern Europe. This remote origin is also reflected in the similarity of levels and seasonal variations of ozone concentrations at the two widely separated stations Ulborg and Frederiksborg shown in Figures 2.3.4 and 2.3.9. Although there is no discernible trend with time in the data presented here, Granby *et al* 1997 have shown that ozone concentrations in the growing season from April to September for 1985 - 1994 had a slight upward trend of 2.25 ppb yr^{-1}.

Decreasing emissions

For comparison the trends of the total emissions in EMEP are shown in the last column of Table 2.3.1 (EMEP MSC-W 1999). The trends are valid for 1980-1997 for SO_2 and for 1988-1997 for NH_3 and NO_2. These trends are also negative but do not otherwise seem to be intimately connected to the concentration trends.

Decreasing ammonium ?

The decreasing trend for particulate ammonium should perhaps be seen in the stoichiometric context discussed in connection with Figure 2.1.9. Here it was shown that the occurrence of ammonium can be seen as a result of neutralisation of atmospheric acids, particularly sulphuric acid by ammonia, and in that case the decrease of ammonium may to a large extent be the results of decreasing concentrations of sulphate.

Low pollutant levels

It can therefore be concluded that the atmospheric pollutant concentrations measured in Denmark have fallen to very low levels over the last two decades, with the notable exceptions of oxidised nitrogen and ozone.

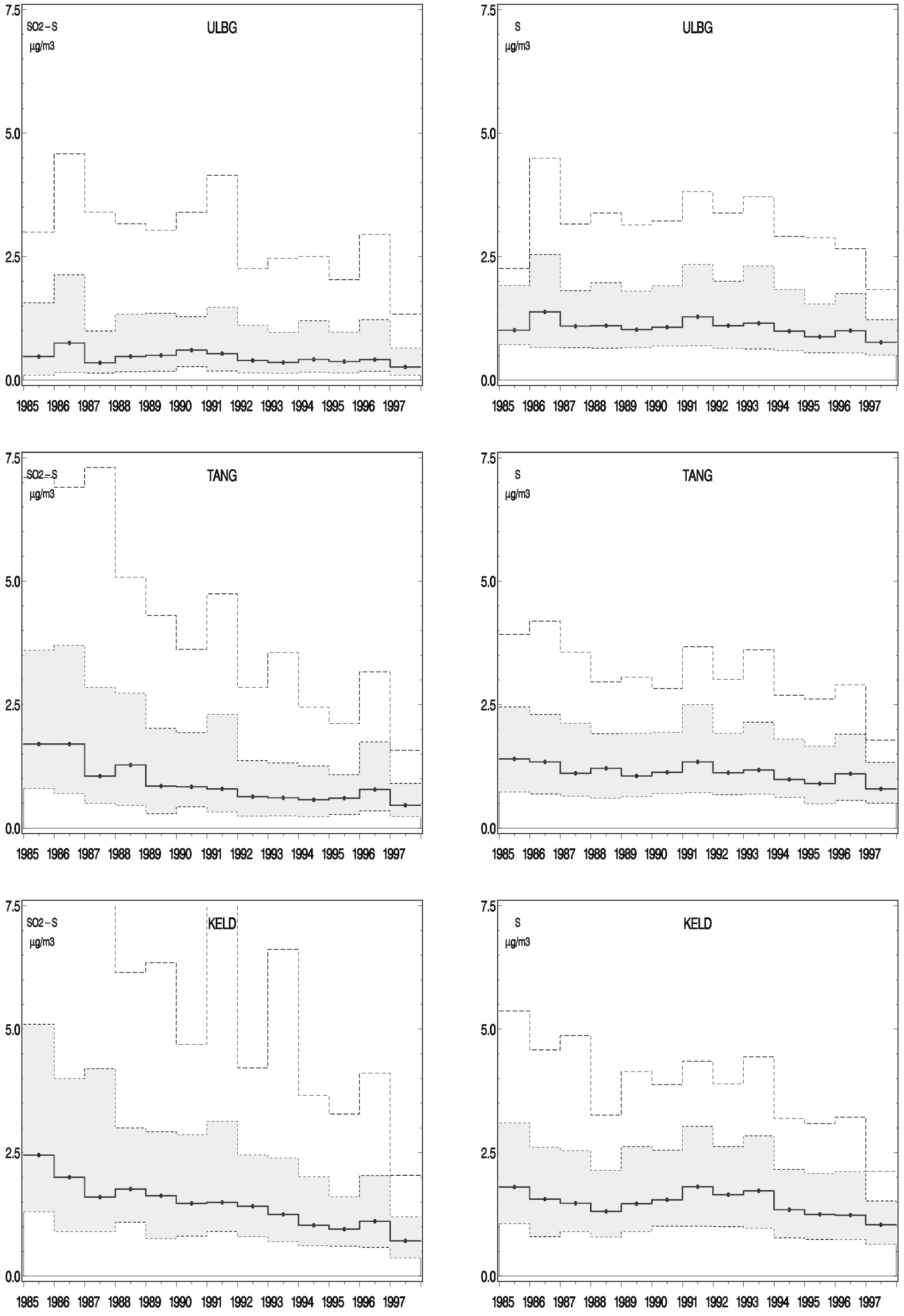


Figure 2.3.1 Annual medians, upper and lower quartiles (shaded) and the 90-percentile of 24h air concentrations of gaseous and particulate sulphur since 1985.

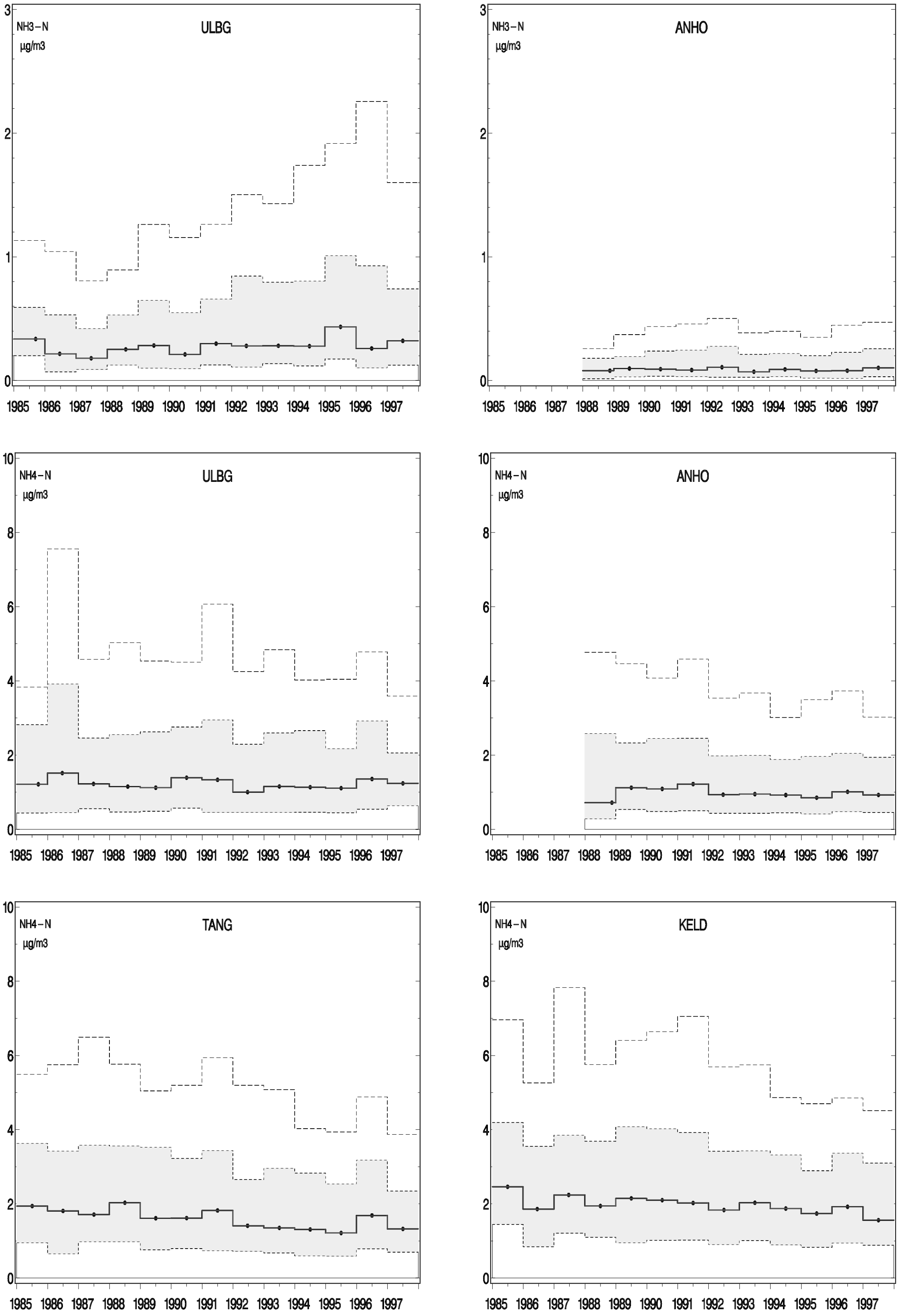


Figure 2.3.2 Annual medians, upper and lower quartiles (shaded) and the 90-percentile of 24h air concentrations reduced nitrogen compounds, gaseous NH_3 -N and particulate NH_4^+-N since 1985.

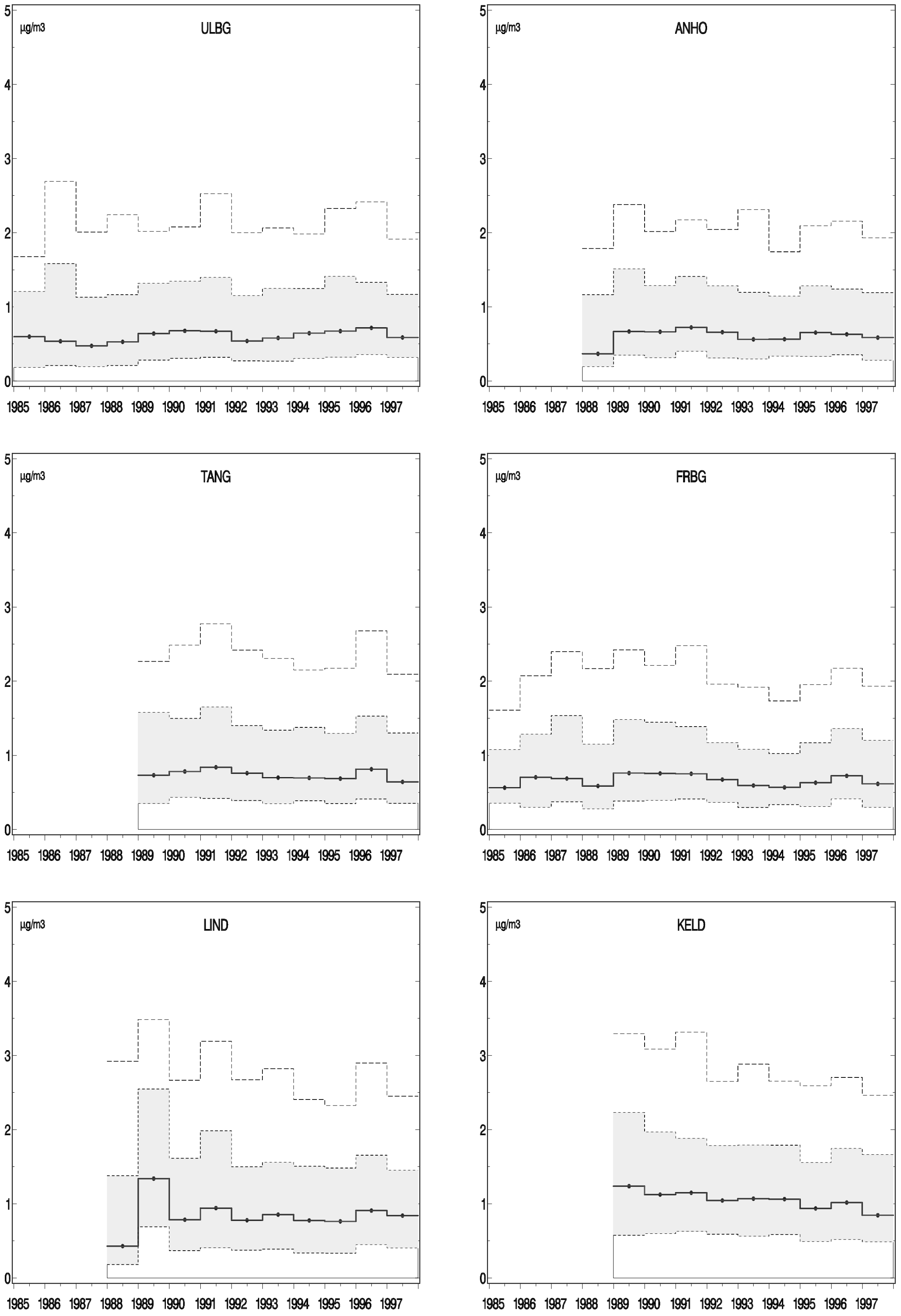


Figure 2.3.3 Annual medians, upper and lower quartiles (shaded) and the 90-percentile of 24h air concentrations of total nitrate, TNO_3 since 1985.

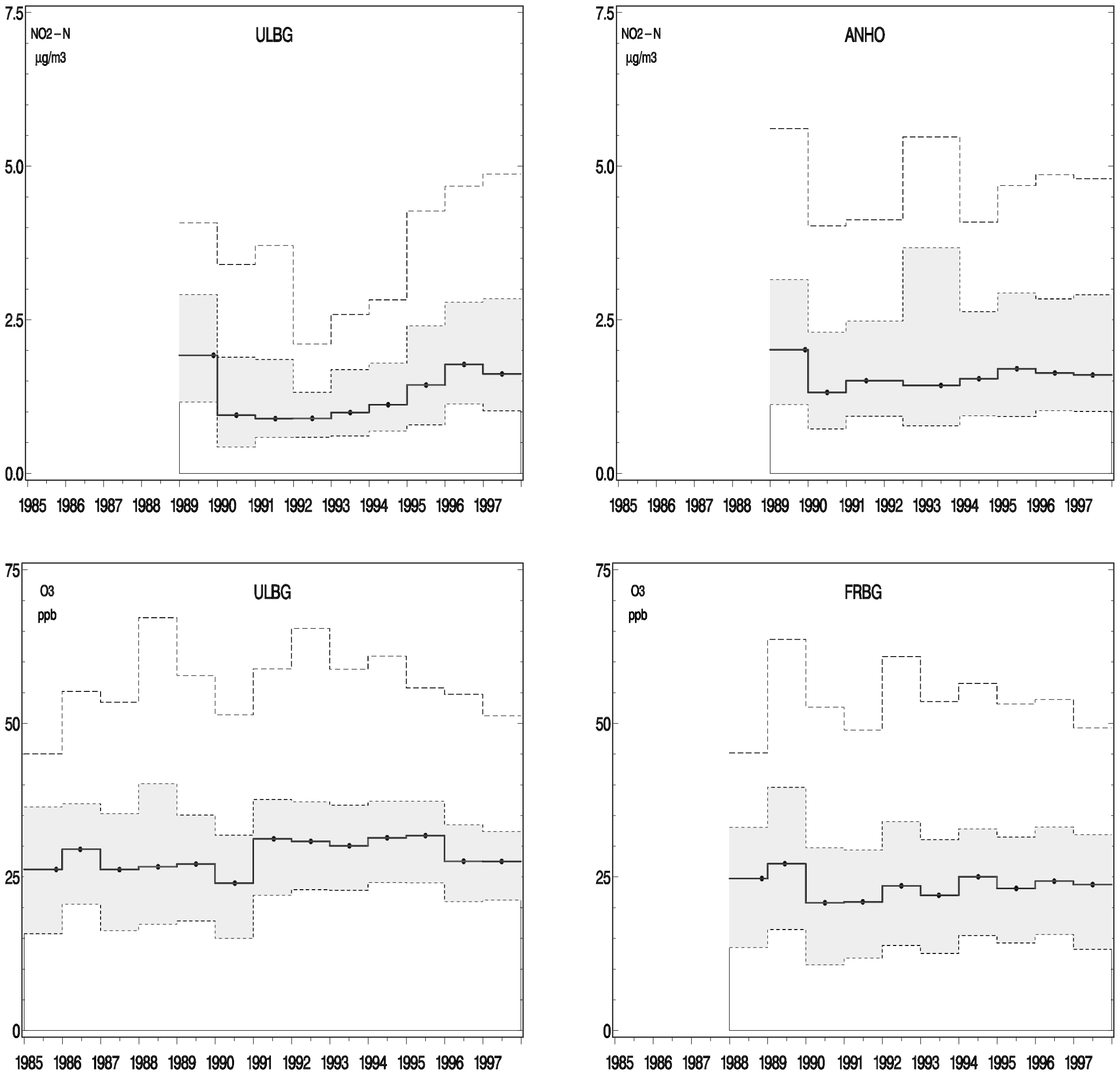


Figure 2.3.4 Annual medians and upper and lower quartiles (shaded) for 24h concentrations of NO_2 - N and 1h concentrations of O_3 since 1985. For NO_2 the uppermost curve is the 90-percentile and for Ozone it represents the 98-percentile.

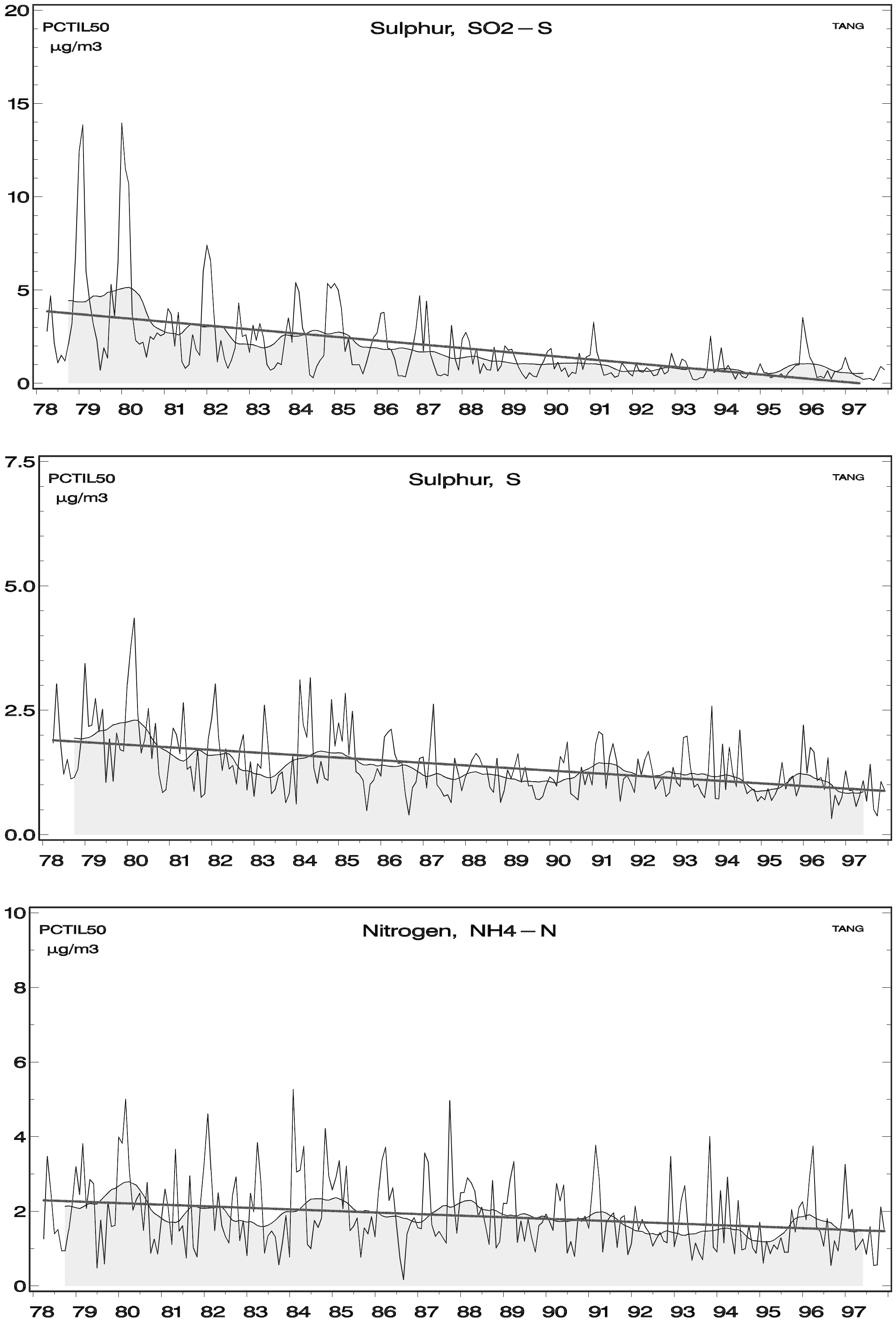


Figure 2.3.5 Trends for monthly medians of SO_2-S, particulate S, and NH_4 -N at Tange. The thin jagged line shows the monthly medians of the measured concentrations, the smooth curve delineating the shaded area represents a moving average over 12 months, and the full straight line is a linear regression line representing the long term trend. See also text.

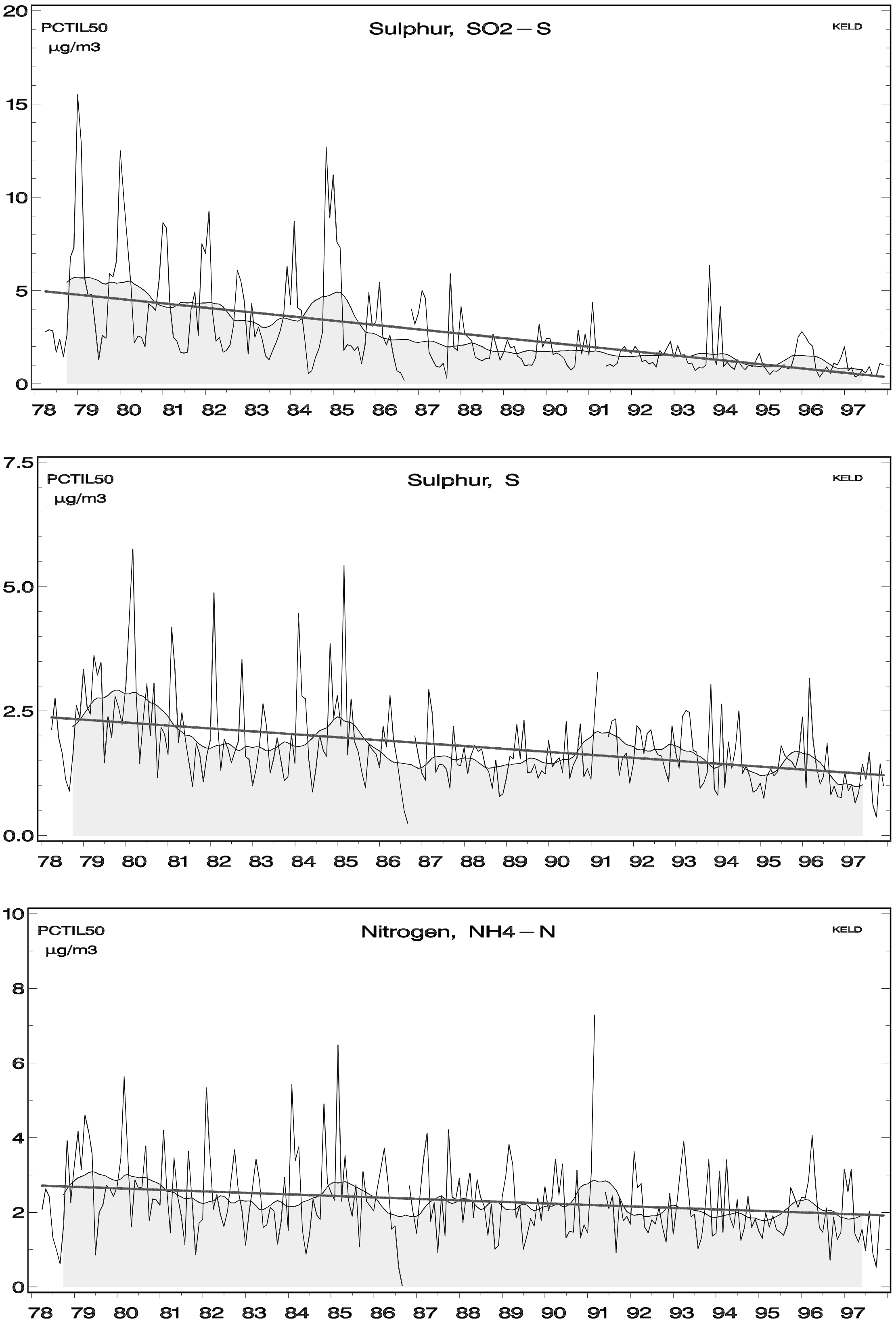
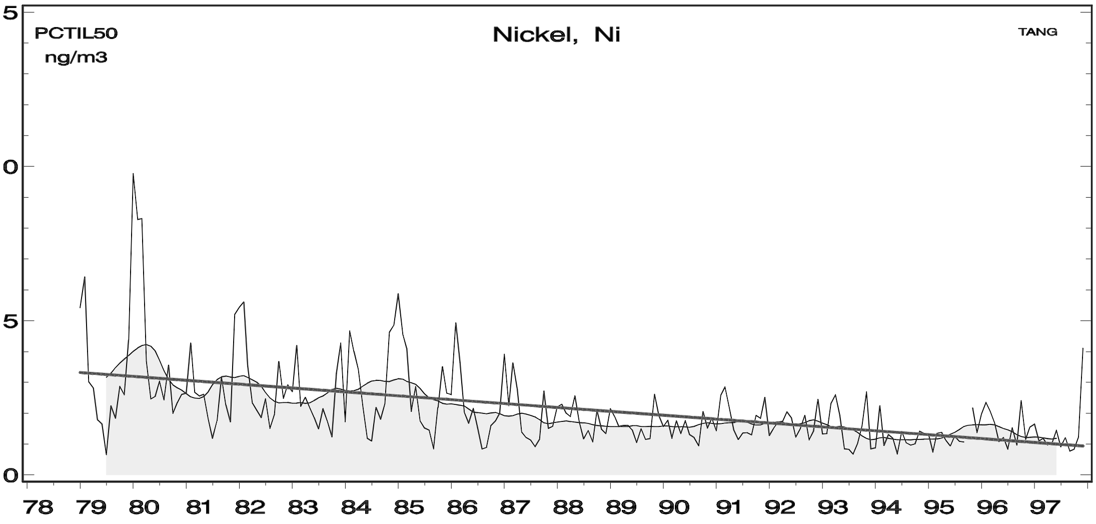
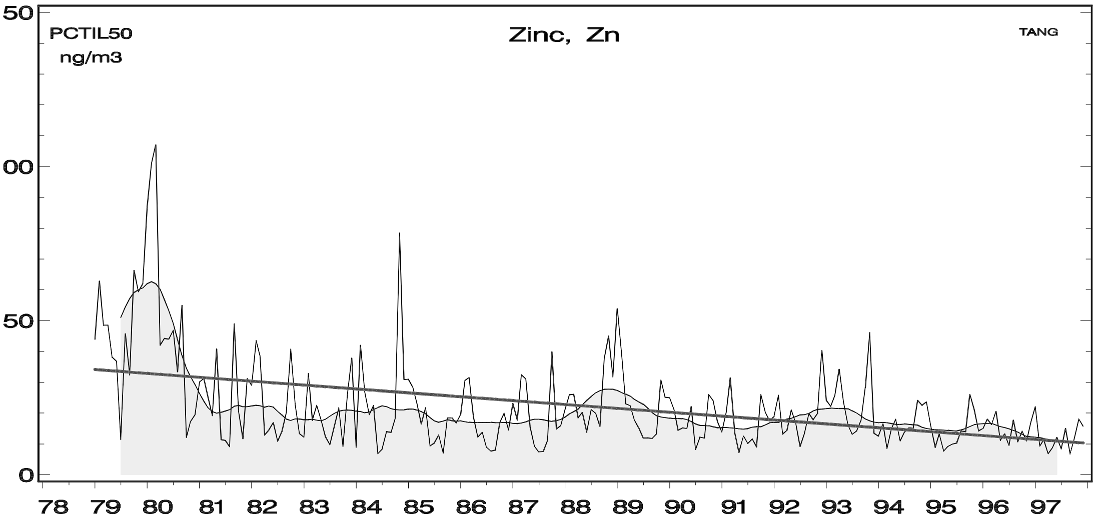


Figure 2.3.6 Trends for monthly medians of SO_2-S, particulate S, and NH_4 -N at Keldsnor. For explanation see caption of Figure 2.3.5.





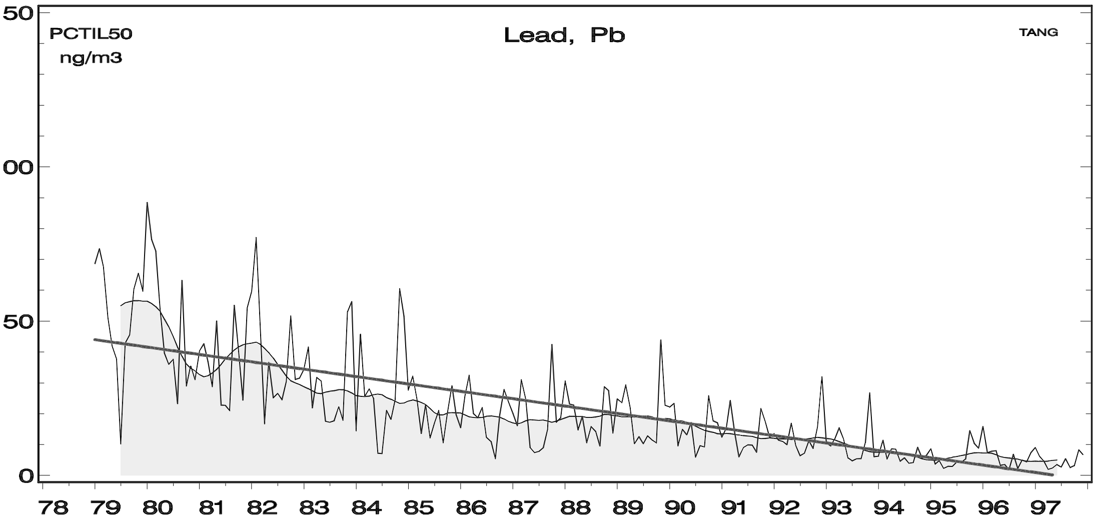


Figure 2.3.7 Trends for monthly medians of particulate Nickel, Zinc, and Lead at Tange. For explanation see caption of Figure 2.3.5.

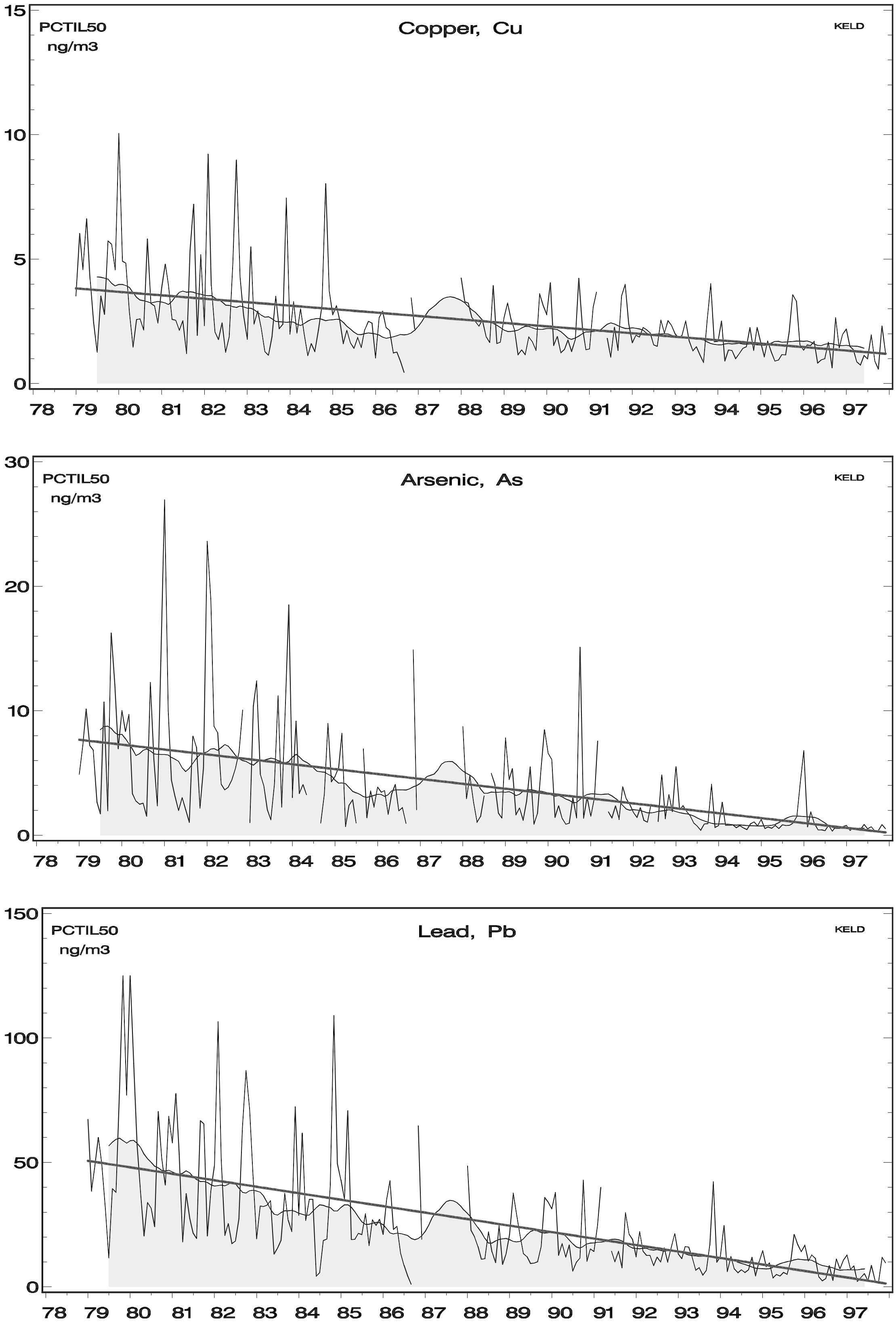


Figure 2.3.8 Trends for monthly medians of particulate Copper, Arsenic, and Lead at Keldsnor. For explanation see caption of Figure 2.3.5.

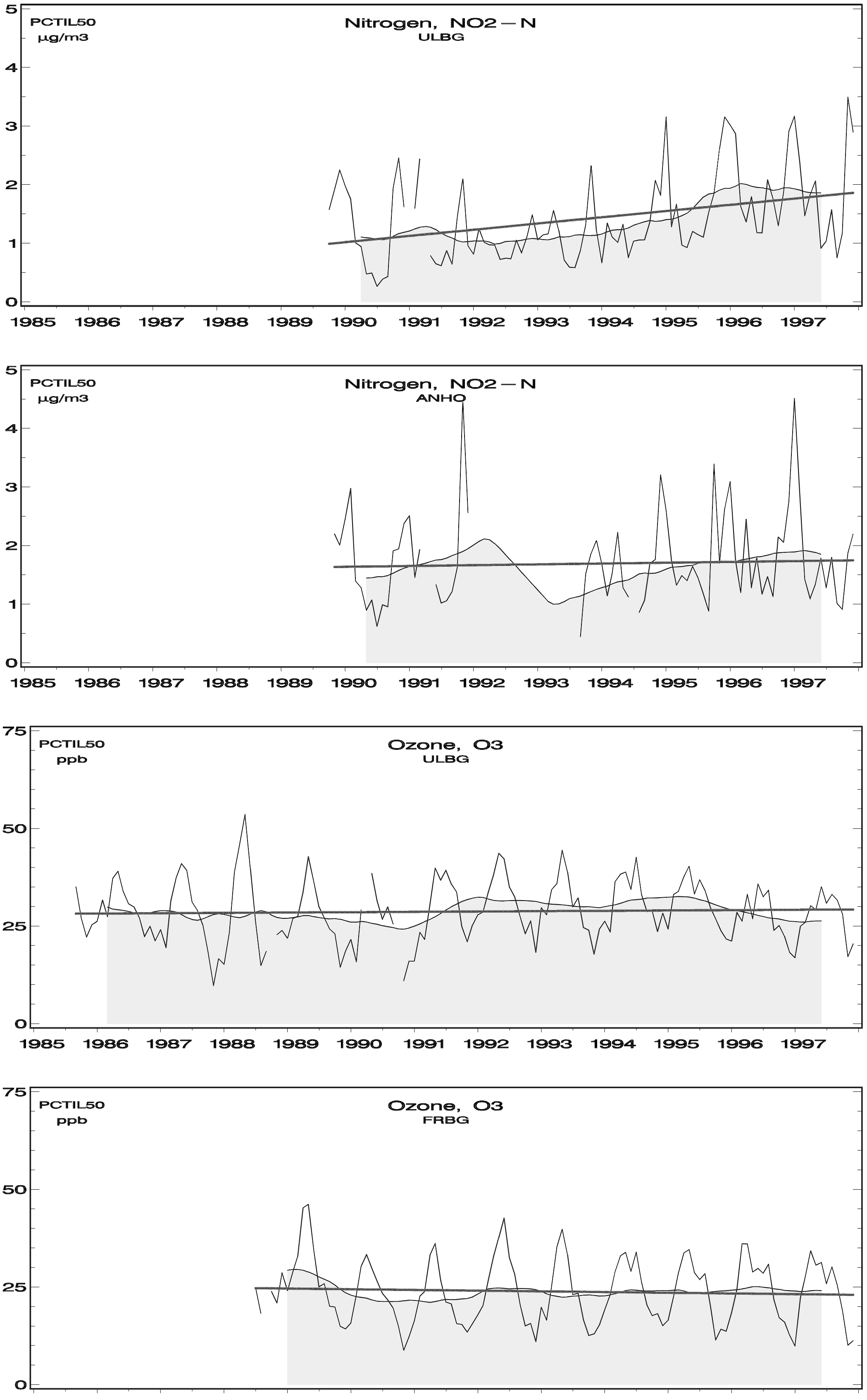


Figure 2.3.9 Trends for monthly medians of NO_2 and O_3. For explanation see caption of Figure 2.3.5.

Table 2.3.1 Significant trends of monthly medians of air concentrations. Trend values are average annual percentage changes relative to the grand means of the 50-percentiles, measured in $\mu g \cdot m^{-3}$ for the sulphur and nitrogen compounds, in $ng \cdot m^{-3}$ for the elements and in ppb for O_3.

Component	Grand-mean Median	Trend Pct per year	Std. dev. relative	Grand-mean Median	Trend Pct per year	Std. dev. relative	Trend Pct per year
	TANGE 1978 - 1997			**KELDSNOR 1978 - 1997**			**EMISSIONS in EMEP**
SO_2-S	1.87	-10.8	0.10	2.69	-8.65	0.10	-4.20
S	1.39	-3.73	0.13	1.79	-3.30	0.15	-
NH_4^+-N	1.88	-2.24	0.25	2.30	-1.75	0.29	-
NH_3-N	1.38	-	-	0.90	-	-	-2.15
TNO_3-N	0.80	-	-	1.14	-4.32	0.34	(-1.8)
Cr	1.90	-2.64	0.17	2.20	-3.75	0.14	-
Ni	2.13	-5.90	0.11	2.79	-4.19	0.13	-
Cu	2.03	-3.26	0.14	2.47	-5.61	0.11	-
Zn	22.2	-5.67	0.13	26.80	-6.23	0.13	-
As	2.62	-9.74	0.08	3.84	-10.20	0.11	-
Cd	1.66	-	-	1.95	-2.02	0.21	-
Pb	21.4	-11.2	0.06	25.50	-10.20	0.08	-
	ULBORG 1989 -1997			**ANHOLT 1989 -1997**			
NO_2-N	1.42	7.48	0.27	1.75	-	-	-1.8
	ULBORG 1985 - 1997			**FREDERIKSBORG 1985 - 1997**			
O3	28.8	-	-	23.9	-	-	-

2.4 Periodicities

Average patterns

Here we shall pursue the question of recurrent behaviour of ambient atmospheric concentrations, which was introduced previously in connection with the autocorrelation functions (section 2.1). On the basis of multiannual datasets the *average* patterns on an annual, a weekly, and a diurnal basis are calculated and described.

Average annual cycles

The average variations through the year at the two stations Tange and Keldsnor are illustrated for 3 subperiods by monthly concentration medians in Figures 2.4.1. - 2.4.3. For each subperiod the ratios of the monthly to the annual medians have been averaged to remove trends and multiplied with the total median value for that subperiod. The figures also include these subperiodic median concentrations (1).

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(1) Formally the method can be represented as $\{MD_{50}\}_P = <(MD_{50} / M_{50})_Y>_P \cdot M_{50;P}$, where MD and M represent, respectively, monthly and yearly medians of daily values for the year Y, and $< * >_P$ represents a mean value over the (sub-) period P.

Sulphur cycles

The average annual cycles for SO_2 and S are shown in Figure 2.4.1 for each of the 3 subperiods 1978-1984, 1985-1990, and 1991-1997. As can be seen the annual variations of the primary gaseous component SO_2 which in the beginning was dominated by large concentrations in the winter, caused *i.a.* by domestic/district heating, has diminished considerably as a result of regulations imposed on the emissions and the use of cleaner fuel. In contrast the particulate phase of sulphur, which is a secondary pollutant that contains a larger part of aged pollutants and which therefore has a more remote (*i.e.* foreign) origin has not changed so drastically, cf. also Figures 2.3.5-6 and Table 2.3.1. For both compounds the diminished annual variations are centred on the steadily reduced subperiodic medians.

Nitrogen cycles

The monthly medians of TNH_z and its components and of TNO_3 are shown in Figure 2.4.2 for the periods since 1985. The annual variations of TNH_z are dominated by high winter levels of NH_4^+, a secondary pollutant that may be of foreign origin and associated with sulphate or nitrate, and by high midyear levels of ammonia, NH_3 from domestic agricultural activities. As already demonstrated earlier in Figures 2.3.2, 2.3.5, 2.3.6 and Table 2.3.1 particulate ammonium has fallen somewhat whereas there is no trend for NH_3. The annual variations for TNO_3 shown in Figure 2.4.2 are dominated by high concentrations values in spring and autumn, most pronounced at Keldsnor which is more exposed to transport form the European continent. It is a secondary pollutant deriving from emissions from traffic and probably dominated by particulate nitrates of foreign origin. In the absence of national trends (Figure 2.3.3 and Table 2.3.1) only results from the most recent subperiod are shown.

Pb cycles

For lead in particles - Pb, deriving mainly from traffic emissions both at home and abroad, the average year in the early 1980s was, as shown in Figure 2.4.3, dominated by high winter levels that diminished considerably in the second half of that decennium to reach almost negligible levels in the 1990s. It is noted that the annual minimum has shifted from midsummer to September, a similar shift can be observed for SO_2 (Figure 2.4.1).

Ozone cycles

The average annual cycles of ozone concentrations are shown in Figure 2.4.4 as monthly median daytime (9-17) concentrations for the period 1991 - 1997 at Ulborg & Frederiksborg. The seasonal variation is considerable with the highest concentrations occurring in the summer period where higher temperatures and enhanced solar radiation induce photochemical production of ozone from NO_x and hydrocarbons. The concentrations are typically higher than the mean annual median from March to September with a tendency for the highest concentrations to appear in April - May with a smaller secondary maximum in August.

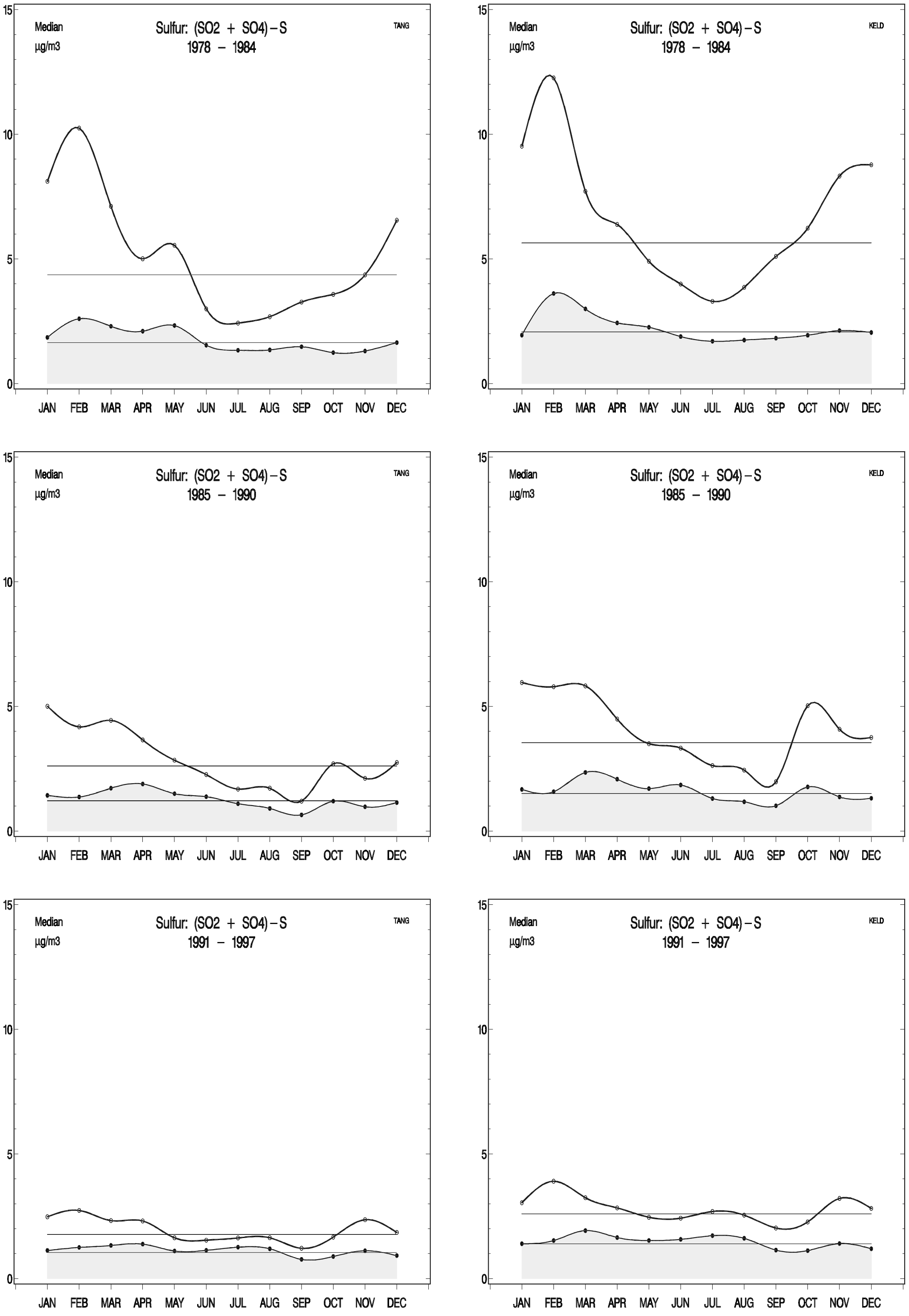

Figure 2.4.1 Average annual behaviour of the sum of monthly median concentrations of sulphur compounds in 3 subperiods. Particulate phases are shaded. Results from station Tange at left and from Keldsnor at right. The component medians of each subperiod are shown as horizontal lines.

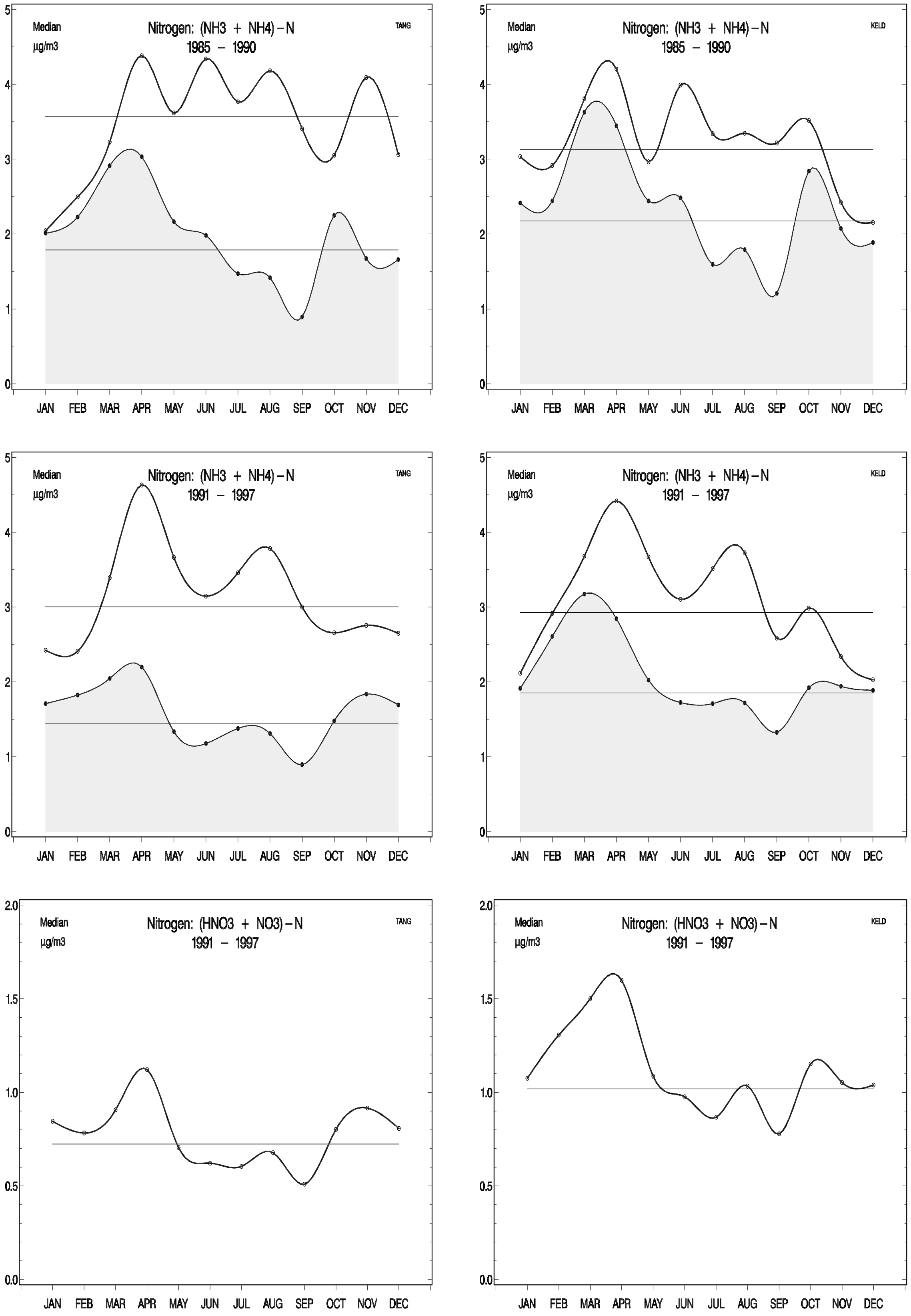

Figure 2.4.2 Average annual behaviour of monthly median concentrations of reduced (summed) and oxidised nitrogen compounds in two subperiods. Particulate phases are shaded. Results from station Tange at left and from Keldsnor at right. The component medians of each subperiod are shown as horizontal lines.

