EMEP/CCC-Report 7/2000

A contribution from CCC to the reevaluation of the observed trends in sulphur and nitrogen in Europe 1978–1998

Input for further evaluation by the national laboratories and for use in the TFMM assessment work

EMEP Chemical Co-ordinating Centre

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EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe

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Preface

During the spring of 2000 EMEP-CCC began a review of the long-term acid monitoring data assembled under the EMEP programme. This report presents results for this review. It is hereby presented as a discussion document to the Task Force on Measurements and Modelling (TFMM) in Vienna, 23-25 October, 2000, convened under the Convention on Long Range Transboundary Air Pollution as an input to its work on trends.

The observations under the programme have been conducted by the countries themselves. In truth, therefore, this report is the product of considerable effort over a considerable period by a large number of organisations and individuals. Furthermore, whilst the data collated and presented here by EMEP benefits from collection with concern for comparability between countries and across time, and with attention to procedures of quality control, it nevertheless must remain only a fraction of the information available to those countries, and to the international community. Reflecting its duties within the field of transboundary pollution, EMEP-CCC has endeavoured to review the assembled data with a view to regional patterns which may be observed across national boundaries. With TFMM intending to construct a much more comprehensive Assessment Report in the coming period, we submit this report on the EMEP data as an assistance to countries in both framing and answering the questions which arise. We also present the report as a simple statement on the information available from the monitoring work of EMEP alone. EMEP's activities have also been concerned with reliable modelling of the transport of air pollutants across Europe. Measurement data has been used to validate and improve these modelled estimates. Clearly, there are ways in which modelled estimates may now in feedback be used to complement and analyse the trends presented here. By presenting the state of knowledge which monitoring alone affords us, we invite discussion as to the means which modelling work can be used to take this further.

In summary, this report represents one assessment of the state of the environment, or more accurately the state of change of the acidifying environment, as is revealed simply by the EMEP monitoring network. We trust it provides a valuable input to comprehensive analysis to trends in acidification in Europe conducted by countries and by the whole EMEP framework in the coming