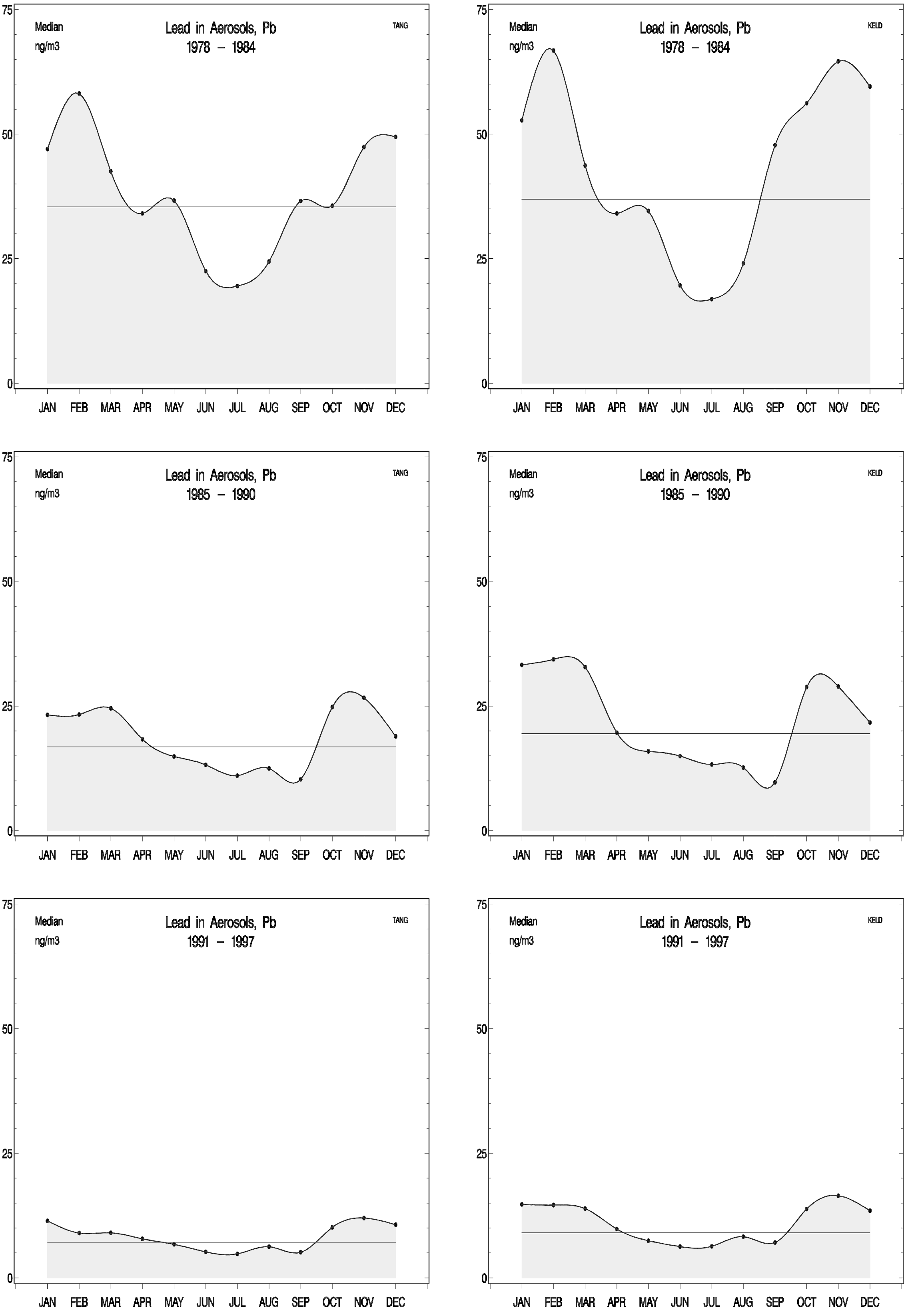

Figure 2.4.3 Average annual behaviour of monthly median concentrations of lead in aerosols in 3 subperiods. Results from station Tange at left and from Keldsnor at right. The medians of each subperiod are shown as horizontal lines.

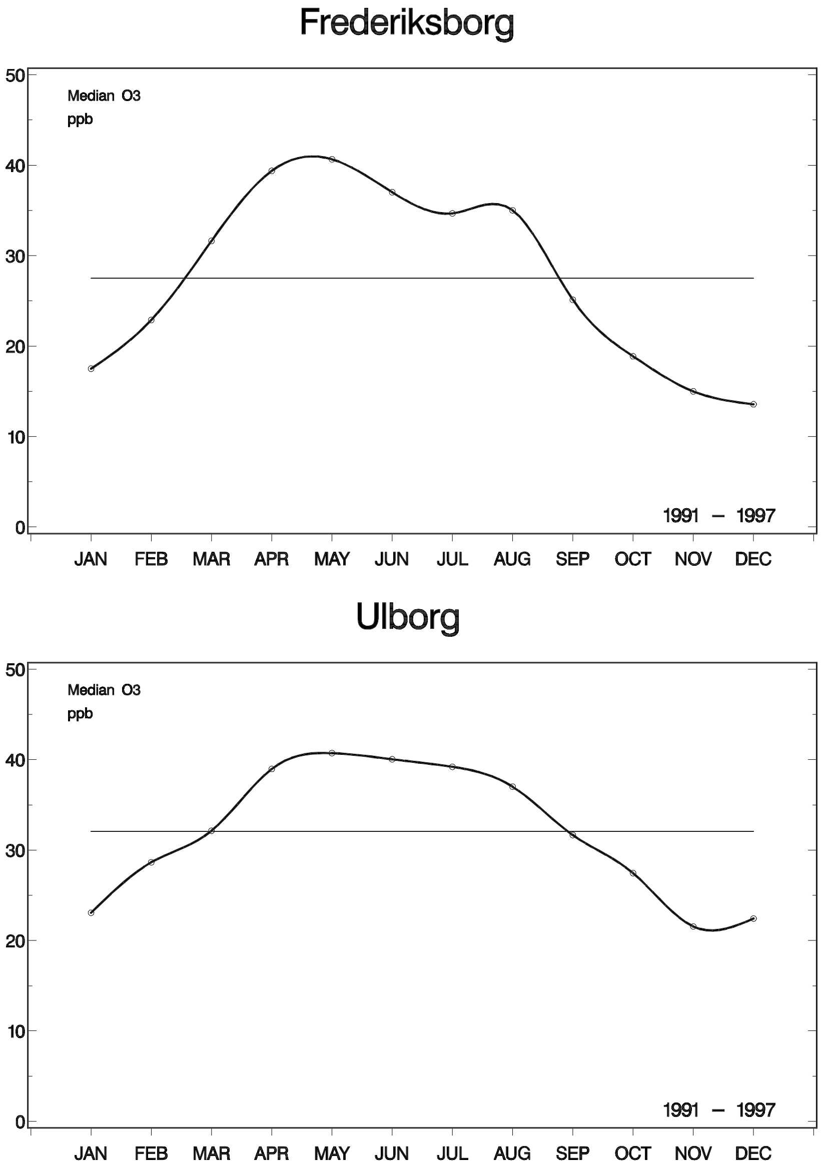

Figure 2.4.4 Average annual behaviour of monthly median daytime (9-17) concentrations of ozone 1991 - 1997 and the medians of the subperiod shown as horizontal lines.

Average weekly cycles

In this section we investigate whether the background air concentrations exhibit any systematic variation on a weekly basis. In a background area this is not *á priori* expected to be very pronounced since the whole idea of a background station is to obtain data that are not - or only minimally - influenced by activities in the local area and local community. On the other hand, the autocorrelation functions clearly revealed a memory effect extending over roughly a week. Notwithstanding, systematic weekly variations can be expected to depend on the time of the year, which has been divided into the four seasons Spring (March-May), Summer (June-August), Autumn (September - November), and Winter (December - February).

Pattern identification

To reveal any weekly pattern the calculations proceed in a manner similar to that which was used above for the average annual variations. For each year in a subperiod the ratio of the concentration median for a particular weekday to the median of all weekdays in the particular season of that year is calculated. This ratio is then averaged over all the years of the subperiod to remove trends and multiplied with the median of the whole set of seasonal concentrations in the period [2]. Finally a selection based on the standard errors of the mean ratio and of the total seasonal median is made. Only systematic cases with at least one weekday differing significantly (5%) from the average seasonal median are considered.

Spurious weekly behaviour

The investigation has been limited to the stations Tange and Keldsnor in the subperiod 1985-1990. This middle subperiod has been preferred over the most recent one where concentrations may have fallen to such low levels that any variation through the week could be purely spurious. Nevertheless, the cases with indications of a systematic weekly behaviour constitute a rather odd and incoherent selection of compounds and seasons that in several cases exhibit patterns which defy explanation. Despite the significance criterion applied it seems that the *à priori* expectation that these patterns are purely spurious is confirmed.

Patterns defy explanation

Almost all the cases with significant weekly patterns are presented in Figures 2.4.5 -2.4.6. Most of the weekly variations are related to smaller concentrations during weekends (by ~10%) where community activities are low. This is the case for Lead on summer Sundays, shown in Figure 2.4.5 but note that in winter, which has only been included for comparison, no weekdays differ significantly from the overall median. The remainder of the cases are difficult to explain in terms of recurrent community activities. It is thus not obvious why TNH_z in Figure 2.4.5 at Keldsnor is high on Fridays in the spring but low on Thursdays in the fall and why the minimum at Tange falls on Saturdays in the spring but on Sundays in the fall. Similarly, for TNO_3 at Tange, shown in Figure 2.4.6 the maximum shifts from Thursdays in the spring (why a maximum here?) to Saturdays in the winter whereas at Keldsnor the minimum in winter mysteriously occurs on Mondays.

Average daily ozone cycles

Ozone is measured on a 10 min to ½-hourly basis and it is therefore possible to see the detailed behaviour of this reactive gas. The average seasonal variations in 1991-1997 of hourly concentrations with time of day are shown in Figure 2.4.7. The calculations proceed in an analogous manner with hourly and particular hours replacing daily and particular weekday values above.

Ozone cycles by season

The diurnal variations are most pronounced in spring and summer. Peak values are generally attained in the afternoon caused by a build-up from photochemical reactions and/or influx from aloft. Ozone

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[2] Formally the method can be represented as $\{WD_{50;S}\}_P = \langle (WD_{50;S}/D_{50;S})_Y \rangle_P \cdot D_{50;S;P}$, where WD and D represent daily medians for, respectively, a particular and all weekdays. Subscripts S, Y, and P refer to season, year and (sub-)period, respectively and < * > represents a mean value.

decreases during the night because of the absence of photochemistry and the normally stable meteorological conditions that reduce the influx from above. In winter the variations with time of day are insignificant. The seasonal median concentrations are somewhat higher at Ulborg than at Frederiksborg whereas variations through the day are higher at Frederiksborg.

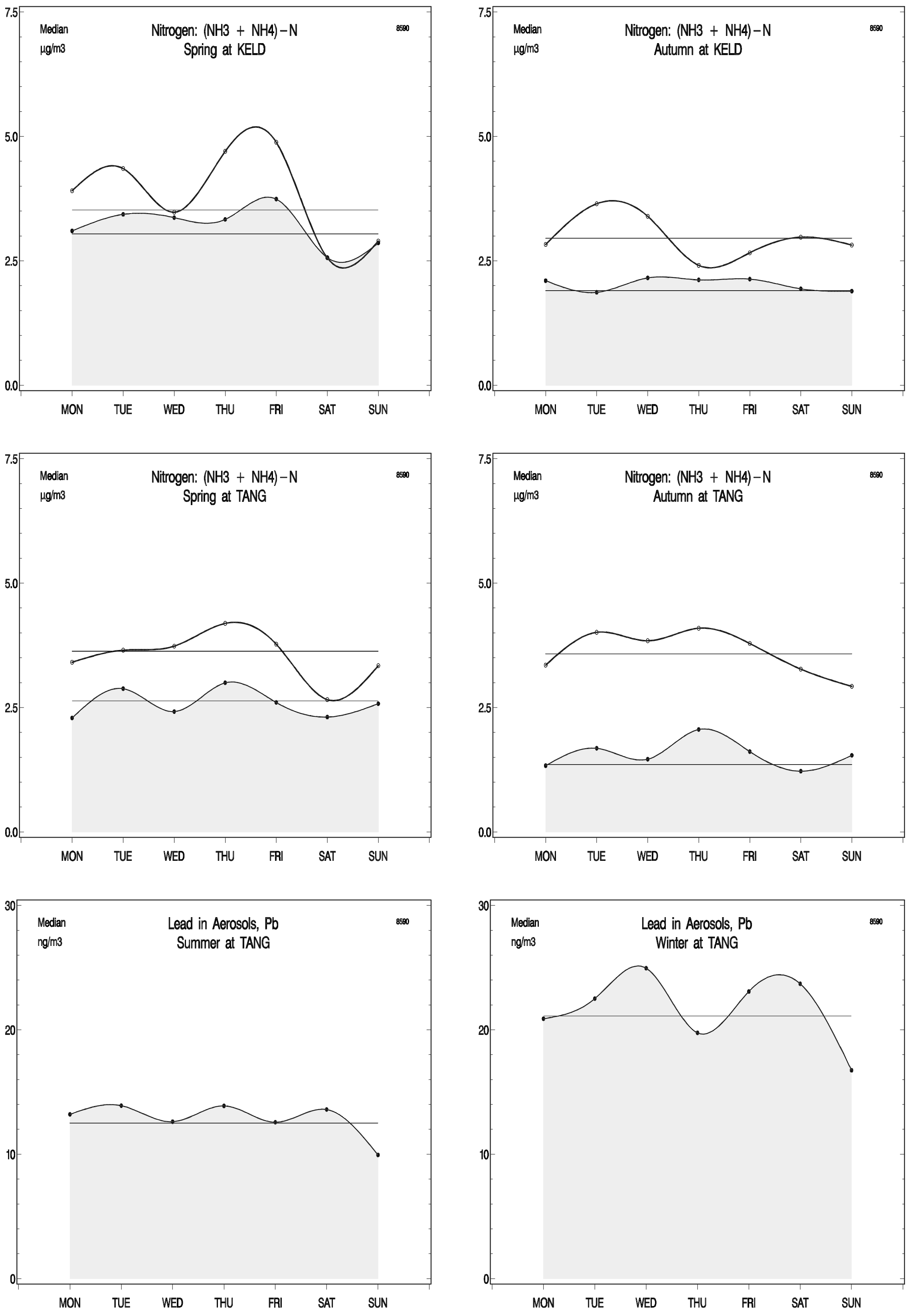

Figure 2.4.5 Apparent weekly patterns: Average seasonal medians of reduced nitrogen compounds and lead in 1985-1990. Only cases with seemingly significant weekly variations are shown. Horizontal lines indicate the seasonal median values for daily concentrations.

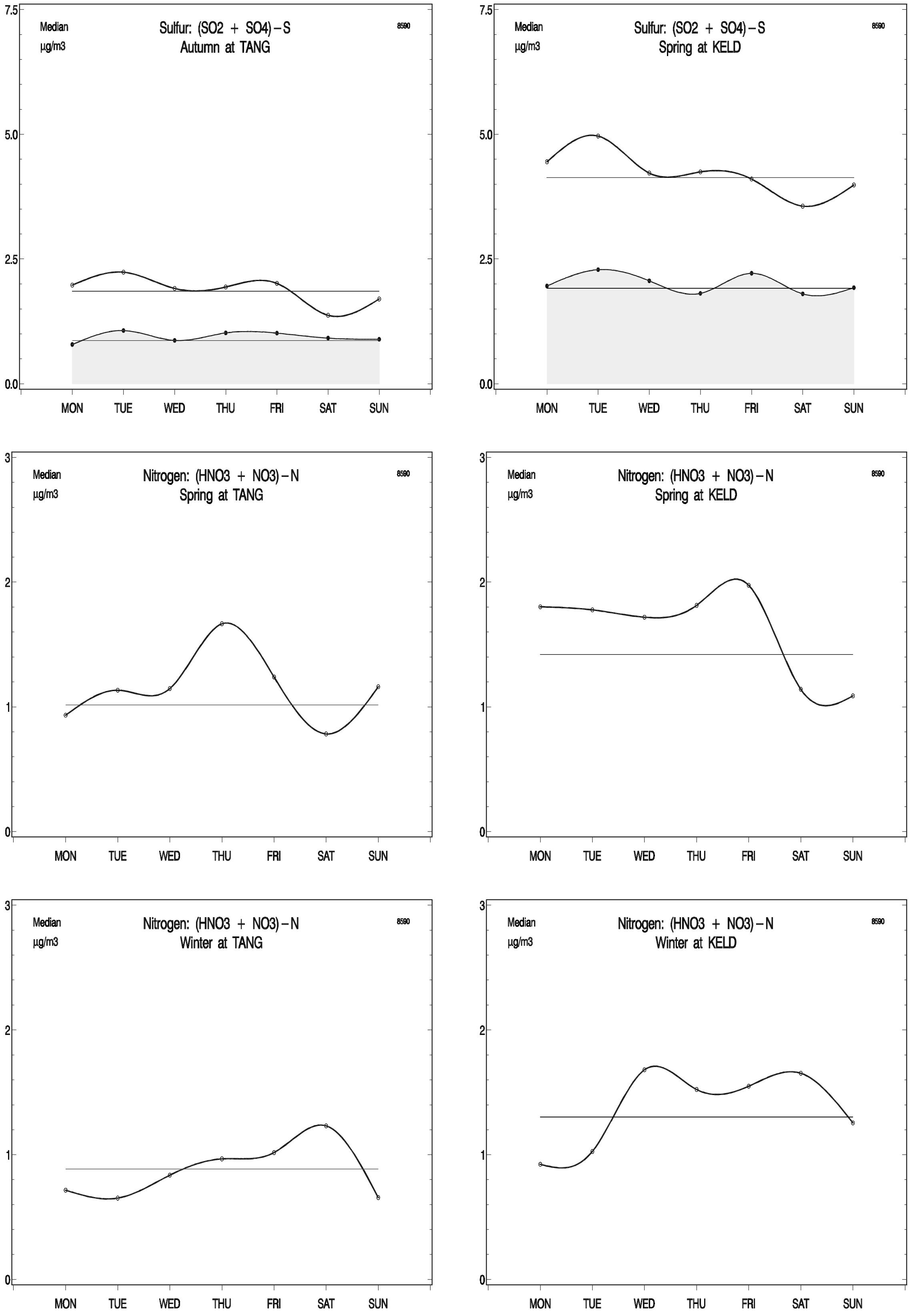

Figure 2.4.6 Apparent weekly patterns: Average seasonal medians of sulphur and oxidised nitrogen compounds in 1985-1990. Only cases with seemingly significant weekly variations are shown. Horizontal lines indicate the seasonal median values for daily concentrations.

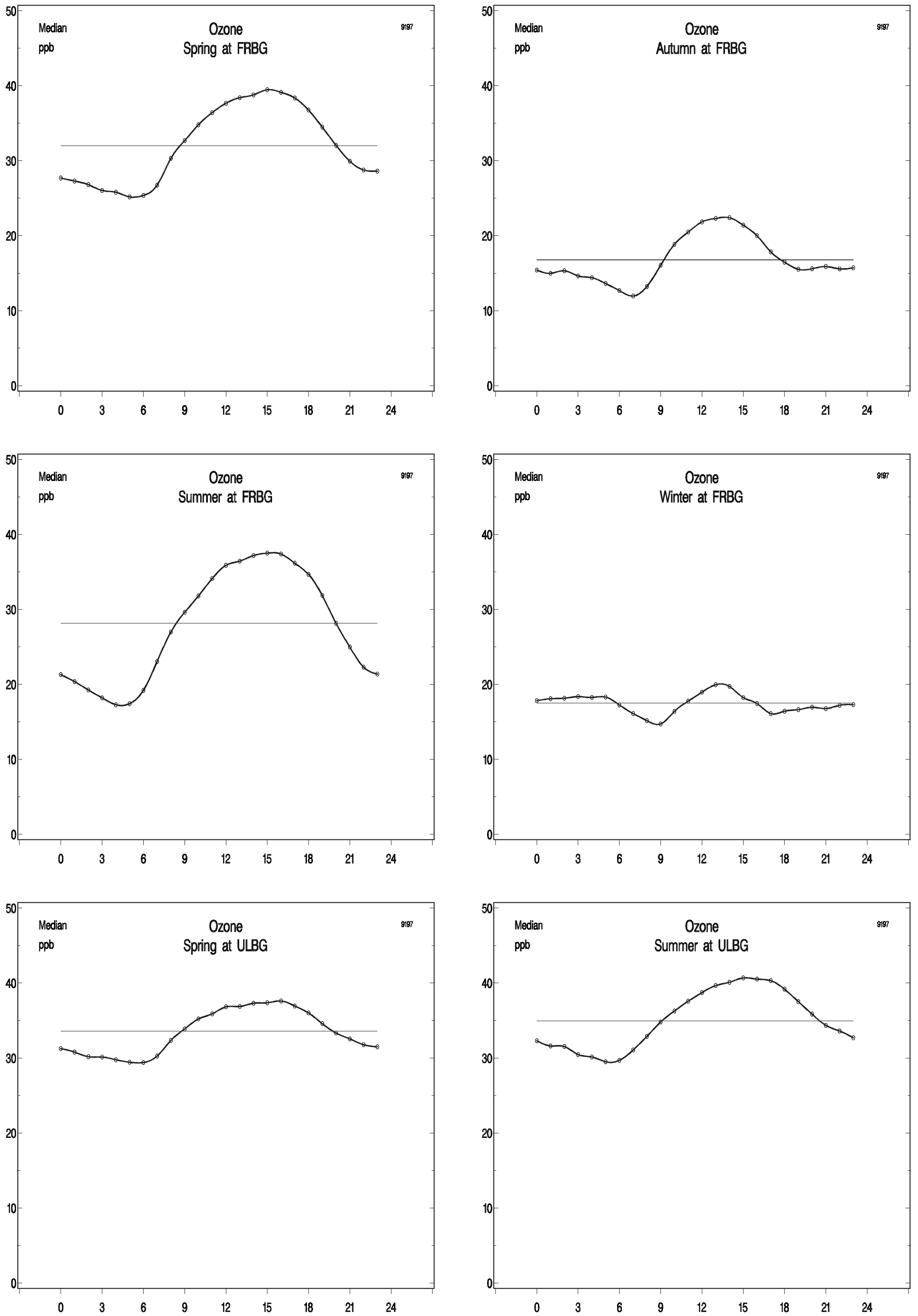

Figure 2.4.7 Daily patterns of ozone 1991 - 1997: Average seasonal medians of hourly concentrations at 2 stations with 4 seasons at one station (upper figures) and 2 seasons at the other (lower figures). Horizontal lines indicate the seasonal median values for all hours.

2.5 Episodes and Exceedances

Episodes controlled by meteorology

The atmospheric pollutant concentrations in rural areas in Denmark are generally fairly low and usually do not give rise to concern regarding possible health effects. However, in short periods and under special circumstances the concentrations do reach abnormally high levels - the so-called episodes.

The conditions that favour the occurrence of episodes usually fall in two categories:

- Stagnant weather conditions where local pollution concentrations build up because there is very little dispersion in the atmosphere.
- Stable conditions accompanied by a steady flow from the SE - SW wind sectors carrying pollutants from major source areas in Europe.

Quite often the episodes occur as a mixture of both types and the situations may be aggravated by the existence of a low inversion layer that prevents vertical dispersion.

Sulphur, nitrogen and heavy metals

Episodes that lead to a nation-wide build-up of high concentrations of atmospheric pollutants occur 3-8 times a year. In the background areas they are most often observed in midwinter and they are usually also observed in urban air. A number of severe episodes since 1985 have been observed and reported in various reports from DMU.

Well described episodes

One example is an episode in January 1985 in the coldest winter in Denmark since 1942. (Heidam 1987). It extended all the way to Frankfurt a. M. and was extensively documented in a German study (Umwelt 1986). Another episode in January - February 1987 (Heidam 1989, Palmgren *et al.* 1987) was part of a widely distributed system of mainly local episodes all over Northern Europe. Other episodes, mostly urban in character, occurred in 1989 (Palmgren *et al* 1990), in 1994, and in 1995 (Kemp *et al* 1996a, 1996b).

Here we present data on two episodes not mentioned above.

Early episode

The first one is shown in Figure 2.5.1. It occurred early in the history of the BOP-programme in February- March 1979 and was observed at both the existing stations Keldsnor and Tange. In this episode 20- 30 % of the SO2, $SO_4^=$, and NH_4^+ concentrations were higher than the 95-percentiles for the 7-year subperiod 1978-1984 and 10-15 % were higher than the corresponding 99-percentiles. It should be noted that this subperiod exhibits the highest percentiles compared to later subperiods.

Recent episode

The second episode is illustrated in Figures 2.5.2 - 2.5.3. It occurred in November 1993 and was observed at all 6 main stations. In all the cases shown the concentrations exceeded the nation-wide 99-percentiles for the period 1991-1997.

Decreasing episode frequency and severity

The frequency and severity of episodes have been decreasing over the years in step with the steadily diminishing concentrations. This is illustrated in Figures 2.5.4 - 5 where the occurrence of all episodes at Tange and Keldsnor of sulphur compounds, ammonium, lead and zinc is shown. Episodes have been selected among the upper 5% of data that span at least 4 consecutive days and contain at most two consecutive non-episodic results. The frequency of episodes have fallen from about 7 per year in the early 1980s to about 3 per year in the period 1991-1997. The severities of the episodes, defined as the sum of concentrations over the episode, have as can be seen also fallen considerably.

Ozone

For ozone high concentration episodes usually occur in the summer period and may be aggravated by constant sunshine and stagnant weather or constant atmospheric transport from Central Europe. In these and other instances critical levels may be exceeded at the Danish stations. As can be seen from the tables below that happens quite often.

Exceedance of critical levels

The annual number of exceedances of the Danish critical levels for vegetation, 1 hour maximum of 200 $\mu g/m^3$ (100 ppb) and 24 hour mean of 65 $\mu g/m^3$ (32.5 ppb), are shown in Table 2.5.1 for each year since 1985. The limit on the daily mean value is being transgressed two - six times a week as an average for the summer season where exceedances usually occur. In Denmark this is mainly due to LRTAP of ozone from the south. These high ozone levels may cause substantial losses of crop yield but unfortunately it is quite a normal situation at most European ozone stations. However, the limit on the hourly values is only rarely exceeded, it happened only 16 times in the 13 years shown in the table.

Exceedance in AOT40

The accumulated AOT40 values of UN_ECE are listed in table 2.5.2 and it can be seen that the critical levels for crops of 3000 ppb·hours for May-July and for trees of 10 000 ppb·hours for April-October were exceeded in almost all years. The only real exception occurred at Ulborg in 1990 since the other two cases at Frederiksborg in 1988 and Ulborg in 1985 were probably caused by measurements being started fairly late in those years.

Uncertain consequences

It is estimated that the exceedances of the AOT40 limit value lead to crop losses that amount to several hundred million Danish kroner each year (Dimov 1999). However, in this context it should be mentioned that the estimated AOT40 values for Denmark could be very uncertain. This is because Denmark is located in a transition zone where ozone concentrations often are very close to the limit value of 40 ppb (see Figures 2.4.4 and 2.4.7). The number of hours that contribute to AOT40 is therefore highly dependent on the meteorological conditions.

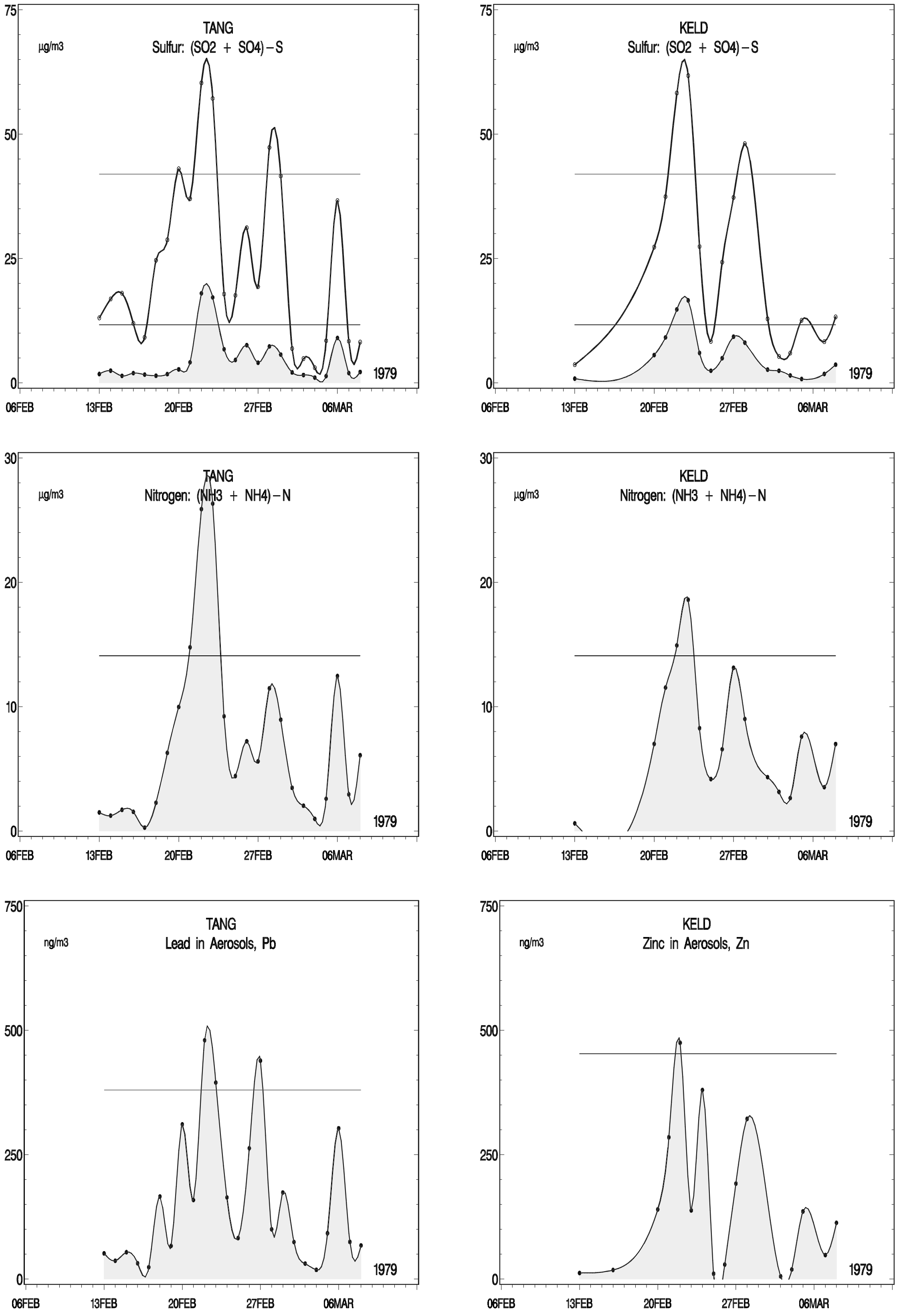

Figure 2.5.1 Episode in February 1979 at Tange and Keldsnor. Concentrations of total and particulate (shaded) phase on a day-by-day basis. Horizontal lines are the nation-wide 99-percentiles for particulate and total phases in 1978-1984.

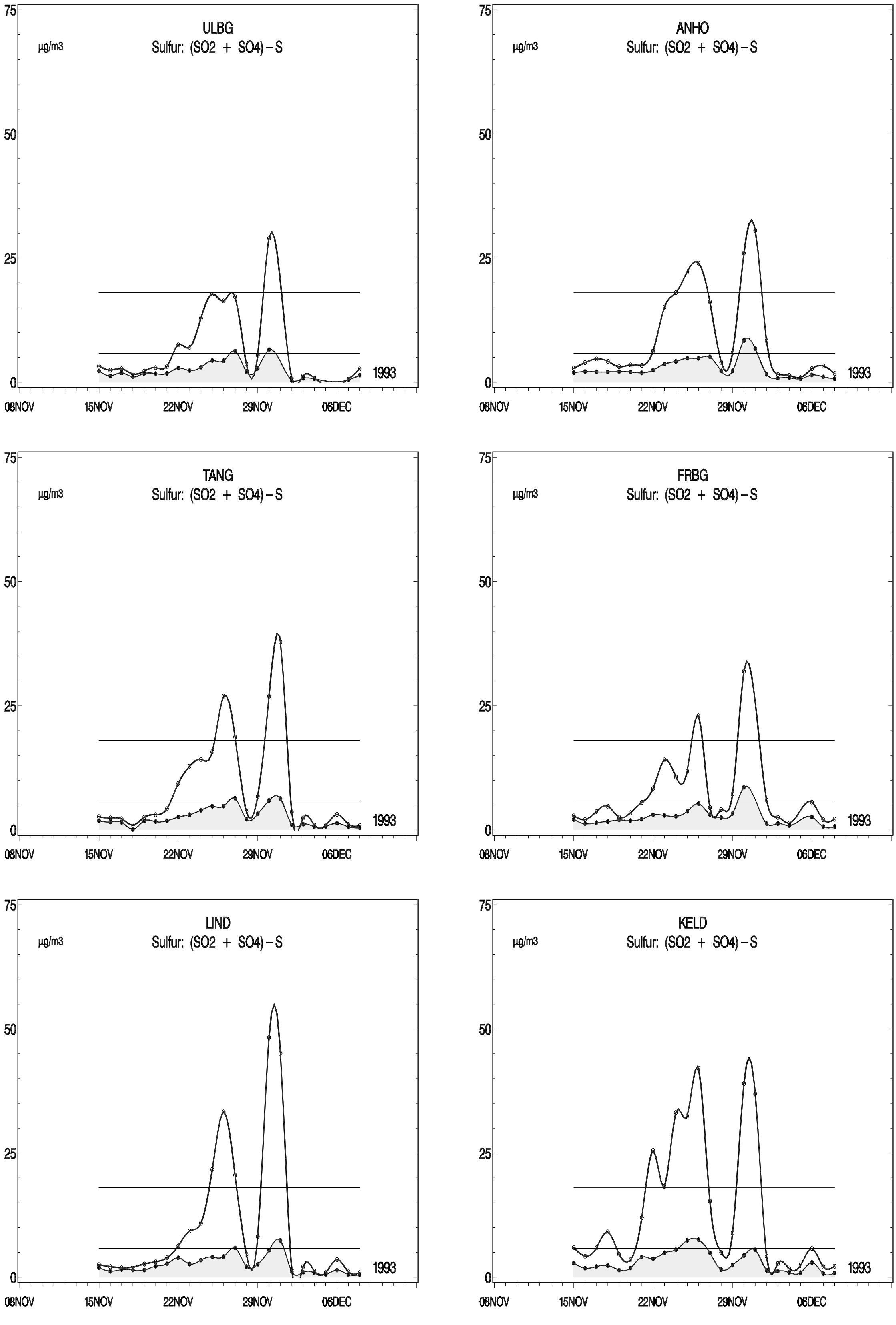

Figure 2.5.2 Episode in November 1993 with enhanced sulphur concentrations at all stations. Concentrations of total and particulate (shaded) phase on a day-by-day basis. Horizontal lines are the nation-wide 99-percentiles for particulate and total phases in 1978-1984.

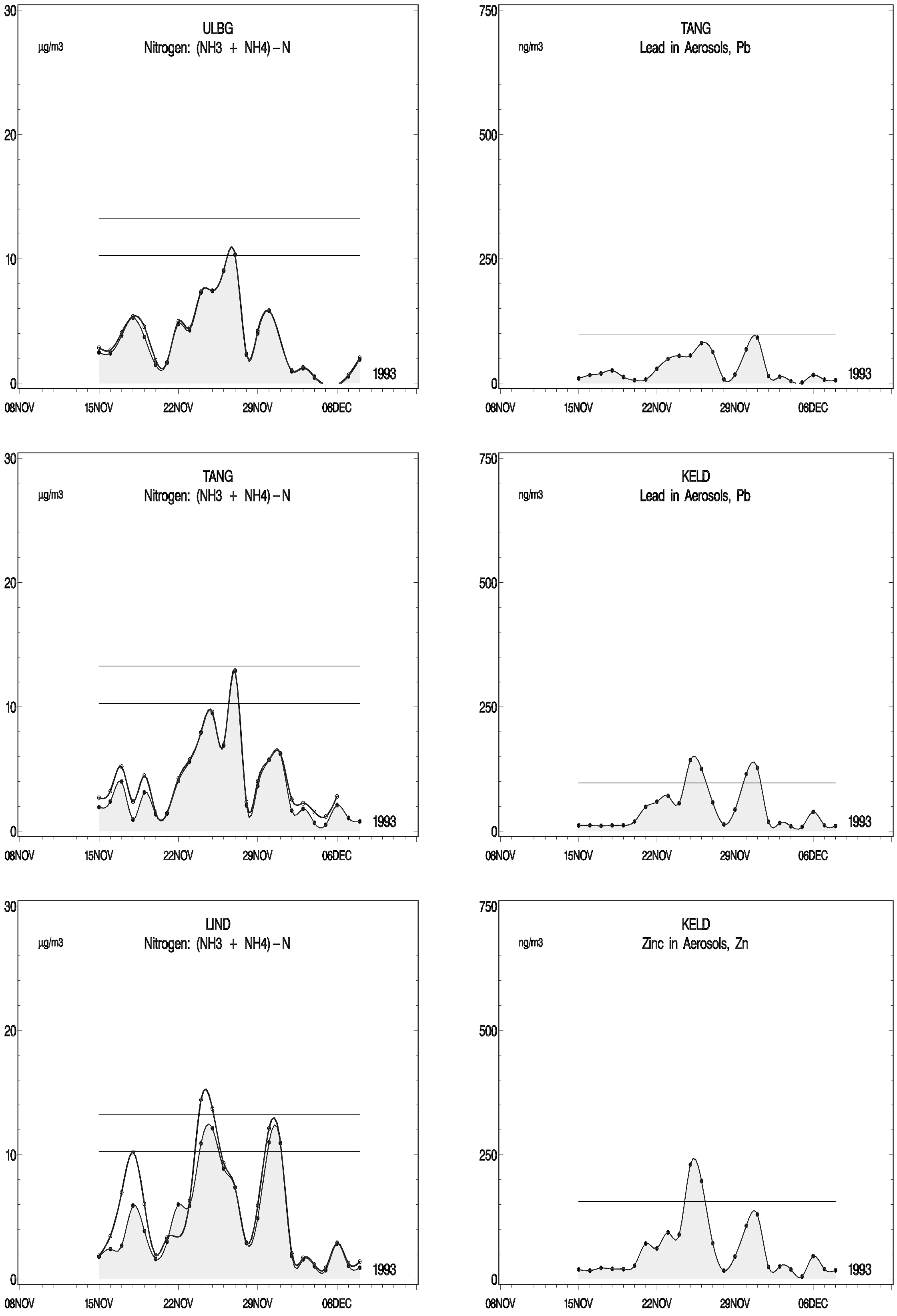

Figure 2.5.3 Episode in November 1993 with enhanced concentrations of reduced nitrogen, lead and zinc. Concentrations of total and particulate (shaded) phase on a day-by-day basis. Horizontal lines are the nation-wide 99-percentiles for particulate and total phases in 1978-1984.

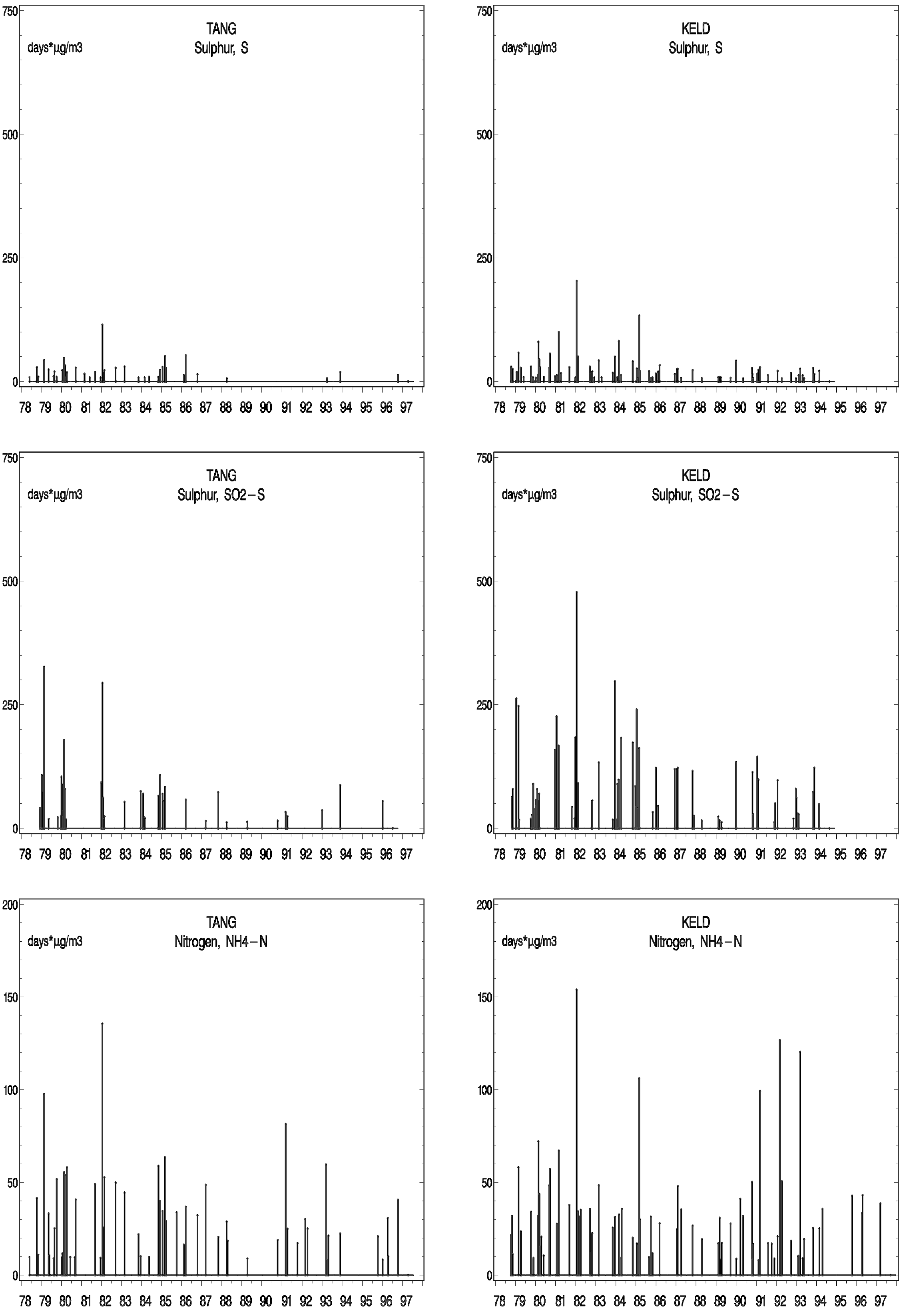

Figure 2.5.4 Episodes of sulphur compounds and ammonium at Tange and Keldsnor, 1978 - 1997. The episode severity is shown vertically as the sum of episode concentrations.

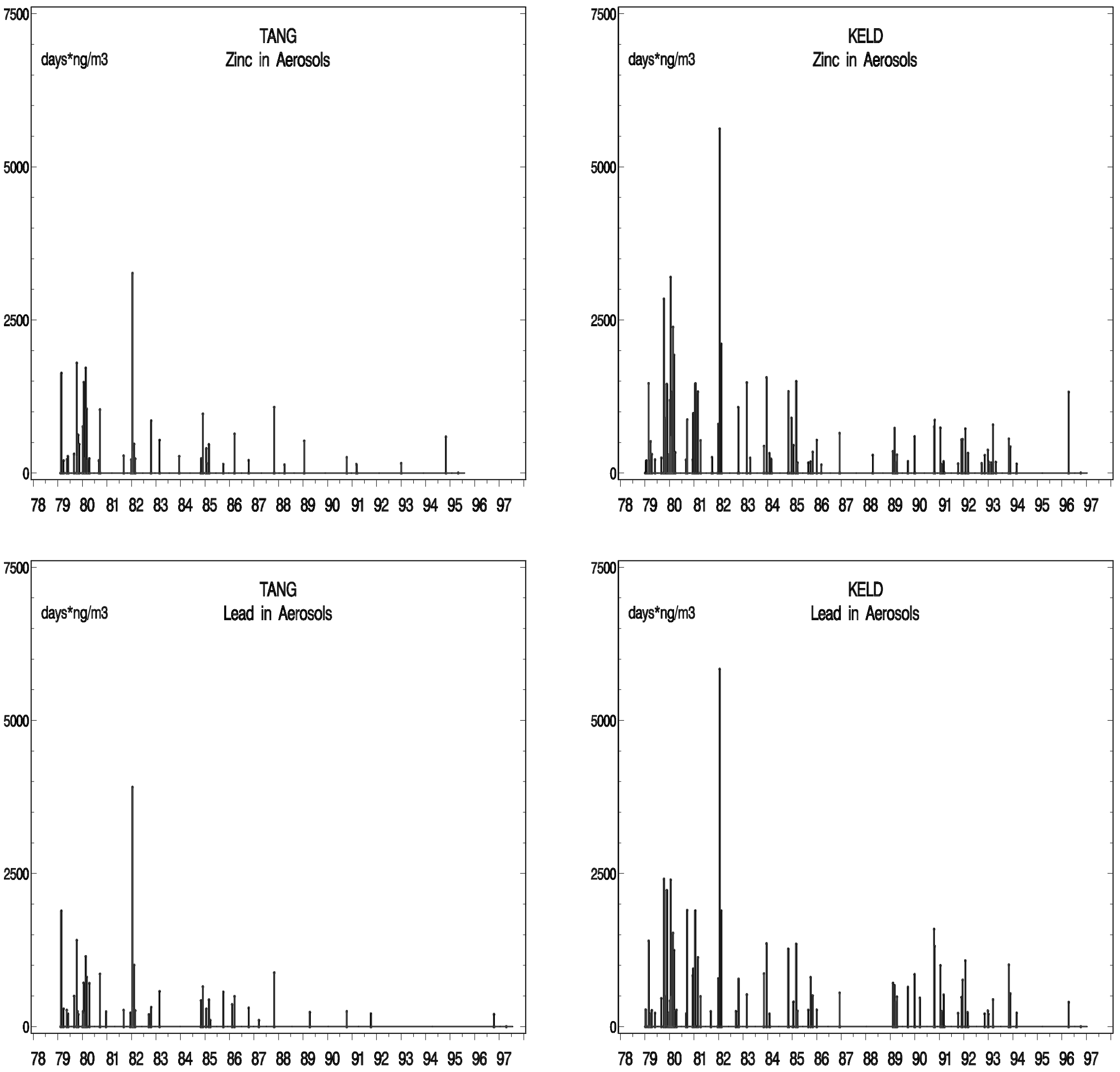

Figure 2.5.5 Episodes of lead and zinc at Tange and Keldsnor, 1978 - 1997. The episode severity is shown vertically as the sum of episode concentrations.

Table 2.5.1 Annual number of exceedances of ozone limits (see Table 1.5.1).

Site	ppb	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997
FRBG	32.5				14	100	28	40	94	60	70	60	85	66
	100					6			3					
KELD	32.5											131	141	200
	100													
ULBG	32.5	22	102	96	99	99	40	148	149	143	156	172	97	65
	100						2		5					

Table 2.5.2 AOT40: Annually accumulated daytime (9-16) ozone concentrations above 40 ppb in the growth seasons (see Table 1.5.2). Units: ppm·hours.

Site	ppm.hr	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997
FRBG	3					17.7	7.4	9.5	24.2	11.9	14.4	9.3	7.1	8.0
	10				0.3	29.5	14.2	16.2	31.6	18.0	21.9	18.0	17.9	17.7
KELD	3											9.4	7.8	19.6
	10											15.9	16.7	37.5
ULBG	3		13.4	13.1	19.9	19.5	5.7	16.5	21.4	16.6	16.1	16.2	8.7	5.4
	10	1.8	20.0	22.1	28.7	26.7	9.2	26.1	30.6	25.2	27.1	27.1	17.6	10.7

3 Precipitation Quality

3.1 Overview and statistics

Pollutant concentrations

The pollutants measured in precipitation are sulphur in sulphate $SO_4^{=}$ - S, nitrogen in ammonium NH_4^{+}-N and in nitrate, $NO3^{-}$ -N, acidity pH, the minor constituents K^{+} and Ca^{++}, the marine tracers Na^{+}, Cl^{-}, Mg^{++}, and the precipitation amount, mm. From these data results on non-seasalt sulphur NSS_S of anthropogenic origin, total nitrogen TOT_N, and H^{+} concentrations are calculated and included in the analysis. Precipitation is, as detailed in Tables 1.2.2 and 1.3.1, collected in both wet-only samplers, normally on a 24-h basis, and in bulk samplers on a ½-monthly basis. The bulk concentrations reported are as noted earlier calculated as precipitation weighted averages over several co-located samplers and they contain a certain amount of dry deposited material.

One year of data

Examples of these data are presented in Figures 3.1.1 and 3.1.2, which show concentrations for one year (1996) for daily wet-only and ½-monthly bulk sampling, respectively. The lower panel in Figure 3.1.1 shows that anthropogenic NSS_S at Keldsnor constitutes a major fraction of the sulphate in precipitation. Figure. 3.1.2 shows that the concentrations of marine tracers are high at Husby on the West Coast but moderate to low at the Baltic station at Pedersker. It also shows that the seasonal pattern of total nitrogen at Keldsnor differs from that at the island site Anholt, probably because of an agricultural impact.

Statistical overview

To give a general overview of the levels in precipitation in background areas in Denmark aggregated results are presented in Tables 3.1.1 and 3.1.2 for all measured and calculated components at all seven bulk stations of Table 1.2.2 in the recent subperiod 1991 - 1997. The tables contain precipitation weighted mean values, standard deviations, maximum values, and number of results. In both tables the measuring sites are arranged with the four northern stations above southern ones and otherwise listed in the order west to east.

Major ions

The results for the major ions of sulphur, nitrogen and acidity are shown in Table 3.1.1 together with the calculated components NSS_S and Tot_N. It seems to be a general characteristic that NSS_S constitute a major part of sulphate in precipitation and that the nitrogen components, NO_3^{-} and NH_4^{+} contribute about equal amounts to the total nitrogen content in precipitation.

Trace species

Table 3.1.2 shows results for the minor, soluble ions, including the marine tracers Na^{+}, Mg^{++}, and Cl^{-} as well as K^{+}, a nutrient tracer, and Ca^{++}. The latter two have their highest concentrations at Keldsnor, which is under some agricultural influence. All the marine tracers Na^{+}, Mg^{++}, and Cl^{-} have as expected the highest abundance at the marine stations Husby, Keldsnor, and Anholt

Statistical distributions

Several of the pollutant concentrations in precipitation are to a good approximation distributed log-normally as illustrated in Figures 3.1.3 and 3.1.4 for some of the compounds. These plots are similarly constructed as for the airborne pollutants, the circles show the 16-, 50-, and 84-percentiles, and the line shows the ideal log-normal distribution with indications of the geometric mean and standard deviations. Note that the vertical axes describe the distribution in two different ways and that the horizontal concentration axes are logarithmic.

Log-normal distributions

The figures show the distribution of results over the most recent subperiod 1991 - 1997, in figure 3.1.3 for the two 24-h wet-only stations and in Figure 3.1.4 for some of the components collected in bulk samplers. Most of the wet-only concentrations show a reasonable agreement with the log-normal line, especially for the central part of the distributions, but it is clear that the concentrations of hydrogen ions are not log-normally distributed, *i.e.* pH is not normally distributed. For the bulk concentrations in Figure 3.1.4 a majority of the compounds are not log-normally distributed in the strict sense, but in most cases the fits for the central parts are reasonably good.

Concentrations and accumulated precipitation

The various pollutants are scavenged from the atmosphere during the precipitation events. These processes are quite effective so that even small rainfalls may have a considerable cleaning effect on the atmosphere. For extended precipitation events this mechanism usually leads to higher concentrations in the beginning and quite soon the concentrations start to decrease as a consequence of dilution by the accumulating precipitation in the sampler. The concentrations in rain therefore tend to decrease with the amount of precipitation. This is illustrated in Figure 3.1.5 where daily concentrations of NO_3^--N and $SO_4^=$-S are plotted against the amount of precipitation collected by the wet-only samplers at Tange and Keldsnor.

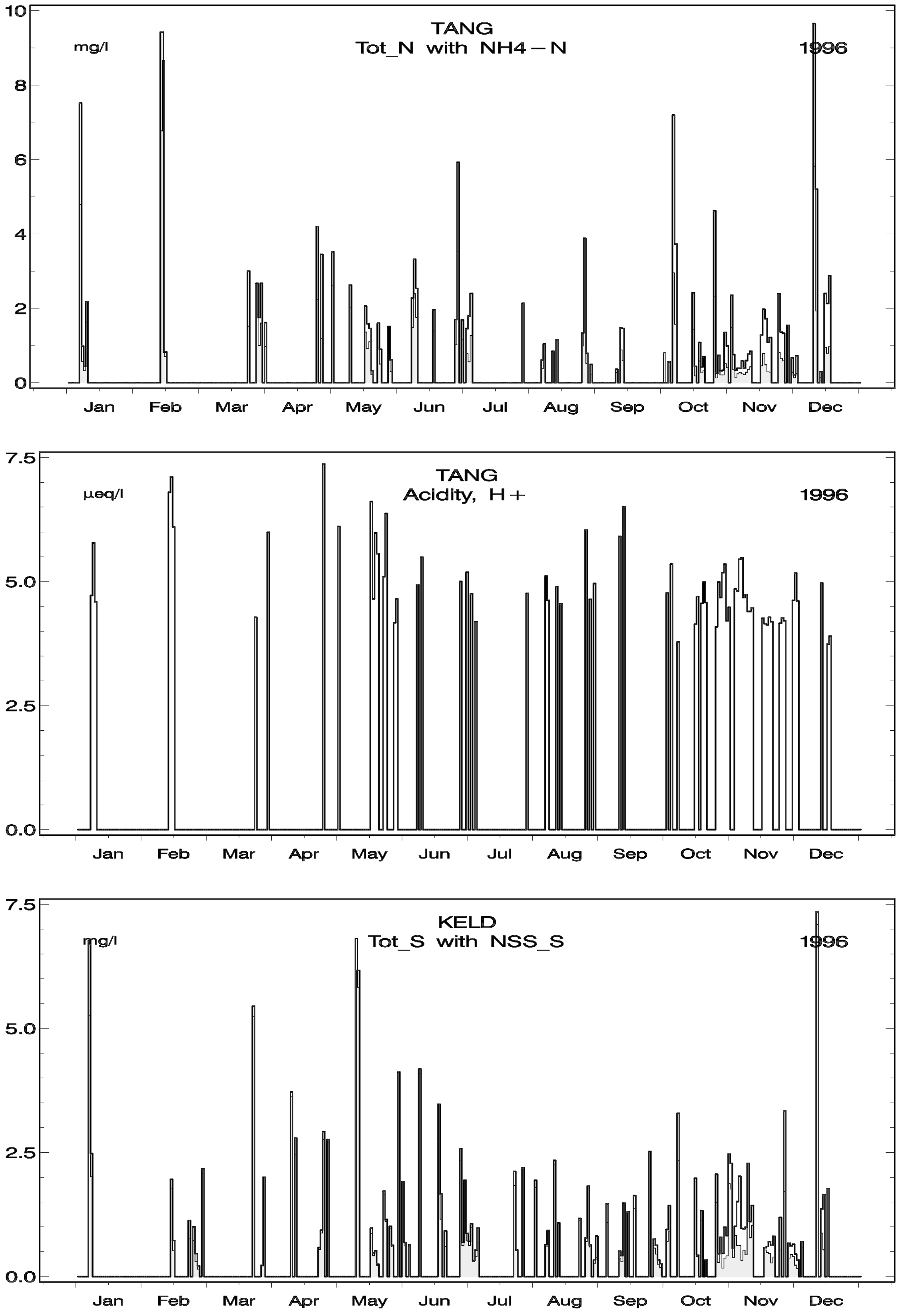

Figure 3.1.1 Daily concentrations in wet-only precipitation at Tange and Keldsnor in 1996.

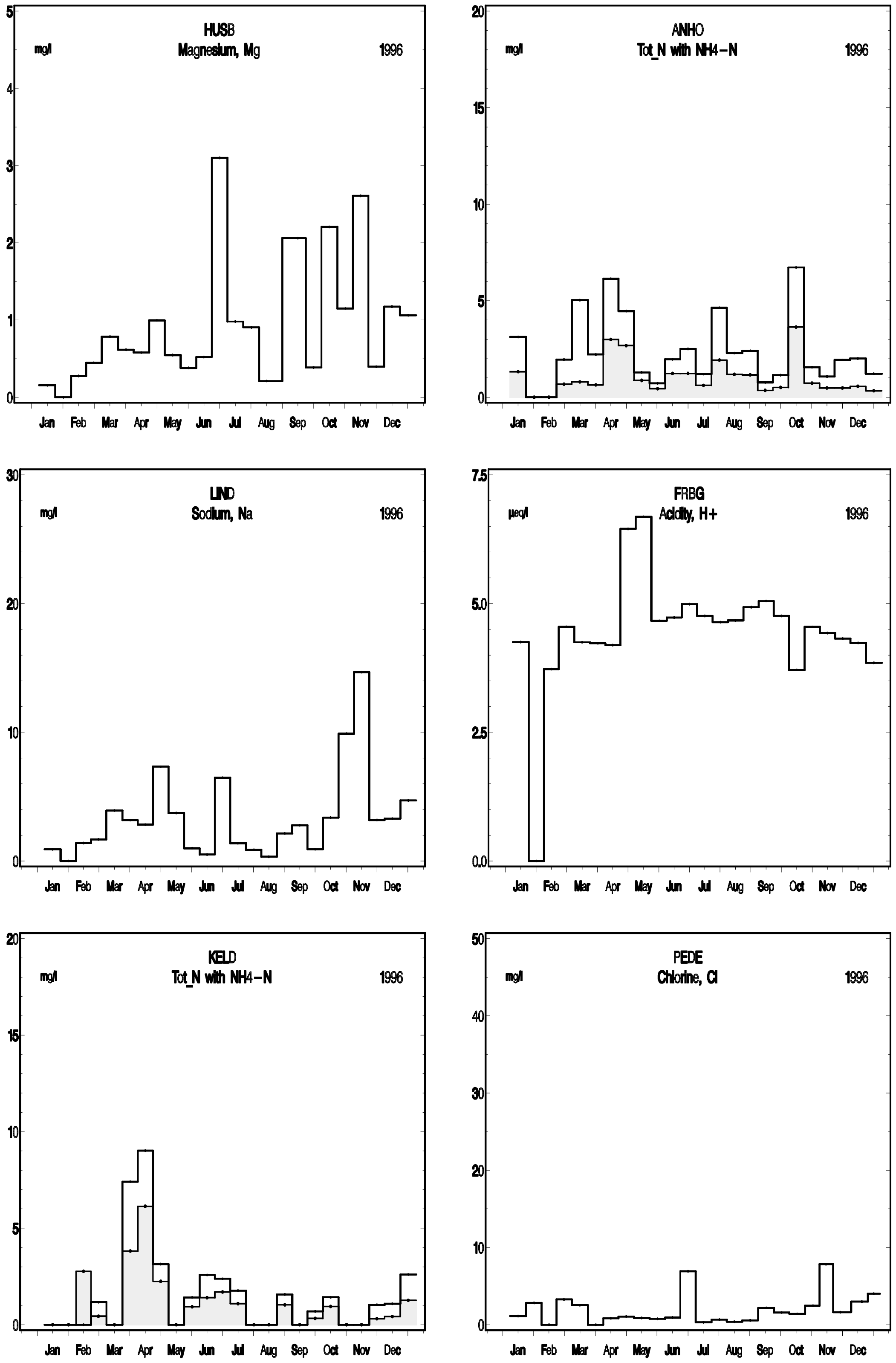

Figure 3.1.2 ½-monthly concentrations in bulk precipitation in 1996.

Table 3.1.1 Weighted mean concentrations of major ions in mg/l (H^+ in µg/l) at 7 bulk precipitation stations 1991-1997.

Site	W_mean	W_std	Maximum	W_mean	W_std	Maximum
		NSS_S			**SO4-S**	
HUSBY	0.69	2.72	10.04	1.57	4.32	17.40
SEPSTRUP	0.70	2.59	11.22	0.88	2.52	11.44
ANHOLT	0.82	2.51	6.68	1.24	2.94	11.74
FREDERIKSBORG	0.83	3.00	11.79	0.93	3.06	12.45
LINDET	0.76	2.81	13.01	1.05	3.00	13.35
KELDSNOR	0.97	3.21	11.60	1.48	7.06	17.61
PEDERSKER	0.91	2.49	9.45	1.03	2.51	10.44
		NO3-N			**NH4-N**	
HUSBY	0.62	2.40	5.68	0.60	2.58	14.30
SEPSTRUP	0.51	1.53	5.18	0.62	2.28	10.96
ANHOLT	0.70	2.03	7.17	0.60	1.96	5.21
FREDERIKSBORG	0.56	1.62	4.48	0.70	3.25	14.82
LINDET	0.58	1.90	7.18	0.79	3.55	16.06
KELDSNOR	0.72	2.43	7.05	0.90	3.79	10.16
PEDERSKER	0.64	1.59	5.06	0.70	3.04	39.60
		TOT_N			**H+**	
HUSBY	1.22	4.75	19.23	32.74	196.44	346.74
SEPSTRUP	1.14	3.69	16.14	29.27	100.61	201.31
ANHOLT	1.30	3.77	12.38	38.16	102.09	180.49
FREDERIKSBORG	1.26	4.38	17.54	33.53	126.14	241.47
LINDET	1.38	5.24	18.40	21.11	87.18	160.59
KELDSNOR	1.63	5.82	17.21	16.18	84.05	193.58
PEDERSKER	1.35	4.11	42.56	41.23	138.99	229.09

Table 3.1.2 Weighted mean concentrations of minor ions in mg/l in bulk precipitation 1991-1997.

Site	W_mean	W_std	Maximum	W_mean	W_std	Maximum
		K			**Ca**	
HUSBY	0.47	2.08	6.00	0.52	2.00	5.90
SEPSTRUP	0.14	0.95	4.55	0.20	1.67	3.65
ANHOLT	0.31	1.94	6.23	0.38	1.69	13.81
FREDERIKSBORG	0.19	2.10	14.07	0.22	1.26	4.70
LINDET	0.34	2.38	9.88	0.39	2.20	11.30
KELDSNOR	0.92	6.35	22.30	1.23	12.02	36.31
PEDERSKER	0.18	1.03	4.48	0.24	1.26	7.33
		Mg			**Na**	
HUSBY	1.31	5.97	14.50	10.27	44.61	120.00
SEPSTRUP	0.27	1.40	2.05	2.06	9.88	14.30
ANHOLT	0.65	3.72	9.77	5.00	21.86	75.72
FREDERIKSBORG	0.15	0.73	1.76	1.14	6.08	8.76
LINDET	0.44	2.17	2.67	3.40	17.77	28.60
KELDSNOR	0.78	8.16	12.19	5.66	65.64	103.07
PEDERSKER	0.19	0.82	4.40	1.42	6.11	13.79
		Cl				
HUSBY	18.34	79.36	208.00			
SEPSTRUP	3.65	17.64	26.03			
ANHOLT	8.69	38.05	136.14			
FREDERIKSBORG	2.01	11.09	15.83			
LINDET	6.09	32.55	56.31			
KELDSNOR	10.64	122.47	184.82			
PEDERSKER	2.42	10.93	21.88			

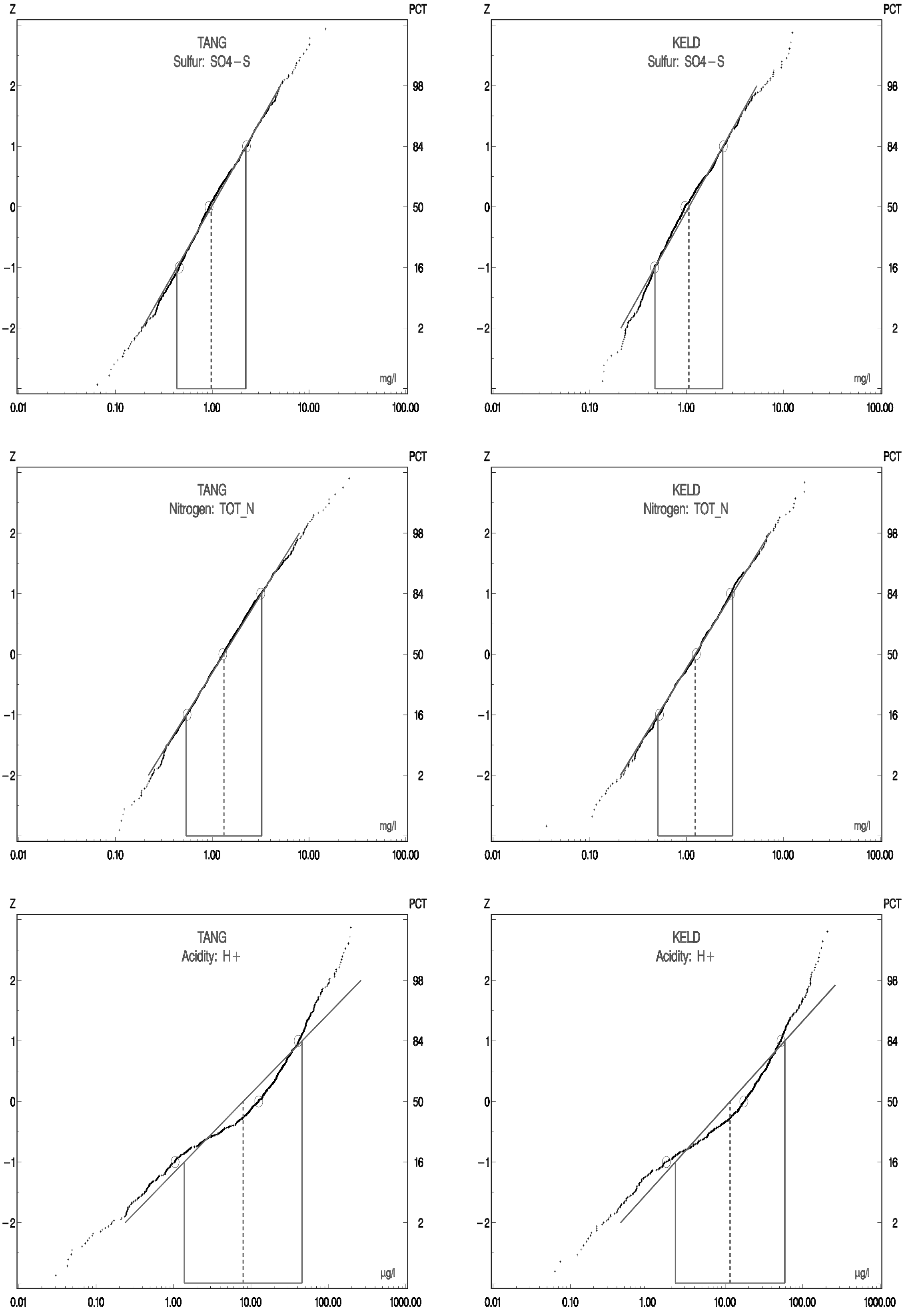

Figure 3.1.3 Statistical distributions of log-concentrations on the horizontal axis for selected pollutants in 24-h wet-only precipitation 1991-1997. Circles denote the 16-, 50-, and 84-percentiles and the straight line is the log-normal fit through the indicated geometric mean and standard deviations.

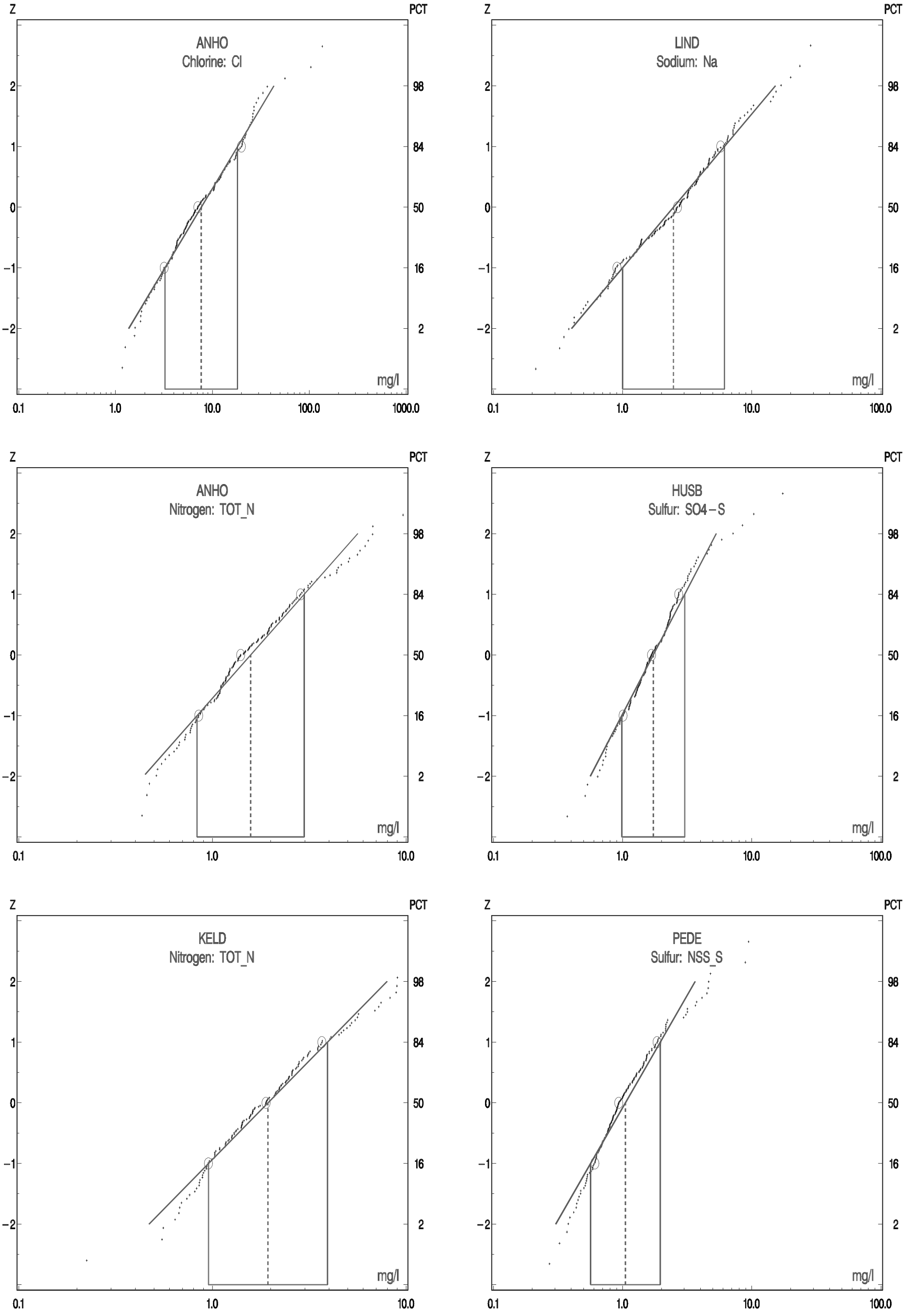

Figure 3.1.4 Statistical distributions of log-concentrations on the horizontal axis for selected pollutants in ½-monthly bulk precipitation 1991-1997. Circles denote the 16-, 50-, and 84-percentiles and the straight line is the log-normal fit through the indicated geometric mean and standard deviations.

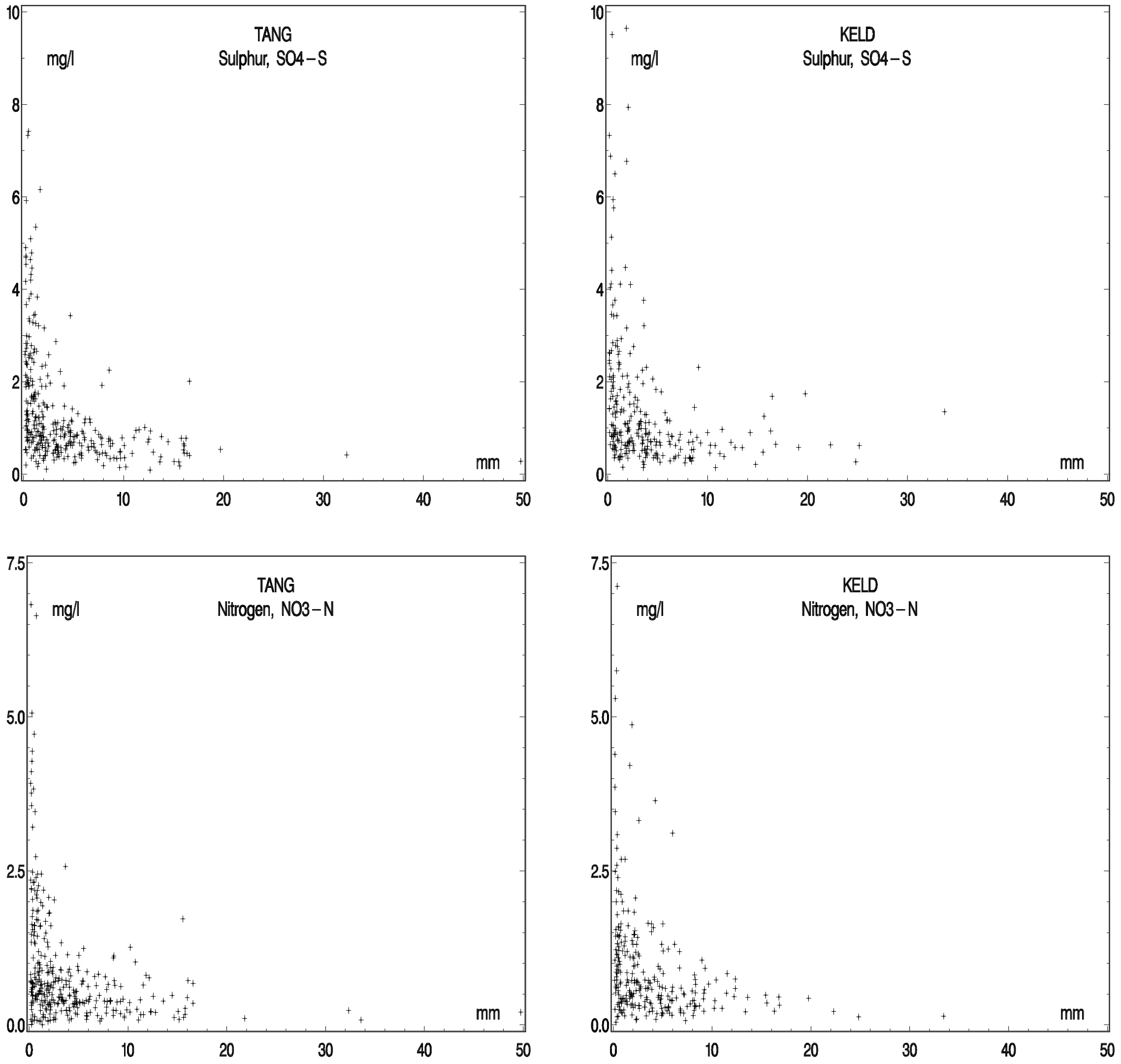

Figure 3.1.5 Daily wet-only concentrations versus amount of precipitation, 1991-1997.

3.2 Geography

Means and percentiles

The parameters of the distributions presented in Figures 3.1.3 and 3.1.4 are described in more detail and for different sub-periods in Tables 3.2.1 - 3.2.5. For selected components these tables contain non-weighted *arithmetic* as well as *geometric* means and standard deviations, 50- and 90-percentiles, and number of observations as well as an indication of whether the distribution can be considered to be lognormal. Table 3.2.1 is for wet-only results and Tables 3.2.2 - 3.2.5 for bulk concentrations. Note that for most datasets the geometric mean is much closer to the 50-percentile than the arithmetic mean, an indication of the approximate lognormal distributions. The column 'History' concerns time trends, which are considered below.

Wet-only and bulk concentrations

The level of the wet-only concentrations as expressed by the geometric means or the medians are as expected smaller than the bulk concentrations which may contain a certain amount of dry deposition or even be influenced by some precipitation evaporation during sampling. On the other hand, the relative ranges of concentrations as expressed by the geometric standard deviations are larger for the wet-only data, which have a time resolution of 24 hours, than for the bulk concentrations measured on a ½ monthly basis.

Geometric and precipitation weighted means

The variation of the average precipitation concentrations among stations across the country can be studied both from the geometric mean concentrations in Tables 3.2.1 - 3.2.5 and from the precipitation weighted mean concentrations in Tables 3.1.1 and 3.1.2. The conclusions reached are quite similar.

Wet-only concentrations

The variation of the geometric mean concentrations in wet-only precipitation (Table 3.2.1) show that the daily concentrations of sulphate, total nitrogen, and acidity in all three sub-periods are lower at Tange compared to Keldsnor which is more directly exposed to long range transport from the continent to the south.

Bulk concentrations

Bulk sulphate concentrations, shown as precipitation weighted means in table 3.1.1 and as geometric means in table 3.2.2, vary considerably, not only among the stations but also - as can be seen from the standard deviations - within stations. The highest concentrations occur at the marine stations Husby, Keldsnor, and Anholt where marine sulphur accounts for 30-55 % of the total and where the fractions of anthropogenic sulphur NSS_S are smallest. The levels of anthropogenic NSS_S concentrations (Tables 3.1.1 and 3.2.3) are more evenly distributed across the country. The highest concentrations occur at Keldsnor and Pedersker, which are exposed to LRTAP from the south. The standard deviations are also smaller but the largest and - oddly enough also the smallest - ranges of variation of these two components occur at these two stations (Table 3.1.1).

Uniform nitrogen concentrations

For nitrogen the concentrations are fairly uniform across the country (Tables 3.1.1 and 3.2.4). The concentrations at the non-agricultural stations Sepstrup, Husby, and Frederiksborg are the lowest whereas the combined influence of local agriculture and LRTAP give rise to the largest values and the largest standard deviations at Lindet and Pedersker and in particular at Keldsnor.

Acidity variations

The variations of acidity have a different pattern (Tables 3.1.1 and 3.2.5), the H+ bulk concentrations are in fact at a minimum at Keldsnor and at Lindet. That is probably a result of agricultural influence since acid precipitation may be neutralised by the presence of NH_3. This agricultural influence may also be at least part of the explanation for the fact that bulk acidity is by far the lowest at Keldsnor. The general level of the mean concentrations of hydrogen ions in precipitation are 30 - 40 μg/l, corresponding to pH values of 4.7 - 4.4. But in the bulk samplers at Keldsnor the precipitation weighted mean concentration of H+ is below 20 μg/l and the geometric means are in the range 3 - 6 μg/l, corresponding to pH-values of 5.5 - 5.5. This very large difference from the rest of the country does indicate that some local phenomenon may be at work during the two weeks of sampling. The deviations from the corresponding H+ concentration in the wet-only sampler at the same site (Table 3.2.1) that amount to a factor of 2 - 10 may even mean that some of the bulk results are in fact erroneous, *e.g.* contaminated by bird-droppings or other organic material.

Minor ions

For the minor ions in Table 3.1.2 it has already been noted that the marine tracers have the highest abundance at the marine stations Husby, Anholt, and Keldsnor and that the nutrient tracer K has a maximum at this station.

Variations against a national average

The geographic differences between local variations are illustrated in more detail in Figures 3.2.1-3. In these figures the precipitation weighted monthly bulk concentrations at various sites are shown against the corresponding values averaged over all stations. The latter data represent Grand National averages. The lines are orthogonal regression lines, which are the best least-squares fit to the data. In almost all cases the intercept with the vertical axis is of no significance, it is either not statistically different from zero or much smaller than typical concentration values. The slopes depend on the correlation's and the standard deviations, which for the station means do not depend on the site. Therefore much of the information on geographic differences resides in the slopes of the regression lines. However, since the geographic variation of precipitation in a given period is large and since concentrations depend on the amount of precipitation (see Figure 3.1.5) such comparisons of precipitation concentrations should be viewed with caution.

Natural and anthropogenic influences

In Figure 3.2.1 the left hand panels shows that the abundance and variation of sulphate at the marine station Husby are considerably larger than at the inland stations whereas anthropogenic non-seasalt sulphur is more abundant the more southerly the station is, a clear indication of a pronounced LRTAP component. Geographic variations of nitrogen in precipitation are illustrated in Figures 3.2.2-3. Nitrate is quite prominent at the marine and agricultural stations shown in the left-hand panels. Ammonium concentrations at the two southerly stations, which are under agricultural influence, are larger and have greater variations than the national average whereas concentrations at the island stations Anholt and Pedersker are below the national levels, represented in the figures by the stations Husby and Lindet. The geographic variation of Acidity in precipitation across the country is quite smooth as seen from the right hand panels of Figure 3.2.3.

Homogeneous precipitation chemistry

A complete overview is presented in Table 3.2.6, which contain all regression parameters for all major components at all the bulk stations. The last column of the table contains an indication whether the slopes are significantly larger or smaller than 1, *i.e.* whether the concentrations at the individual sites deviate in variation from a national average. Since the majority of the slopes are not statistically different from each other or only slightly so, the general picture that emerges is that the precipitation quality is fairly homogeneous across the country, and that annual and monthly mean concentrations differ at most with a factor of 2 among sites.

Table 3.2.1 Statistics of 24_h wet-only concentrations in mg/1 (H^+ in µg/1) in 3 sub-periods. Significant decreases between two sub-periods are denoted *D,* increases by U. An "X" in the column Log_N 9197 indicates that data in the period 1991-1997 fit a log-normal distribution at a significance level of 5%.

Quantity	Log_N	7884	8590	9197	History	Log_N	7884	8590	9197	History
					NSS_S					
			KELDSNOR					**TANGE**		
Mean_arit.		2.41	1.67	1.19			1.54	1.29	1.09	
Std.dev.		3.37	1.58	1.44			1.55	1.40	1.36	
Mean_geom.	X	1.65	1.22	0.77	Da, Db	X	1.08	0.90	0.70	Da, Db
Std_geom.		2.38	2.20	2.49			2.42	2.44	2.57	
P50		1.59	1.21	0.73			1.07	0.93	0.68	
P90		5.16	3.49	2.49			3.30	2.70	2.37	
N		863	599	807			1041	791	980	
					SO4_S					
			KELDSNOR					**TANGE**		
Mean_arit.		3.12	2.11	1.51			1.82	1.56	1.38	
Std.dev.		4.51	1.88	1.64			1.82	1.47	1.44	
Mean_geom.		2.09	1.61	1.06	Da, Db	X	1.35	1.18	0.98	Da, Db
Std_geom.		2.35	2.05	2.24			2.17	2.11	2.27	
P50		1.99	1.58	0.96			1.30	1.18	0.93	
P90		5.75	4.10	2.98			3.66	3.05	2.78	
N		864	599	807			1045	792	981	
					TOT_N					
			KELDSNOR					**TANGE**		
Mean_arit.		2.58	2.26	1.82			1.96	1.91	2.03	
Std.dev.		2.91	1.87	1.99			3.97	1.93	2.67	
Mean_geom.	X	1.61	1.71	1.23	Db	X	1.05	1.31	1.32	Ua
Std_geom.		3.03	2.15	2.43			3.45	2.51	2.45	
P50		1.74	1.71	1.26			1.20	1.36	1.28	
P90		5.49	4.45	3.64			4.14	3.87	4.13	
N		863	588	715			1044	771	881	
					H+					
			KELDSNOR					**TANGE**		
Mean_arit.		66.2	46.6	27.6			53.0	39.7	21.5	
Std.dev.		86.3	46.9	32.6			65.7	45.1	28.5	
Mean_geom.		27.1	24.2	11.6	Db		20.3	20.6	7.9	Db
Std_geom.		6.22	4.71	5.10			6.77	3.91	5.77	
P50		42.7	33.1	17.4			33.9	25.7	12.6	
P90		154.9	112.2	64.6			120.2	93.3	51.3	
N		859	587	643			1042	773	796	

Table 3.2.2 Statistics of sulphate concentrations in mg S/l in bulk precipitation in 2 sub-periods. For other details see caption of Table 3.2.1.

Quantity	Log_N	8590	9197	History	Log_N	8590	9197	History
		HUSBY				**SEPSTRUP**		
Mean_arit.		2.89	2.08			1.27	1.31	
Std.dev.		2.68	1.78			0.61	1.44	
Mean_geom.	X	2.28	1.73	D		1.15	1.03	
Std_geom.		1.89	1.75			1.56	1.81	
P50		2.07	1.68			1.07	0.93	
P90		5.58	3.19			2.22	2.20	
N		48	161			23	163	
		ANHOLT				**FREDERIKSBORG**		
Mean_arit.		2.59	1.76			1.67	1.46	
Std.dev.		2.35	1.42			0.97	1.55	
Mean_geom.		2.07	1.47	D		1.46	1.11	D
Std_geom.		1.83	1.73			1.66	1.93	
P50		1.97	1.33			1.39	1.03	
P90		4.07	2.98			2.97	2.98	
N		55	155			137	160	
		LINDET				**KELDSNOR**		
Mean_arit.		1.61	1.59			3.48	2.29	
Std.dev.		0.66	1.64			2.60	2.44	
Mean_geom.		1.49	1.26	D		2.84	1.64	D
Std_geom.		1.50	1.81			1.87	2.13	
P50		1.49	1.15			2.35	1.47	
P90		2.47	2.65			5.93	4.44	
N		66	164			23	150	
		PEDERSKER						
Mean_arit.		1.79	1.47					
Std.dev.		1.30	1.31					
Mean_geom.		1.53	1.20	D				
Std_geom.		1.67	1.77					
P50		1.37	1.11					
P90		3.19	2.29					
N		38	158					

Table 3.2.3 Statistics of non-seasalt sulphate concentrations in mg S/1 in bulk precipitation in 2 sub-periods. For other details see caption of Table 3.2.1.

Quantity	Log_N	8590	9197	History	Log_N	8590	9197	History
		HUSBY				**SEPSTRUP**		
Mean_arit.		1.18	1.13			1.00	1.12	
Std.dev.		0.76	1.22			0.61	1.37	
Mean_geom.		0.99	0.86			0.87	0.82	
Std_geom.		1.80	1.99			1.71	2.00	
P50		0.97	0.77			0.83	0.74	
P90		2.26	2.01			1.54	1.98	
N		48	161			23	163	
		ANHOLT				**FREDERIKSBORG**		
Mean_arit.		1.60	1.19			1.54	1.32	
Std.dev.		1.08	0.97			0.96	1.49	
Mean_geom.		1.33	0.96	D		1.32	0.97	D
Std_geom.		1.80	1.90			1.73	2.02	
P50		1.28	0.91			1.26	0.91	
P90		3.45	2.23			2.83	2.86	
N		55	155			137	160	
		LINDET				**KELDSNOR**		
Mean_arit.		1.23	1.27			1.90	1.56	
Std.dev.		0.61	1.52			0.92	1.64	
Mean_geom.		1.10	0.92	D		1.69	1.17	D
Std_geom.		1.62	2.02			1.66	2.02	
P50		1.06	0.86			1.72	1.05	
P90		2.07	2.23			3.49	2.96	
N		66	164			23	150	
		PEDERSKER						
Mean_arit.		1.61	1.33					
Std.dev.		1.27	1.25					
Mean_geom.		1.35	1.05	D				
Std_geom.		1.75	1.86					
P50		1.16	0.93					
P90		3.03	2.17					
N		38	158					

Table 3.2.4 Statistics of total nitrogen concentrations in mg N/l in bulk precipitation in 2 sub-periods. For other details see caption of Table 3.2.1.

Quantity	Log_N	8590	9197	History	Log_N	8590	9197	History
		HUSBY				**SEPSTRUP**		
Mean_arit.		1.91	2.06			1.46	1.80	
Std.dev.		1.55	2.43			0.81	1.95	
Mean_geom.		1.54	1.50			1.29	1.37	
Std_geom.		1.87	2.06			1.65	1.95	
P50		1.42	1.35			1.13	1.23	
P90		3.20	3.62			2.70	3.06	
N		48	161			23	163	
		ANHOLT				**FREDERIKSBORG**		
Mean_arit.		2.32	1.98			1.97	1.96	
Std.dev.		1.71	1.66			1.35	1.99	
Mean_geom.		1.96	1.57	D		1.65	1.51	
Std_geom.		1.74	1.89			1.80	1.95	
P50		1.97	1.40			1.59	1.41	
P90		3.72	3.80			3.80	3.31	
N		55	155			137	160	
		LINDET				**KELDSNOR**		
Mean_arit.		1.92	2.26			2.44	2.54	
Std.dev.		1.13	2.55			1.23	2.33	
Mean_geom.		1.66	1.67		X	2.19	1.94	
Std_geom.		1.71	2.01			1.60	2.03	
P50		1.56	1.48			2.14	1.89	
P90		3.67	4.38			3.94	5.13	
N		66	164			23	134	
		PEDERSKER						
Mean_arit.		2.04	2.17					
Std.dev.		1.47	3.63					
Mean_geom.		1.72	1.61					
Std_geom.		1.73	1.89					
P50		1.55	1.49					
P90		3.75	3.42					
N		38	152					

Table 3.2.5 Statistics of H^+-concentrations in µg/l in bulk precipitation in 2 sub-periods. For other details see caption of Table 3.2.1.

Quantity	Log_N	8590	9197	History	Log_N	8590	9197	History
		HUSBY				**SEPSTRUP**		
Mean_arit.		60.80	37.90			38.20	33.50	
Std.dev.		48.90	35.90			28.20	28.80	
Mean_geom.		47.90	27.30	D		30.40	22.00	D
Std_geom.		2.06	2.54			2.04	3.28	
P50		47.70	27.90			27.50	28.40	
P90		113.50	78.50			58.40	60.70	
N		48	160			23	162	
		ANHOLT				**FREDERIKSBORG**		
Mean_arit.		59.00	45.20			61.50	40.40	
Std.dev.		34.60	31.80			57.40	37.50	
Mean_geom.		49.30	35.50	D		45.00	25.10	D
Std_geom.		1.96	2.19			2.46	3.69	
P50		52.50	38.70			53.30	32.80	
P90		102.90	78.20			108.60	71.10	
N		55	153			137	159	
		LINDET				**KELDSNOR**		
Mean_arit.		35.90	22.80			9.60	19.30	
Std.dev.		24.90	22.70			11.90	26.90	
Mean_geom.		24.00	11.30	D		2.92	5.82	U
Std_geom.		3.32	4.92			6.36	6.68	
P50		31.60	18.70			3.63	11.50	
P90		65.60	46.50			25.50	48.40	
N		66	163			23	139	
		PEDERSKER						
Mean_arit.		53.80	51.50					
Std.dev.		36.80	39.80					
Mean_geom.		38.70	32.30					
Std_geom.		2.81	3.75					
P50		43.70	44.30					
P90		110.70	98.80					
N		38	154					

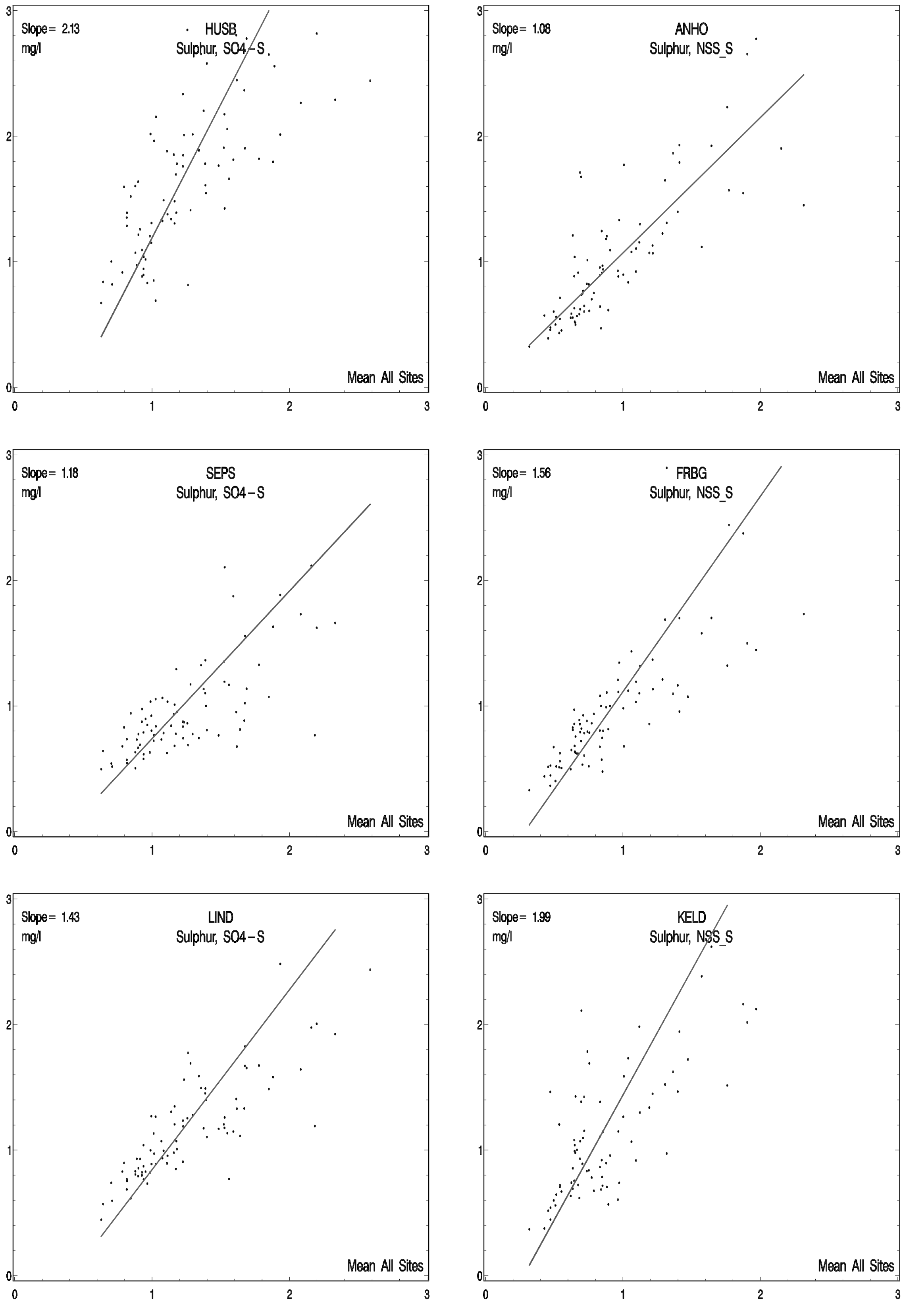

Figure 3.2.1 Monthly precipitation weighted bulk concentrations of sulphur compounds 1991- 1997. Site concentrations plotted and regressed orthogonally against the means at all sites. Calculations are based on all data, whereas displayed data amount to minimum 95% of all.

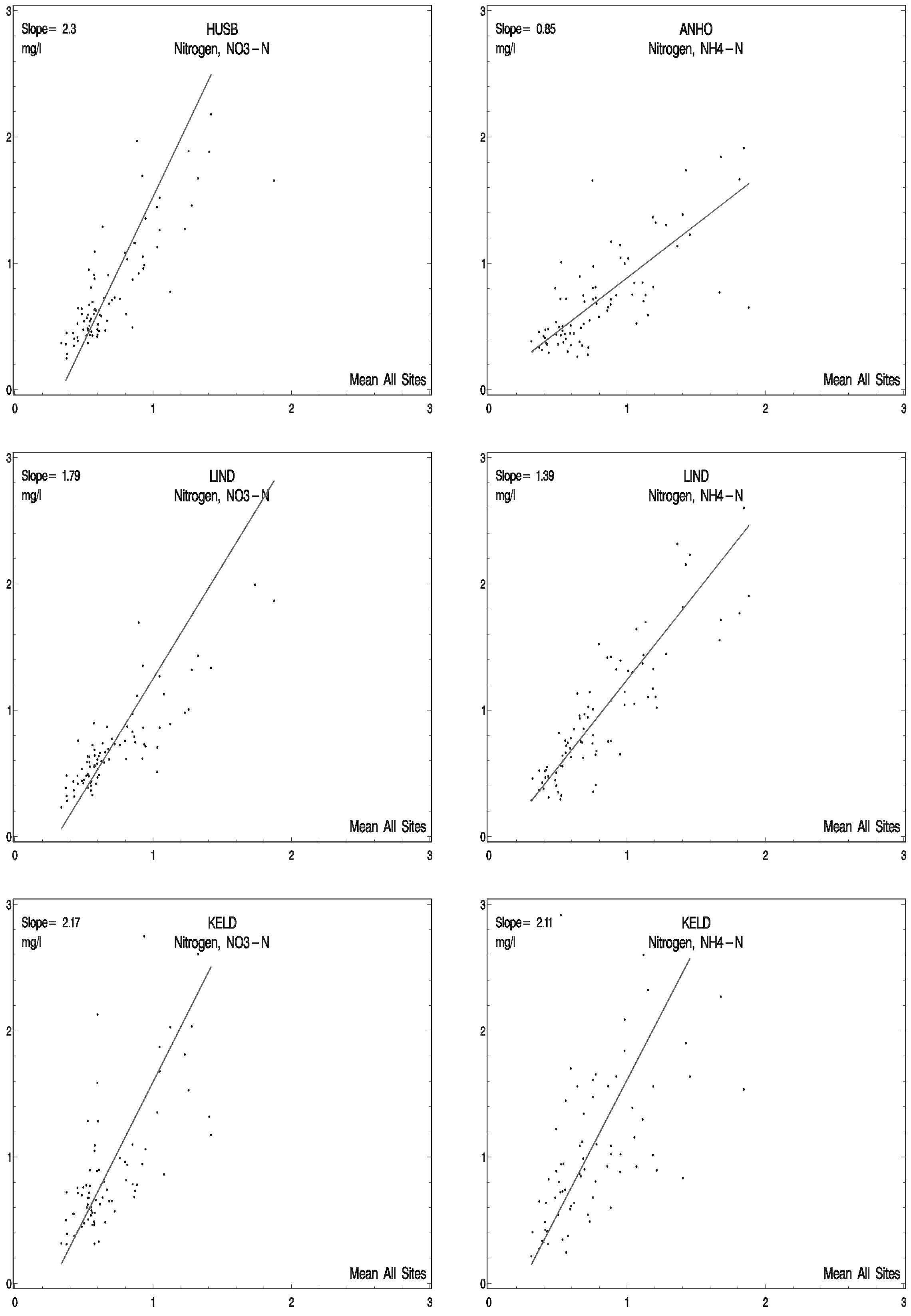

Figure 3.2.2 Monthly precipitation weighted bulk concentrations of nitrogen compounds 1991-1997. Site concentrations plotted and regressed orthogonally against the means at all sites. Calculations are based on all data, whereas displayed data amount to minimum 95% of all.

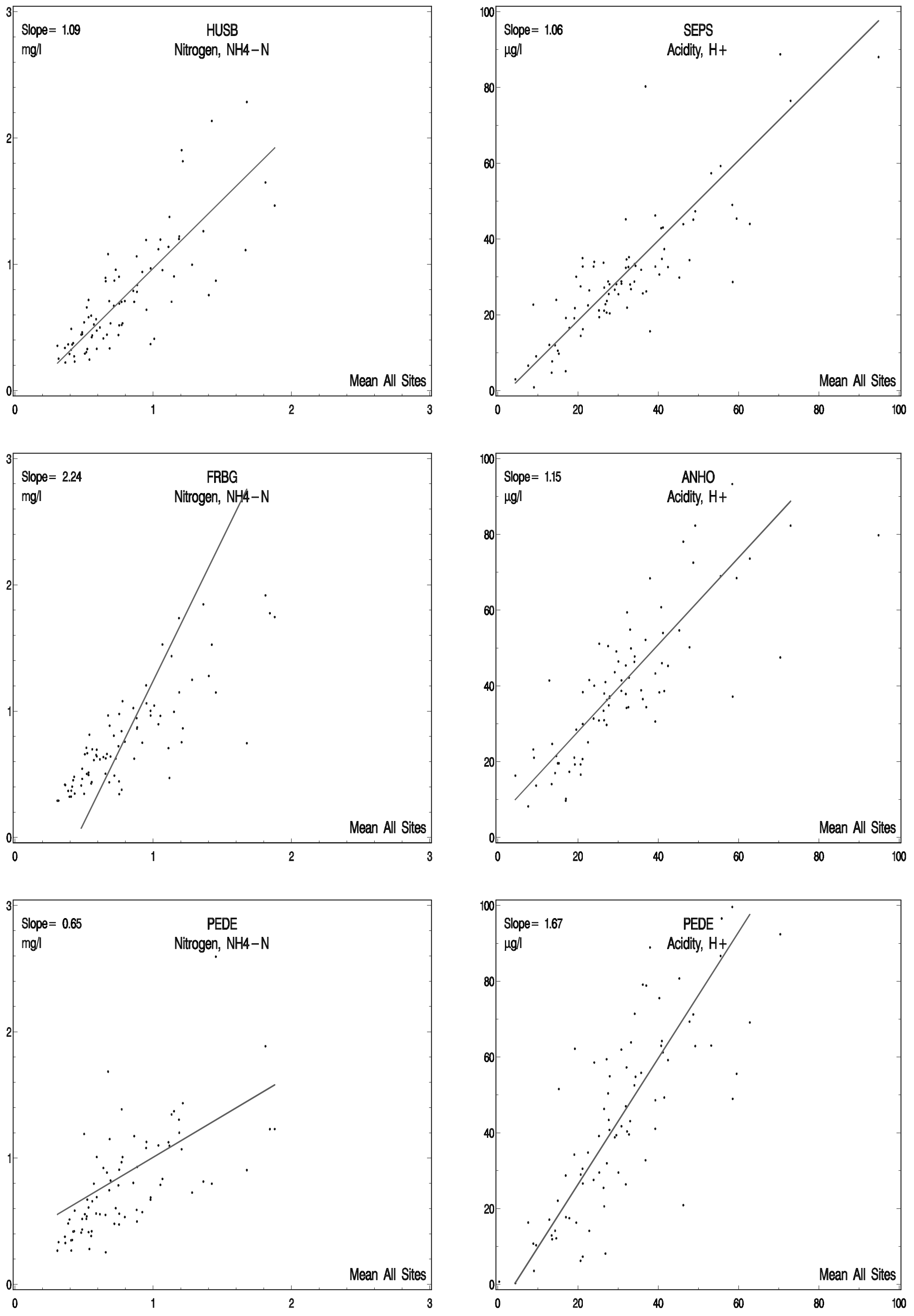

Figure 3.2.3 Monthly precipitation weighted bulk concentrations of nitrogen compounds and acidity 1991-1997. Site concentrations plotted and regressed orthogonally against the means at all sites. Calculations are based on all data, whereas displayed data amount to minimum 95% of all.

Table 3.2.6 Orthogonal regression parameters for monthly bulk concentrations 1991-1997.

Site	Slope	Std_ Slope	Intercep	Std_ Intcep	Rsq	Slope # 1
			SO4-S			
HUSB	2.13	0.29	-0.94	0.37	0.40	1
SEPS	1.18	0.16	-0.44	0.20	0.41	
ANHO	1.05	0.14	0.13	0.18	0.42	
FRBG	1.56	0.15	-0.87	0.20	0.56	1
LIND	1.43	0.16	-0.59	0.21	0.50	1
KELD	4.93	0.66	-4.30	0.83	0.42	1
PEDE	1.48	0.35	-0.64	0.46	0.18	
			NSS-S			
HUSB	1.64	0.18	-0.61	0.17	0.51	1
SEPS	1.34	0.11	-0.37	0.11	0.63	
ANHO	1.08	0.09	-0.01	0.08	0.65	1
FRBG	1.56	0.12	-0.44	0.12	0.66	1
LIND	1.47	0.14	-0.42	0.13	0.59	1
KELD	1.99	0.25	-0.55	0.23	0.44	
PEDE	1.50	0.29	-0.30	0.28	0.25	
			NH4- N			
HUSB	1.09	0.12	-0.12	0.10	0.50	
SEPS	1.13	0.09	-0.15	0.07	0.68	
ANHO	0.85	0.07	0.04	0.06	0.65	-1
FRBG	2.24	0.09	-1.00	0.08	0.88	1
LIND	1.39	0.10	-0.14	0.10	0.68	1
KELD	2.11	0.29	-0.50	0.24	0.42	1
PEDE	0.65	0.20	0.35	0.18	0.12	
			NO3-N			
HUSB	2.30	0.31	-0.78	0.22	0.40	1
SEPS	1.15	0.11	-0.18	0.08	0.58	
ANHO	1.40	0.12	-0.11	0.08	0.64	1
FRBG	1.14	0.10	-0.13	0.07	0.64	
LIND	1.79	0.22	-0.54	0.16	0.44	1
KELD	2.17	0.25	-0.58	0.17	0.51	1
PEDE	0.81	0.12	0.19	0.09	0.36	
			H+			
HUSB	1.28	0.16	-5.83	5.23	0.44	
SEPS	1.06	0.09	-2.66	2.97	0.62	
ANHO	1.15	0.10	4.93	3.23	0.62	
FRBG	1.24	0.11	-2.59	3.53	0.61	1
LIND	0.75	0.08	-2.77	2.41	0.54	-1
KELD	0.90	0.11	-10.94	3.44	0.48	
PEDE	1.67	0.15	-6.94	4.75	0.60	1

3.3 Trends

Decreasing concentrations

It is seen from Tables 3.2.1 - 3.2.5 that in a majority of instances the concentration levels appear to decrease from one period to the next. Where this is a true and significant decrease according to the Student's T-test for the lognormal case it has been noted in the *History* column, with D denoting significant decreases between two subperiods. The occasional upward trends are similarly marked by U. Both sulphate concentrations and acidity have decreased by 20 - 50 % or more from the late 1980's to the first half of the 1990's. This is however not the case for total nitrogen where hardly any discernible trends have been noted. Once again the acidity in the bulk samplers at Keldsnor behave differently, exhibiting in fact an apparent doubling of the H+ concentration.

Precipitation weighted means

The development on a national level since 1985 is further illustrated in Figures 3.3.1 - 3.3.3 by the annual precipitation weighted mean concentrations of the major ions for six of the ½-monthly bulk samplers. Annual precipitation amounts at these stations are shown in Figure 3.3.4.

Decreasing sulphate concentrations and acidity

The decreases in precipitation concentrations of sulphate and acidity from the 1980's to the 1990's are clearly seen. As can be seen from Figure 3.3.1 the decrease in sulphate is caused mainly by the anthropogenic NSS_S but the figure also illustrates the important role of the sea salt sulphate component at the marine stations Husby, Anholt and Keldsnor. In Figure 3.3.3 on acidity the data from Pedersker, which have been preferred over the apparently abnormal behaviour at Keldsnor, show a clear decrease in concentrations although that is not apparent from Table 3.2.5, mainly because very few data exist before 1991. Figure 3.3.2 on nitrogen confirms on an annual basis the roughly equal division between reduced and oxidised ions pointed out earlier and also illustrates the lack of development in nitrogen concentrations.

Data gaps and trend statistics

Data from a full year of daily precipitation sampling were presented in Figure 3.1.1. It is seen that although rain is quite frequent the absence of rain is equally frequent so these series are characterised by great many gaps. Trend statistics must therefore be based on rather long-term averages and therefore the more numerous 24-h wet-only precipitation results at the two oldest stations Tange and Keldsnor have been chosen for illustration. However, since concentrations depend on the amount of precipitation (see Figure 3.1.5) trend statistics for precipitation concentrations should be viewed with caution.

Trends over 20 years

The development with time of the monthly precipitation weighted means are shown in Figures 3.3.5 - 3.3.6. Each figure contains three curves that are, respectively, the monthly precipitation weighted means (jagged line), a moving 12-month average (delineating the shaded area) and a trend (straight line) calculated as a regression line. The figures are in several instances characterised by quite large excursions, which make the trend estimates rather uncertain. Nevertheless, significant negative trends are observed in the majority of the cases illustrated. The exceptions where no significant trend can be seen are the nitrogen components, nitrate at both stations and ammonium at Tange

Negative trends

The complete set of numerical trend values for all components measured in precipitation are presented in Table 3.3.1. and they are all negative. The trend values are listed as annual changes in percent of the grand mean concentration for the various components. The trends are only presented if considered significant, *i.e.* if the relative uncertainties are less than 0.5. Note that Na, Mg, Ca, and Cl are mainly of natural origin. The negative trend for [Ca^{++}] at Tange will be considered in the next chapter in the context of depositions.

Short term variations.

The variations from year to year in precipitation amount, frequency, and occurrence are too large to allow an average annual behaviour to be described. There are only very few extended precipitation episodes with high concentrations since, as explained earlier, one rainfall normally suffices to clean the atmosphere and also because precipitation normally occurs with a separation of several days. Coincident episodes of high concentrations of airborne pollutants and high concentrations of precipitation-borne pollutant cannot be expected either since absence of precipitation is almost always a prerequisite for extended atmospheric episodes. In fact such coincidences are virtually absent in the 20-year record.

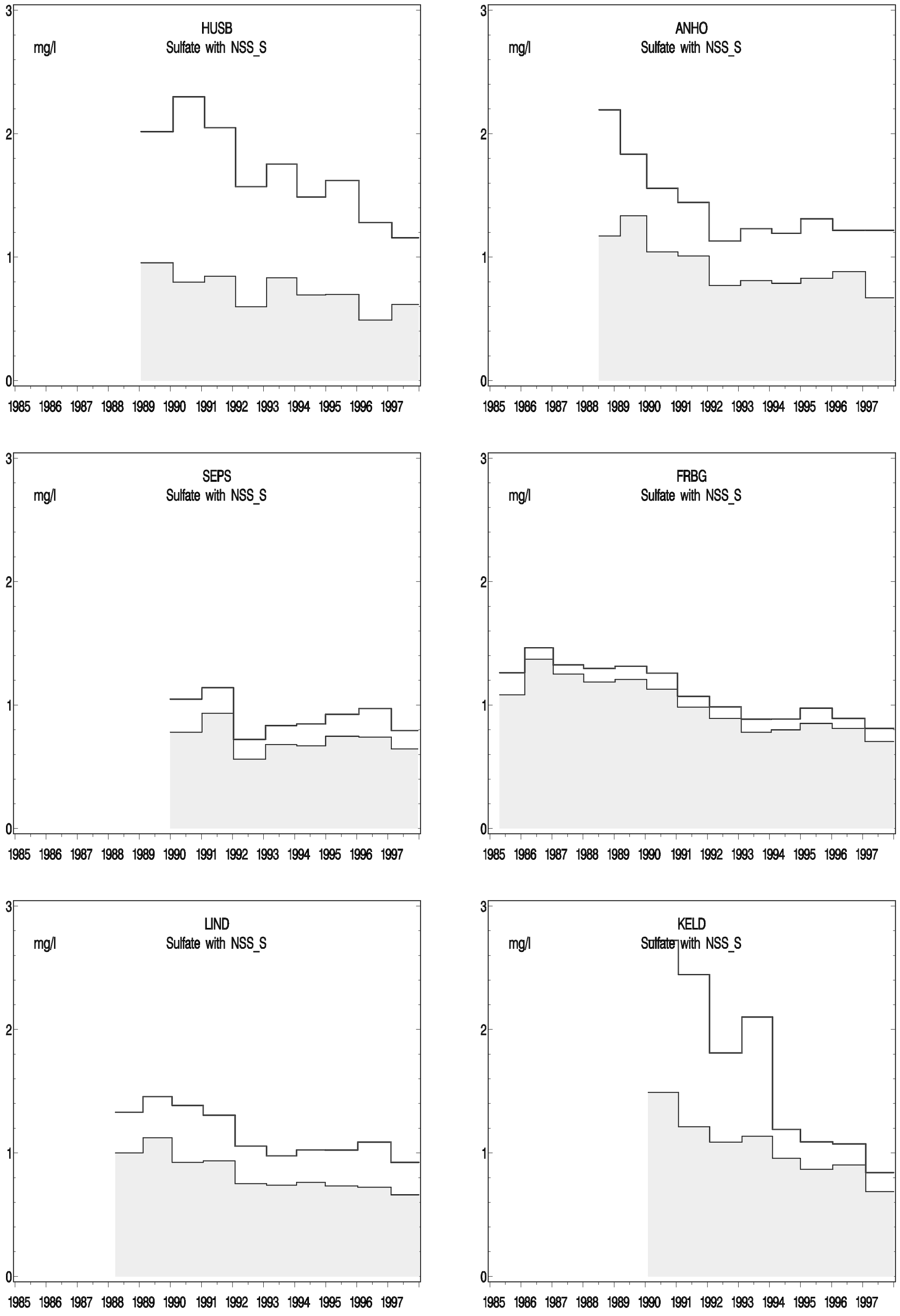

Figure 3.3.1 Annual precipitation weighted mean bulk concentrations for sulphate, SO4 and the anthropogenic part NSS_S in mg S/l, 1985 - 1997.

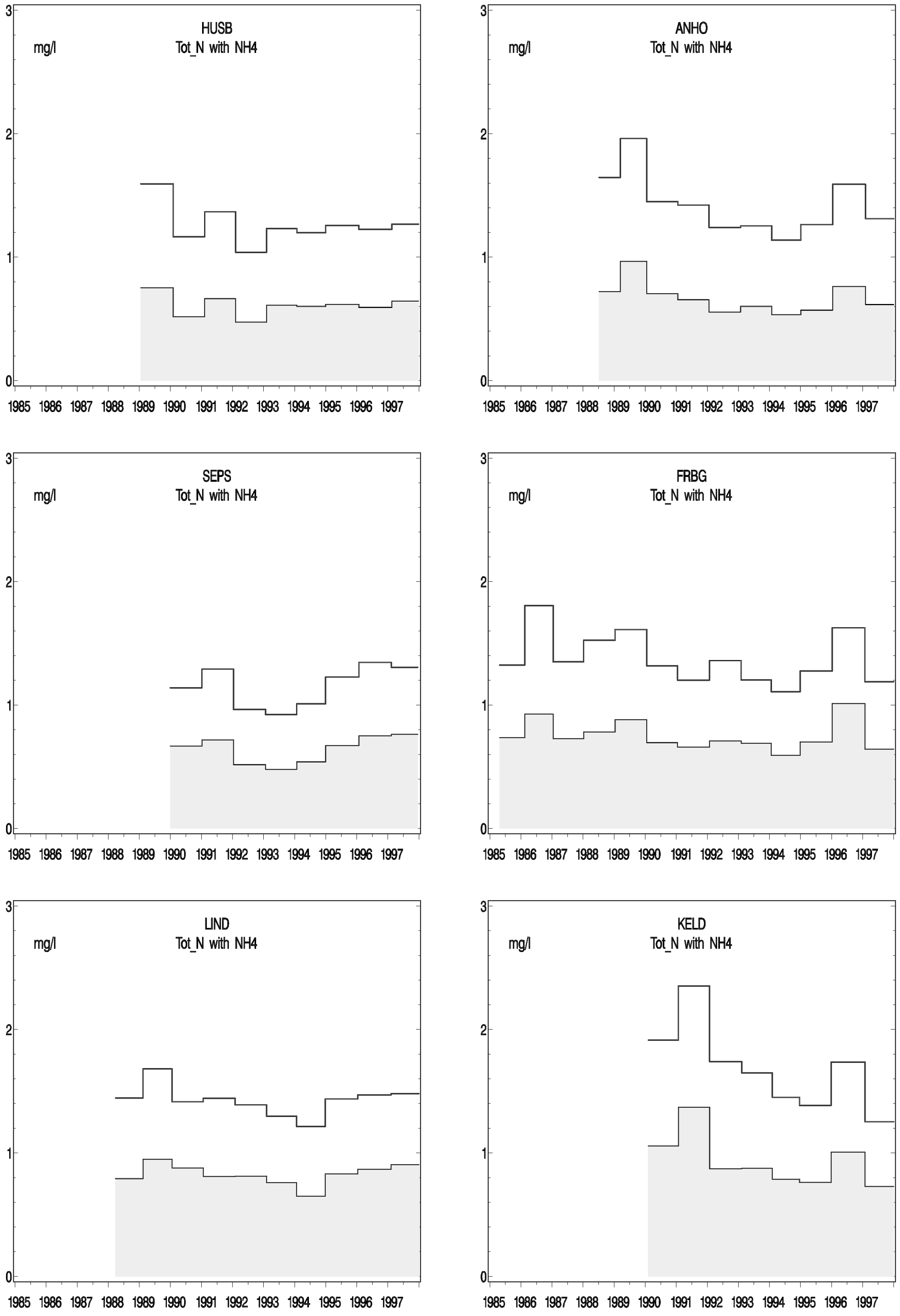

Figure 3.3.2 Annual precipitation weighted mean bulk concentrations for total nitrogen and the ammonium part in mg N/l, 1985 - 1997.

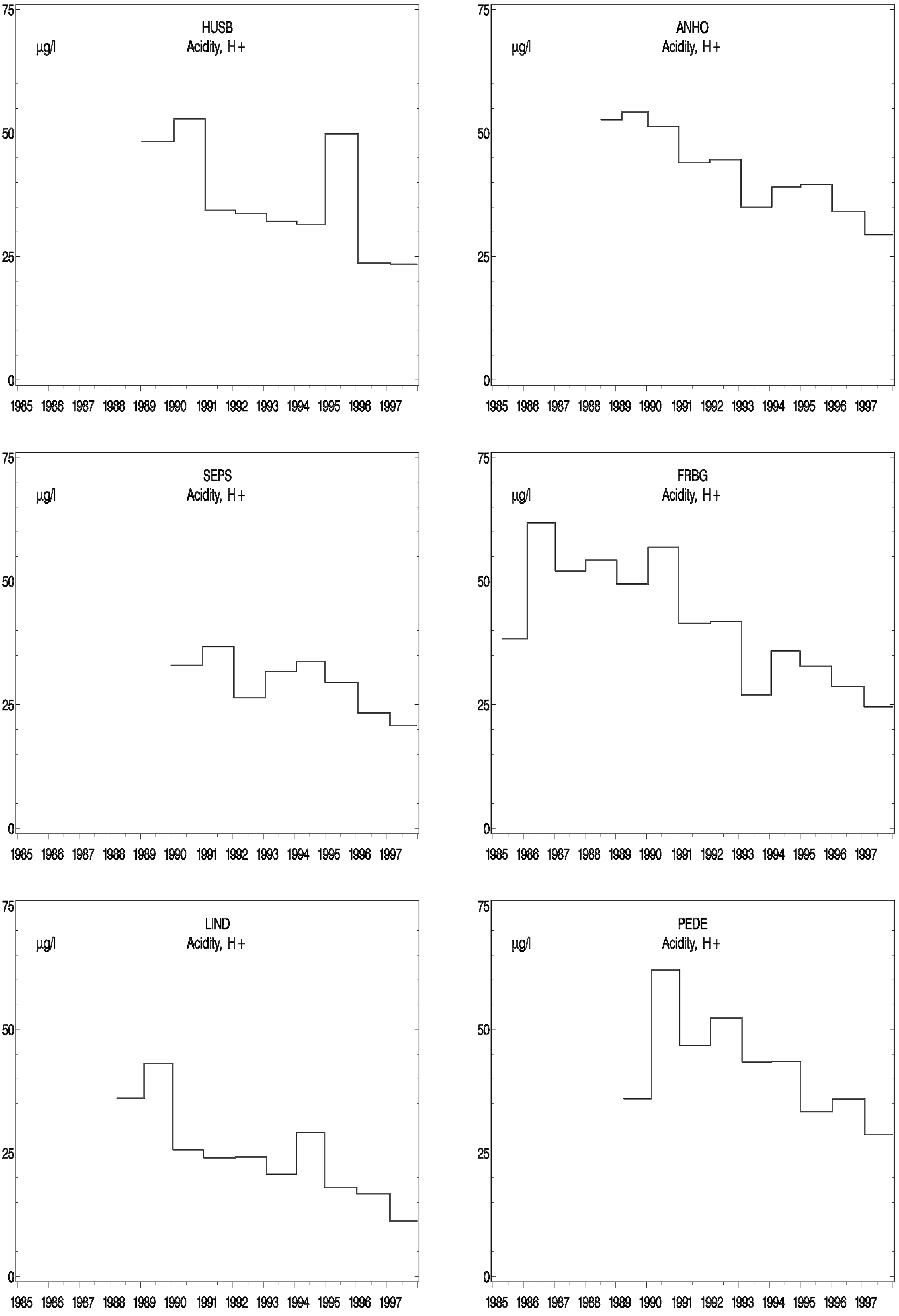

Figure 3.3.3 Annual precipitation weighted mean bulk concentrations for acidity, H^+ in µg/l, 1985 - 1997.

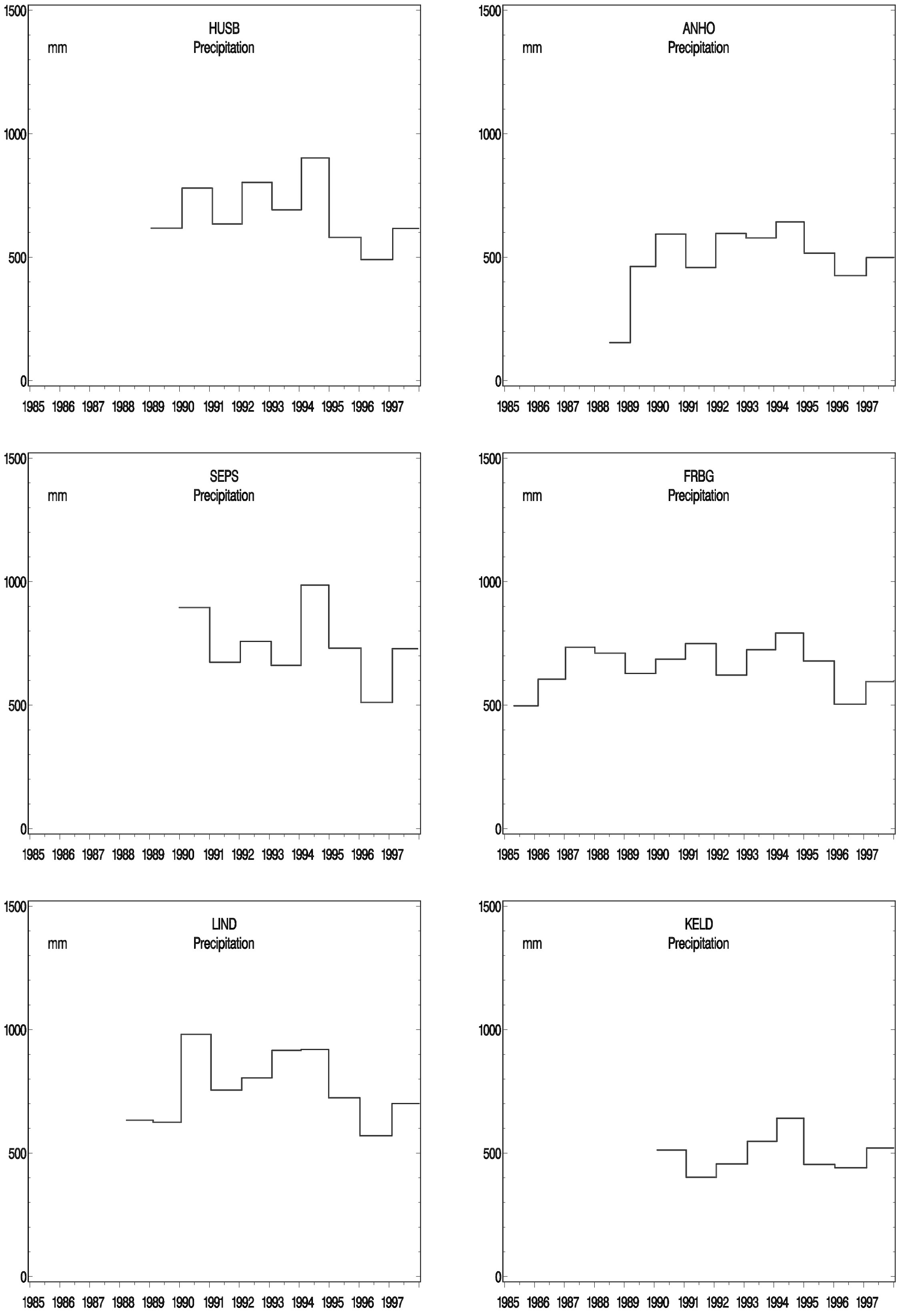

Figure 3.3.4 Precipitation amounts at six bulk stations 1985 - 1997.

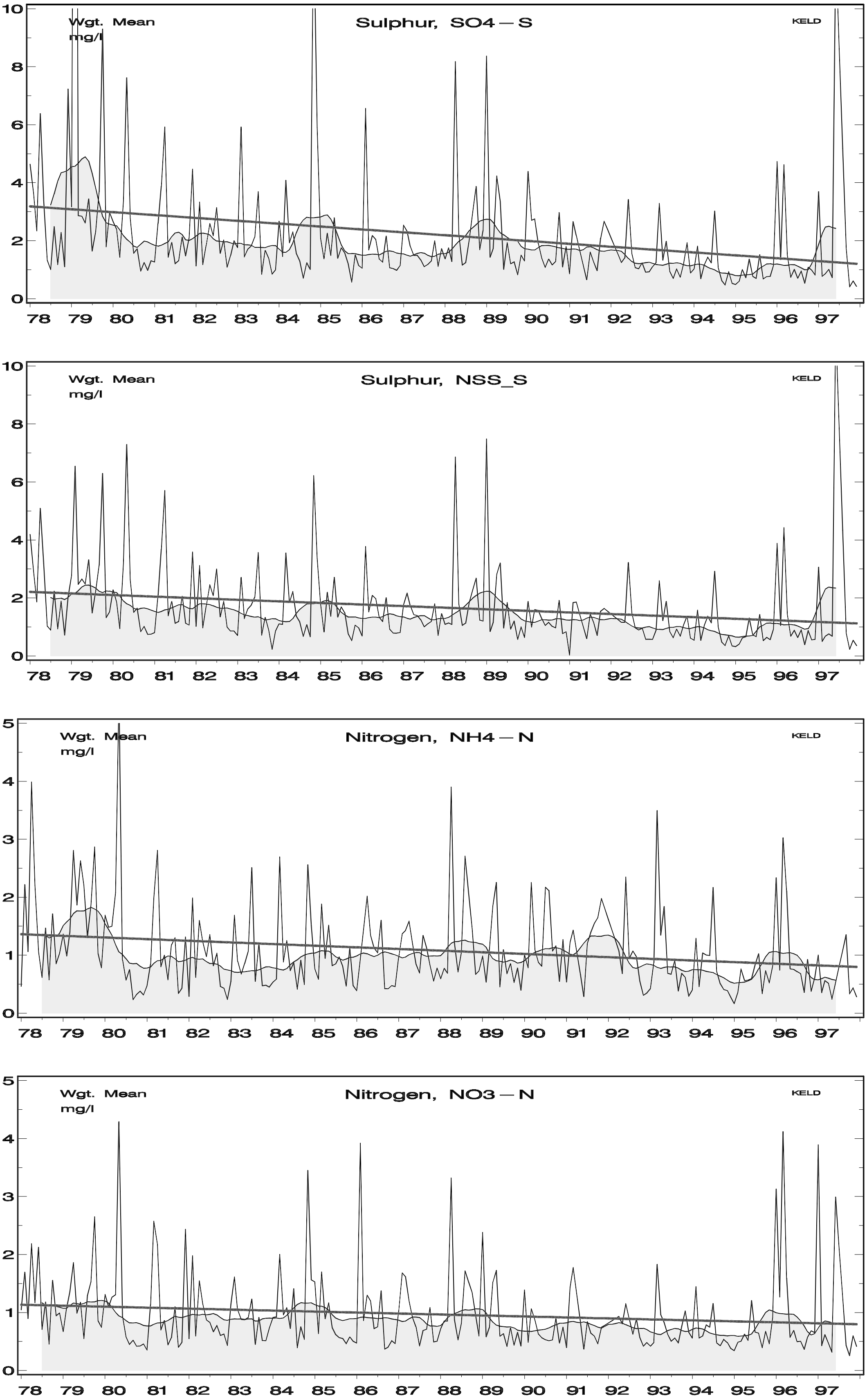

Figure 3.3.5 Trendplots for monthly precipitation weighted means at Keldsnor. The thin jagged line shows the monthly medians of the measured concentrations, the smooth curve delineating the shaded area represents a moving average over 12 months, and the full straight line is a linear regression line representing the long term trend. See also text.

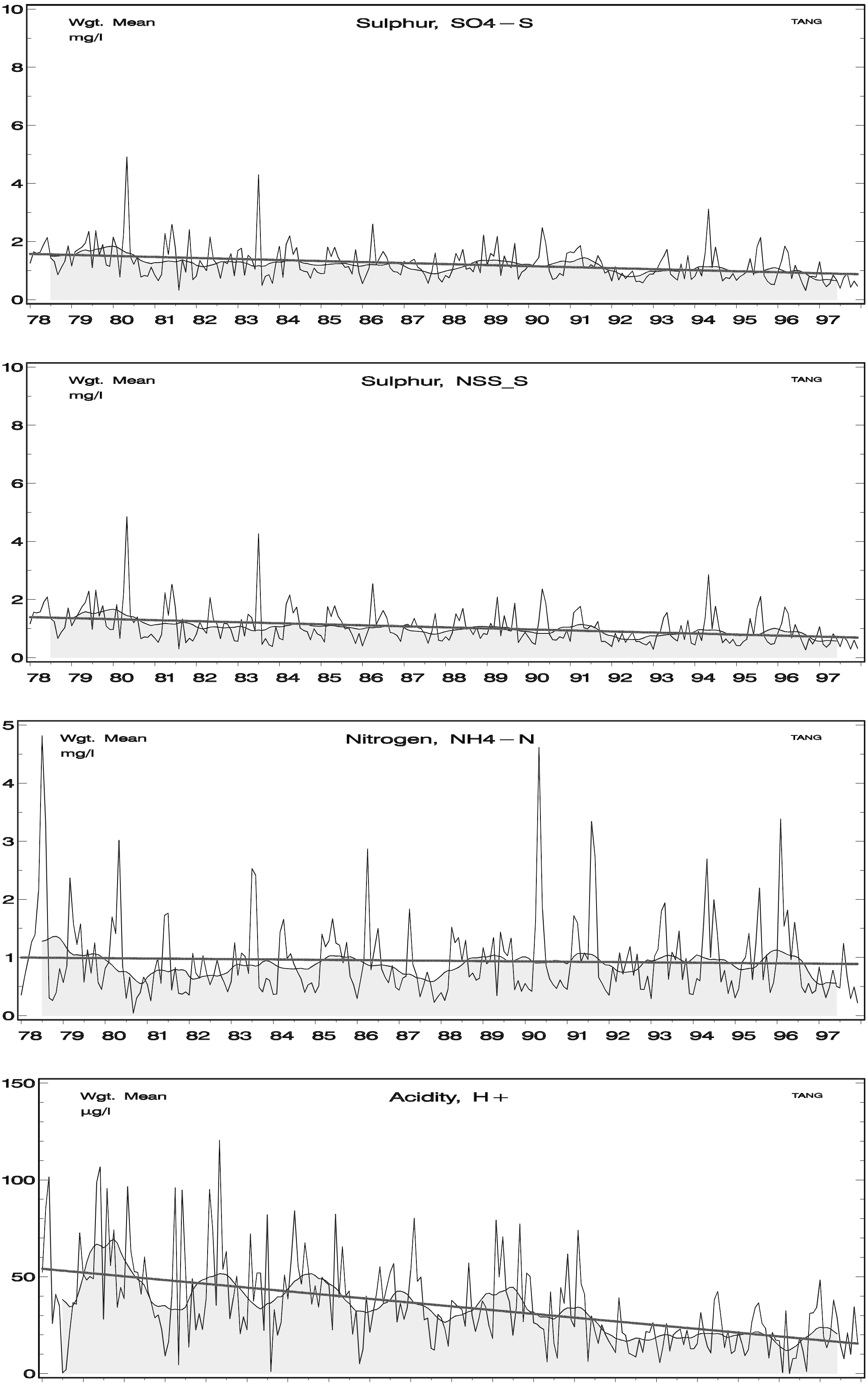

Figure 3.3.6 Trendplots for monthly precipitation weighted means at Tange. For explanation see caption of Figure 3.3.5.

Table 3.3.1 Significant trends of precipitation weighted monthly means of 24h wet-only concentrations. Trend values are average annual percentage changes relative to the grand mean, measured in mg·l^{-1} for all compounds, except H^+ which is measured in µg·l^{-1}.

Component	Grand Mean Concentration	Trend Pct. per Year	Relative Std_Dev
		KELDSNOR	
SO4-S	1.68	-5.9	0.3
NSS_S	1.26	-4.3	0.3
NH4-N	0.85	-3.3	0.3
NO3-N	0.75		
TOT_N	1.59	-3.4	0.3
H+	41.92	-5.5	0.1
Na	2.92		
Mg	0.36	-14.2	0.3
K	0.28		
Ca	0.46		
Cl	8.88		
		TANGE	
SO4-S	1.14	-3.1	0.2
NSS_S	0.95	-3.7	0.2
NH4-N	0.81		
NO3-N	0.52		
TOT_N	1.32		
H+	34.51	-5.6	0.1
Na	2.24		
Mg	0.28		
K	0.18		
Ca	0.28	-8.1	0.3
Cl	4.14		

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4 Depositions

Deposition - the final stage

Airborne pollutants are with time transported to the ground or other surfaces by various mechanisms. Washout by precipitation leads to wet deposition whereas advection and diffusion processes may lead to dry deposition as a consequence of direct contact between the pollutants and the surfaces. Particles may also settle directly on surfaces by gravity induced sedimentation. Together wet and dry deposition make up the total deposition.

Acidification and eutrophication

Deposition of pollutants such as sulphur or nitrogen compounds often have undesirable ecological consequences such as acidification of soils, forests and lakes or eutrophication of soil or sea because of too large a supply of nutrients such as nitrogen compounds. For these reasons depositions should be below the critical loads described earlier.

Wet and dry deposition

From an experimental point of view wet deposition is fairly easy to measure whereas dry deposition is normally not included in regular monitoring because of experimental difficulties. Instead it may be estimated by model calculations. On the experimental side one remedy is to measure bulk deposition in an open sampler that collects both wet and dry deposition. In most cases dry deposition is only of major importance for reactive gases such as NH_3 and O_3, but wet deposition may dominate anyway. Thus ammonia usually reacts very quickly to be converted to ammonium-containing particles for which wet deposition is the primary removal process. We shall therefore concentrate on the experimentally determined wet and bulk depositions and leave out a separate treatment of the dry deposition.

4.1 Overview and statistics

Statistical distributions

The distributions of monthly depositions in 1991-1997 are shown for some of the compounds in Figures 4.1.1 and 4.1.2 for the two wet-only stations and in Figures 4.1.3 and 4.1.4 for the bulk stations. Note that the deposition is shown logarithmically and that the unit of kg/km^2 is equal to deposition measured in mg/m^2. In these plots the circles show the 16-, 50-, and 84-percentiles, and the line shows the ideal lognormal distribution with indications of the geometric mean and standard deviations.

Approximately lognormal

Only a minor part of the monthly wet-only depositions at the two stations are strictly log-normally distributed *e.g.* $SO_4^{=}$-S and NH_4^+ -N at Keldsnor, but the approximation is reasonably good in a fair number of cases. Notable exceptions are NO_3^--N and H^+. About half of the monthly bulk depositions at the seven bulk stations are log-normally distributed in the strict sense, some examples are shown in Figure 4.1.3. None of the distributions in Figure 4.1.4 are log-normally distributed, however, but the lognormal approximation seems to be quite fair for all the nitrogen compounds shown for Anholt, whereas the distributions of the depositions of hydrogen ions are quite different with very long tails.

Bulk and wet-only deposition

The monthly depositions as measured by bulk collectors are compared to the results from the wet-only samplers in Figure 4.1.5. The orthogonal regression lines shown represent the best linear fits between the results from the two types of sampler. In almost of the cases the intercept of the lines on the bulk axis is positive as an indication of the dry deposition that takes place in the bulk samplers. In most of the cases (not all are shown) and in view of the uncertainties the slopes of the lines are essentially 1. The deviations from this situation, which only occurs for H^+ and $SO_4^=$-S at Keldsnor, are caused by some atypically large or small depositions in either type of sampler. So the two types of samplers collect precipitation equally well as corroborated by the comparisons for the precipitation amount shown in Figure 4.1.6.

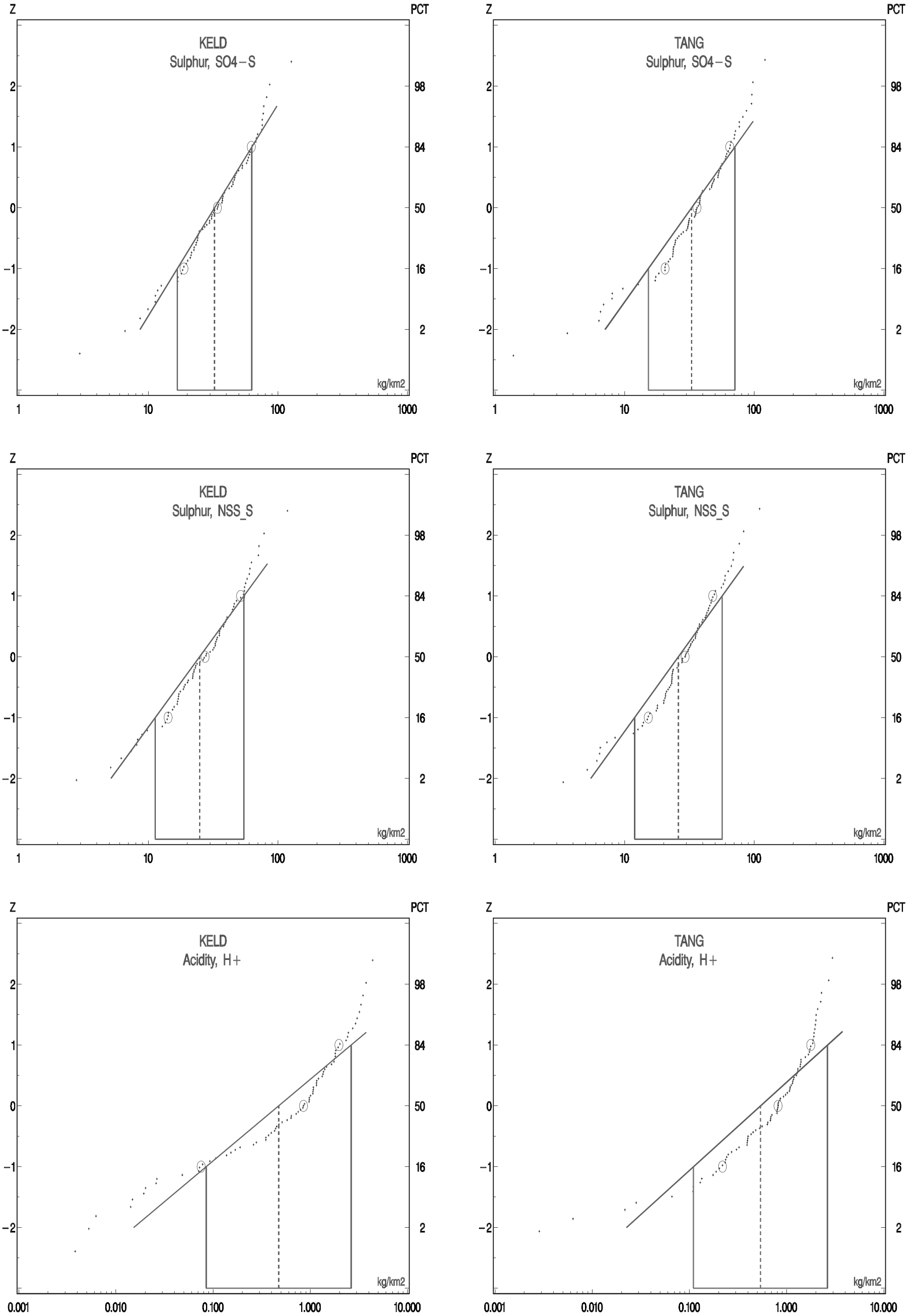


Figure 4.1.1 Statistical distributions of monthly wet-only depositions since 1991 of sulphur compounds and acidity, H^+. The depositions are shown logarithmically on the horizontal axis and circles denote the 16-, 50-, and 84-percentiles. The straight line is the log-normal fit through the indicated geometric mean and standard deviations.

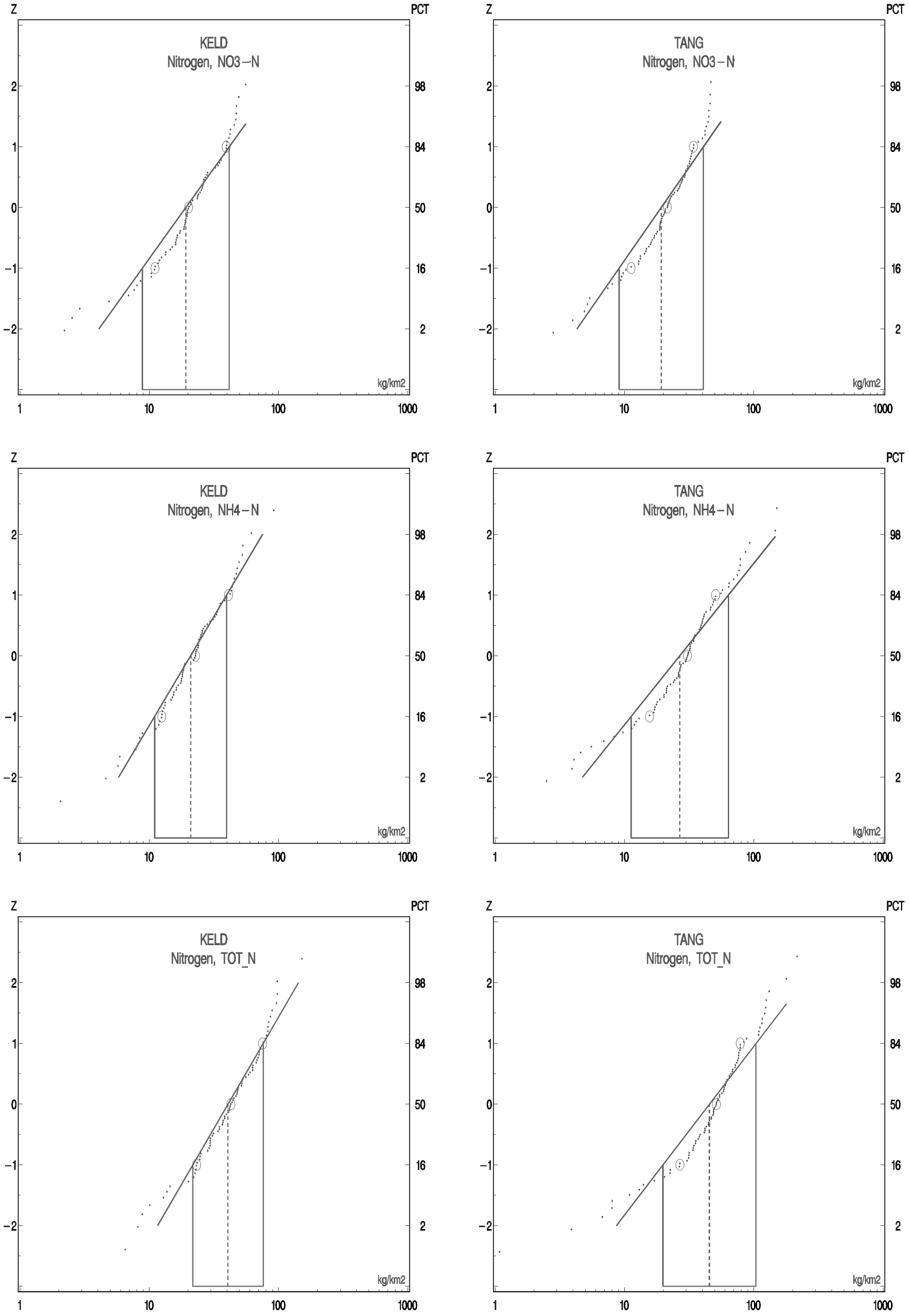


Figure 4.1.2 Statistical distributions of monthly wet-only depositions since 1991 of nitrogen compounds. The depositions are shown logarithmically on the horizontal axis and circles denote the 16-, 50-, and 84-percentiles. The straight line is the log-normal fit through the indicated geometric mean and standard deviations.

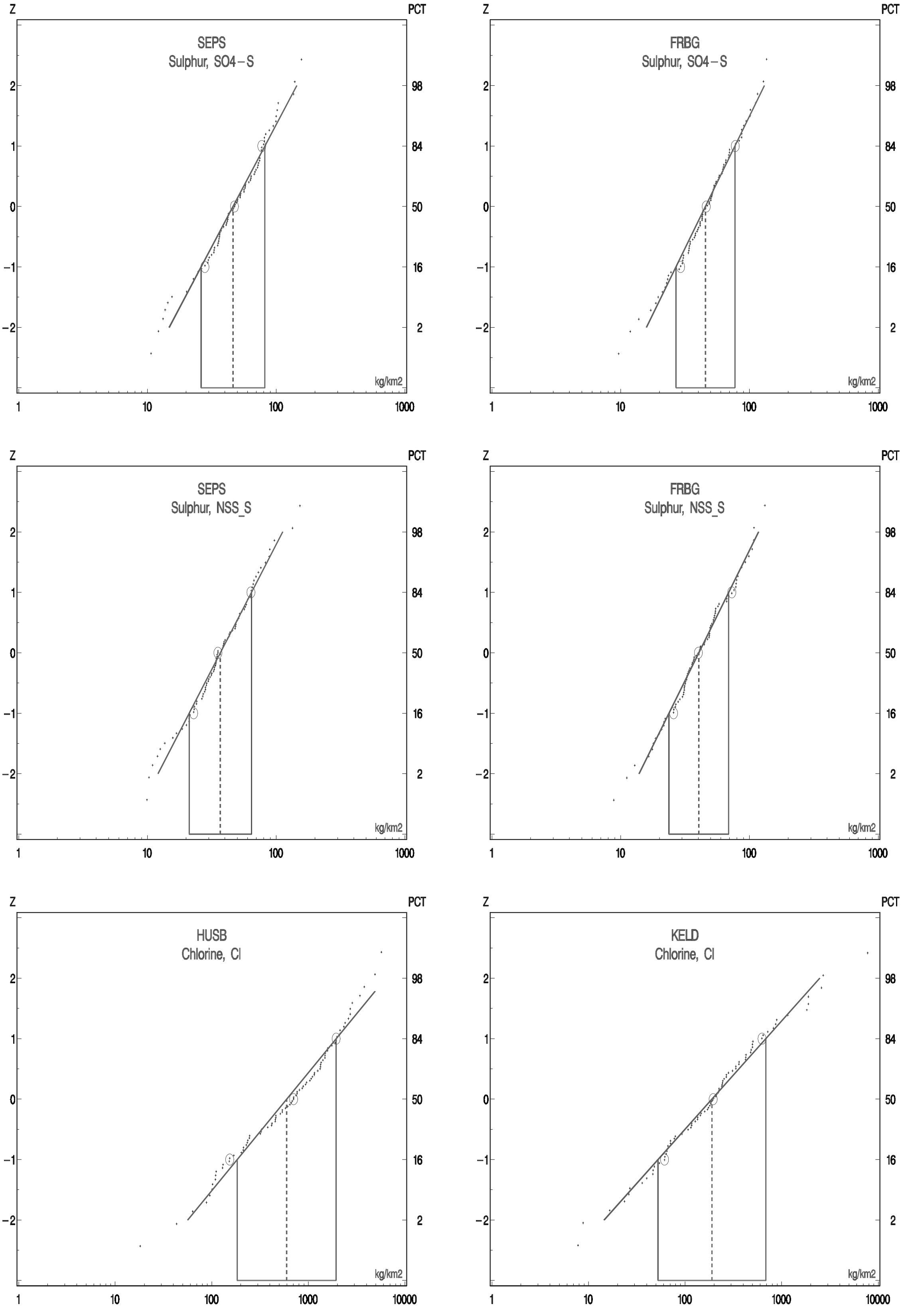


Figure 4.1.3 Statistical distributions of monthly bulk depositions since 1991 of sulphur compounds and chlorine. The depositions are shown logarithmically on the horizontal axis and circles denote the 16-, 50-, and 84-percentiles. The straight line is the log-normal fit through the indicated geometric mean and standard deviations.

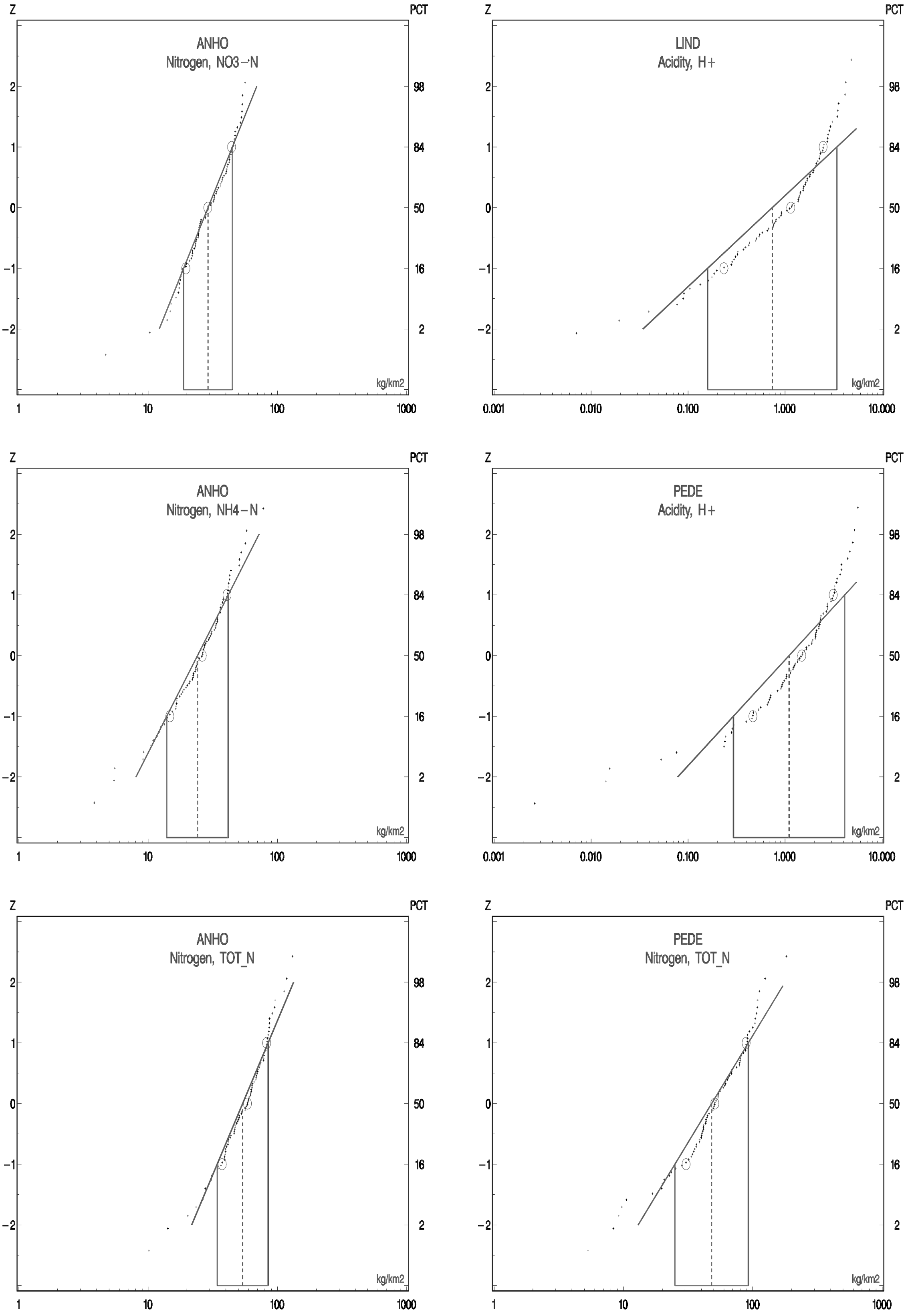


Figure 4.1.4 Statistical distributions of monthly bulk depositions since 1991 of nitrogen compounds and acidity, H^+. The depositions are shown logarithmically on the horizontal axis and circles denote the 16-, 50-, and 84-percentiles. The straight line is the log-normal fit through the indicated geometric mean and standard deviations.

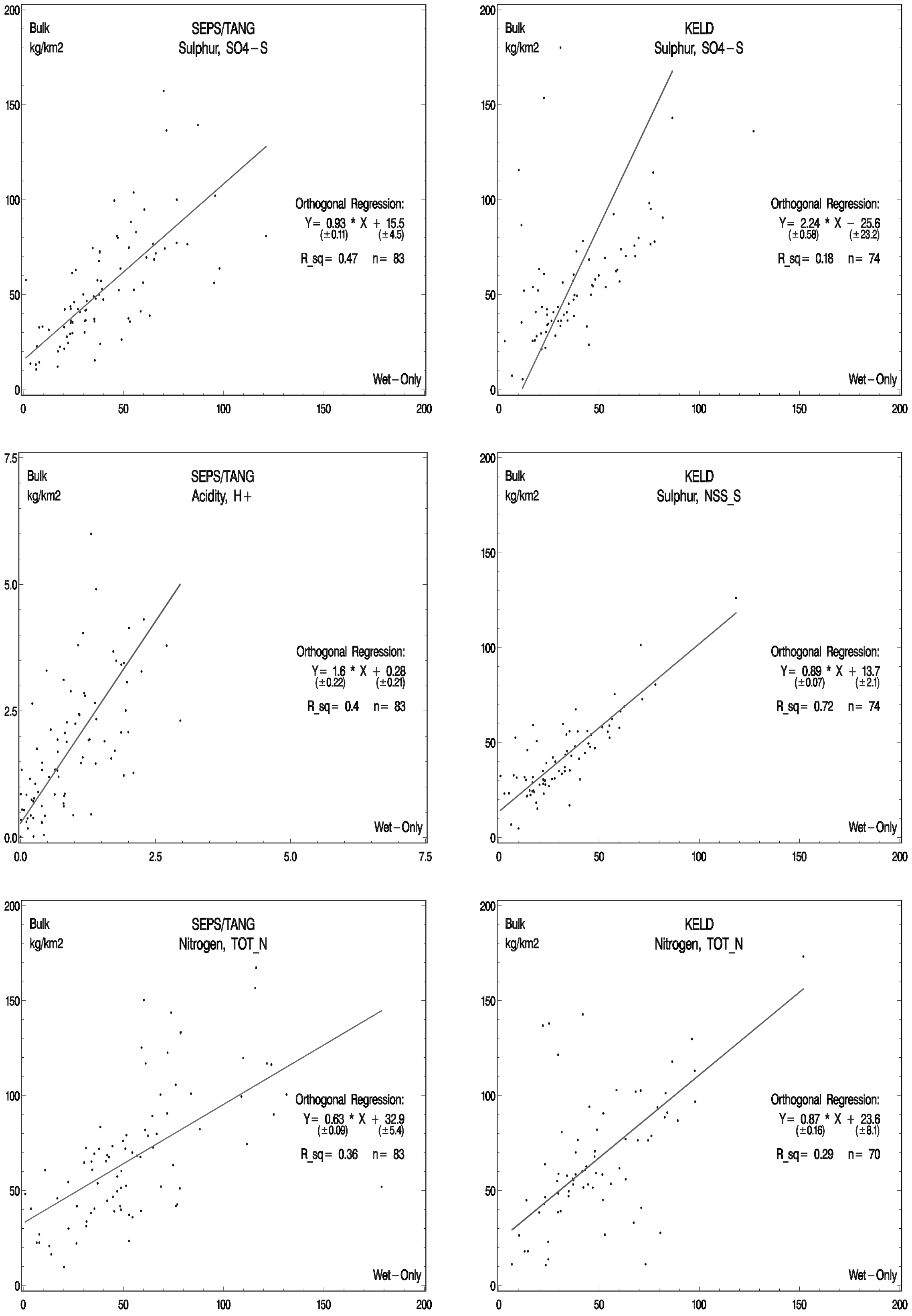


Figure 4.1.5 Monthly depositions in bulk collectors compared to wet-only samplers for the period 1991 - 1997. The results are fitted by orthogonal regression lines.

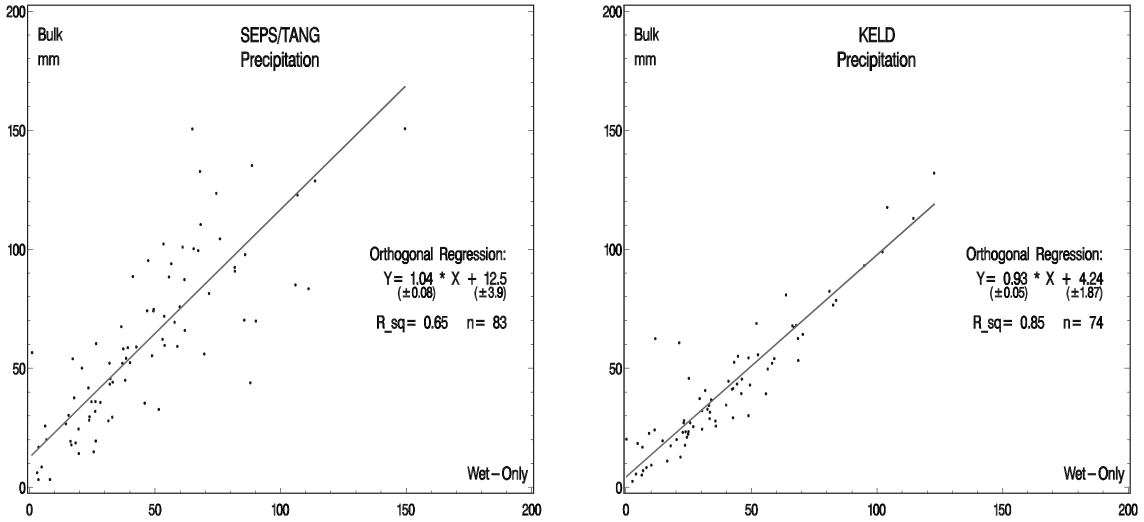


Figure 4.1.6 Monthly precipitation in bulk collectors compared to wet-only samplers for the period 1991 – 1997. The results are fitted by orthogonal regression lines.

4.2 Geography

Distribution parameters

The parameters of the distributions presented in Figures 4.1.1 - 4.1.4 are described in more detail and for different sub-periods in Tables 4.2.1 for monthly wet-only depositions and in Tables 4.2.2- 4.2.5 for monthly bulk depositions. For selected components these tables contain non-weighted *arithmetic* as well as *geometric* means and standard deviations, 50- and 90-percentiles, and number of observations as well as an indication of whether the distribution (in 1991-1997) can be considered to be lognormal. Note that for most datasets the geometric mean is much closer to the 50-percentile than the arithmetic mean, an indication of the approximate lognormal distributions. The column 'History' concerns time trends that are considered below.

Time resolution and deposition ranges

The level of the wet-only depositions as expressed by the means or the medians are as expected and already illustrated in Figure 4.1.5 considerably smaller than the bulk depositions, which also contain a certain amount of dry deposition. However, the relative ranges of depositions as expressed by the geometric standard deviations are larger for the wet-only data, which have a time resolution of 24 hours, than for the bulk depositions with a time resolution of a half month.

Similar wet-only deposition

For wet-only precipitation it is observed from Table 4.2.1 that the monthly depositions of sulphate, total nitrogen, and acidity in all three sub-periods are quite similar at the two stations. However, it is also observed that the 50-percentiles are larger at Tange compared to Keldsnor although this station is more directly exposed to long range transport from the continent to the south. With the exception of sulphate in the earliest sub-period this is also true for the geometric means of the monthly depositions.

Variable bulk depositions of sulphate

Bulk sulphate depositions, shown in Table 4.2.2, vary considerably among the stations. The variations within stations are also considerable since the geometric standard deviation factors in many cases are close to a value of 2. The highest deposition values occur, as for the concentrations, at the marine stations Husby, Keldsnor and Anholt where marine sulphur accounts for 30-55 % of the total and where the fractions of anthropogenic sulphur, NSS_S are smallest. The depositions of anthropogenic NSS-S (table 4.2.3) are more evenly distributed across the country, particularly in the most recent sub-period in the 1990's. The geometric standard deviations are also smaller and the highest depositions at Lindet, Keldsnor and Frederiksborg are not significantly higher than the depositions at the four other stations.

Uniform bulk depositions of nitrogen

The bulk depositions of nitrogen are fairly uniform across the country (table 4.2.4) and the only systematic differences seem to be that depositions at the coastal stations are less than at the agriculturally influenced stations further inland. Also the smaller precipitation at the coast may be of importance.

Acidity depositions

The bulk depositions of acidity H^+, shown in Table 4.2.5 reveal no systematic geographical variation. If the atypical low levels and high variations for the bulk depositions at Keldsnor are ignored the lowest values occur at such disparate stations as Lindet and Pedersker.

Variations against a national average

The geographic differences are illustrated in more detail in Figures 4.2.1-4. In these figures the monthly bulk depositions at various sites are shown against the corresponding values averaged over all stations. The latter data represent Grand National averages. The lines are orthogonal regression lines, which are the best least squares fit to the data, and their location relative to the national means reflect the geographical differences. However, in several cases the intercept with the vertical axis is of no significance, it is either not statistically different from zero or much smaller than typical deposition values. In these cases much of the information on geographic differences resides in the slopes of the regression lines, since they depend on the correlations and the standard deviations at the site. An overview of the parameters is given in Table 4.2.6 for all major compounds at all sites. Note that the calculations of these parameters are based on all data, whereas the data displayed in the figures amount to minimum 95% of all.

North-South sulphur gradient

Variations of sulphur compounds are shown for a selection of stations in Figure 4.2.1 with SO_4 in the left-hand panels and anthropogenic NSS_S in the right-hand panels. The marine influence at Husby and Keldsnor is quite evident from the large SO_4 -deposition compared to depositions at the other stations which are typical of the national levels as can be seen in Table 4.2.6 (a. and b.). The pattern of depositions of the anthropogenic component NSS_S is somewhat different however. The depositions at the stations to the north, Husby and Anholt are considerably smaller than in the rest of the country (Table 4.2.6). This gradient is clear evidence of LRTAP from the south. This geographical variation in the deposition of NSS_S is also found for the depositions of NH_4^+, compare Table 4.2.6, so also this component is of predominant European origin. The depositions of NH_4^+ are shown for 6 of the seven bulk stations in Figure 4.2.2.

Homogeneous nitrate depositions

Nitrate depositions are as seen in the table quite homogeneous across the country, only Anholt differs by a smaller slope of the line. The same applies to the deposition of Tot_N despite the site differences for NH_4^+. These features are illustrated in Figure 4.2.3.

Homogeneous acidity depositions

The acid depositions as well as the precipitation amounts are geographically quite homogeneous as illustrated in Figure 4.2.4 for a selection of sites. Table 4.2.6 shows that precipitation tends to be scarcer at the coastal stations in the inner Danish waters (see also Figure 3.3.4).

Table 4.2.1 Statistics of monthly wet-only depositions in 3 sub-periods in kg/km^2 Significant decreases between two sub-periods are denoted *D*. An "X" in the column Log_N 9197 indicates that data in the period 1991-1997 fit a log-normal distribution at a significance level of 5%.

Quantity	Log_N	7884	8590	9197	History	Log_N	7884	8590	9197	History
					NSS_S					
			KELDSNOR					**TANGE**		
Mean_arit.		60.9	39.8	31.5			65.1	46.9	32.4	
Std.dev.		44.3	25.4	20.3			53.0	24.6	19.5	
Mean_geom.		45.7	31.6	24.9	Da. Db		48.3	40.5	26.0	Db
Std_geom.		2.37	2.12	2.20			2.27	1.78	2.18	
P50		47.1	34.4	27.4			58.3	42.2	29.3	
P90		118.1	75.1	57.8			126.5	78.4	59.5	
N		84	71	76			84	70	83	
					SO4-S					
			KELDSNOR					**TANGE**		
Mean_arit.		87.8	48.5	39.1			76.6	56.7	41.0	
Std.dev.		143.3	28.1	23.0			58.0	27.4	24.2	
Mean_geom.	X	59.1	40.2	32.4	Da. Db		57.4	49.8	32.9	Db
Std_geom.		2.38	1.97	1.94			2.27	1.71	2.16	
P50		60.5	44.8	34.1			68.0	52.3	36.2	
P90		133.9	86.7	75.1			145.2	95.8	71.5	
N		84	71	76			84	70	83	
					TOT_N					
			KELDSNOR					**TANGE**		
Mean_arit.		65.2	52.6	48.1			75.0	66.7	58.1	
Std.dev.		39.7	33.8	26.5			57.6	34.5	37.4	
Mean_geom.		52.4	41.7	40.7	Da		56.8	57.2	45.4	Db
Std_geom.		2.13	2.17	1.87			2.20	1.82	2.29	
P50		55.5	43.9	42.8			58.9	59.9	51.3	
P90		125.2	91.9	83.2			158.2	112.8	111.6	
N		84	71	75			84	70	83	
					H+					
			KELDSNOR					**TANGE**		
Mean_arit.		1.98	1.30	1.07			2.51	1.77	0.94	
Std.dev.		1.57	1.08	1.04			2.14	1.13	0.70	
Mean_geom.		1.26	0.83	0.47			1.65	1.36	0.54	Db
Std_geom.		3.42	3.12	5.57			3.16	2.30	4.89	
P50		1.52	1.07	0.85			2.04	1.58	0.82	
P90		4.22	2.63	2.73			4.37	3.33	1.95	
N		84	71	75			84	70	83	

Table 4.2.2 Statistics of monthly bulk deposition of sulphate in 2 sub-periods in kgS/km^2. For other details see caption of Table 4.2.1.

Quantity	Log_N	8590	9197	History	Log_N	8590	9197	History
		HUSBY				**SEPSTRUP**		
Mean_arit.		126.6	89.1			78.2	53.6	
Std.dev.		77.9	58.4			36.6	29.4	
Mean_geom.	X	111.0	72.4	D	X	70.9	45.7	D
Std_geom.		1.63	1.96			1.59	1.83	
P50		99.0	76.8			73.1	48.0	
P90		227.4	164.8			111.0	88.4	
N		24	83			12	83	
		ANHOLT				**FREDERIKSBORG**		
Mean_arit.		75.4	56.3			76.1	51.8	
Std.dev.		30.2	25.0			33.5	26.3	
Mean_geom.	X	68.9	50.5	D	X	69.0	45.6	D
Std_geom.		1.58	1.64			1.58	1.69	
P50		73.1	56.3			70.0	46.2	
P90		122.5	85.3			118.1	87.3	
N		28	82			67	84	
		LINDET				**KELDSNOR**		
Mean_arit.		94.2	67.6			116.3	64.1	
Std.dev.		46.0	30.3			60.0	52.0	
Mean_geom.		83.9	60.5	D	X	102.5	52.7	D
Std_geom.		1.65	1.64			1.71	1.87	
P50		90.2	61.4			113.4	53.9	
P90		136.1	109.7			168.7	106.3	
N		33	84			12	80	
		PEDERSKER						
Mean_arit.		62.7	45.2					
Std.dev.		22.5	27.0					
Mean_geom.		58.8	37.1	D				
Std_geom.		1.45	2.00					
P50		56.8	37.5					
P90		97.2	85.4					
N		19	84					

Table 4.2.3 Statistics of monthly bulk deposition of non-seasalt sulphate in 2 sub-periods in kgS/km^2. For other details see caption of Table 4.2.1.

Quantity	Log_N	8590	9197	History	Log_N	8590	9197	History
		HUSBY				**SEPSTRUP**		
Mean_arit.		50.4	39.1			58.2	42.9	
Std.dev.		16.6	18.8			25.2	25.4	
Mean_geom.		47.7	35.8	D	X	53.7	36.5	D
Std_geom.		1.42	1.62			1.51	1.80	
P50		49.6	40.0			51.3	35.3	
P90		70.2	62.2			100.2	69.6	
N		24	83			12	83	
		ANHOLT				**FREDERIKSBORG**		
Mean_arit.		50.6	37.0			69.6	46.3	
Std.dev.		23.6	19.4			31.9	24.9	
Mean_geom.	X	44.7	33.2	D	X	62.7	40.4	D
Std_geom.		1.71	1.68			1.60	1.71	
P50		51.0	32.5			62.9	40.2	
P90		91.5	63.8			108.1	81.3	
N		28	82			67	84	
		LINDET				**KELDSNOR**		
Mean_arit.		67.9	48.7			63.7	42.1	
Std.dev.		28.3	20.2			26.0	19.8	
Mean_geom.	X	62.0	44.6	D		59.5	37.6	D
Std_geom.		1.57	1.54			1.46	1.67	
P50		62.9	44.1			62.9	38.2	
P90		107.5	76.6			95.4	64.5	
N		33	84			12	80	
		PEDERSKER						
Mean_arit.		55.2	39.9					
Std.dev.		22.2	24.9					
Mean_geom.		51.3	32.6	D				
P50		47.7	33.0					
P90		90.5	74.6					
N		19	84					

Table 4.2.4 Statistics of monthly bulk deposition of total nitrogen in 2 sub-periods in kgN/km^2. For other details see caption of Table 4.2.1.

Quantity	Log_N	8590	9197	History	Log_N	8590	9197	History
		HUSBY				**SEPSTRUP**		
Mean_arit.		78.3	69.2			85.0	69.2	
Std.dev.		25.9	28.7			30.5	36.7	
Mean_geom.		74.0	62.5	D	X	80.1	59.6	D
Std_geom.		1.43	1.62			1.44	1.78	
P50		78.4	68.6			83.8	64.8	
P90		112.4	102.4			132.1	122.6	
N		24	83			12	83	
		ANHOLT				**FREDERIKSBORG**		
Mean_arit.		72.2	59.0			85.7	70.0	
Std.dev.		29.1	24.0			36.4	33.2	
Mean_geom.		65.3	53.6	D	X	77.4	62.7	D
Std_geom.		1.64	1.60			1.62	1.62	
P50		78.8	58.7			88.5	63.8	
P90		107.7	87.0			132.3	123.5	
N		28	82			67	84	
		LINDET				**KELDSNOR**		
Mean_arit.		101.5	88.1			81.7	66.7	
Std.dev.		40.5	35.3			34.5	33.7	
Mean_geom.		93.2	80.6			74.6	57.3	D
Std_geom.		1.55	1.56			1.59	1.83	
P50		95.8	81.8			78.0	59.0	
P90		166.5	133.5			124.9	113.1	
N		33	84			12	76	
		PEDERSKER						
Mean_arit.		69.1	57.2					
Std.dev.		26.3	34.4					
Mean_geom.		64.1	47.2	D				
Std_geom.		1.51	1.97					
P50		61.6	49.6					
P90		116.6	104.2					
N		19	82					

Table 4.2.5 Statistics of monthly bulk deposition of acidity H^+ in 2 sub-periods in kg/km^2. For other details see caption of Table 4.2.1.

Quantity	Log_N	8590	9197	History	Log_N	8590	9197	History
		HUSBY				**SEPSTRUP**		
Mean_arit.		2.96	1.86			2.46	1.78	
Std.dev.		1.87	1.99			1.59	1.26	
Mean_geom.		2.51	1.32	D		1.99	1.25	D
Std_geom.		1.79	2.44			2.05	2.76	
P50		2.87	1.54			1.99	1.56	
P90		5.25	3.21			4.83	3.49	
N		24	83			12	83	
		ANHOLT				**FREDERIKSBORG**		
Mean_arit.		2.27	1.73			3.04	1.88	
Std.dev.		0.99	1.05			1.68	1.28	
Mean_geom.		1.98	1.35	D		2.54	1.37	D
Std_geom.		1.83	2.22			1.93	2.68	
P50		2.61	1.54			2.84	1.72	
P90		3.36	3.26			5.65	3.25	
N		28	82			67	83	
		LINDET				**KELDSNOR**		
Mean_arit.		2.27	1.34			0.52	0.67	
Std.dev.		1.36	1.12			0.76	0.78	
Mean_geom.		1.80	0.74	D		0.15	0.23	
Std_geom.		2.14	4.64			6.73	6.29	
P50		2.24	1.14			0.23	0.41	
P90		4.13	2.87			1.46	1.88	
N		33	84			12	79	
		PEDERSKER						
Mean_arit.		2.30	1.75					
Std.dev.		1.58	1.35					
Mean_geom.		1.85	1.08	D				
Std_geom.		2.01	3.82					
P50		1.93	1.44					
P90		4.11	3.81					
N		19	84					

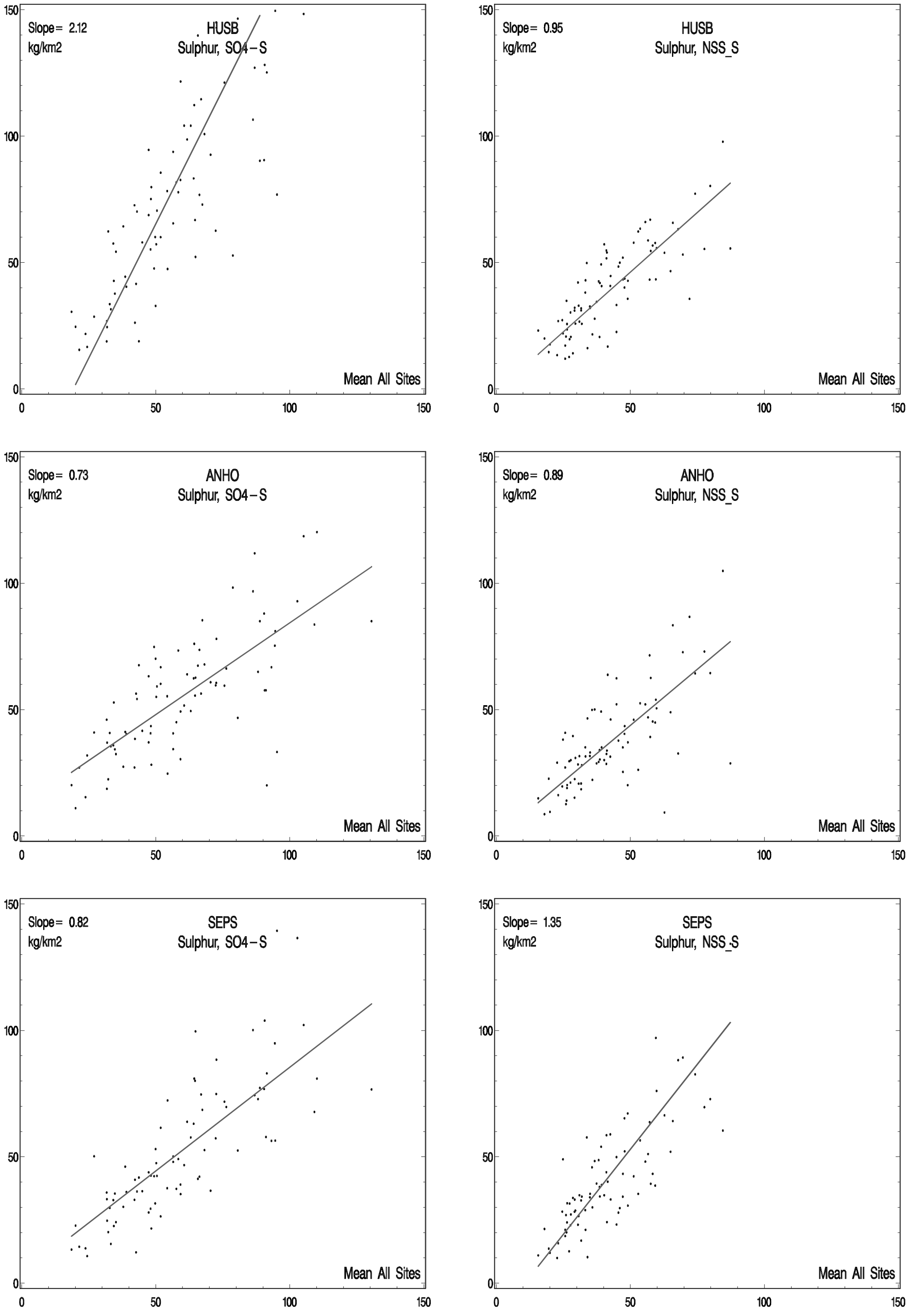


Figure 4.2.1 Monthly bulk depositions of sulphur compounds 1991- 1997. Site depositions plotted and regressed orthogonally against the means at all sites.

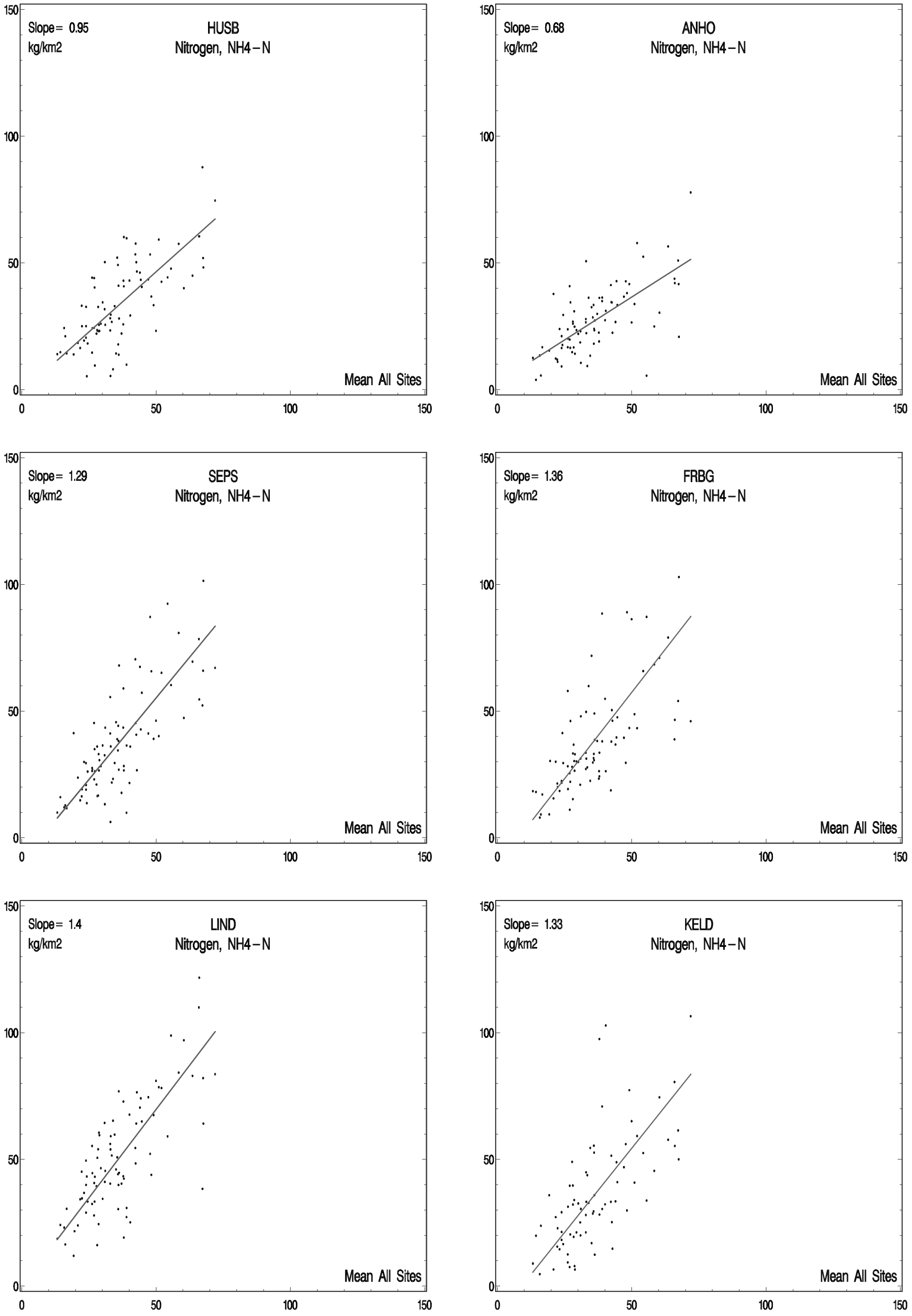


Figure 4.2.2 Monthly bulk depositions of ammonium 1991-1997. Site depositions plotted and regressed orthogonally against the means at all sites.

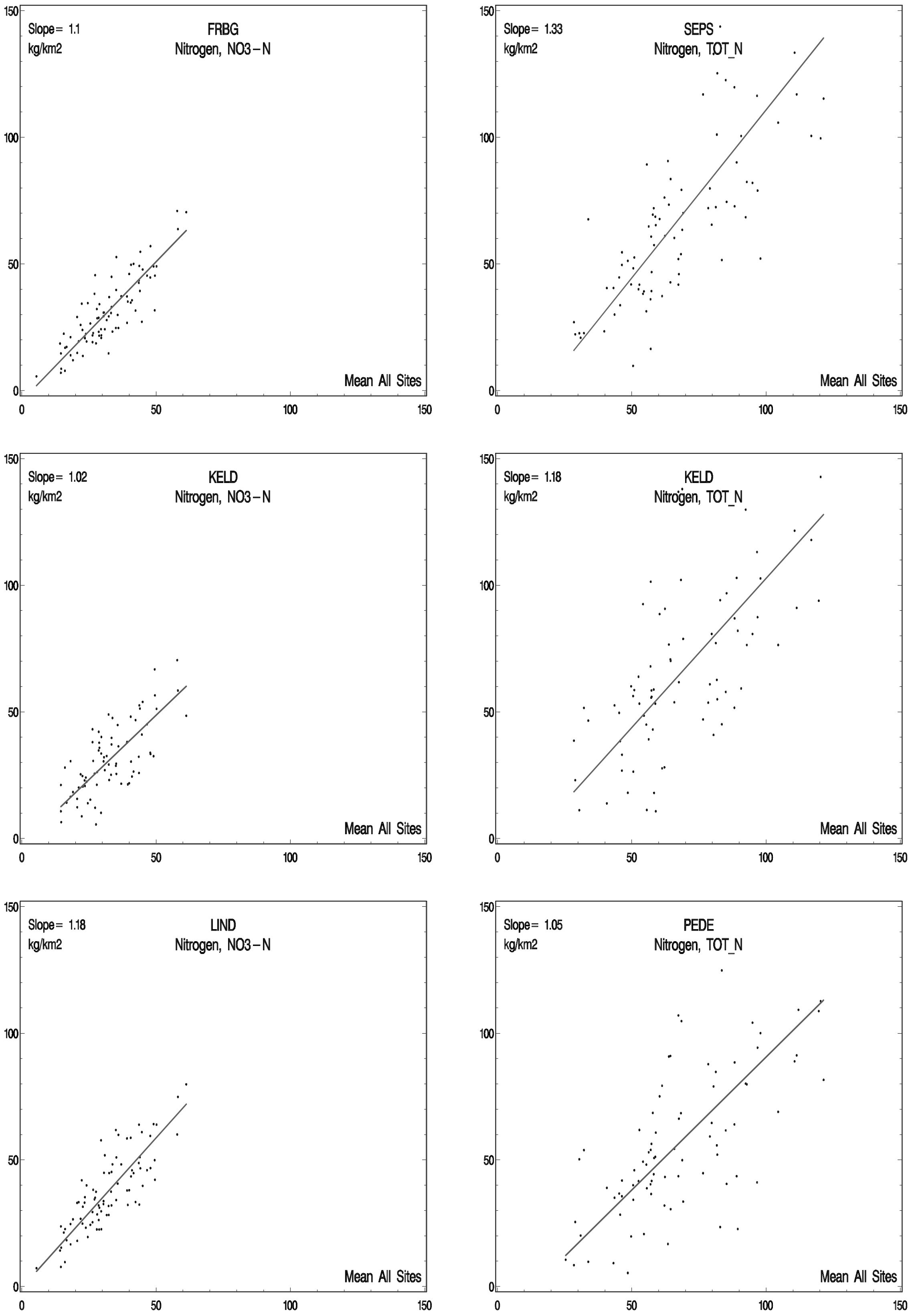


Figure 4.2.3 Monthly bulk depositions of nitrate and total nitrogen 1991-1997. Site depositions plotted and regressed orthogonally against the means at all sites.

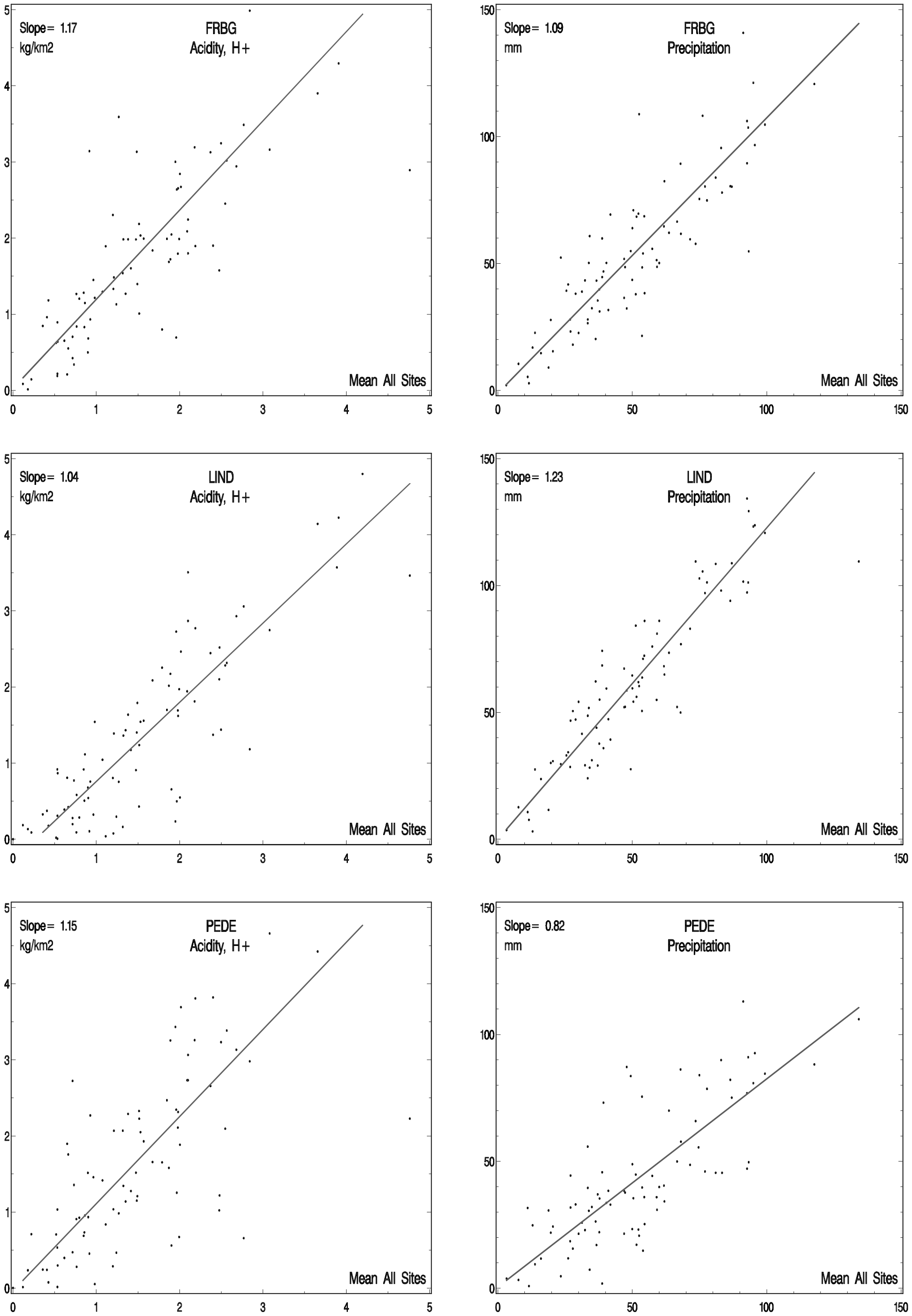


Figure 4.2.4 Monthly bulk depositions of acidity and precipitation 1991-1997. Site depositions plotted and regressed orthogonally against the means at all sites.

Table 4.2.6.a Orthogonal regression parameters for monthly bulk depositions in kg/km^2 1991-1997.

Site	Slope	Std- Slope	Intercept	Std- Intcep	Rsq	Slope # 1
			SO4-S			
HUSB	2.12	0.12	-40.92	7.45	0.79	1
SEPS	0.82	0.09	3.29	5.79	0.48	
ANHO	0.73	0.07	11.64	4.38	0.56	-1
FRBG	0.68	0.09	10.60	5.29	0.43	-1
LIND	1.00	0.07	7.12	3.99	0.74	
KELD	1.80	0.17	-46.56	10.30	0.60	1
PEDE	0.63	0.09	6.92	5.56	0.37	-1
			NSS_S			
HUSB	0.95	0.09	-1.12	3.73	0.59	
SEPS	1.35	0.12	-14.36	4.97	0.62	1
ANHO	0.89	0.10	-0.77	4.44	0.48	
FRBG	1.32	0.11	-9.13	4.57	0.64	1
LIND	1.03	0.09	5.46	3.74	0.62	
KELD	1.04	0.10	-1.70	4.33	0.57	
PEDE	1.17	0.13	-9.59	5.49	0.50	
			NH4-N			
HUSB	0.95	0.10	-0.90	3.81	0.51	
SEPS	1.29	0.12	-9.24	4.50	0.58	1
ANHO	0.68	0.09	2.62	3.19	0.43	-1
FRBG	1.36	0.16	-10.82	5.76	0.48	1
LIND	1.40	0.14	-0.14	4.99	0.56	1
KELD	1.33	0.17	-12.07	6.35	0.45	
PEDE	1.13	0.15	-11.36	5.43	0.42	
			NO3-N			
HUSB	1.11	0.07	-0.71	2.41	0.73	
SEPS	1.20	0.10	-7.61	3.35	0.62	
ANHO	0.85	0.09	4.12	2.94	0.52	
FRBG	1.10	0.08	-4.09	2.45	0.72	
LIND	1.18	0.09	-0.56	2.93	0.67	1
KELD	1.02	0.12	-2.26	3.79	0.51	
PEDE	1.10	0.09	-7.11	3.06	0.62	
			TOT_N			
HUSB	1.08	0.09	-5.06	5.95	0.66	
SEPS	1.33	0.12	-21.97	8.25	0.60	1
ANHO	0.72	0.09	9.35	6.33	0.43	-1
FRBG	1.18	0.12	-10.53	8.12	0.55	
LIND	1.32	0.12	-1.89	7.85	0.62	1
KELD	1.18	0.15	-15.15	10.36	0.46	
PEDE	1.05	0.12	-14.51	8.46	0.47	

Table 4.2.6.b Orthogonal regression parameters for monthly bulk depositions in kg/km^2 1991-1997.

Site	Slope	Std- Slope	Intercept	Std- Intcep	Rsq	Slope # 1
				H+		
HUSB	1.91	0.20	-1.16	0.31	0.54	1
SEPS	1.13	0.10	-0.01	0.15	0.62	
ANHO	0.85	0.09	0.38	0.15	0.52	
FRBG	1.17	0.09	0.02	0.15	0.66	
LIND	1.04	0.07	-0.28	0.11	0.73	
KELD	0.58	0.07	-0.26	0.11	0.47	-1
PEDE	1.15	0.11	-0.04	0.17	0.59	
				mm		
HUSB	1.23	0.07	-7.97	3.43	0.81	1
SEPS	1.24	0.07	-4.75	3.94	0.77	1
ANHO	0.87	0.07	-0.73	3.53	0.68	
FRBG	1.09	0.06	-1.13	3.37	0.77	
LIND	1.23	0.06	-0.05	3.19	0.83	1
KELD	0.85	0.07	-3.60	3.97	0.63	
PEDE	0.82	0.07	0.39	3.85	0.60	-1

4.3 Trends

Decreasing depositions

It is seen from Tables 4.2.1 - 4.2.5 that in a majority of instances the average monthly bulk depositions appear to decrease from one period to the next. Where this is a true and significant decrease according to the Student's T-test for the lognormal case it has been noted in the *History* column, with D denoting significant decreases between two sub-periods. The decreases in bulk depositions from the late 1980's to the first half of the 1990's amount to 25-35% for NSS_S and to 25-50% for total sulphate. For total nitrogen depositions decreased by 15-25%, which even if modest is in contrast to what was observed for the concentrations. The acidity of the deposition has however decreased most dramatically, by 35 -60%, except at Keldsnor where the bulk samplers behave differently, exhibiting an apparent, but in fact insignificant increase by more than 50% of the H$^+$ deposition.

Annual bulk depositions

The development on a national level since 1985 is further illustrated in Figures 4.3.1 - 4.3.3 by the annual bulk depositions of the major ions at six of the ½-monthly bulk sampling sites. Annual precipitation amounts at these stations were shown in Figure 3.3.4.

Athropogenic NSS_S

The figures confirm in more detail the general picture of the variations found above. The considerable variations among stations of depositions of sulphur are mainly due to the influence of marine sulphate and the variations within stations are mainly caused by a rather persistent decrease in depositions of anthropogenic NSS_S since the late 1980s. The reductions of nitrogen depositions are more modest and seem to be equally caused by decreases for ammonium and for nitrate, whereas the deposition reductions for acidity are quite dramatic.

Persistent trends

In general the deposition tendencies are sufficiently strong to override the fluctuations caused by the different meteorological conditions and precipitation amounts in the individual years.

Trends in quarterly depositions

As noted earlier the character of precipitation data series calls for rather long-term statistics. Consequently quarterly depositions have been selected for illustration of the development with time in bulk deposition. Trendplots for the six bulk stations are shown in Figures 4.3.4 - 4.3.6 for a number of selected pollutants. As in previous trendplots the figures contain three curves that are, respectively, the quarterly depositions (full line), a moving 4-quarter average (delineating the shaded area) and a trend (straight line) that is calculated as a regression line. Clear downward trends have existed at all sites since the mid-1980s for the sulphur compounds and for acidity whereas the tendencies for Tot_N are most pronounced at the southern stations. However, it should be noted that only a minority of these bulk deposition trends are significant, presumably because of rather short time series and/or because of a late start compared to the really important years in the 1980s (see next paragraph). Thus despite appearances, no significant trends were found at Anholt, Sepstrup, and Pedersker. On the other hand all trends shown for Keldsnor are significant.

Deposition trends over 20 years

Similar trendplots for the quarterly wet-only depositions measured since 1978 at the two 24-h stations Tange and Keldsnor are shown in Figures 4.3.7 - 4.3.10. Also here clear trends are found and again, most pronounced for sulphur and acidity. These longer time series do reveal, however, that the period since the mid-1980s have contributed only little, if at all, to the overall trends. This is most pronounced at Keldsnor, particularly for nitrogen, and may be ascribed to the quite large depositions in the early 1990s seen in the figures. For Keldsnor this is probably caused by the rather large amounts of precipitation in this period, see Figure 4.3.11.

Significant negative trends

For the whole period since 1978 the trends are however significant, except for NO_3^- at Tange, and reflect the changes in emissions in Europe, see the last column of Table 2.3.1. This can be seen from Table 4.3.1, which shows annual changes in percent of the grand mean deposition for the various components. The trend uncertainties are given as relative standard deviations and if they are larger than 0.5 the trends are not considered significant and are not presented.

Counteracting base cations

As expected that is the case for the minor, predominantly natural, components with the exception of Ca. The negative trend for the deposition of this soil component at Tange can be ascribed to very large depositions in 1987-1988 and to very small depositions in 1996-1997. These small depositions might have an origin in the increasing use of 'green' fields' in the winter season. Calcium belongs to the group of base cations, which neutralise the acidic deposition. But this effect is diminished if such a component has a negative trend. Similar negative trends for Ca have also been seen in UK, Finland, and Canada (DETR 1997; Kulmala *et al.* 1998; Nordlund and Sirois, 1999). Negative trends for base cations may thus offset the benefits from reduced sulphur emissions.

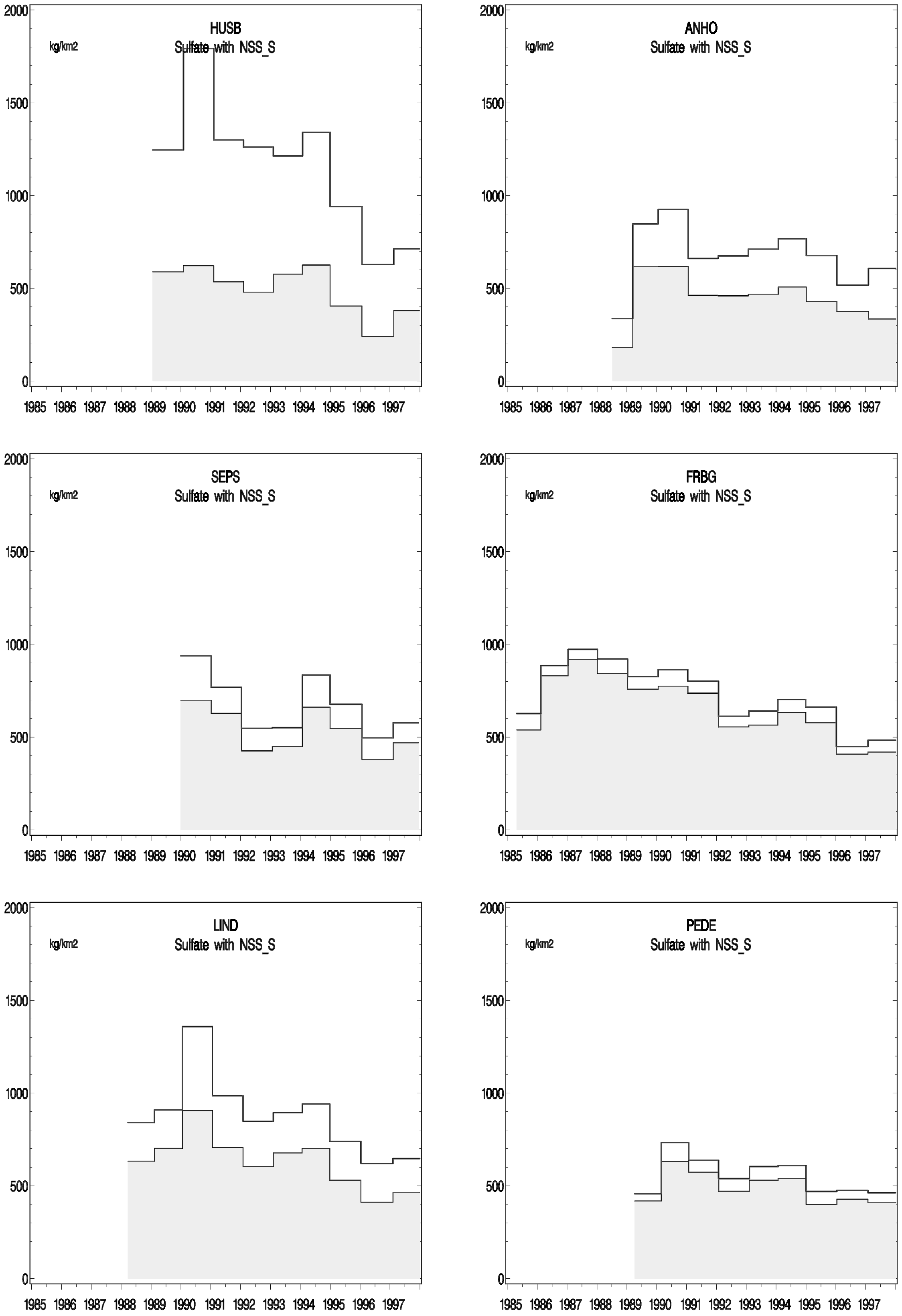


Figure 4.3.1 Annual bulk depositions of sulphate, SO4 and the fraction of NSS_S (shaded) in kg S/km^2, 1985 - 1997.

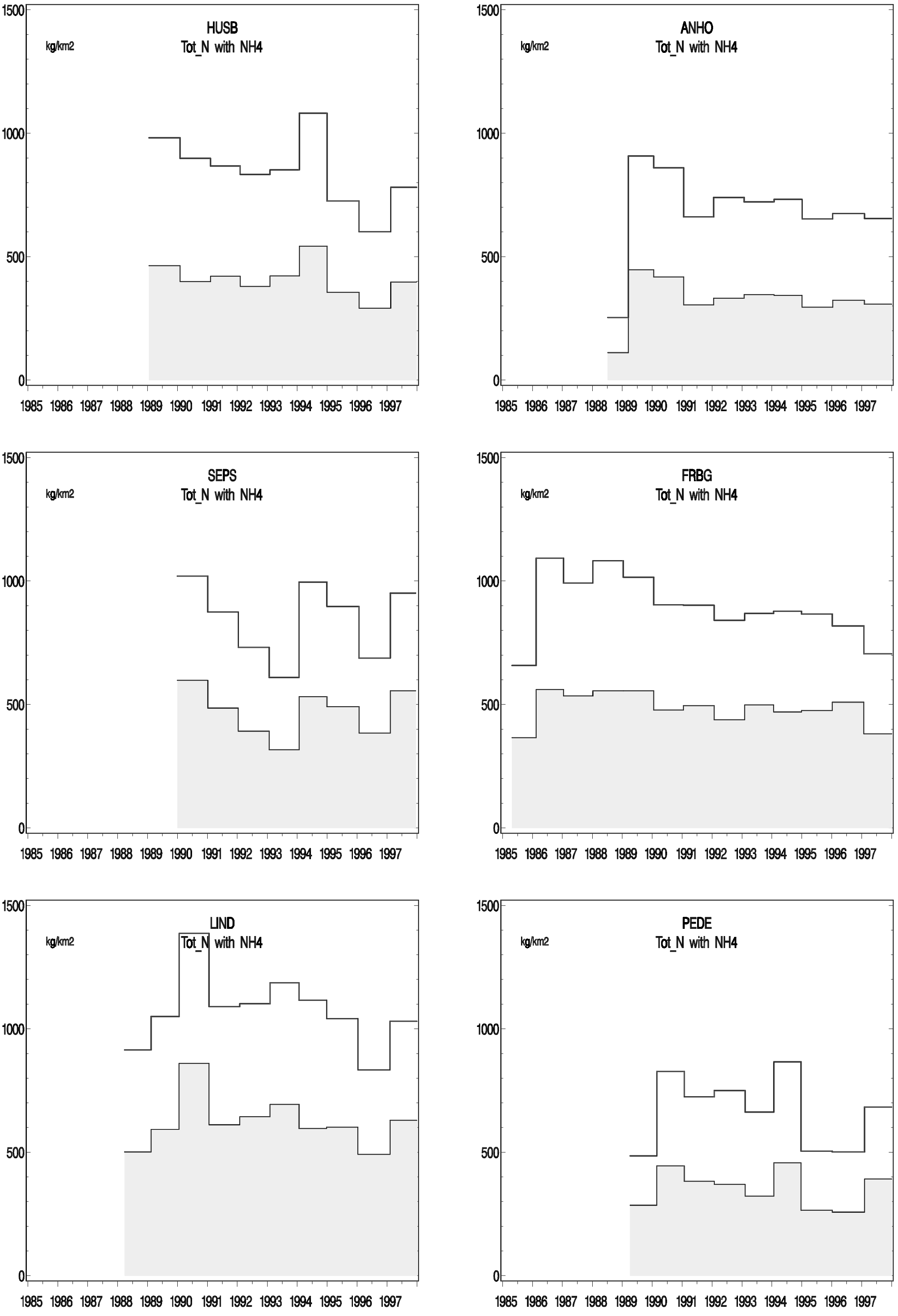


Figure 4.3.2 Annual bulk depositions of total nitrogen, the sum of nitrate and ammonium (shaded) in kg N/km^2, 1985 - 1997.

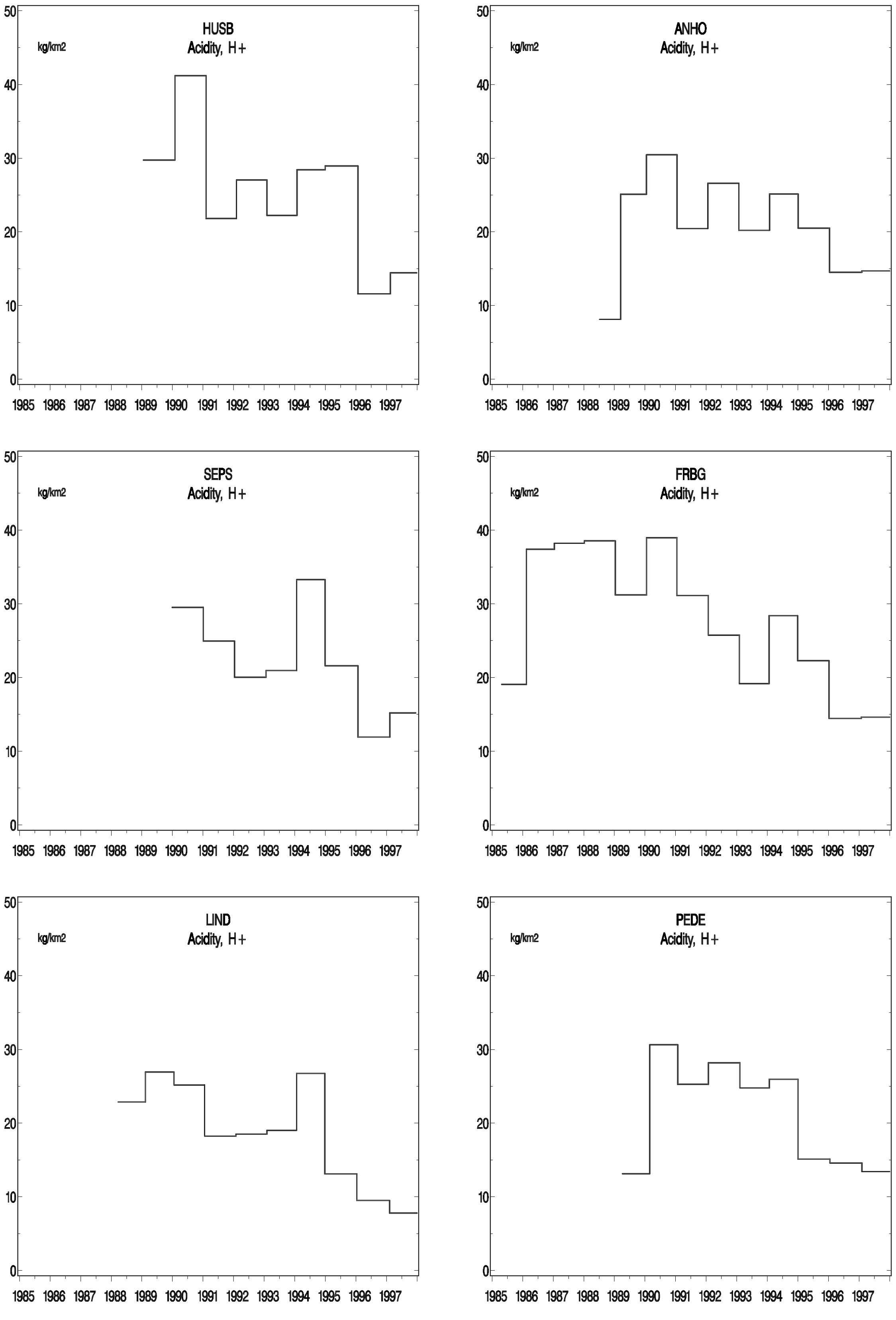


Figure 4.3.3 Annual bulk depositions of acidity, H^+ in kg/km^2, 1985 - 1997.

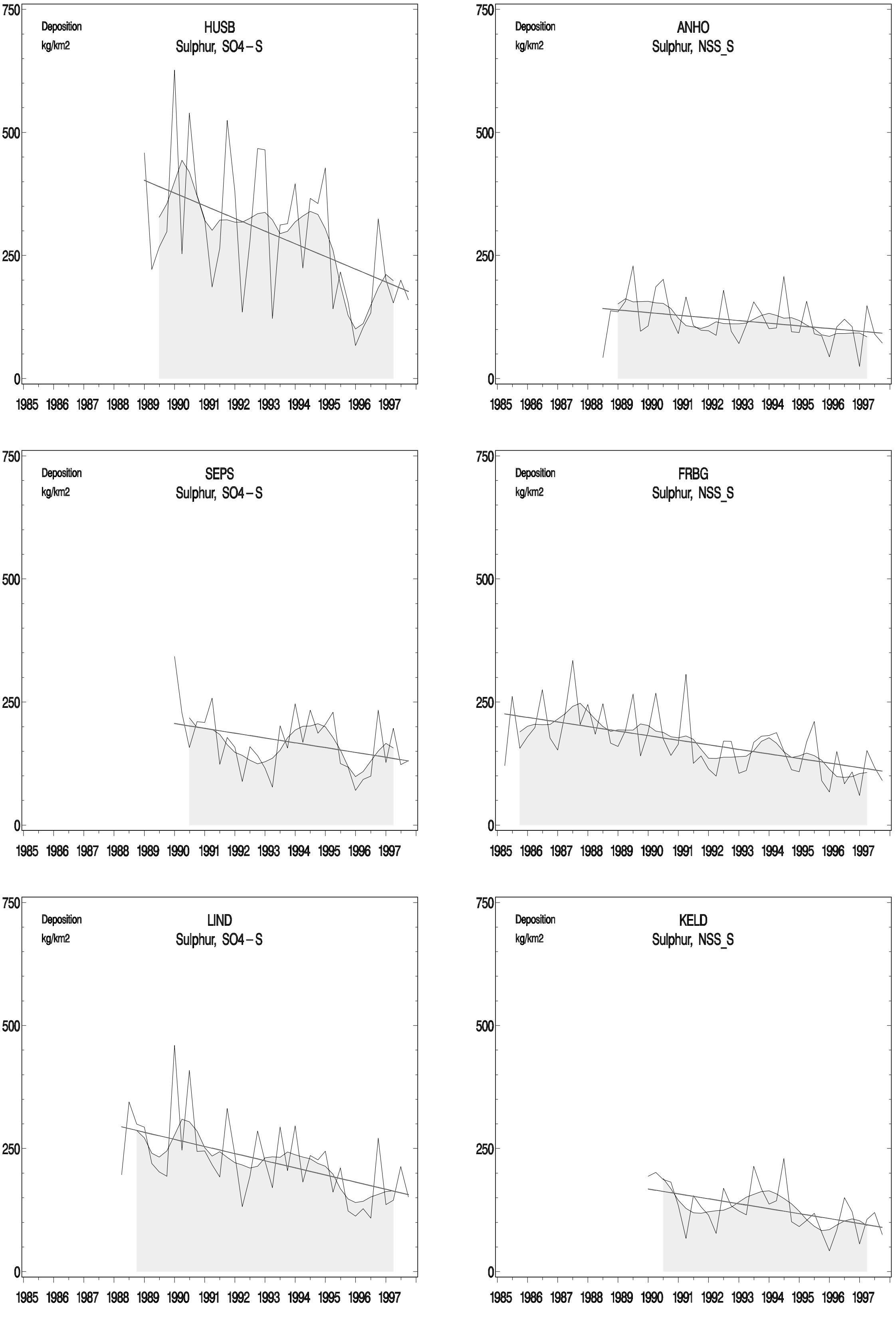


Figure 4.3.4 Quarterly bulk depositions (thin jagged line) of sulphate and NSS_S, moving annual (4-quarter) average (shaded) and trend.

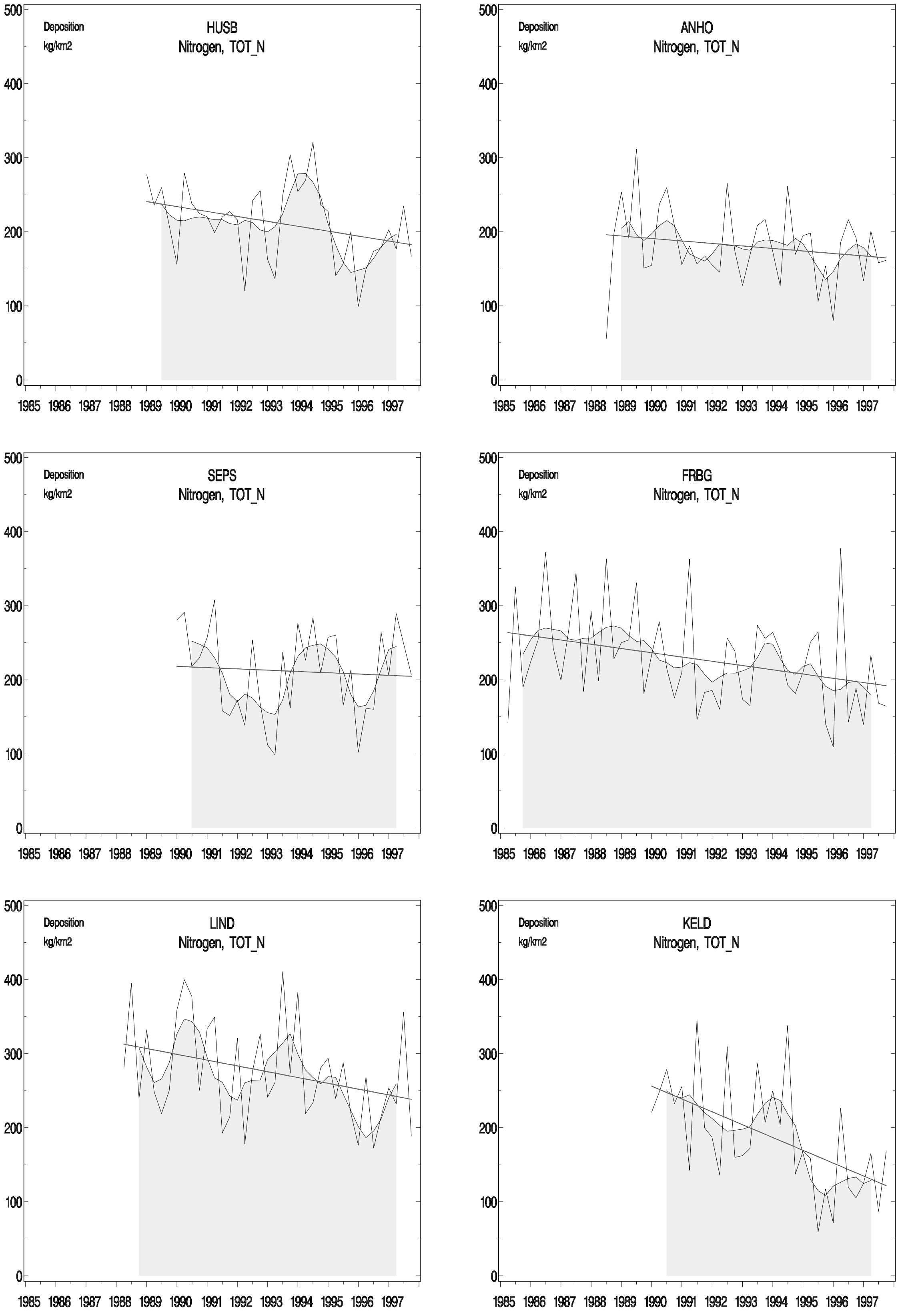


Figure 4.3.5 Quarterly bulk depositions (thin jagged line) of total nitrogen, moving annual (4-quarter) average (shaded) and trend.

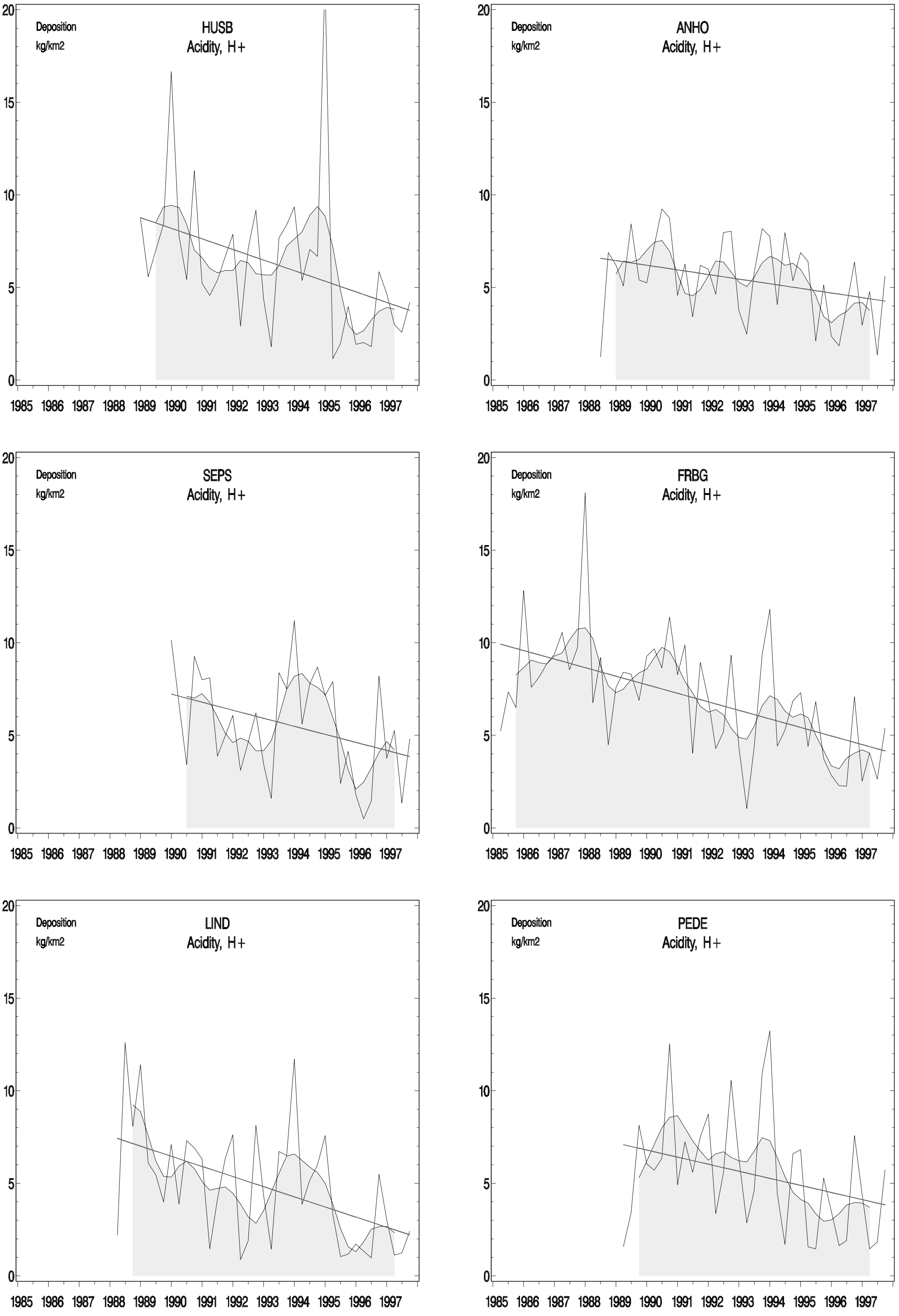
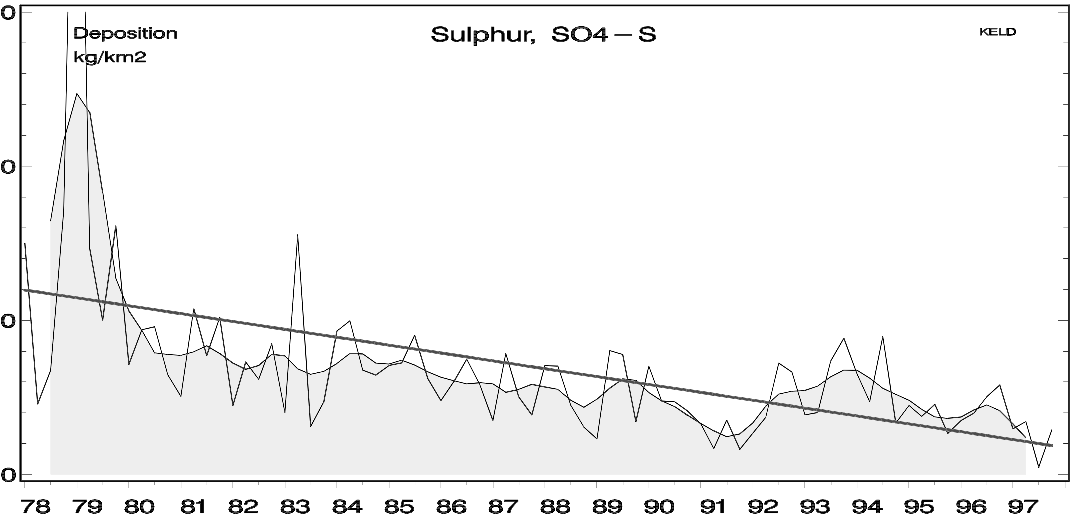
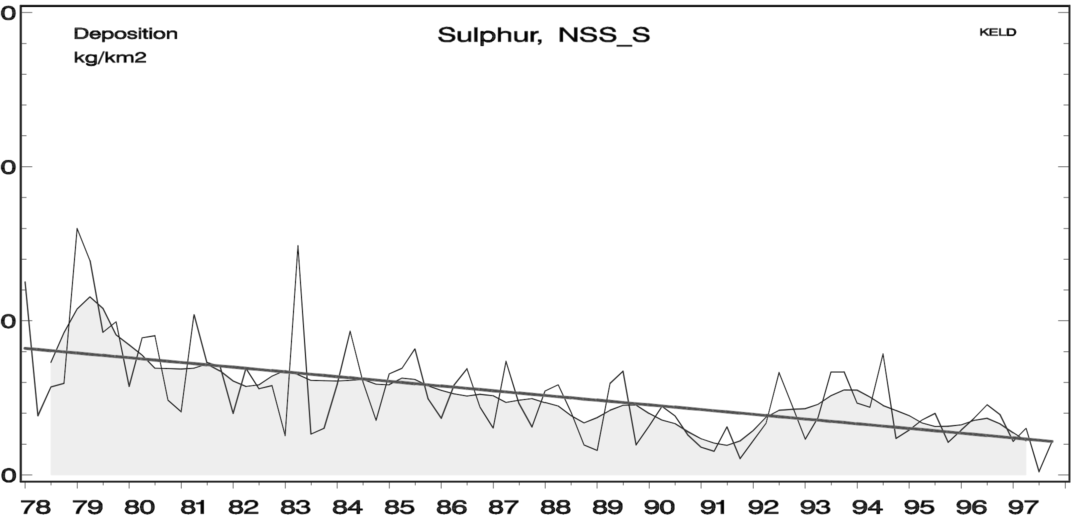


Figure 4.3.6 Quarterly bulk depositions (thin jagged line) of acidity H^+, moving annual (4-quarter) average (shaded) and trend.





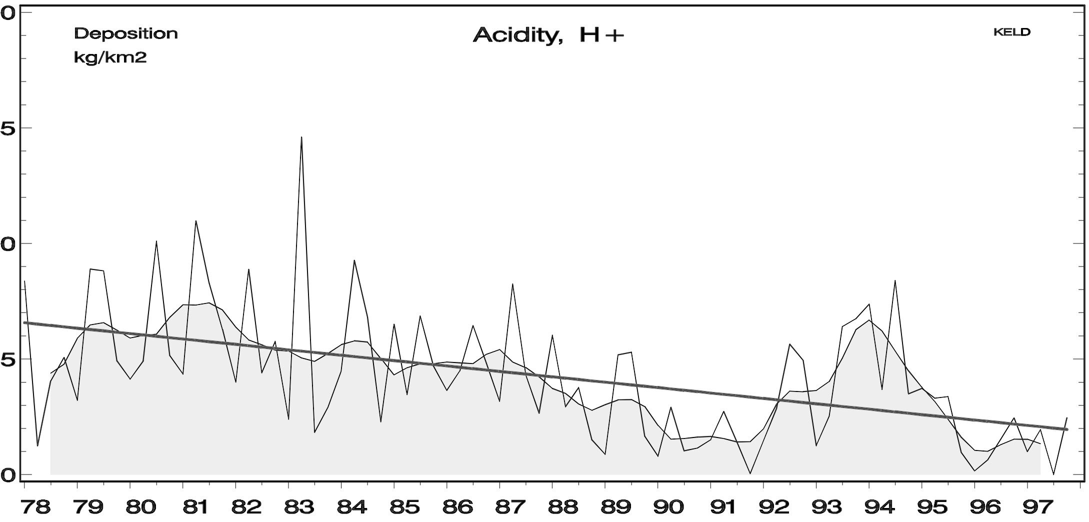


Figure 4.3.7 Quarterly wet-only depositions (thin jagged line) of sulphur and acidity at Keldsnor 1978 - 1997, moving annual (4-quarter) average (shaded) and trend.

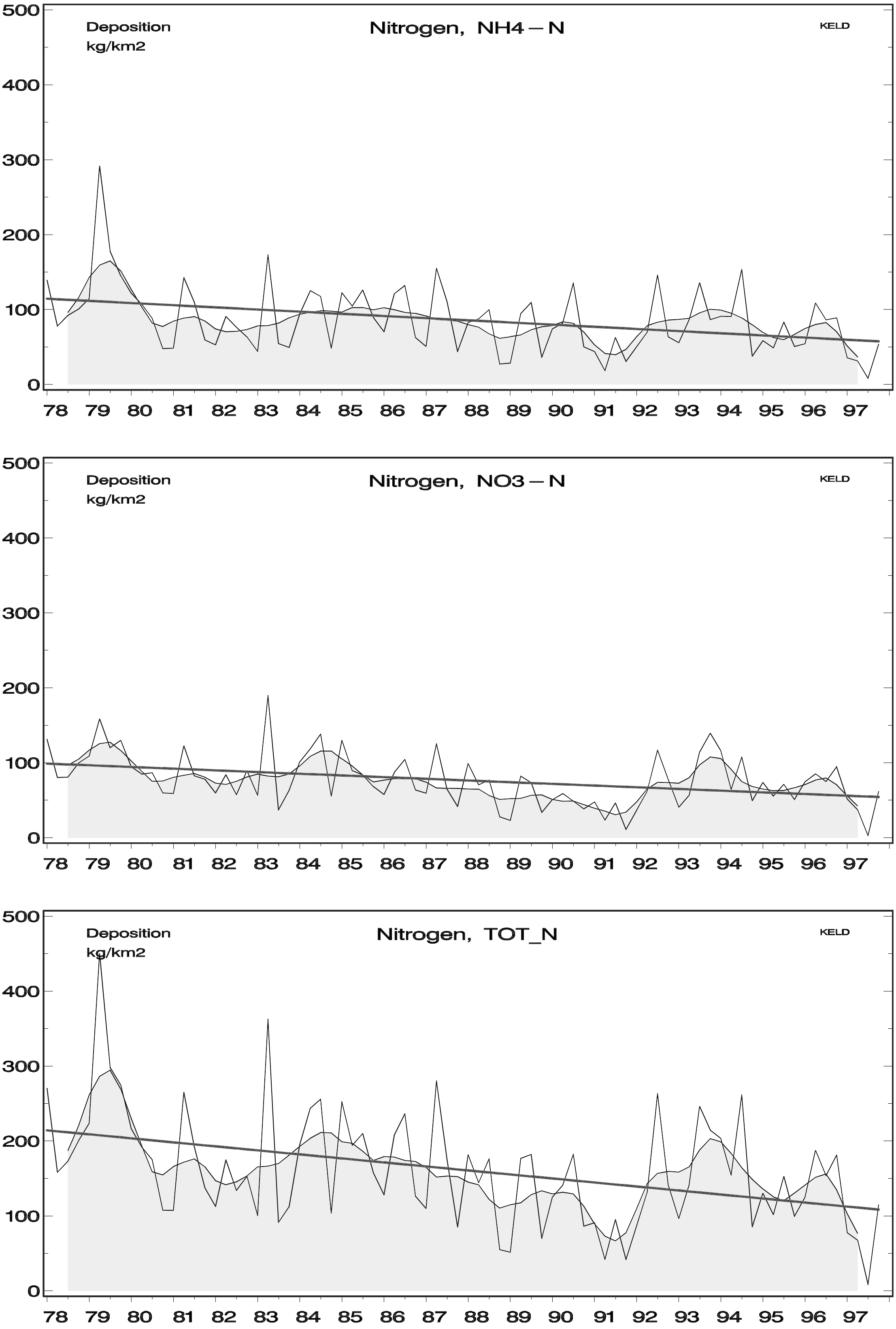
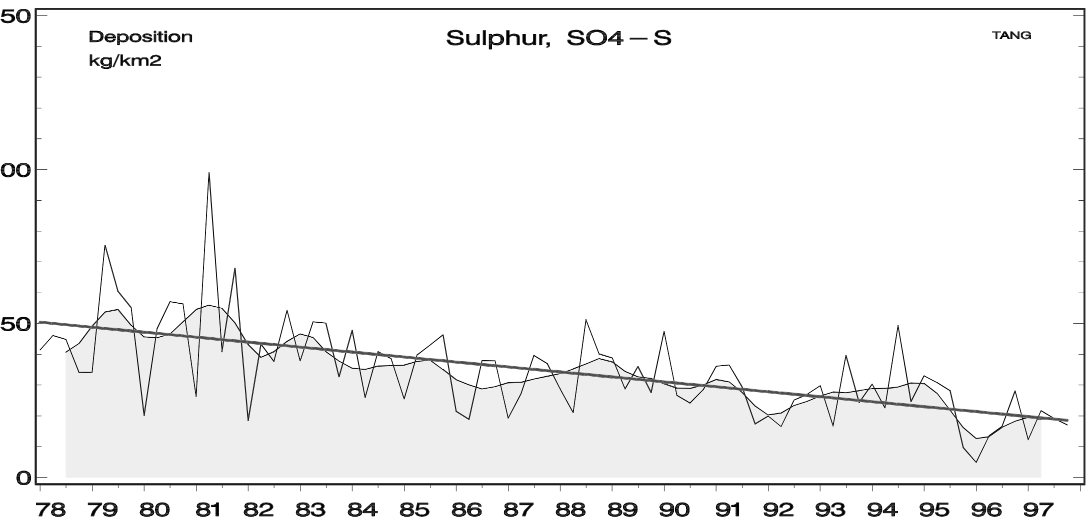
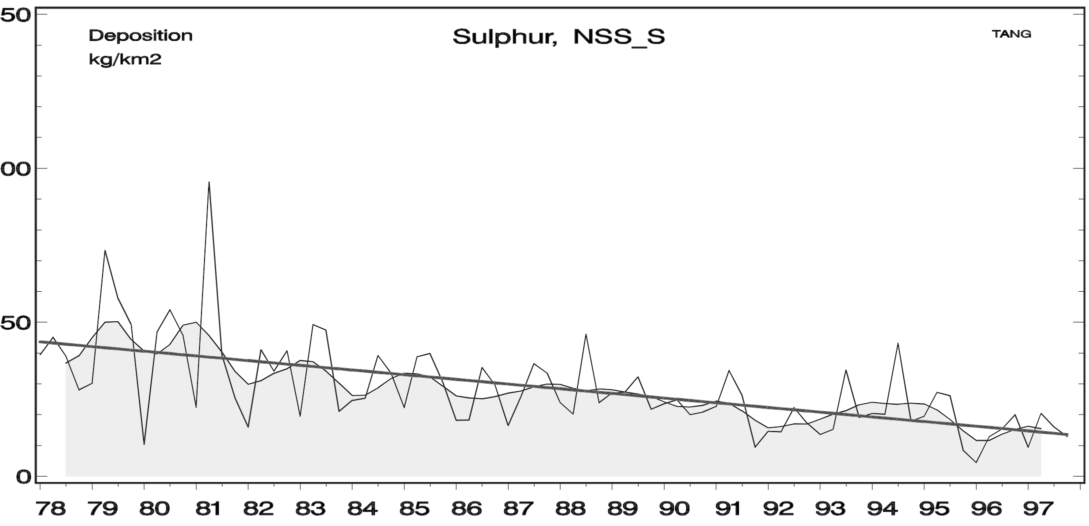


Figure 4.3.8 Quarterly wet-only depositions (thin jagged line) of nitrogen compounds at Keldsnor 1978 - 1997, moving annual average (shaded) and trend.





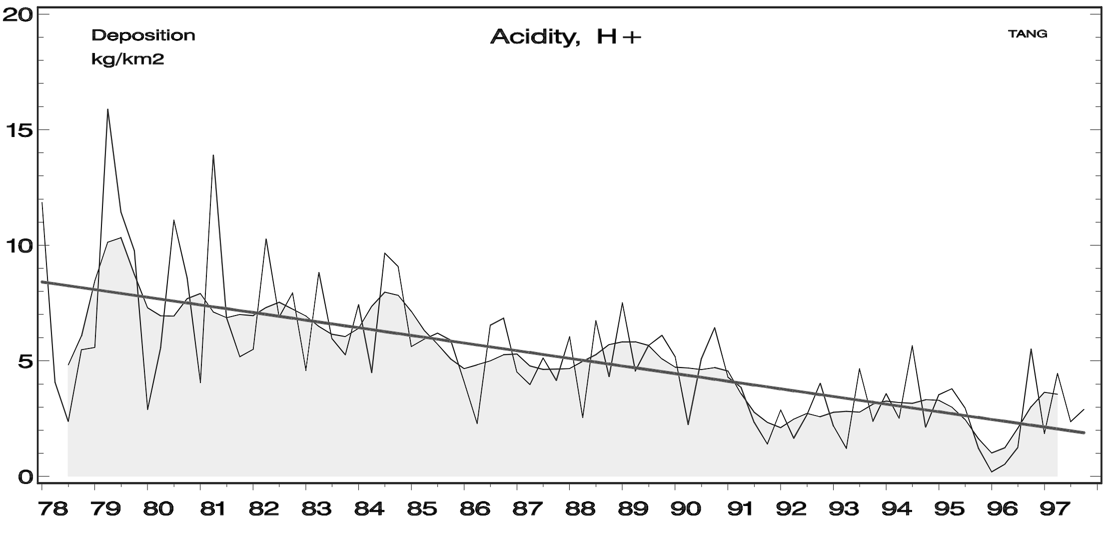


Figure 4.3.9 Quarterly wet-only depositions (thin jagged line) of sulphur and acidity at Tange 1978 - 1997, moving annual average (shaded) and trend.

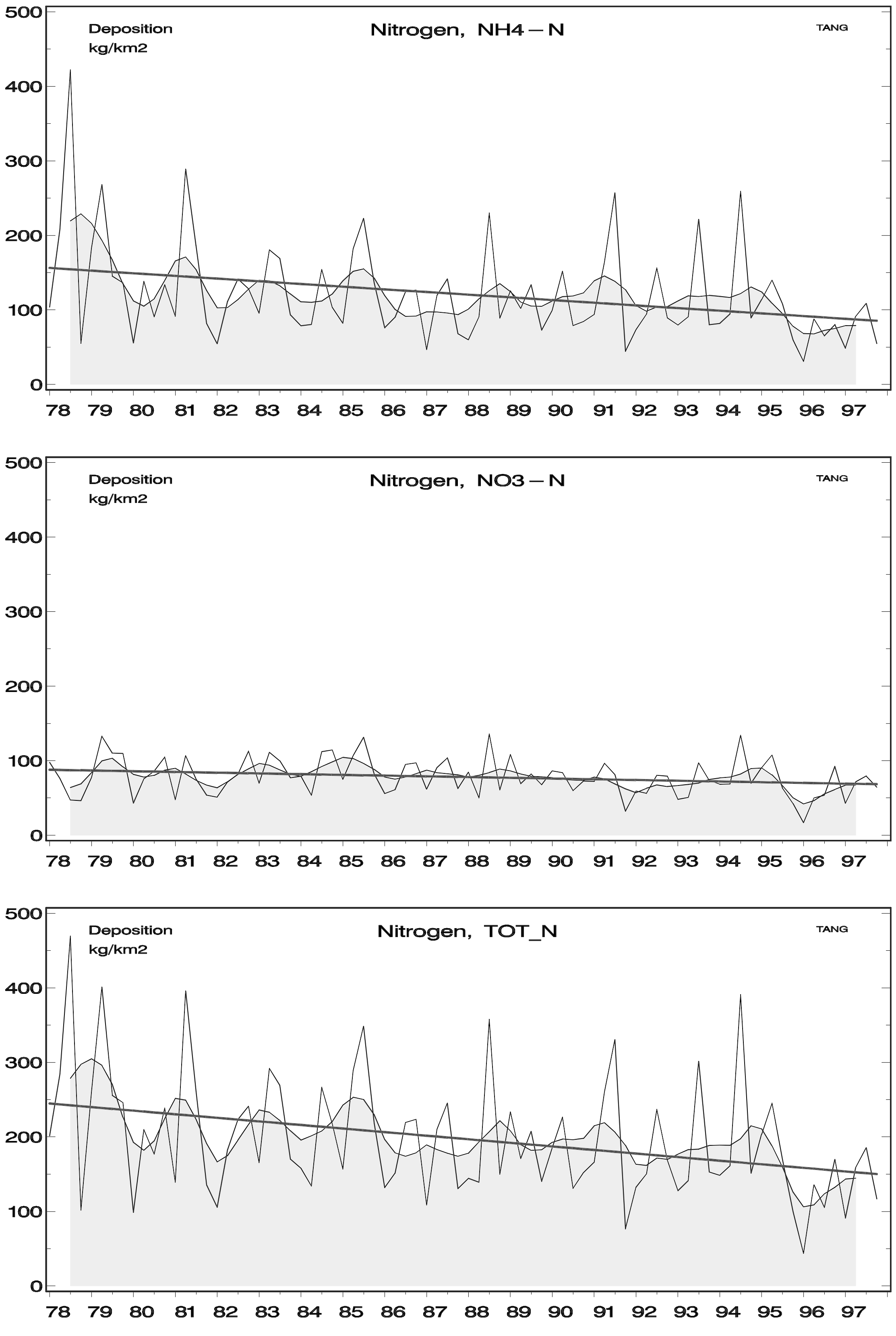
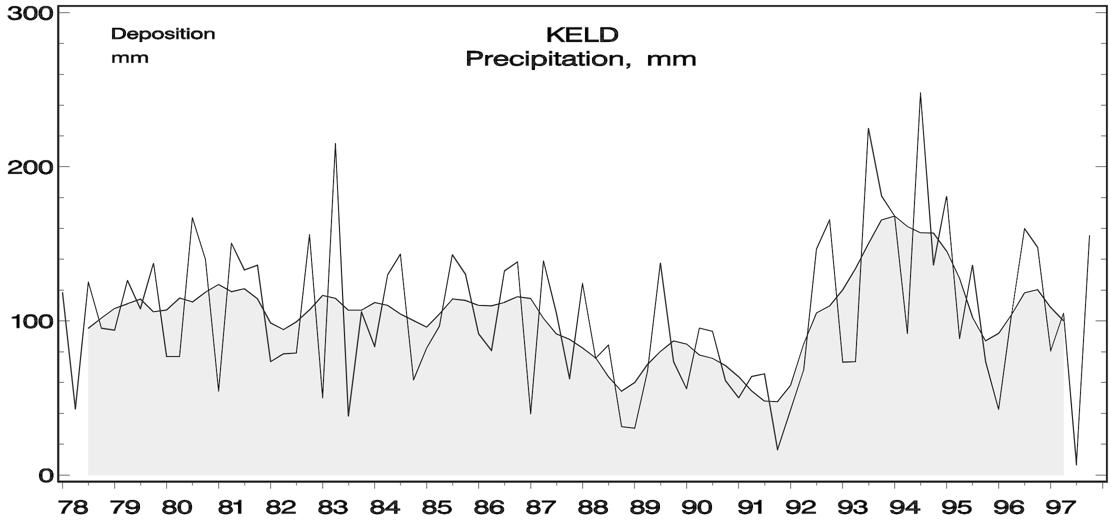


Figure 4.3.10 Quarterly wet-only depositions (thin jagged line) of nitrogen compounds at Tange 1978 - 1997, moving annual average (shaded) and trend.



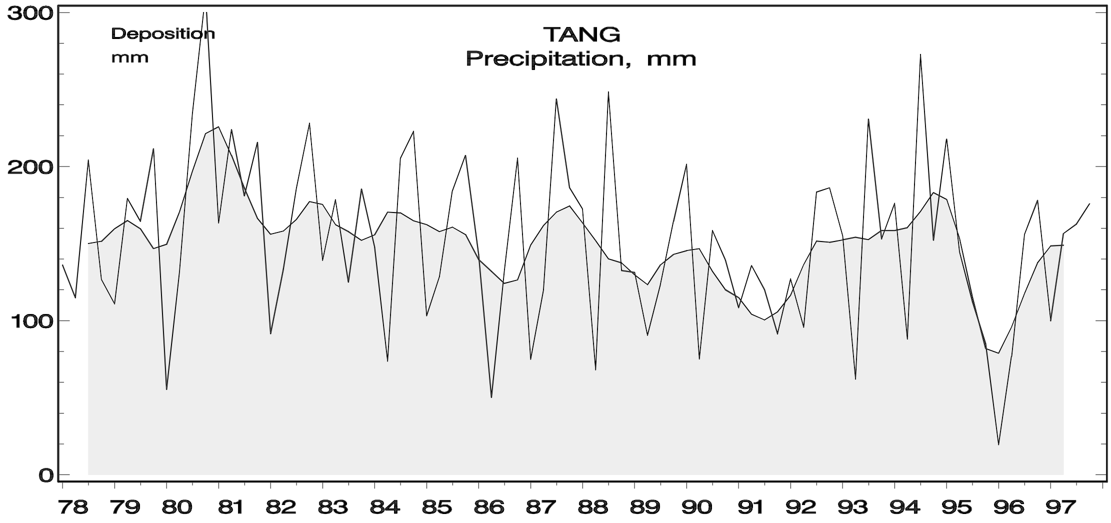


Figure 4.3.11 Quarterly wet-only precipitation (thin jaged line) and moving annual (4-quarter) average (shaded) at Keldsnor and Tange 1978 - 1997

Table 4.3.1 Trends in quarterly wet-only depositions for the two decades 1978- 1997. Trend values are average annual percentage changes relative to the grand mean deposition, measured in kg·km^{-2}.

Component	Grand Mean Deposition	Trend Pct. per Year	Relative Std_Dev	Grand Mean Deposition	Trend Pct. per Year	Relative Std_Dev
		KELDSNOR			**TANGE**	
SO4-S	174.50	-7.3	0.2	172.50	-4.7	0.1
NSS_S	130.80	-5.8	0.2	143.00	-5.3	0.2
NH4-N	86.50	-3.3	0.3	120.90	-3.0	0.3
NO3-N	77.10	-2.9	0.3	78.10		
TOT_N	162.30	-3.3	0.3	197.40	-2.4	0.3
H+	4.30	-5.4	0.2	5.15	-6.4	0.1
Na	290.50			317.20		
Mg	36.10			39.30		
K	27.20			24.80		
Ca	46.40			39.60	-9.6	0.3
Cl	923.50			624.10		

4.4 Total deposition

Detrimental effects

The depositions of sulphur and nitrogen compounds have detrimental effects on Danish eco-systems, both terrestrial, aquatic and marine. Effects of eutrophication, *i.e.* a surplus supply of nitrogen compounds that serve as nutrients, can be seen in all three types of eco-systems. The most adverse effects are seen in the marine systems and for that reason much effort has in recent years been directed at mapping the depositions and their detrimental effects and not least in reducing the emissions through the Danish Action Plan for the Aquatic Environment.

Calculated dry deposition

The total deposition to land and water surfaces is composed of dry and wet deposition. Since dry depositions are difficult to determine experimentally the results presented in this section are based on model calculations. Most of the results shown have been published previously by DMU, notably in connection to VMOP, the monitoring programme under the Danish Action Plan for the Aquatic Environment (VMOP_89, ..., VMOP_97). It should be noted that model calculation of deposition rests on a number of approximations and simplifying assumptions, which lead to uncertainties in the results. The uncertainty in the results is estimated to be about 40%, and the results must therefore be considered with some caution.

The ACDEP model

For these calculations the ACDEP model is used. It is a Lagrangian transport model with a chemical module in which air parcels are followed along 96-hours back-trajectories from given receptor points. Horizontally it operates on a 30 x 30 km grid net and vertically in up to ten layers, although two layers often suffice. A more detailed description of the ACDEP model has been given elsewhere (Hertel et al 1995). The model has primarily been used to calculate the deposition of nitrogen to Danish marine waters and to give information on the geographical distribution and the development with time. Calculations with the ACDEP model have however also been carried out for sulphur.

Sulphur deposition to the sea

Sulphur is a natural component of ocean water where it occurs as sulphates at a concentration of about 1 g S $\cdot l^{-1}$ (Brewer, 1975). Atmospheric deposition of sulphur to seawater is therefore of no environmental importance.

Sulphur deposition to land areas

The geographical distribution of total deposition fluxes in 1997 of sulphur to Danish land surfaces is shown in Figure 4.4.1 on a 30·30 km^2 grid. It should be noted that the deposition fluxes within each square only pertain to land surfaces. The deposition ranges from 0.3 to 1.0 ton S/km^2 with a tendency for the larger fluxes to occur in the central and southern parts of the country. These high depositions are probably caused by LRTAP from source areas in Europe combined with contributions from domestic sources.

Dry and wet deposition of sulphur

The average dry, wet and total deposition fluxes to Danish land areas in 1997 of both gaseous and particulate sulphur are shown in Table 4.4.1. In general the deposition of gaseous sulphur is dominated by dry deposition whereas wet deposition dominates the deposition of particulate sulphur, but locally the situation may be reversed. In periods of precipitation wet deposition dominates but since such periods occur irregularly, cf. Figure 3.1.1, the relative contributions of dry and wet deposition also vary irregularly.

Table 4.4.1 The average dry, wet and total deposition fluxes in to Danish land areas (43312 km^2) in 1997 of both gaseous and particulate sulphur (Frohn: personal communication 1999).

kg S / km^2	Dry	Wet	Total
Gas	329	38	367
Aerosol	33	210	243
Total	362	248	610

Annual deposition flux

The estimated total annual deposition flux compares quite well with the measured bulk depositions for 1997 shown in Figure 4.3.1. It also agrees with the recently published 1997 estimate of 500-1000 $kgS \cdot km^{-2}$ for the region comprising Denmark from the EMEP Eulerian model (EMEP 1999, Figure 1.3b).

Total sulphur deposition

The above deposition flux is equivalent to a total sulphur deposition of 26 kt $S \cdot yr^{-1}$ to Danish land areas which measure 43 312 km^2. This deposition is also comparable to the recent EMEP-estimates. The total deposition of sulphur to Denmark has been estimated by EMEP at 37 kt $S \cdot yr^{-1}$ in both 1996 (EMEP MSC-W 1998a, table 3.5) and 1997 (EMEP MSC-W 1998b, appendix E) with an average value of 54 kt $S \cdot yr^{-1}$ in 1985-1996 (EMEP MSC-W 1998a, table 3.2). The differences between the estimates from the ACDEP and the EMEP models may possibly be ascribed to different definitions of the total area involved.

Decreasing depositions

As already shown in Figures 4.3.7 and 4.3.9 the sulphur deposition to Denmark has been considerably reduced in the last decade. Results from EMEP (MSC_W 1998a, table 3.5) show that where the total sulphur deposition in the 1980's was about 70 kt S $\cdot yr^{-1}$, it decreased to 50-60 kt S$\cdot yr^{-1}$ in the early 1990's, and has now reached the above mentioned value of 37 kt S$\cdot yr^{-1}$ (ACDEP: 26 kt S$\cdot yr^{-1}$). These reductions are as already pointed out primarily the result of the international agreements on emission reductions within CLRTAP, which have resulted in a total reduction of European sulphur emissions to less than 60% of the 1985-emissions.

Nitrogen depositions to Danish land and water surfaces

For nitrogen the total deposition fluxes in 1997 to Danish waters, marine as well as aquatic, and to land surfaces are shown in Figures 4.4.2 and 4.4.3, respectively. It should be noted that the deposition fluxes within each square only pertain to assumed water surfaces, respectively assumed land surfaces. The deposition ranges from 0.5 to 1.8 ton N/km^2 with a tendency for the larger fluxes to water surfaces to occur in fjords, bays and lakes and in the north-western part of the open Danish waters whereas the highest depositions to land areas are found in the southern part of the country. The short distances to agricultural ammonia sources cause high depositions to land areas, coastal waters and lakes and the maxima in open waters coincide with high frequencies of precipitation. The magnitude of the deposition and the flux of nitrogen to the Danish part of the Baltic agree with recent estimates from HELCOM (1997) for the southern Baltic.

Dry and wet deposition of nitrogen

The average dry, wet and total deposition fluxes of nitrogen to Danish land areas and water surfaces in 1997 are shown in Table 4.4.2. In general the deposition to land is dominated by dry deposition due to the short distances to agricultural emissions of NH_3 whereas wet deposition dominates the deposition to water, but locally the situation may be reversed. In periods of precipitation wet deposition dominates but since such periods occur irregularly, cf. Figure 3.1.1, the relative contributions of dry and wet deposition also vary irregularly.

Table 4.4.2 The average dry, wet and total deposition fluxes of nitrogen in to Danish land areas and water surfaces in 1997. (Frohn: personal communication 1999).

kg N / km^2	Dry	Wet	Total	Area, km^2
Land	709	460	1169	43312
Water	294	461	755	113073

Annual deposition flux

The estimated total annual deposition flux compares quite well with the measured bulk depositions for 1997, shown in Figure 4.3.2. The bulk depositions are shown at land stations in the left-hand side of that figure and at two island and coastal stations in the right panels.

Deposition of reduced nitrogen dominates

The average composition of the nitrogen deposition flux to all Danish waters in 1996 is shown in figure 4.4.4. The deposition of the reduced components, gaseous ammonia - NH_3, and particulate ammonium - NH^+_4, constitutes the main part of the deposition, 66 % on a national basis. In the inner waters and fjords (dry) deposition of NH_3 caused by local activities becomes so large that the agricultural contribution to deposition approaches 80 %. Both components derive from the agricultural sector, but ammonia is mainly of indigenous origin whereas a considerable part of ammonium may derive from foreign sources. The remaining 34% of the load consists of oxidised compounds, including nitrates, NO_3^-, and a number of nitrogen oxides NO_y which mainly originate from combustion processes (in the figure gas NO_y denotes the sum of the oxidised components NO, NO_2, HNO_2, HNO_3, HNO_4, N_2O_5, NO_3 and PAN). A comparison of these deposition fluxes with the recently published 1997 estimates of nitrogen fluxes for the region comprising Denmark from the EMEP Eulerian model (EMEP 1999, Figure 1.3a and c) show reasonable agreement for the reduced compounds, but the EMEP estimate for oxidised compounds is considerably larger.

Total nitrogen deposition

The geographical distribution of total atmospheric nitrogen deposition in Danish waters and its development with time is shown in Table 4.4.3. The total deposition is close to 100 000 tonnes N per year and the flux is close to 1 ton $N\cdot km^{-2}$ in all main waters. Variations in depositions of 10-20% from year to year appear to be normal both in the various sub-basins and in the total figure but no consistent trend can be observed.

Importance of atmospheric nitrogen deposition

The importance of atmospheric deposition of nitrogen is emphasised when the recent estimates of atmospheric loads are compared to other important nitrogen sources. The total nitrogen loads to Danish waters in 1995 are given in Table 4.4.4 (the minor deviations between the 1996-results in tables 4.4.2 and 4.4.3 are caused by a re-appraisal of the areas involved). In several instances atmospheric deposition is the main contributor of nitrogen. For all Danish waters as a whole the atmospheric deposition, which was previously believed to constitute 30 % of the total (VMOP_94), is now estimated to contribute 51% of the total load (Hertel and Frohn 1997).

Acidification, eutrophication and critical loads

The depositions of sulphur and nitrogen have, as mentioned above, adverse effects on the eco-systems. However, the decreasing trends of concentrations in air and thus in dry deposition, as well as in precipitation and thus in wet deposition, that have been demonstrated earlier, will of course have beneficial effects, also on the Danish eco-systems. But the depositions still exceed the critical loads in many parts of the country. Since both sulphur and nitrogen cause acidification damages the exceedances of the critical loads cannot easily be related to the individual depositions of either of these compounds. By convention the critical acidifying loads for *e.g.* sulphur are given as conditional upon the nitrogen deposition, fixed at the existing level – and *vice versa*. The case is simpler for eutrophication, which can be related directly to the deposition of nitrogen.

Depositions in Denmark and Europe

The development on the national as well as on the European level is illustrated in Figure 4.4.5, which shows the percentage of land area where the critical load pentiles are exceeded. Note that the curves for conditional exceedance for acidifying sulphur and nitrogen are almost completely overlapping.

Improvements for acidifying depositions

As can be seen the situation for acidification has improved considerably, probably mainly as a result of the decreases in sulphur emissions, which have led to significantly smaller concentrations in both air and precipitation during the last ten years. In Denmark the exceedances are not so widespread anymore. For sulphur the exceeding deposition has fallen to less than 500 kg $S{\cdot}km^{-2}{\cdot}yr^{-1}$ (0.35 $keq{\cdot}ha^{-1}{\cdot}yr^{-1}$) in most of the country. The present maximum exceedances of about 800 kg $S{\cdot}km^{-2}{\cdot}yr^{-1}$ (0.5 $keq{\cdot}ha^{-1}{\cdot}yr^{-1}$) are attained in only a small part of the country (Holten-Andersen et al. 1998). As shown in Figure 4.4.5a the fraction of Danish land area where critical loads are exceeded has in recent years fallen to less than 2%. On a European level the areas of exceedance of the critical loads for acidifying sulphur and nitrogen have also decreased. As shown in the figure the exceedance areas in EU decreased in the period 1985 - 1997 from about 25% of the total land area in the member countries to a value of about 13% (Figure 4.4.5b) and to 7.5% of the total land area in EMEP as a whole (Figure 4.4.5c).

Eutrophying depositions remain a problem

The situation is considerably worse for eutrophication since the critical loads are still exceeded in large parts of the country with about 500 - 1000 kg $N{\cdot}km^{-2}{\cdot}yr^{-1}$ (0.35-0.75 $keq{\cdot}ha^{-1}{\cdot}yr^{-1}$). The exceedances reach maximum values of more than 1000 kg $N{\cdot}km^{-2}{\cdot}yr^{-1}$ (0.75 $keq{\cdot}ha^{-1}{\cdot}yr^{-1}$) in the southern part of Jutland (Holten-Andersen et al. 1998). That represents a serious national problem, since they are close to the total annual deposition to both land and sea areas. Also there seems to be no trend in the land area of exceedance. In Denmark it has according to Figure 4.4.5a remained constant at a level of 5-8 % since the middle of the 1980-s. A similar lack of improvement is seen on a European scale but the percentages of the areas of exceedance are higher. For EU the area of exceedance has remained close to 20% and for all countries in EMEP the eutrophication area of exceedance has until recently constituted about 35% of the total land area, but a rather dramatic drop to about 20% appears to have set in since 1995.

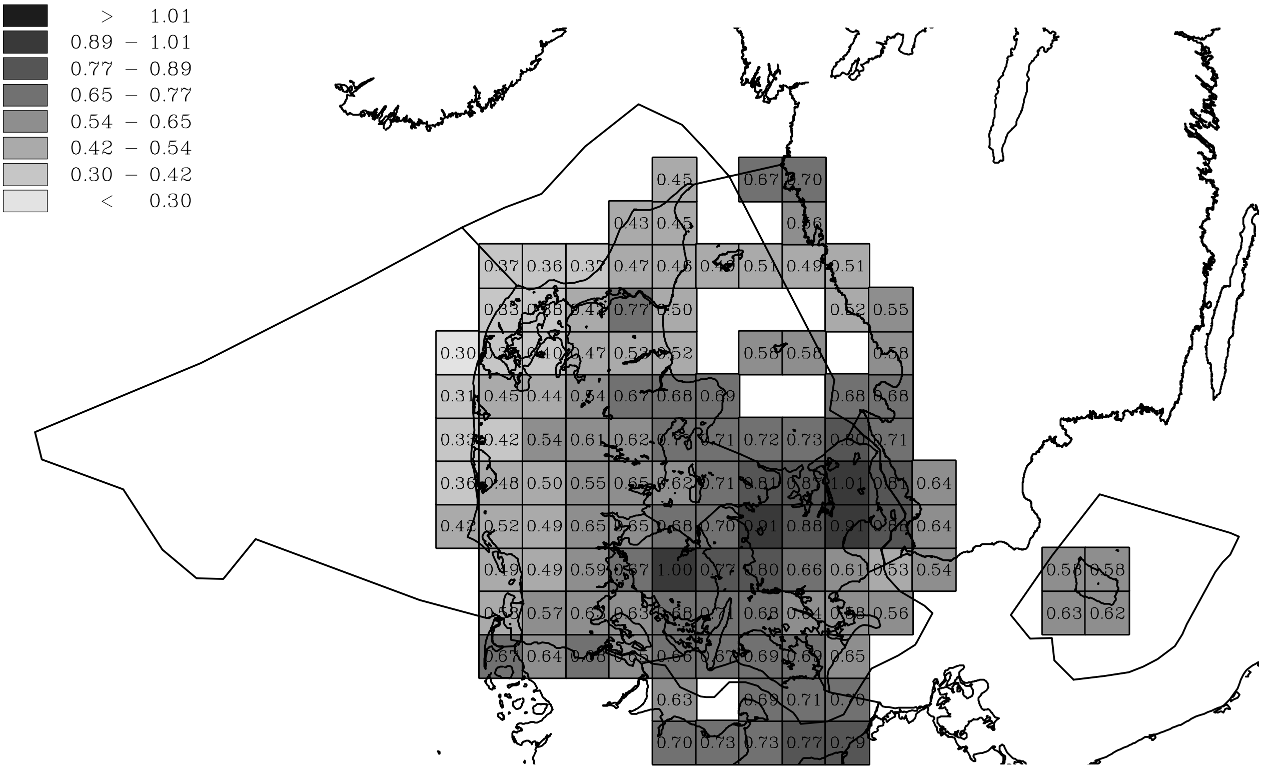


Figure 4.4.1 Total deposition flux of sulphur compounds to assumed land surfaces in Denmark calculated for 1997. The deposition averages in the 30·30 km^2 grids are in ton S·yr^{-1} per km^2 (Hertel, Frohn: personal communication 1999).

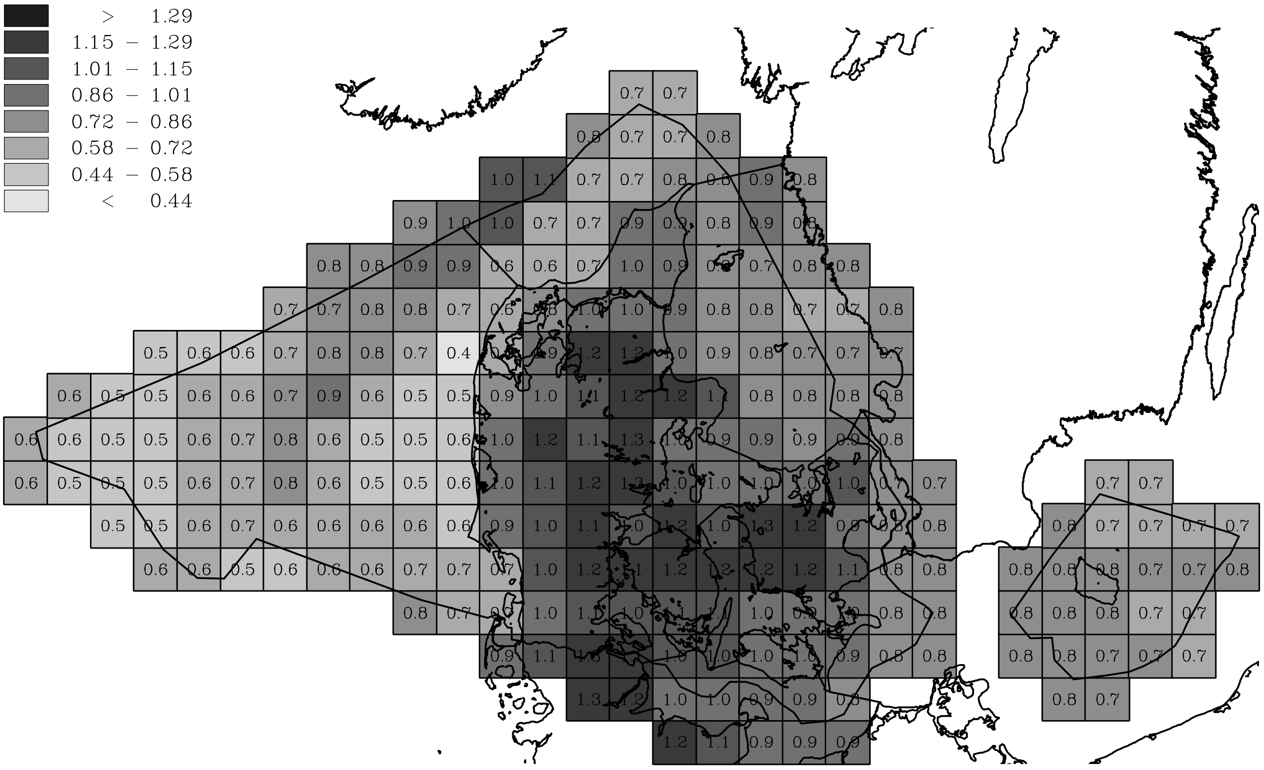


Figure 4.4.2 Total deposition flux of nitrogen compounds to assumed water surfaces in Denmark calculated for 1997. The deposition amounts are in ton N·yr^{-1} per km^2. (Adapted from VMOP_97 by L. Frohn).

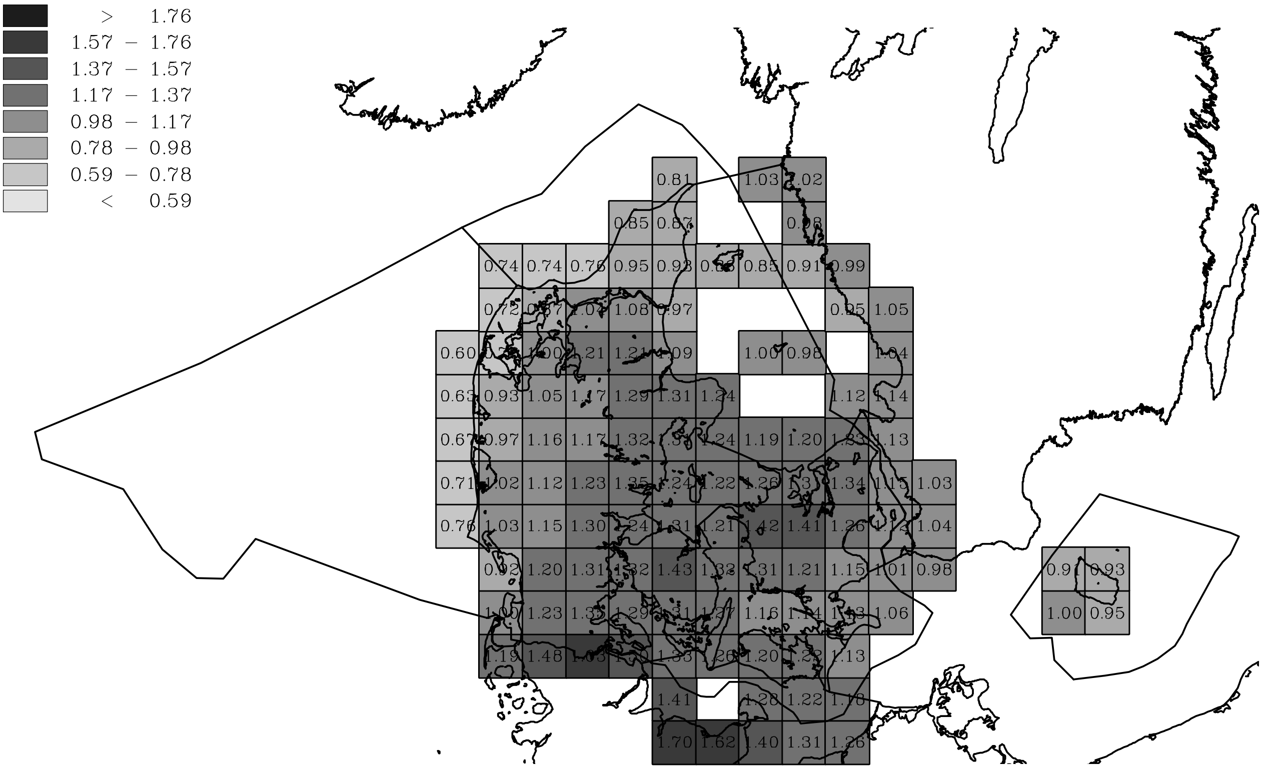


Figure 4.4.3 Total deposition flux of nitrogen compounds to assumed land surfaces in Denmark calculated for 1997. The deposition amounts are in ton N·yr^{-1} per km^2. (Adapted from VMOP_97 by L. Frohn).

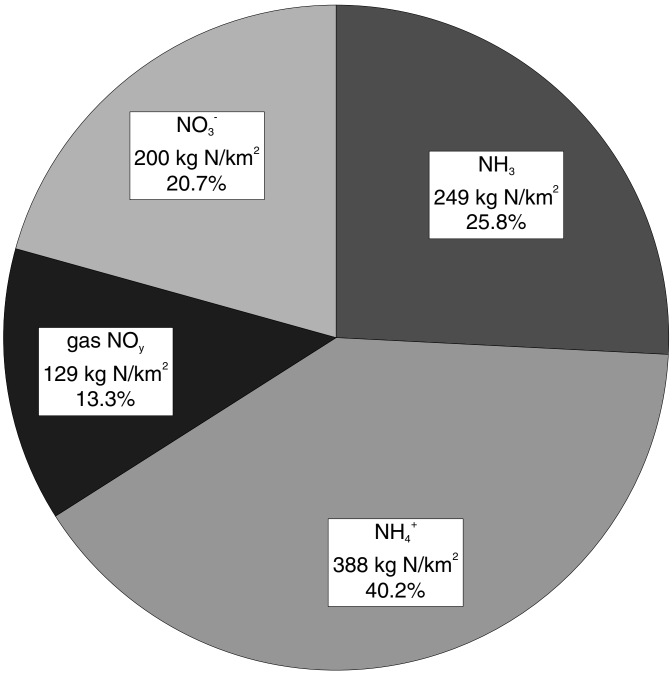


Figure 4.4.4 Average distribution among compounds of the total nitrogen deposition flux in kgN·km^{-2} for all Danish waters in 1996 (adapted from VMOP_96).

Table 4.4.3 Total annual depositions of nitrogen to main Danish waters for the period 1989-1996.

	Area	1989	1990	1991	1992	1993	1994	1995	1996	1996-flux
	km^2	kton N	kton N	kton N	kton N	kton N	kton N	kton N	kton N	ton N per km^2
North Sea	48.886	36.1	45.3	37.6	42.1	35.3	44.7	40.1	48.4	0.99
Skagerrak	10.122	8.9	11.7	10.0	10.8	8.4	10.1	9.8	9.3	0.91
Kattegat, Danish part	16.773	15.5	17.7	15.4	21.6	18.7	21.6	17.1	15.0	0.89
Kattegat, Swedish part	*6.859*	*6.7*	*7.0*	*7.4*	*8.8*	*6.2*	*7.0*	*6.4*	*5.6*	*0.82*
Northern Belt Sea	3.878	4.4	4.6	4.4	5.2	4.5	5.2	4.3	4.1	1.07
Lillebælt	2.399	3.0	2.8	3.0	2.7	2.5	2.4	2.6	2.8	1.14
Storebælt	4.472	5.3	5.2	5.8	5.0	4.6	4.8	4.7	4.8	1.09
Øresund, Danish part	1.334	1.3	1.3	1.5	1.5	1.3	1.4	1.3	1.3	0.99
Øresund, Swedish part	*993*	*0.9*	*0.9*	*1.1*	*1.1*	*1.0*	*1.0*	*1.0*	*0.9*	*0.95*
Southern Belt Sea	2.457	2.8	2.6	2.9	2.5	2.3	2.1	2.9	2.5	0.95
Baltic, Danish part	14.816	15.0	15.0	16.5	15.5	12.4	11.9	14.0	13.5	0.91
Total, Danish waters	105.137	92.3	106.2	97.0	106.9	90.0	104.2	96.8	101.7	0.97

Adapted from VMOP_96

Table 4.4.4 The total nitrogen load in kton N in 1995 to the open Danish waters from streams, direct point sources and the atmosphere. (from Hertel and Frohn, 1997).

Water	Streams[a]	Point sources	Atmosphere	Atm. %
North Sea	21	0.56	40	65
Skagerrak	2.25	0.36	9.9	73
Kattegat	31.7	1.41	15.2	31
Northern Belt Sea	6.1	0.48	3.8	37
Lillebaelt	7.9	0.54	2.2	21
Storebaelt	10.6	0.7	3.9	26
Oresund	1.85	4.13	1.3	18
Southern Belt Sea	0.75	0.02	2.7	78
Dk total	84.4	8.45	98	51

[a] Including point sources received by the streams

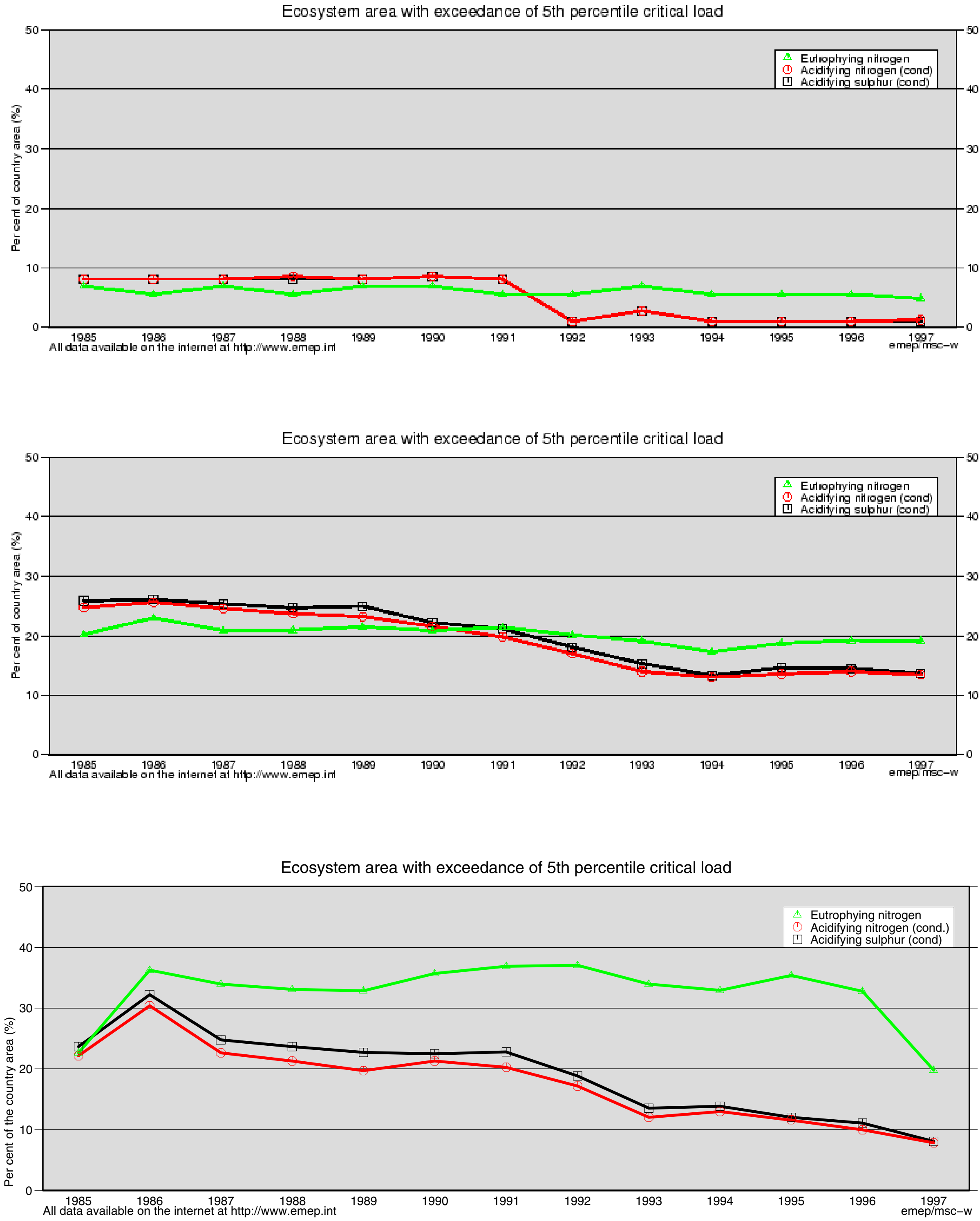


Figure 4.4.5 Ecosystem area with exceedance of critical loads for acidification and eutrophication as percentages of total area of a. Denmark; b. countries in the European Union; c. countries in the EMEP-area. (EMEP 1999; a. and b. from EMEP's homepage: www.emep.int; c. Jerzy Bartnicki, EMEP MSC-W, personal communication).

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5 Transport and Sources

5.1 Origins and directional transport sectors

Long transport distances

Air pollutants measured at a given location originate from a number of different sources. Since many air pollutants have a lifetime of several days they can travel considerable distances in the atmosphere. The sources may therefore be from a few kilometres to several hundred and even up to a thousand kilometres away. Thus the sources for air pollution measured in *e.g.* Denmark may be located anywhere in Europe. However, the main transport parameter is the wind and the direction of this wind may be a clue to the origin of the pollution.

Daily wind sectors

The air pollution concentrations measured in BOP are based on sampling through 24 hours so use of the wind direction can only be meaningfully applied if the wind has a fairly constant direction over this time period. When the directions of the transporting wind during the particular day fulfil some predefined criteria for constancy of direction it is possible to assign a daily wind direction, say one of eight 45^0- sectors, to a measuring site. In all other cases, when the wind is highly variable in direction or if there is little or no wind, the wind direction must be classified as indeterminate.

Wind sector analysis

For an extended measuring period the average concentrations in each sector can be calculated and that may give a rough picture of which wind directions bring the highest concentrations to the site. Results of such an analysis are shown for the period 1991-1997 in Figures 5.1.1 - 5.1.4 for sulphur dioxide SO_2, particulate S and total ammonium TNHz, and for Nickel, Zinc, and Lead. The data have been taken from the two EMEP-sites, Tange and Keldsnor.

Air from SE is more polluted

In Figures 5.1.1 – 5.1.2 the mean concentrations are shown in dependence on the wind sector. The results are typical and show that for most pollutants the highest concentrations are found when the transport is from the south to the south-east, *i.e.* when the air comes from the European continent, notably Germany and the East European countries.

Degree and dose of air pollution

Whereas these two figures show the *degree of pollution* of the air coming to Denmark by different directions, the following two Figures 5.1.3 - 5.1.4 show the *dose of pollution* these winds bring to Denmark. These latter results have been obtained by multiplying the sector-means by the frequencies of occurrence of wind from the various directions. The resulting values are in fact equal to the sector's contribution to the overall annual mean concentrations.

Largest dose from SW

In contrast to the pollution degree, which had maxima in the SE and S sectors, Figures 5.1.3 – 5.1.4 show that the largest pollution doses arrive in Denmark from south-westerly directions. It can therefore be concluded that the overall annual means described in earlier chapters are dominated by contributions from the source areas in Western Europe.

Time developments depend on source regions

The development with time of mean sector concentrations in the three southerly sectors are shown in Figure 5.1.5 - 5.1.7 for the gaseous and particulate sulphur compounds, and for the four metals Ni, Cu, Zn, and Pb. The time developments of the concentrations in winds from these sectors are quite different. Whereas concentrations in especially the southwesterly winds from Western Europe generally decrease rather steadily as the result of planned emission reductions, the concentrations in winds from the southeastern sector, *i.e.* from Eastern Europe, behave much more erratically, especially in the late 1980s. The reasons for that could be that the control of the emissions was lost to some degree in this period of political and economic turmoil in Eastern Europe. The subsequent decrease of concentrations in the first half of the 1990's might, at least partly, be the result of the plummeting of industrial activities. The southerly direction can apparently be seen as an intermediate case with influence from both the neighbouring 45^0-sectors.

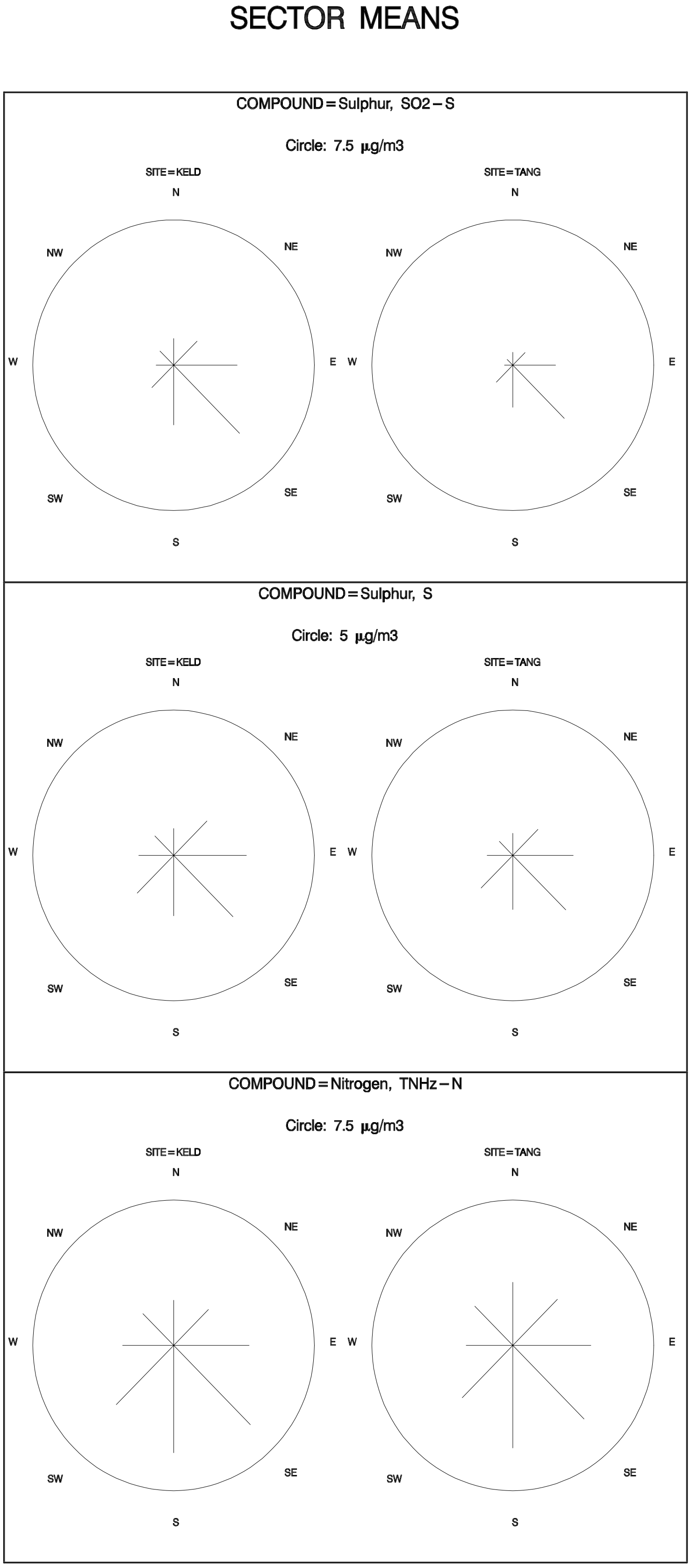

Figure 5.1.1 Mean concentrations of SO_2, S and TNHz at Keldsnor and Tange for 1991 – 1997. The sector value is the mean concentration in winds from that direction. For each compound the scale is given by the radius of the circumscribing circle.

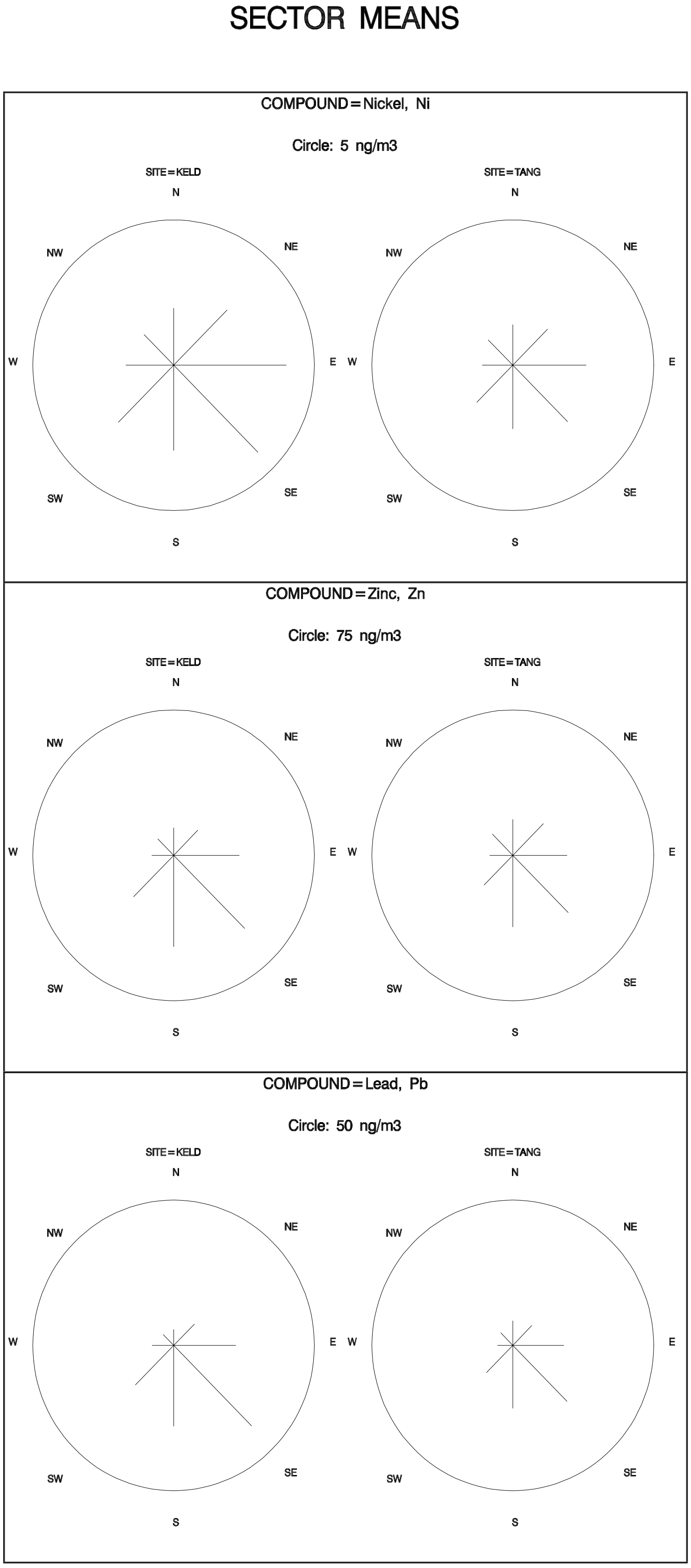

Figure 5.1.2 Mean concentrations of Nickel, Zinc, and Lead in aerosols at Keldsnor and Tange for 1991 - 1997. The sector value is the mean concentration in winds from that direction. For each compound the scale is given by the radius of the circumscribing circle.

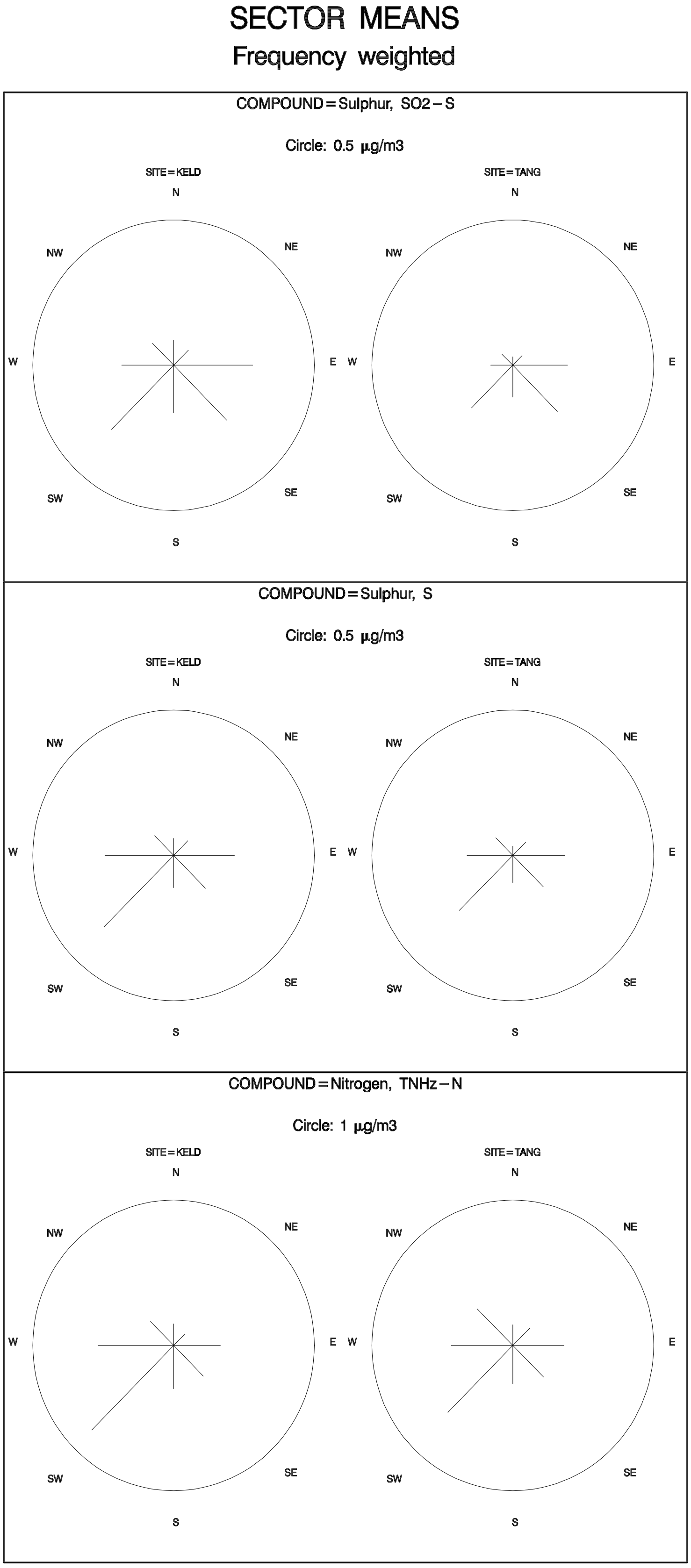

Figure 5.1.3 Wind frequency weighted mean concentrations of SO_2, S and TNHz at Keldsnor and Tange for 1991 - 1997. The sector value is equal to the contribution from that sector to the overall mean value for the period. For each compound the scale is given by the radius of the circumscribing circle.

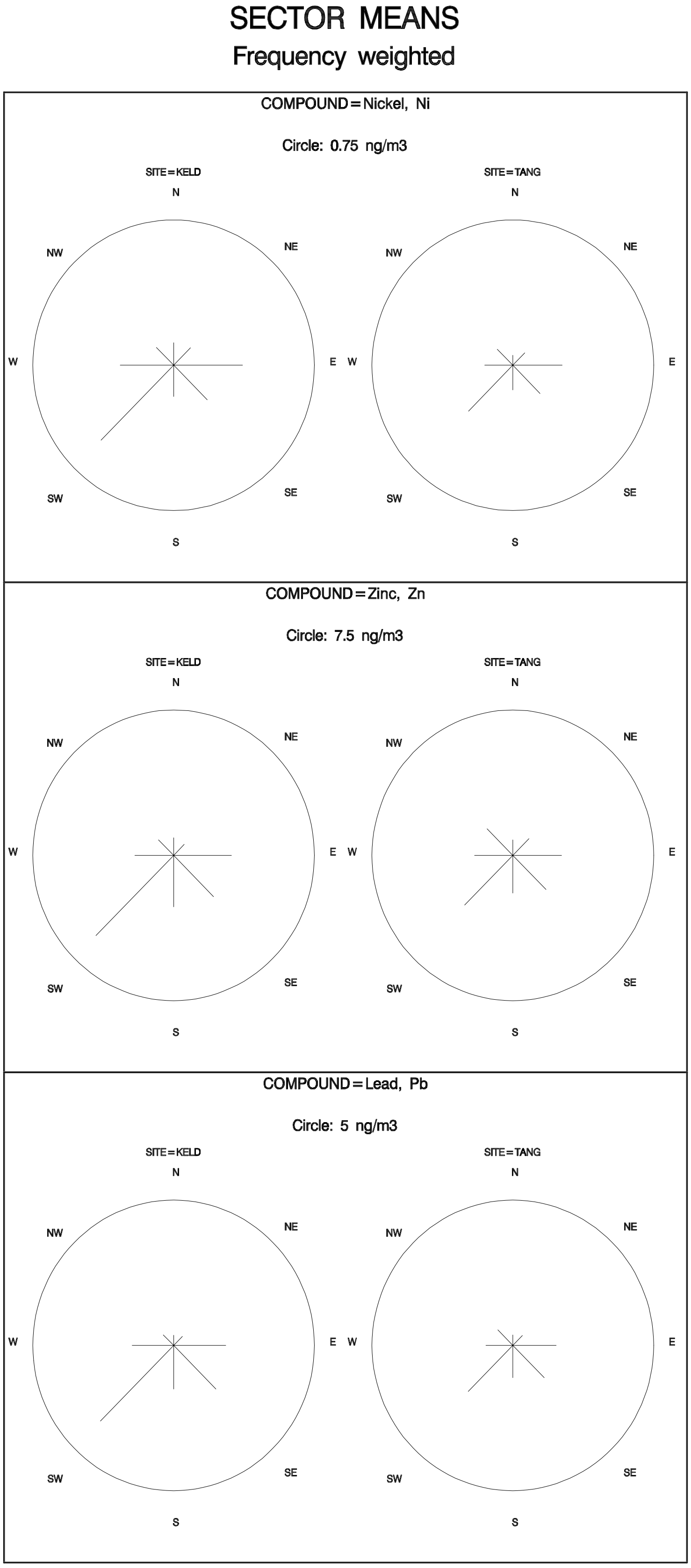

Figure 5.1.4 Wind frequency weighted mean concentrations of Nickel, Zinc, and Lead in aerosols at Keldsnor and Tange for 1991 - 1997. The sector value is equal to the contribution from that sector to the overall mean value for the period. For each compound the scale is given by the radius of the circumscribing circle.

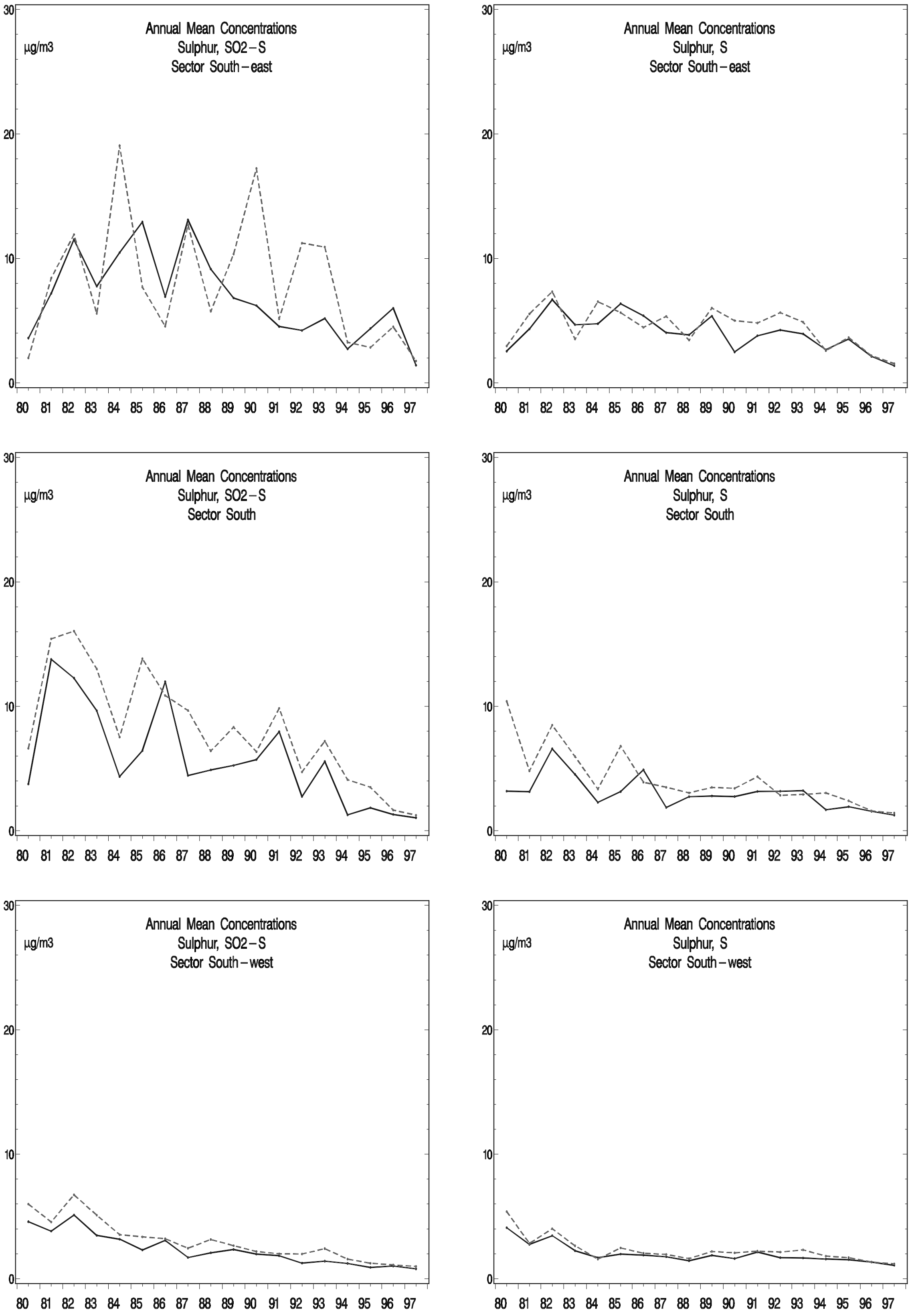

Figure 5.1.5 Annual mean concentrations of SO_2 and S at Tange (full line) and Keldsnor (dashed line) in wind sectors from south-east, south, and south-west.

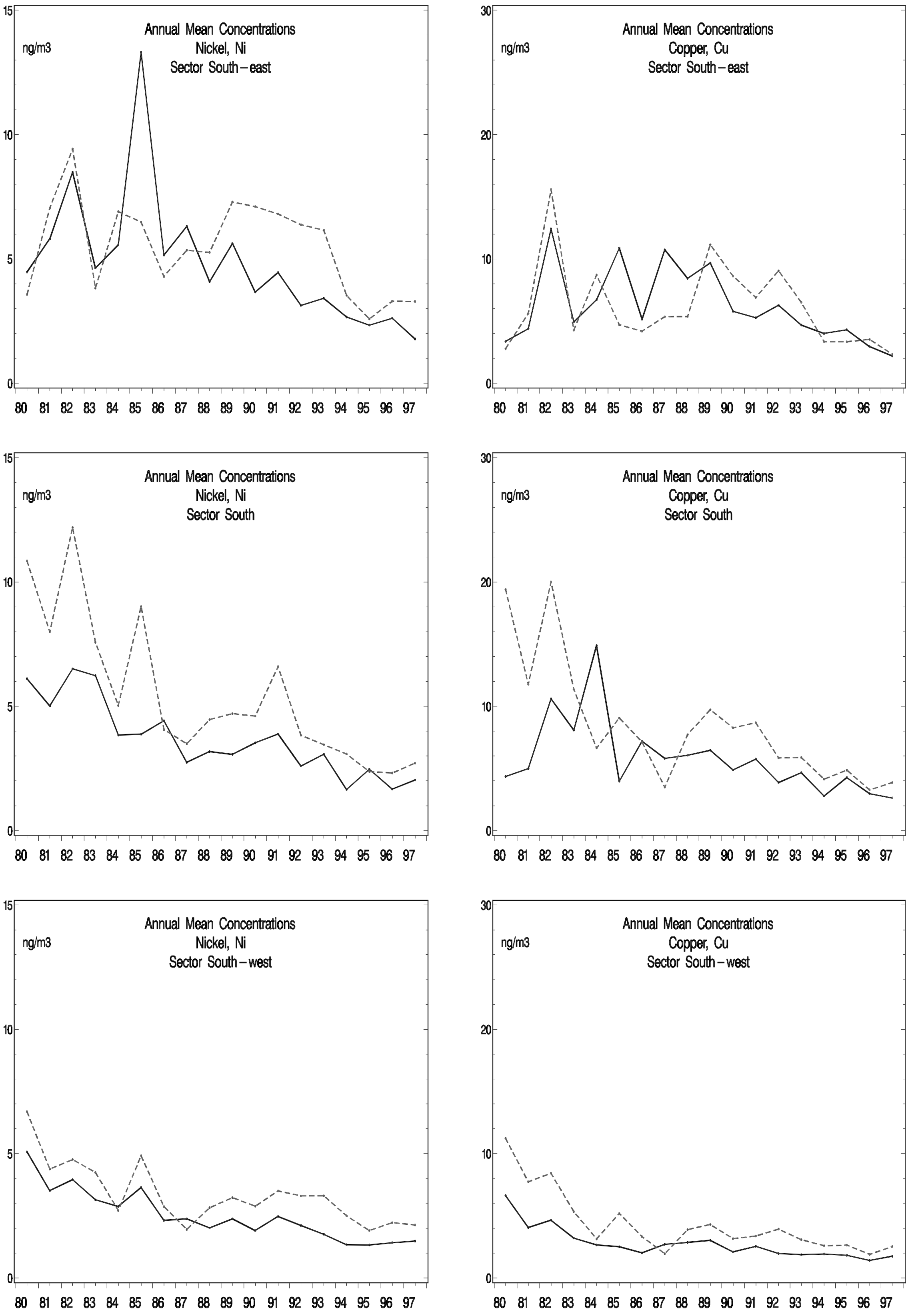

Figure 5.1.6 Annual mean concentrations of the heavy metals Ni and Cu in aerosols at Tange (full line) and Keldsnor (dashed line) in wind sectors from south-east, south, and south-west.

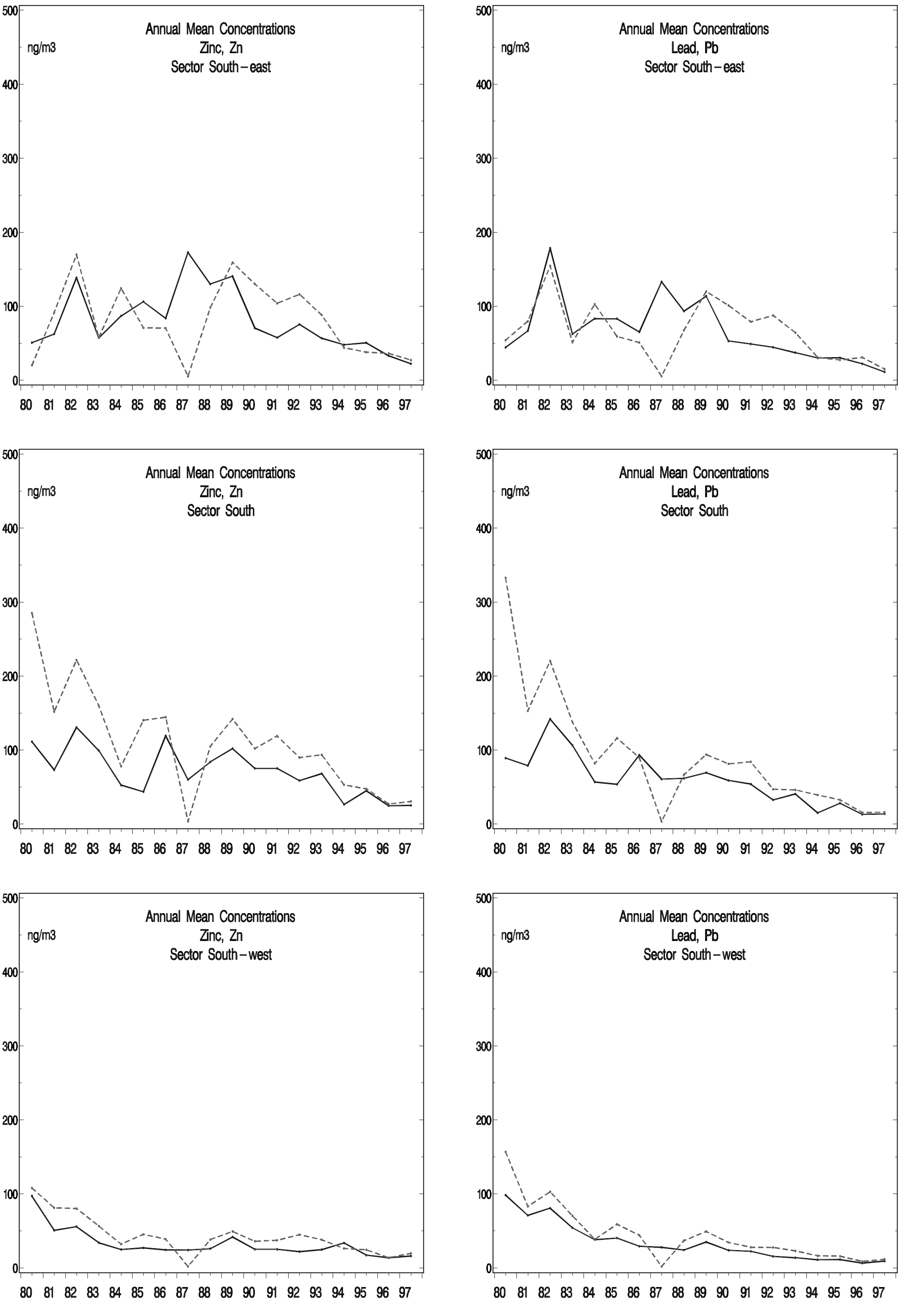

Figure 5.1.7 Annual mean concentrations of the heavy metals Zn and Pb in aerosols at Tange (full line) and Keldsnor (dashed line) in wind sectors from south-east, south, and south-west.

5.2 Depositions from domestic and foreign sources

Depositions in Denmark

The long travel distances of pollutants in the atmosphere make it necessary to use large scale models to trace these movements and to find where the pollutants eventually go. With these models pollutants emitted in one country can be followed as they move across Europe to be deposited somewhere on the continent. Results from calculations with such models can then be used to describe and quantify Danish and foreign source contributions to deposition in Denmark.

Source apportionment by EMEP

In the EMEP model, which has been developed and used extensively in the context of comprehensive European co-operative programme on transboundary air pollution, EMEP, the transport of air pollution emitted from every European country is followed until it is finally deposited (MSC-W 1998a). The model domain is very large and stretches from Nordkap to North Africa and from the Atlantic Ocean (40^0 W) to the Ural Mountains (60^0 E). Even then the pollution is sometimes transported outside the domain and information on its origin and fate is lost. By appropriate summing of all these data it is possible to estimate on, say, an annual basis how much of the deposition in one country can be traced to any other country.

Sulphur

The model estimates of the development with time of the sulphur deposition to Denmark are shown in Figure 5.2.1 for the period 1985 - 1997 (data from EMEP MSC-W 1998b). The depositions have as pointed out earlier fallen by almost 50% in these thirteen years, and this is true for contributions from both Danish and foreign sources. The figure also shows that throughout this period the foreign contribution has dominated and that the contribution from Danish sources to deposition in Denmark has persistently been in the range 15-25% of the total deposition.

Nitrogen

For nitrogen some results from the Danish ACDEP model are presented in Figures 5.2.2 - 5.2.4 below. The development with time of nitrogen deposition to Danish waters from Danish and foreign sources is shown in Figure 5.2.2 for the period 1989 - 1995. As stated earlier no systematic trends can be seen over this period, in particular not for the domestic contributions. However it can also be seen that in all Danish waters, including the more open North Sea, the average Danish contribution amounts only to about 20%.

Foreign nitrogen dominates deposition in Denmark

In the more detailed map shown in Figure 5.2.3 it can be seen that Danish contributions varies from close to 60% in fjords and bays to less than 5% in the North Sea, mainly because of the prevailing westerlies. But apart from the innermost fjords foreign source contributions are everywhere more important than the Danish ones and quite often more than 90% of the deposition of nitrogen to Danish waters come from abroad. This is further illustrated in Figure 5.2.4, which shows how the different components were distributed among Danish and foreign loads in 1997. The major components of the deposition are particle bound nitrates and ammonium that easily travel long distances in the atmosphere before being deposited. The deposition of foreign nitrogen to all Danish waters is clearly dominating and amounts to 83 % of the total, see also Figure 5.2.2. Even in Limfjorden, the inner water with the greatest indigenous influence, foreign sources are responsible for more than half the atmospheric nitrogen load. This result should be viewed in connection with the finding in Table 4.4.4 that the atmosphere contributes 51 % of the total nitrogen load to Danish waters.

Depositions in Europe

The estimates by the EMEP model of country-to-country exchange of depositions can be used to illustrate the situation of Denmark in a European context. With reference to Table 5.2.1 that contains abbreviated names of countries and oceans, the results can conveniently be listed as shown in Tables 5.2.2 - 5.2.4. These tables show the percentage distribution of depositions of oxidised sulphur and of oxidised and reduced nitrogen in European countries over twelve years 1985-1996 (adapted from MSC-W 1998a). It should be noted that these deposition figures refer to deposition on the land area of a country, and do not include depositions to any sea surface that might belong to that country.

"Blame matrices"

The entries in these socalled "blame matrices" are percentages of deposition in a country and they can be followed horizontally or vertically to highlight deposition from a receptor or an emitter point of view, respectively. A horizontal country row shows how the deposition in that country is distributed among the emitter countries listed in the top row. The last column shows the total absolute deposition in the country in kilotonnes. A vertical country column describes how the pollutant in question from this country is deposited across Europe. The tables have been adapted to include only those emitter areas affecting Denmark and those receptor areas affected by Denmark. It is thus only for Denmark that the tables are complete and for which the row entries in principle sum to 100%, corresponding to the total deposition.

Denmark as a
receiver country
- for sulphur

As an example of the receptor viewpoint the origin of oxidised sulphur deposited in Denmark can be traced along the DK-row in Table 5.2.2. It is seen that over these 12 years 17% of the total annual sulphur deposition of 54 kilotonnes (kt) in Denmark came from domestic sources, whereas the rest originated in 13 foreign emitter regions with the major contributions of 24% coming from Germany (DE) and 19% from Great Britain (GB).

- for oxidised nitrogen

For oxidised nitrogen deposited in Denmark Table 5.2.3 shows similarly that only 10% of the total deposition of 26 kt in Denmark was of domestic origin, whereas the rest originated in 15 foreign emitter regions, the main contributors being Germany with 18% and Great Britain with 24%.

- for reduced nitrogen

For reduced nitrogen the pattern is quite different, mainly because of the pronounced tendency for NH_3 to dry deposit close to the source. In this case Table 5.2.4 shows that 78% of the deposition of 51 kt in Denmark was of domestic origin and that the remainder was distributed with minor amounts from 8 neighbouring countries.

Denmark as an
emitter country
- for sulphur

For Denmark as an emitter the DK-column in Table 5.2.2 shows that 17% of the total deposition in Denmark was of indigenous origin and that Danish sulphur was otherwise deposited in 7 other receptor areas where they were of only minor importance to these receivers.

- for oxidised nitrogen

Depositions of oxidised nitrogen emitted in Denmark were as shown in Table 5.2.3 scattered among 13 other northern European countries and receiver areas where they constituted a few percent of the national depositions. The largest relative deposition was the domestic one amounting to 10%.

- for reduced nitrogen

Relative depositions of reduced nitrogen from Denmark are given in the DK-column in Table 5.2.4. Denmark was as pointed out above responsible for 78 % of the total deposition in Denmark, for 9% of total deposition in Sweden (SE) and for 12% of the total deposition in the Baltic Sea (BAS). The Danish depositions in the 11 foreign receiver areas were otherwise of only minor importance.

Export and import budgets

Such figures can conveniently be summarised as export/import budgets for all countries. The export/import budgets for 1996 are shown in Tables 5.2.5 (Tarrason, 1998) and they are quite typical for the twelve years 1985 - 1996 (MSC-W 1998). The key numbers are here the national emissions, the total national depositions and the national self-depositions. Export of a given pollutant is then defined as the national emission minus the self-deposition. It is also given as a percentage of the national emission. Import is similarly defined as the total national deposition minus the national self-deposition. It is also given in percentages of the total national deposition.

Sulphur

In 1996 84.7 kt of sulphur or 91% of the Danish emissions of 93 kt was exported and deposited abroad, with 44% depositing on the adjacent seas. 79% of the emissions was deposited within the modelled area; the remaining 21% were lost to the model, either because it entered the free troposphere above the planetary boundary layer or because it was transported very far before being deposited outside the EMEP domain, probably east of the Urals. Table 5.2.5 also shows that 30.4 kt of sulphur or 79% of the sulphur deposition in Denmark was of foreign origin. The net result was that 54.3 kt (84.7—30.4) of sulphur or 59% of the Danish emissions left the country in 1996.

Nitrogen

Similar figures apply to oxidised nitrogen, whereas the export and import percentages for reduced nitrogen are considerably lower, because a main part of the emissions is gaseous ammonia, that is efficiently deposited in the local area. For all nitrogen compounds the net export in 1996 from Denmark was 104 kt (84.9-19.1 + 49.3-10.8) of nitrogen corresponding to 61% of the total annual emissions of 169 kt N.

A net exporter

Denmark is, as can be seen, a net exporter of both sulphur and nitrogen. But so are most of the European countries as is evident from Table 5.2.5. However a word on scale is in order here. Small countries inherently have larger export percentages than big countries, simply because a pollutant emitted in a small country does not have to travel far before crossing a border. Similarly absolute import figures are smaller in small countries because they present a much smaller area for deposition compared to a big country.

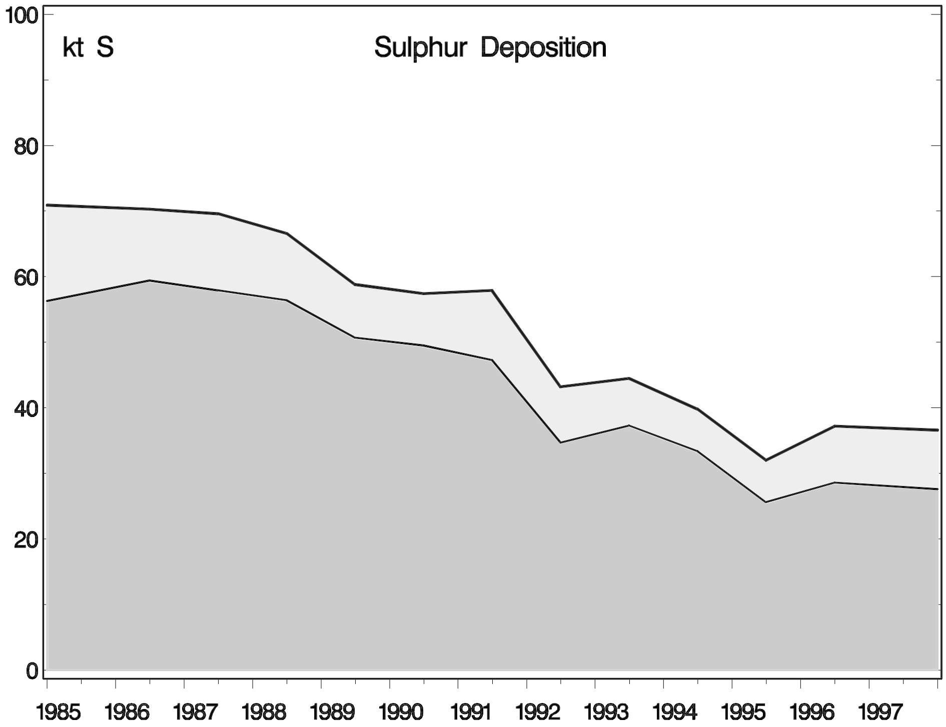

Figure 5.2.1 The total sulphur deposition to Danish land areas from foreign sources (dark) and Danish sources (light). EMEP model estimates for 1985-1997.

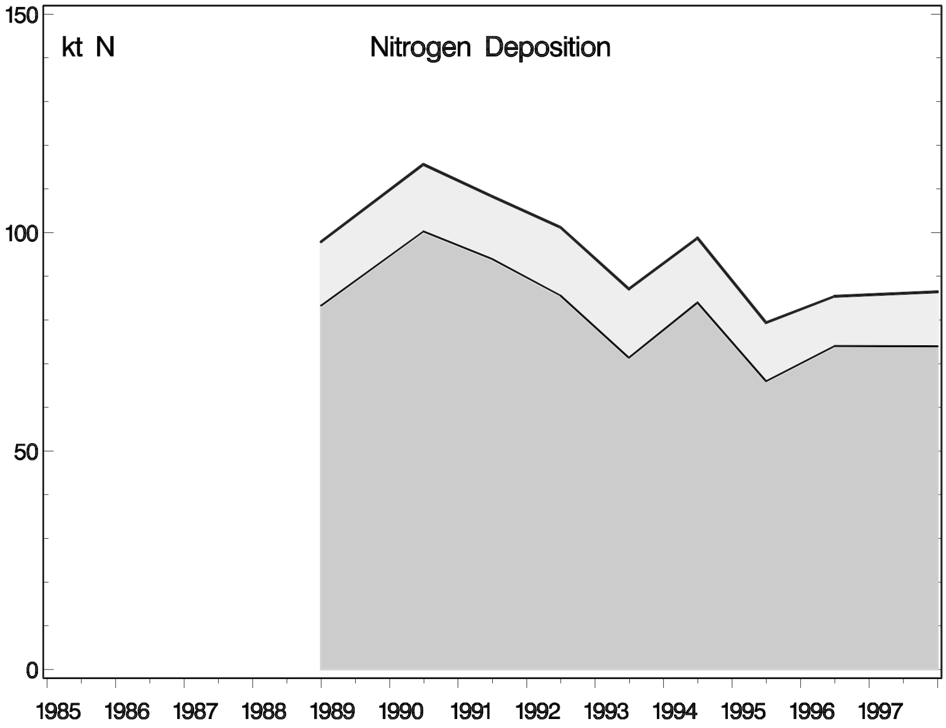

Figure 5.2.2 The total nitrogen deposition to Danish waters from foreign sources (dark) and Danish sources (light). ACDEP model estimates for 1989-1997.

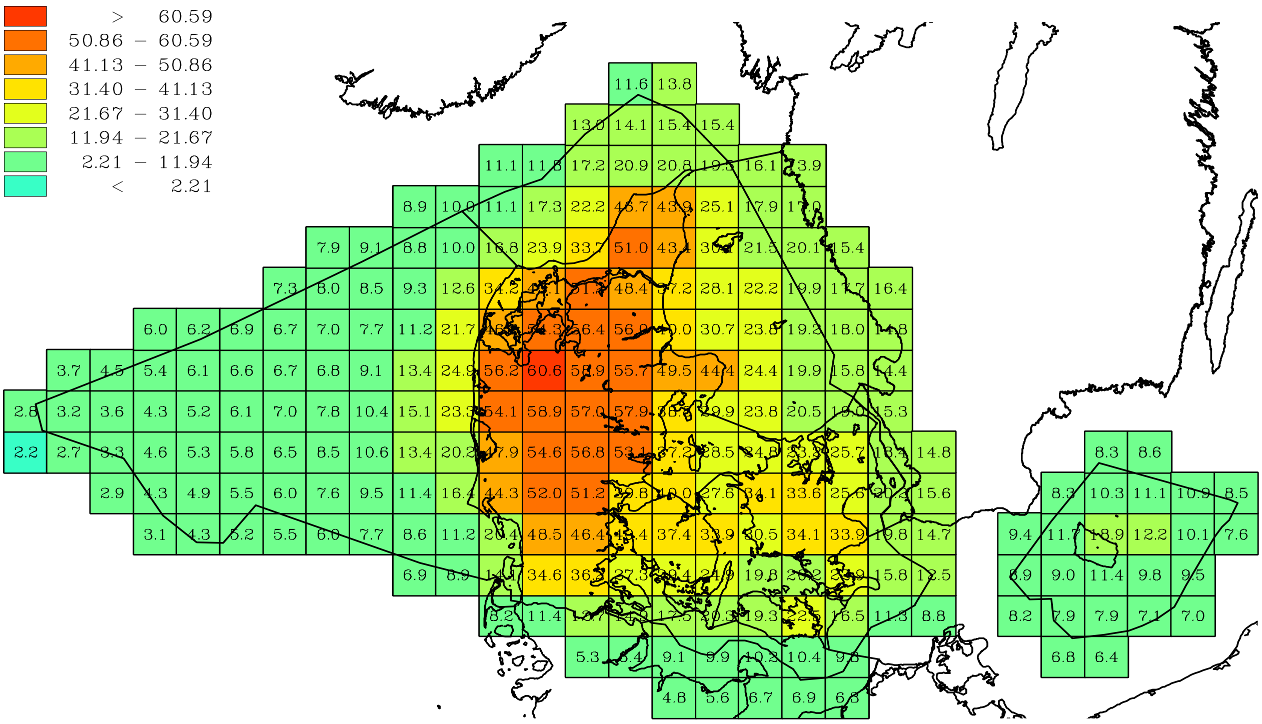

Figure 5.2.3 The relative contribution of Danish atmospheric emissions to total nitrogen depositions to Danish waters given in per cent of the total depositions in 1997 (from VMOP_97).

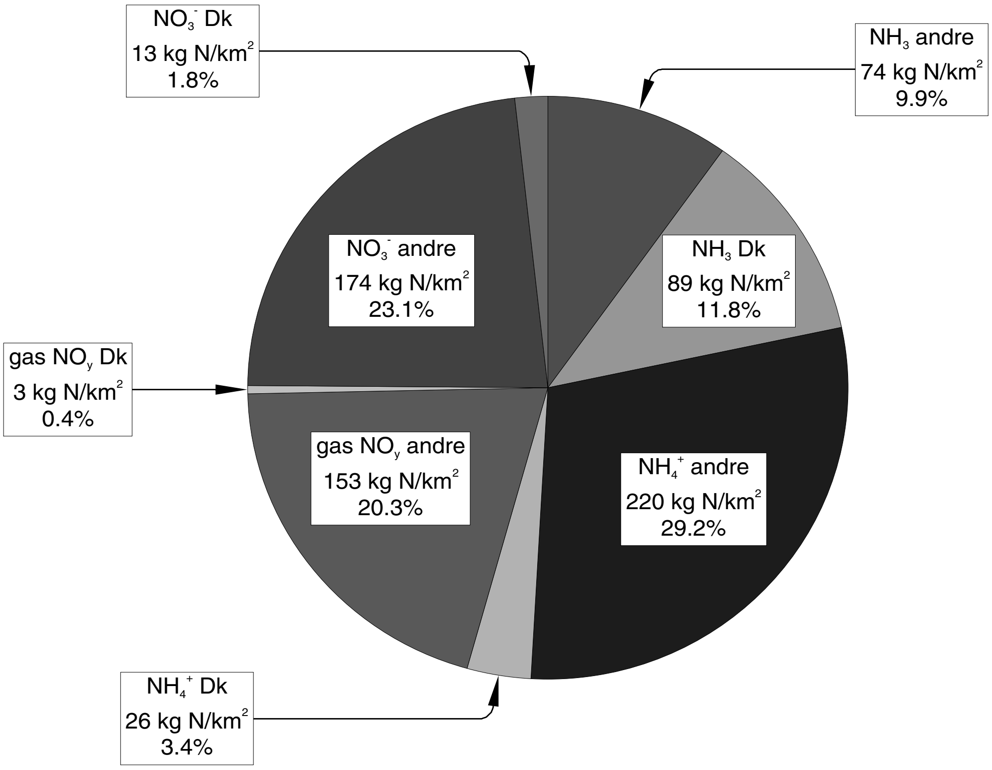

Figure 5.2.4 Total annual nitrogen depositions in 1997 to Danish waters from all atmospheric sources, Danish and foreign, distributed over the components ammonia, particulate ammonium, gas phase NO_y, and particulate nitrate (adapted from VMOP_97) [“andre”= others, *i.e.* foreign].

Table 5.2.1 Emitter and receptor regions in the EMEP model (from MSC-W, 1998).

Albania	AL	Netherlands	NL
Austria	AT	Norway	NO
Belarus	BY	Poland	PO
Belgium	BE	Portugal	PT
Bosnia and Herzegovina	BA	Romania	RO
Bulgaria	BG	Russian Federation (European Part)	RU
Croatia	HR	Slovakia	SK
Czech Republic	CS*	Slovenia	SI
Former Czechoslovakia	CS	Spain	ES
Cyprus	CY	Sweden	SE
Denmark	DK	Switzerland	CH
Estonia	EE	Turkey	TR
Finland	FI	Ukraine	UA
France	FR	United Kingdom	GB
Germany	DE*	USSR former, European part	SU
Greece	GR	Yugoslavia	YU
Hungary	HU	Remaining Land Areas	REM
Iceland	IS	Baltic Sea	BAS
Ireland	IE	Black Sea	BLS
Italy	IT	Mediterranean Sea	MED
Relative	LV	North Sea	NOS
Lithuania	LI	NE Atlantic Ocean	ATL
Luxemburg	LU	Natural Marine Sources	NAT
Former Republic of Macedonia	FYM	Total inattributable sources	IND
Republic of Moldova	MD	Total attributable sources	SUM

Table 5.2.2 Deposition of oxidised sulphur. Percentage contributions by modelled emission sources to total deposition in each country, 1985 - 1996 (adapted from MSC-W, 1998).

		Source Areas of Emission																					%	
A		**BE**	**DK**	**FI**	**FR**	**DE**	**HU**	**NL**	**NO**	**PL**	**SE**	**GB**	**CS**	**RU**	**REM**	**BAS**	**NOS**	**ATL**	**NAT**	**IND**	**DEP kt**		SUM	N>0
r																								
e	**BE**	28	**0**	0	17	18	0	0	0	1	0	14	2	0	0	0	5	1	0	7	70	**BE**	93	9
a	**DK**	**2**	**17**	**0**	**3**	**24**	**1**	**1**	**0**	**8**	**1**	**19**	**4**	**0**	**0**	**1**	**5**	**0**	**1**	**9**	**54**	**DK**	**96**	**14**
s	**FI**	0	**1**	17	1	9	1	0	0	8	2	3	2	20	0	1	1	0	1	20	156	**FI**	87	14
	FR	3	**0**	0	34	11	1	1	0	2	0	8	0	0	1	0	1	2	1	16	457	**FR**	81	12
R	**DE**	3	**1**	0	5	58	1	1	0	4	0	6	9	0	0	0	2	0	0	6	934	**DE**	96	11
e	**HU**	0	**0**	0	1	8	41	0	0	0	0	1	6	0	1	0	0	0	0	7	206	**HU**	65	7
c	**NL**	9	**0**	0	8	25	0	15	0	0	0	23	2	0	0	0	6	0	0	6	81	**NL**	94	8
e	**NO**	1	**2**	1	2	14	1	1	4	6	2	18	3	7	0	0	3	1	2	28	129	**NO**	96	17
i	**PL**	0	**1**	0	1	27	0	0	0	44	0	2	9	0	0	0	0	0	0	8	972	**PL**	92	7
v	**SE**	1	**5**	2	2	19	1	1	1	11	8	10	4	4	0	1	2	0	1	19	216	**SE**	92	17
i	**GB**	1	**0**	0	2	4	0	0	0	1	0	74	1	0	0	0	3	1	1	6	418	**GB**	94	10
n	**CS**	1	**0**	0	1	33	2	0	0	10	0	1	39	0	0	0	0	0	0	5	324	**CS**	92	8
g	**RU**	0	**0**	1	0	4	1	0	0	5	0	1	0	37	1	0	0	0	0	25	2012	**RU**	75	8
D	**REM**	0	**0**	0	1	1	0	0	0	1	0	0	1	8	41	0	0	0	0	35	467	**REM**	88	7
e	**BAS**	1	**5**	4	2	24	1	1	0	18	4	7	5	4	0	3	2	0	1	11	396	**BAS**	93	16
p.	**NOS**	2	**1**	0	4	12	0	3	0	3	0	45	2	0	1	0	8	1	2	11	829	**NOS**	95	13
	ATL	1	**0**	0	3	5	0	1	0	2	0	15	1	7	0	0	1	10	30	0	1297	**ATL**	76	11
																					9018		**%**	
	N>0	12	8	5	16	17	10	9	2	15	5	16	15	7	5	4	12	6	9	16	**19**		**17**	

Table 5.2.3 Depostition of oxidised nitrogen. Percentage contributions by modelled emission sources to total deposition in each country, 1985 - 1996 (adapted from MSC-W, 1998)

Source Areas of Emission

		BE	**DK**	**FI**	**FR**	**DE**	**IE**	**IT**	**NL**	**NO**	**PL**	**SE**	**GB**	**CS**	**RU**	**REM**	**BAS**	**NOS**	**ATL**	**IND**	**DEP kt**		SUM	N > 0
A	**BE**	13	**0**	0	18	18	0	0	9	0	1	0	19	1	0	0	0	8	2	7	31	**BE**	96	10
r	**DK**	**3**	**10**	**0**	**5**	**18**	**1**	**1**	**7**	**1**	**4**	**2**	**24**	**2**	**0**	**0**	**1**	**8**	**1**	**9**	**26**	**DK**	**97**	**16**
e	**FI**	1	**3**	16	2	10	0	0	2	3	7	9	6	2	6	0	2	3	1	17	69	**FI**	90	16
a	**FR**	3	**0**	0	34	11	0	5	3	0	1	0	10	1	0	0	0	4	4	12	253	**FR**	88	11
s	**DE**	6	**1**	0	11	38	0	2	7	0	3	0	11	4	0	0	0	4	1	7	334	**DE**	95	12
	IE	2	**1**	0	6	6	11	0	3	0	1	0	30	1	0	0	0	5	11	19	18	**IE**	96	12
R	**IT**	1	**0**	0	10	7	0	51	1	0	2	0	2	2	0	0	0	1	1	14	150	**IT**	92	11
e	**NL**	7	**1**	0	9	19	1	0	17	0	1	0	25	1	0	0	0	9	2	6	36	**NL**	98	12
c	**NO**	2	**4**	1	3	12	1	0	4	9	3	5	20	2	1	0	1	6	2	20	78	**NO**	96	17
e	**PL**	2	**2**	0	4	24	0	2	3	0	25	1	6	9	1	0	1	2	0	9	222	**PL**	91	14
i	**SE**	2	**6**	4	3	14	0	0	4	5	6	13	12	2	2	0	1	5	1	14	120	**SE**	94	16
v	**GB**	2	**1**	0	5	6	2	0	3	0	1	0	54	1	0	0	0	6	4	9	130	**GB**	94	12
i	**CS**	2	**1**	0	6	32	0	3	3	0	8	1	5	19	0	0	0	2	0	8	70	**CS**	90	12
n	**RU**	0	**1**	3	1	5	0	1	1	1	6	2	2	1	30	1	0	3	6	26	666	**RU**	90	16
g																								
	REM	0	**0**	0	4	2	0	0	1	0	2	0	1	1	12	7	0	0	1	52	131	**REM**	83	10
D	**BAS**	2	**6**	4	4	19	0	1	4	2	9	8	12	3	2	0	2	4	1	10	151	**BAS**	93	17
e	**NOS**	3	**2**	0	7	12	1	0	6	1	2	1	37	1	0	1	0	8	3	13	298	**NOS**	98	15
p	**ATL**	1	**1**	1	6	6	2	0	3	1	1	1	18	1	2	0	0	4	11	38	573	**ATL**	97	16
																					3356		**%**	
	N>0	16	14	6	18	18	7	8	18	8	18	10	18	18	8	3	6	17	16	18	**19**		**18**	

Table 5.2.4 Deposition of reduced nitrogen. Percentage contributions by modelled emission sources to total deposition in each country, 1985 - 1996 (adapted from MSC-W, 1998).

		Source Areas of Emission																		
		BE	**DK**	**FI**	**FR**	**DE**	**NL**	**NO**	**PL**	**SE**	**GB**	**EE**	**LV**	**LT**	**REM**	**IND**	**DEP kt**		SUM	N > 0
A																				
r	**BE**	64	**0**	0	14	5	9	0	0	0	3	0	0	0	0	3	51	**BE**	98	6
e	**DK**	**1**	**78**	**0**	**1**	**8**	**3**	**0**	**2**	**1**	**2**	**0**	**0**	**0**	**0**	**3**	**51**	**DK**	**99**	**9**
a	**FI**	0	**2**	33	1	6	2	1	7	3	1	3	2	2	0	20	45	**FI**	83	13
s	**FR**	2	**0**	0	81	3	1	0	0	0	1	0	0	0	0	6	394	**FR**	94	6
	DE	2	**1**	0	6	73	7	0	1	0	1	0	0	0	0	4	463	**DE**	95	8
R	**NL**	4	**0**	0	3	6	82	0	0	0	2	0	0	0	0	2	90	**NL**	99	6
e	**NO**	1	**6**	1	4	11	4	24	5	3	7	0	0	1	0	26	42	**NO**	93	12
c	**PL**	0	**1**	0	1	9	1	0	69	0	1	0	0	1	0	6	285	**PL**	89	8
e	**SE**	1	**9**	2	2	11	3	2	7	33	3	1	1	1	0	16	77	**SE**	92	14
i	**GB**	1	**0**	0	4	2	2	0	1	0	73	0	0	0	0	4	164	**GB**	87	7
v	**EE**	0	**1**	1	1	5	1	0	6	2	1	44	4	3	0	11	21	**EE**	80	12
i	**LV**	0	**2**	0	1	5	1	0	8	1	1	3	36	10	0	10	32	**LV**	78	11
n	**LT**	0	**1**	0	1	4	1	0	10	1	1	0	2	55	0	6	50	**LT**	82	10
g																				
	REM	0	**0**	0	2	1	0	0	1	0	0	0	0	0	33	34	109	**REM**	71	5
D	**BAS**	1	**12**	2	3	21	4	0	14	6	3	2	2	3	0	13	96	**BAS**	86	13
e	**NOS**	4	**6**	0	16	14	11	1	3	1	20	0	0	0	4	15	166	**NOS**	95	11
p	**ATL**	2	**1**	0	14	6	3	1	2	1	11	0	0	0	0	42	267	**ATL**	83	10
																	2403		%	
	N>0	11	**12**	5	17	17	16	5	14	10	16	5	6	8	2	17	**15**		**17**	

Table 5.2.5 Transboundary Export/Import budget for depositions of oxidised sulphur, oxidised nitrogen and reduced nitrogen in 1996. (Tarrason, 1998).

	Oxidised Sulphur						**Oxidised Nitrogen**						**Reduced Nitrogen**					
	Export		Import		to sea	in area	Export		Import		to sea	in area	Export		Import		to se	in area
	mass	%	mass	%	%	%	mass	%	mass	%	%	%	mass	%	mass	%	%	%
AL	316	88	325	88	13	54	69	95	108	96	11	47	145	57	65	37	9	75
AT	251	84	959	95	10	65	495	93	542	93	10	55	361	50	435	55	5	85
BE	1063	89	340	71	30	78	977	96	225	85	27	73	485	61	155	33	20	93
BG	6117	86	784	44	13	49	723	92	242	79	9	44	385	56	256	46	5	69
DK	**847**	**91**	**304**	**79**	**44**	**79**	**849**	**97**	**191**	**87**	**32**	**73**	**493**	**61**	**108**	**25**	**31**	**93**
FI	364	76	827	88	20	73	682	87	459	81	15	66	119	47	248	65	11	87
FR	3859	75	2590	67	29	72	4096	82	1661	65	24	67	2453	45	801	21	20	89
DE*	6785	73	3166	56	21	77	4648	82	1745	63	22	72	2310	43	1055	26	14	93
GR	2497	90	886	76	24	46	1016	93	234	77	16	39	375	58	179	40	11	66
HU	2713	81	966	60	10	75	515	90	369	86	10	71	510	53	276	38	5	88
IS	106	88	106	88	43	48	66	94	96	96	27	36	14	55	40	78	24	69
IE	612	86	257	71	57	72	328	94	172	89	41	64	522	50	84	14	32	93
IT	5735	80	2583	64	23	59	5635	86	712	43	18	51	1513	47	466	22	12	77
LU	38	95	32	94	18	75	60	98	22	96	21	71	43	65	15	39	12	91
NL	601	88	448	85	41	80	1483	96	256	83	31	73	746	60	159	25	21	93
NO	140	80	868	96	35	70	591	87	627	88	23	58	97	47	307	74	21	88
PL	8294	71	2934	46	16	75	2846	83	1135	67	15	69	1419	45	845	33	10	88
PT	1176	86	182	50	16	37	715	92	122	68	12	34	452	60	52	15	11	62
RO	3388	74	1895	62	6	60	809	83	533	77	6	53	874	48	590	38	4	77
ES	8327	81	754	28	22	47	3180	85	565	50	16	42	1468	52	277	17	11	66
SE	370	79	1173	92	31	74	968	88	796	86	23	66	252	50	396	61	21	90
CH	124	83	349	93	9	62	370	93	254	91	11	51	304	52	188	40	5	83
TR	1373	78	1348	77	18	48	1771	84	469	58	12	39	2135	62	398	24	9	54
GB	8075	80	907	31	49	74	5842	90	604	48	39	68	1317	50	350	21	30	90
BY	1068	78	1332	81	7	69	527	89	510	89	9	64	886	49	552	38	5	88
UA	4487	69	3186	62	9	67	1143	80	1173	81	9	63	2637	44	1105	25	6	85
MD	264	89	259	89	8	64	73	96	73	96	7	57	232	60	127	45	5	82
RU	8034	61	8741	63	7	53	3659	67	3652	67	4	47	2446	38	3195	45	3	72
EE	520	89	254	80	15	74	128	96	139	96	14	68	138	58	95	48	15	90
LV	163	86	437	94	17	74	84	95	201	98	14	67	81	58	173	75	11	89
LT	446	83	497	85	15	72	192	94	219	95	14	67	199	55	195	54	10	89
SI	483	88	216	77	8	53	205	96	118	94	8	45	106	59	78	51	6	77
HR	254	88	604	94	20	66	160	94	245	96	12	57	141	57	153	59	9	81
BA	2044	85	443	55	9	54	227	93	196	92	10	48	141	55	120	51	5	74
YU*	1693	78	1071	69	7	65	152	88	333	94	6	57	373	50	243	40	3	76
FYM	479	90	242	83	5	43	116	97	70	96	4	37	83	59	68	54	3	65
CS*	4675	86	1166	60	17	77	1161	93	474	84	16	70	367	52	374	52	8	89
SK	967	85	825	83	9	73	372	94	260	92	10	68	232	56	215	54	5	87
CY	209	91	31	60	8	39	63	98	13	93	11	36	0	0	11	100	0	100
REM	1435	94	2261	72	30	52	1004	91	1240	92	7	34	974	69	751	63	6	50
BAS	257	71	2486	96	40	78	214	88	1206	98	25	71	0	0	856	100	0	0
NOS	1441	66	6136	89	51	80	1655	85	2846	91	37	71	0	0	1809	100	0	0
ATL	3232	69	1187	89	33	39	3053	77	6670	88	26	35	0	0	3460	100	0	0
MED	58	97	1274	100	3	13	38	95	3909	100	5	15	0	0	2140	100	0	0
BLS	0	0	2180	100	0	0	0	0	651	100	0	0	0	0	892	100	0	0

Last update from October 1998.
Mass in 100 tonnes of Sulphur/Nitrogen.
Export is % of emission, so are depositions to sea and depositions within the model area.
Import is % of deposition.

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6 Concluding summary

Monitoring in 20 years

In this report results from 20 years of air quality monitoring in rural areas in Denmark are presented.

Network history

The monitoring of background air quality in Denmark has been carried out since 1978. Initially the network comprised two stations with a quite simple measurement programme, but increasing demands and needs have over the years led to the development of a full national Background Air Quality Monitoring Programme (BOP). It is a framework programme, which covers both national needs and Denmark's obligations in international conventions and programmes.

Network stations

Since the mid-1980s BOP has comprised 6 main stations and a number of satellite precipitation stations. At the main stations both air and precipitation sampling takes place. Air samples are collected on filters over 24 hours by semi-automatic filterpack samplers and precipitation is collected as wet-only and in most cases also as bulk samples. Precipitation is usually collected on a ½-monthly basis, but at two of the stations wet-only measurements have been on a 24-hour basis. The precipitation satellite stations supplement the main stations with bulk samples on a ½-monthly basis.

Measurement programme

The components measured in BOP comprise sulphur and nitrogen compounds in air and precipitation, elements in airborne aerosols, and at some stations also nitrogen dioxide and ozone. For the ammonia/ammonium and nitric acid/nitrate systems the phase sums are determined. All these components may have both indigenous and foreign origins.

Network is both necessary and sufficient

It is the conclusion of this report that with respect to the measurement programme this network is both necessary and sufficient for a qualified description of the air quality in the Danish rural areas. The stations are found to be representative both of the region where they are situated and of the type of their surroundings. The number of stations and the frequency of sampling are sufficient for describing the air and precipitation quality but also necessary for obtaining both the temporal variations over the years and the geographic variations across the country. The network density is however insufficient for a closer study of urban influences in the open countryside. The value of really long time series have been revealed from differences between conclusions based on series of 20 years compared to those possible from results that only span about 10 years.

Log-normal air concentrations

For the concentrations in air it has been found that most of the components are to a good approximation log-normally distributed; consequently the median rather than the mean is used extensively in this report as the most representative aggregate quantity. The main exception is ozone, which appears to be distributed normally.

Memory of past concentrations,

Most components carry a memory of past concentrations, an effect that extends for about a week. The autocorrelation functions also show that periodicities of one or two weeks occur and, not surprisingly, that there are annual patterns in the concentrations.

Aerosol stoichiometry

The aerosol in Danish rural areas consists mainly of compounds containing ammonium, sulphate and nitrate. A stoichiometric analysis has shown that this aerosol is normally fully neutralised and consists of a stoichiometric mixture of ammonium sulphate and ammonium nitrate.

Geographic variations

The geographic variations of air concentrations are not large although there is some dependence on site surroundings, whether marine or agricultural. But a N-S gradient for SO_2, S, TNHz, and TNO_3 as well as the heavy metals Pb and Zn is clearly visible and is probably caused by LRTAP from the south. A weaker W-E gradient can also be discerned in many cases, but for TNHz the gradient is reversed.

Trends

The temporal variations occur on both long and short time scales. The long-term trends show that the air concentrations of most pollutants have fallen dramatically and continuously by factors of 3-10 over the last 20 years. These changes have been brought about by coordinated international efforts to reduce emissions in Europe and they have affected not only the average but also the maximally occurring concentrations. There is however no trend in the concentrations of the agriculturally related NH_3, and TNO_3 appears to have decreased only in eastern Denmark. For NO_2 no trends can be seen although emissions on a European scale have dropped by almost 2% per year in the last 10 years. As expected no trends can be seen for ozone.

Reduced annual variations

The annual variations have for these reasons been reduced considerably so that the winter maxima of sulphur compounds and lead that occurred in the early 1980s have all but disappeared. In contrast the annual variations of nitrogen compounds have not changed much. Similarly ozone has consistently maintained a broad summer maximum.

Frequency and severity of episodes

On the short term scale episodes of the anthropogenic and/or long-range transported compounds still occur under special conditions, notably in situations with cold stagnant air. But the severity of the episodes has decreased and the frequency of occurrence has also fallen from the original average of about 7 episodes per year to 3-4. For ozone, which is mostly caused by LRTAP from the southern part of Europe, the 24-h limit value of 65 $\mu g \cdot m^{-3}$ introduced by EU for protection of vegetation and adopted by Denmark have been and are still regularly exceeded 2-6 times a week in the growth season. The accumulated AOT40 limit for protection of vegetation is also regularly exceeded each year. These exceedances may cause substantial losses in crop yield.

Concentrations in precipitation

For concentrations in precipitation it is found that total nitrogen is quite evenly distributed among reduced and oxidised nitrogen, *i.e.* ammonium and nitrate. Also the predominantly anthropogenic non_sea_salt sulphur constitutes a major fraction of sulphur in precipitation. The concentrations are approximately log-normally distributed with the exception of Hydrogen H^+, which seems to be neither log-normally nor normally distributed.

Concentrations and accumulated precipitation

Precipitation concentrations tend to decrease with increasing precipitation because already in the beginning of a precipitation event the atmosphere is cleaned quite efficiently by scavenging.

Geographic variations

The type of surroundings of the various stations influences the geographic variations of precipitation concentrations. At agricultural stations precipitation is less acid than at other sites, *e.g.* coastal sites, which may have higher concentrations of sulphate and nitrate, and/or sites exposed to long-range transport where the precipitation is more acid and has higher contents of ammonium and non-sea salt sulphate. But these variations are generally rather small.

Concentration trends

The concentrations of anthropogenic pollutants in precipitation have since the early 1980s fallen considerably, by 20-50 % and in some cases more. The main exceptions are the nitrate concentrations that cannot be seen to have changed.

Wet-only and bulk depositions

The wet depositions as monitored by wet-only and bulk collectors at the stations are approximately log-normally distributed with the exception of nitrate and H^+. A comparison of deposition results from these two collector-types show that they agree quite well, both types collect precipitation equally well. But wet-only deposition is smaller than bulk deposition because of a contribution that is only present in the bulk samplers and which probably represents dry deposition.

Geographic variations

The geographic variations are rather similar to those found for the concentrations, which are under some influence from the station surroundings. The largest variations are found for sulphate, where bulk depositions vary considerably among stations as well as within stations; at the coastal stations marine sulphate constitutes up to 50% of the deposition. The depositions of non-sea_salt sulphate are more evenly distributed over the country but an LRTAP-induced N-S gradient, most pronounced over land, is evident. A similar variation is also found for ammonium, another LRTAP-component. The bulk depositions of nitrate are fairly uniform across the country although depositions at the coastal stations are somewhat smaller. Acidity depositions do not seem to have any systematic geographic variation.

Deposition trends

Both wet-only and bulk depositions of anthropogenic components have, with some reservation for nitrate, decreased markedly in the two decades, usually by factors of 2-5. This decrease is most pronounced for non-sea_salt sulphate and acidity and is without doubt caused by the internationally agreed restrictions on emissions. For the long time series of 20 years for the wet-only depositions the negative trends are significant more often than for the shorter bulk series of 7-12 years. This agrees with the observation that the major decrease in the wet-only depositions occurred before the mid-1980s.

A notable case is that of the base cation Calcium, which as the only dominantly natural component has been found to have a significant negative trend. This phenomenon, which may be caused by the increasing agricultural practice of green winter fields, may reduce the neutralisation of the precipitation and thereby offset the benefits from reduced sulphur emissions.

Total deposition by models

The total deposition of both wet and dry deposition to Danish land and water surfaces is calculated by the ACDEP model that simulates a number of physical and chemical atmospheric processes.

Sulphur deposition

The deposition of sulphur, which is environmentally important for land areas only, is dominated by dry deposition of SO_2 and wet deposition of $SO_4^{=}$. The total deposition is composed of about equal amounts from dry and wet deposition and amounts on the average to an annual value of about 600 kg $S \cdot km^{-2}$. The largest depositions occur in the southern part of the country, indicating a large LRTAP-component.

Deposition trend

Because of the international emission reductions the deposition of sulphur has decreased markedly, by about 50%, in the period from the early 1980s to the middle of the 1990s.

Nitrogen deposition

The deposition of nitrogen compounds to water surfaces vary considerably from low values in the open (North) sea, about 500 kg $N \cdot km^{-2} \cdot yr^{-1}$, to depositions as high as 1300 kg $N \cdot km^{-2} \cdot yr^{-1}$ in the inner waters, notably the fjords and lakes. Depositions to land areas vary less and are largest in the south. About 66% of this deposition is caused by reduced nitrogen, in particular ammonia releases from nearby agricultural areas and ammonium of less local origin. The total depositions calculated by different models and in different years vary somewhat because of model improvements and improved emission estimates but unfortunately also because of varying area definitions.

Deposition trend

The total deposition of nitrogen to Danish waters amount to about (100 ± 5) kt N annually and no trend can be discerned. This atmospheric contribution to eutrophying nitrogen inflow to Danish waters is very large, about 50% of the total supply.

Critical loads

The areas in Europe where critical loads for acidification and eutrophication are exceeded have been calculated within the EMEP programme.

Acidification

For acidification the situation has improved considerably over the last 20 years because of the emission reductions. On the European level the areas of exceedance have decreased from about 25% of the total land area before 1990 to 8-13% in 1996-1997. In Denmark the corresponding figures reveal a decrease from 7-8% to about 2%.

Eutrophication

The situation is considerably more serious for eutrophication where the areas of exceedance since the mid-1980s have remained virtually constant at about 20% in the EU countries, at 35% in Europe as a whole, and at 5-8% in Denmark.

Atmospheric pollution transport from abroad

Much of the atmospheric pollution in Denmark has been transported here from abroad. An analysis of transport directions reveals that the atmospheric concentrations of sulphur, reduced nitrogen and heavy metals are enhanced in winds from east over south to south-west, *i.e.* from the European continent, compared to directions from the north-west or north. The maximum concentrations occur in the southeasterly winds, so the most polluted air arrives in Denmark from Eastern Europe. But when the frequencies of wind from the different directions are included it is found that the southwesterly wind sector contributes the most to the annual mean concentrations, the main dose of foreign air pollution arrives in Denmark from Western Europe. The variations over time of the air concentrations vary considerably with wind direction. In winds from Western Europe concentrations have been falling steadily through two decades, but in the south-easterly sector concentrations vary quite erratically around 1990, the period of political and economic upheavals in Eastern Europe, and have only recently started to decrease more systematically.

Origin of deposited of pollutants

The depositions of pollutants in European countries, including Denmark can be traced back to the original place of emission. This is done regularly in the European co-operation under the EMEP programme by application of the large-scale EMEP models for transport and transformation. For Denmark in particular the Danish ACDEP model has also been used.

Depositions in Denmark dominated by foreign sources

In this way it has been shown that Danish sources contribute only about 15-20% to the depositions of sulphur and nitrogen in Denmark, the remaining 80-85% derive from foreign sources. The decrease of 50% in sulphur deposition over the last 15-20 years as well as the lack of such tendencies for nitrogen depositions are found in both domestic and foreign contributions. The major foreign contributions to nitrogen deposition consist of nitrates and ammonium salts that easily travel long distances in the atmosphere before being deposited. The Danish deposition contributions have a considerable geographic variation, for nitrogen from less than 5% in the North Sea to more than 60% in the inner Danish waters.

Pollutant "import" to Demnark

For the period 1985-1996 it has been estimated by EMEP that Denmark imported on the average 80% of the sulphur deposited in the country from a total of 13 foreign and neighbouring countries, mainly from Germany and the United Kingdom. Similarly 90% of the deposited oxidised nitrogen was imported from 15 foreign countries, and again with Germany and the United Kingdom as the main contributors. For reduced nitrogen that is prone to rapid deposition the import from neighbouring countries accounted for only about 22% of the deposition, the remainder was of domestic origin.

Pollutant "export" from Denmark

However, Denmark also exports pollution that is deposited outside the country. For the same 12-year period as above it has been estimated by EMEP that 91% of the Danish sulphur emissions are transported outside the country, notably to the east. The main part of this pollution (44%) is deposited in the Baltic where it has no effect and in 7 neighbouring countries, mainly in Norway and Sweden. The Danish contributions to the sulphur depositions in these countries are however of no great importance compared to the total deposition there. Similar figures and conclusions apply to the export of oxidised nitrogen whereas the export percentages for reduced nitrogen are considerably lower, because a main part of the emissions is gaseous ammonia, that is efficiently deposited in the local area.

Net exports from Denmark

In conclusion it can be stated that along with most of the European countries Denmark is a net pollutant exporter of deposited sulphur and nitrogen. This is to a large degree caused by the small size of the country where the pollutants do not have far to go to cross a border. For sulphur the net result was in 1996 that 54 kt or 59% of the Danish emissions of 93 kt S left the country in 1996. For all nitrogen compounds, both oxidised and reduced, the net export in 1996 from Denmark was 104 kt corresponding to 61% of the total annual emissions of 169 kt N.

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Danish Summary - Dansk resumé

Luftkvaliteten i baggrundsområder i Danmark 1978 – 1997

Faglig rapport fra DMU nr. 341

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Atmosfærisk overvågning igennem 20 år

Denne rapport præsenterer resultater fra 20 års overvågning af luftkvaliteten i landdistrikter eller baggrundsområder i Danmark. Formålet med rapporten er at give et generelt overblik over luftkvaliteten i danske baggrundsområder, som den har manifesteret sig i de eksperimentelle resultater. Det har ikke været hensigten at give en komplet redegørelse for forekomsten af alle forureninger alle steder, men derimod at illustrere hovedtrækkene i udviklingen med udvalgte, men typiske resultater fra forskellige stationer.

Udbygning af stationsnettet

Kvaliteten af baggrundsluften i Danmark har været overvåget siden 1978. Oprindeligt bestod netværket af to stationer med et enkelt måleprogram, men stigende krav og behov har gennem årene før til udviklingen af et fuldt udbygget nationalt Baggrunds-Overvågnings-Program (BOP) for atmosfæren. Det er et paraplyprogram, som dækker Danmarks forpligtelser for atmosfærisk overvågning, både nationalt og internationalt.

Stationsnettet i dag

Siden midten af 1980-erne har BOP omfattet 6 hovedstationer, hvor der indsamles både luft- og nedbørprøver, og et antal satellitstationer alene til nedbørmåling. Luftprøverne opsamles på filtre over 24 timer med halvautomatiske filterpack opsamlere og nedbør opsamles i såvel wet-only som bulkopsamlere, normalt på ½-månedsbasis, men to af wet-only opsamlerne har været drevet på døgnbasis. Satellitstationerne supplerer hovedstationerne med nedbørprøver på ½-månedsbasis.

Måleprogram

De komponenter, som måles i BOP, omfatter svovl- og kvælstofforbindelser i luft og nedbør, grundstoffer i atmosfæriske aerosoler og ved nogle stationer også kvælstofdioxid og ozon. For ammoniak/ammonium og salpetersyre/nitrat systemerne bestemmes fasesummerne. Alle disse komponenter kan have deres oprindelse både indenlands og udenlands.

Nødvendigt og tilstrækkeligt stationsnet

Det konkluderes i rapporten, at i relation til det anvendte måleprogram er *omfanget dette netværk både nødvendigt og tilstrækkeligt* til at give en kvalificeret beskrivelse af luftkvaliteten i danske baggrundsområder. Stationerne er repræsentative for både det område, hvor de er placeret og for de specifikke lokale omgivelser. Antallet af stationer såvel som midlingstid og hyppighed for prøverne er tilstrækkelige til en beskrivelse af luft- og nedbørkvaliteten, men også nødvendige for at fremskaffe pålidelige vurderinger af tidsvariationer over årene og geografiske variationer henover landet. Værdien af lange tidsserier er blevet demonstreret gennem forskellene i de konklusioner, der kan drages fra tidsserier over 20 år sammenlignet med serier som kun dækker 10 år.

Log-normale luftkoncentrationer

Koncentrationer i luft er for de fleste komponenter log-normalt fordelte med god tilnærmelse; derfor anvendes medianen i stor udstrækning i denne rapport som den mest repræsentative aggregerede størrelse, snarere end den aritmetiske middelværdi. Ozon indtager i fordelingsmæssig sammenhæng en særstilling, idet den synes at være normalt fordelt.

Hukommelse om tidligere koncentrationer

De fleste stoffer udviser hukommelse om tidligere koncentrationer, som strækker sig omtrent en uge tilbage i tiden. Autokorrelationsfunktionen viser også, at der optræder perioder på en til to uger, og at der ikke overraskende er årlige mønstre i koncentrationerne.

Aerosol støkiometri

De atmosfæriske aerosoler i danske baggrundsområder består hovedsageligt af ammonium-, svovl- og nitratholdige forbindelser. En støkiometrisk analyse viser, at disse aerosoler normalt er fuldt neutraliserede og består af en støkiometrisk blanding af ammonimsulfat og ammoniumnitrat.

Geografisk variation

Luftkoncentrationernes geografiske variationer er ikke store omend der er nogen afhængighed af om stationerne er placeret i nærhed af havet eller i landbrugsområder. Men for SO_2, S, TNH_z, and TNO_3 såvel som for tungmetallerne Pb og Zn er der en tydelig N-S gradient, som sandsynligvis skyldes LRTAP[1] fra syd. En svagere V-Ø gradient kan også skelnes i adskillige tilfælde, men den har modsat retning for TNH_z.

Trends

De tidslige variationer forekommer på både kort og lang skala. Langtidsvariationerne viser, at luftkoncentrationerne for de fleste forureninger er faldet dramatisk over de sidste 20 år, så koncentrationerne er reduceret med faktorer på 3-10. Disse ændringer, som kan ses i hele perioden, kan henføres til de fælles internationale bestræbelser på at reducere emissionerne i Europa, og de har påvirket ikke blot de gennemsnitlige men også de maksimale koncentrationer i luft. Der er imidlertid ingen sådan udvikling at spore for NH_3, som har sin oprindelse i landbrugsaktiviteter, og TNH_z synes kun at være faldet noget i det østlige Danmark. For NO_2 kan der heller ikke konstateres noget fald selv om emissionerne i Europa er faldet med næsten 2% om året i de sidste 10 år. Som forvente er der heller ingen udviklingstendens at spore for ozon.

Mindre årlig variation

De årlige variationer er af disse årsager også blevet betragteligt mindre, så de maksimalværdier, der kunne observeres for svovlforbindelser og bly i de tidlige 1980-ere, næsten er forsvundet. I modsætning hertil har de årlige variationer i koncentrationerne for kvælstof-

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[1] LRTAP: Langtransport af atmosfærisk forurening

forbindelser ikke ændret sig meget, og ozon udviser ligeledes bestandigt et bredt sommermaksimum.

Episoder

På den korte tidsskala forekommer der stadig episoder for de menneskeskabte og/eller langtransporterede forbindelser under specielle omstændigheder, især i perioder med kold stillestående luft over landet. Men episodernes styrke er aftaget og hyppigheden er også faldet fra oprindeligt ca. 7 episoder pr. år til 3-4 om året. For ozon, som hovedsageligt stammer fra LRTAP fra det sydlige Europa, overskrides den 24-timers grænseværdi på 65 $mg{\cdot}m^{-3}$, som er indført i EU til beskyttelse af vegetation og som Danmark har tilsluttet sig, regelmæssigt 3-4 gange om ugen i vækstsæsonen. Den årlige akkumulerede grænseværdi AOT40 overskrides også jævnligt. Disse overskridelser kan medføre store tab af udbytte.

Koncentrationerne i nedbør

For koncentrationerne i nedbør er det fundet, at totalt kvælstof forekommer nogenlunde ligeligt fordelt mellem reduceret og oxideret kvælstof, dvs. mellem ammonium og nitrat. Desuden udgør det antropogene, ikke-marine svovl den største del af svovlforbindelserne i nedbør. Koncentrationerne er tilnærmelsesvist logaritmisk normalt fordelte med undtagelse af brintionen, som dog heller ikke synes at være normalt fordelt.

Koncentrationer og nedbørsmængde

Koncentrationerne i nedbør har en tendens til at aftage med mængden af nedbør, fordi atmosfæren renses effektivt allerede i begyndelsen af en nedbørbegivenhed.

Geografisk variation

De geografiske variationer af nedbørkoncentrationerne er påvirket af stationernes omgivelser. Ved stationer i landbrugsområder er nedbøren mindre sur end andre steder, såsom i kystnære omgivelser, hvor der ofte er større koncentrationer af svovl og nitrat. Ved stationer, som er udsat for atmosfærisk langtransport, er nedbøren mere sur og har højere indhold af ammonium og ikke-marint svovl. Men disse variationer er i almindelighed ret små.

Koncentrationsudvikling

Koncentrationerne i nedbør af antropogene forureninger er faldet betragteligt siden begyndelsen af 1980-erne. Nedgangen er typisk på 20-50% men større fald ses også. Hovedundtagelsen udgøres af nitrat, hvor der ikke kan konstateres nogen ændring.

Wet-only og bulk deposition

Depositionerne, som er målt med wet-only og bulk opsamlere, er med tilnærmelse logaritmisk normalt fordelte med undtagelse af nitrat og depositionen af de sure brintioner. En sammenligning mellem de to typer opsamlere viser god overensstemmelse og begge typer opsamler nedbøren lige godt. Men wet-only depositionen er mindre end bulk depositionen, fordi der her forekommer et ekstra bidrag, som sandsynligvis repræsenterer den tørre deposition.

Geografisk variation

De geografiske variationer har stor lighed med variationerne for koncentrationerne, som i nogen grad er påvirket af stationernes omgivelser. De største variationer forekommer for bulkdeposition af sulfat, som har en betydelig variation både mellem og indenfor stationer. Ved de kystnære stationer udgør marint sulfat op til 50% af depositionen. Depositionen af ikke-marint sulfat er mere jævnt fordelt over landet men en N-S gradient, forårsaget af LRTAP, er tydelig, især over land. En tilsvarende variation kan også ses for ammonium, en anden LRTAP-komponent. Bulkdepositionerne af nitrat er ret ens over hele landet, omend depositionerne er lidt mindre ved kystnære stationer. Den sure H^+-deposition ser ikke ud til at have nogen systematisk geografisk variation.

Depositions udvikling

Både wet-only og bulkdepositioner af antropogene forbindelser er, med noget forbehold for nitrat, faldet betragteligt i de seneste to tiår, typisk med en faktor 2-5. Dette fald er tydeligst for ikke-marint sulfat og surhed, og skyldes uden tvivl de internationale aftaler om emissionsreduktioner. For de lange tidsserier på 20 år, som findes for wet-only depositionerne, er de negative udviklingstendenser hyppigere signifikante end for de kortere serier på 7-12 år for bulkdepositionerne. Dette stemmer med den observation, at de største fald i wet-only depositionerne fandt sted i det første tiår. Et særligt tilfælde udgøres af base-kationen Calcium, der som den eneste hovedsageligt naturlige komponent, udviser en negativ trend. Dette fænomen, som måske kan henføres til den stadigt større udbredelse af grønne vintermarker, kan reducere neutraliseringen af nedbøren og dermed modvirke effekten af de formindskede emissioner af svovl.

Total deposition iflg. modeller

Den totale deposition, som omfatter både våd- og tørdeposition, til danske land- og havområder er beregnet med ACDEP-modellen, som simulerer et stort antal fysiske og kemiske processer i atmosfæren.

Svovldeposition

Depositionen af svovl, som kun er af miljømæssig betydning for landområder, domineres af tørdeposition af SO_2 og af våddeposition af $SO_4^{=}$. Den totale deposition udgøres af nogenlunde lige mængder af våd og tør deposition af svovl og beløber sig i gennemsnit til omkring 600 kg $S \cdot km^{-2} \cdot år^{-1}$. De største depositioner forekommer i den sydlige del af landet, hvilket indikerer et stort LRTAP-bidrag.

Trend

Den totale svovldeposition er pga. de internationale emisssionsreduktioner faldet markant med omkring 50% i perioden fra de tidlige 1980-ere til midten af 1990-erne.

Kvælstofdeposition

Depositionen af kvælstofforbindelser til vandoverflader varierer meget, fra lave værdier omkring 500 kg $N \cdot km^{-2} \cdot år^{-1}$ i de åbne farvande, især Nordsøen, til så høje værdier som 1300 kg $N \cdot km^{-2} \cdot år^{-1}$ i de indre farvande, især fjorde og søer. Depositionen til landområderne varierer noget mindre og er størst i de sydlige egne. Omkring 66% af denne deposition udgøres af reduceret kvælstof, hovedsageligt ammonium fra lokale landbrugsudslip såvel som ammonium af mere fjern oprindelse. Den totale beregnede deposition varierer noget med tidspunktet for beregningen pga. forbedringer i både model og i emissionsopgørelser, men desværre også pga. variationer i definitionerne af de forskellige farvandsarealer.

Trend

Den totale kvæstofdeposition til danske favandsområder beløber sig årligt til ca. (100 ± 5) kt. N og der kan ikke konstateres nogen udvikling over tid. Dette atmosfæriske bidrag til eutrofieringen af danske havområder med kvælstof er meget stort, da det udgør henved 50% af den totale kvælstoftilførsel til havet.

Kritiske tålegrænser.

Omfanget af de arealer i Europa, hvor de kritiske tålegrænser for forsuring og eutrofiering er overskredet er beregnet indenfor EMEP programmet.

Forsuring

For forsuringen er situationen forbedret meget de sidste 20 år pga. de internationale nedskæringer af emissionerne. På europæisk plan er arealerne, hvor der sker overskridelser, faldet fra omkring 25% af det totale landområde før 1990 til 8-13% i 1996-1997. I Danmark viser de tilsvarende tal et fald fra 7-8% til ca. 2%.

Eutrofieringen

Situationen er betydeligt værre for eutrofieringen, hvor arealerne med overskridelse af den kritiske tålegrænse, siden midten af 1980-erne har været nærmest uændret på omkring 20% af arealet i EU-landene, på ca. 35% i Europa (EMEP-landene) som helhed, og i Danmark på 5-8%.

Luftforurening fra udlandet

I Danmark er en stor del af luftforureningen transporteret hertil fra udlandet. En analyse af transportretninger, opdelt i 45^0-sektorer, viser, at de atmosfæriske koncentrationer af svovl, reduceret kvælstof og tungmetaller er forhøjet i vindretninger fra øst, syd og sydvest, dvs. når vinden kommer fra det europæiske kontinent, sammenlignet med vind fra de nordlige og nordvestlige sektorer. De største koncentrationer optræder under sydøstlige vinde, så den mest forurenede luft kommer fra Østeuropa. Men indregnes hyppigheden af vind fra de forskellige retninger viser det sig, at de største bidrag til den årlige middelværdi stammer fra sydvest, så hovedparten af den forurenende dosis ankommer til Danmark fra Vesteuropa. De tidsmæssige variationer af luftkoncentrationerne er stærkt afhængige af transportvindens retning. I sydvestlige vinde fra Vesteuropa er koncentrationerne faldet konstant gennem to årtier, men i den sydøstlige vindsektor varierede koncentrationerne i Danmark temmeligt vilkårligt omkring 1990, hvor der var økonomisk turbulens i Østeuropa, og de er først i de senere år igen begyndt at falde systematisk.

Kilder til den deponerede forurening

Depositionen af forurenende stoffer i Europa og herunder Danmark kan spores tilbage til det oprindelige udslip. Dette sker rutinemæssigt som led i det europæiske EMEP-samarbejde under anvendelse af EMEPs storskala-modeller for transport og omdannelse af luftforurening. Under BOP har den danske ACDEP-model også været anvendt at belyse disse forhold for Danmark.

Depositionen i Danmark domineres af udenlandske kilder

På denne måde er det påvist, at danske kilder kun bidrager med 15-20% til depositionen af svovl og kvælstof i Danmark, så 80-85% af depositionen kommer fra kilder i udlandet. Den konstaterede nedgang i depositionen af svovl på 50% gennem de sidste 15-20 år, såvel som manglen på udvikling i depositionen af kvælstof, kan findes i både de indenlandske og udenlandske bidrag. De største udenlandske bidrag til depositionen af kvælstof består af ammonium- og nitratsalte, som let transporters over store afstande før de deponeres. De danske bidrag til depositionen af kvælstof har en stor geografisk variation, fra under 5% i Nordsøen til mere end 60% i de indre danske farvande.

Forurenings "import" til Danmark

I perioden 1985-1996 er det under EMEP vurderet, at gennemsnitligt 80% af det svovl, som blev deponeret i landet, blev importeret til Danmark fra i alt 13 fremmede lande, herunder især nabolande som Tyskland og Storbritannien. På tilsvarende måde blev 90% af det oxiderede kvælstof, som deponeredes her i landet, importeret fra 15 lande, hvor hovedbidraget igen kom fra Tyskland og Storbritannien. For reduceret kvælstof, som fortrinsvis deponerer lokalt, udgjorde importen fra udlandet således kun ca. 22% af depositionen, hovedparten var af dansk oprindelse.

Forurenings "eksport" fra Danmark

Danmark eksporterer imidlertid også forurening, som deponeres i udlandet. For den samme 12 års periode er det under EMEP vurderet, at 91% af de danske svovludslip transporteres ud af landet, hovedsageligt mød øst. Hovedparten på 44% deponeres i Østersøen, hvor det er uden miljømæssig virkning og resten i 7 nabolande, fortrinsvis Norge og Sverige. Disse danske bidrag til depositionen er dog ikke af stor betydning, da de kun udgør en lille del af den samlede deposition i disse lande. Tilsvarende tal og tilsvarende konklusioner gælder for eksporten af oxideret kvælstof, hvorimod eksportandelen af reduceret kvælstof er betragteligt lavere, fordi hovedparten af emissionerne er gasformig ammoniak, som fortrinsvis deponeres lokalt.

Netto eksport fra Danmark

Det kan derfor konkluderes, at på linie med de fleste europæiske lande er Danmark nettoeksportør af forureningerne svovl og kvælstof. Dette skyldes dog i høj grad landets størrelse, hvor der kun er korte afstande til grænserne. For svovl var det samlede resultat i 1996, at 54 kt. S eller 59% af de danske udslip på 93 kt. S blev sendt udenlands. For alt kvælstof, både oxideret og reduceret, var nettoeksporten fra Danmark på 104 kt. N i 1996 svarende til 61% af de samlede emissioner på 169 kt. N.

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"The Background Air Quality in Denmark 1978 – 1997" presents 20 years of results from the national Background Air Quality Monitoring Programme. Data are reported for sulphur and nitrogen compounds in rural air and precipitation, a number of elements in aerosols including heavy metals, and ozone and nitrogen dioxide. Background air pollution in Denmark is under considerable influence from the European continent. Because of atmospheric transport from Europe pollutant concentrations in both air and precipitation are larger in the southern than in the northern part of the country. During the two decades concentrations have fallen by factors of 2 – 10 times because of reduced emissions throughout Europe, and the number and severity of air pollution episodes have also decreased. But the levels of the nitrogen compounds emitted from agricultural activities and from traffic remain almost unchanged. Quite similar conclusions can be drawn for the wet depositions; also here very considerable decreases can be followed through the two decennia. Concentrations in air and precipitation as well as depositions are shown to be approximately log-normally distributed.

The main foreign contributions to the general pollution level in Denmark originate from West Europe although concentrations are largest in winds from East Europe. A major part of the depositions of both sulphur and oxidised nitrogen have a foreign origin, domestic sources contribute only 20 %. Nevertheless Denmark is a net exporter of air pollution, but the contributions to depositions in other countries are small.

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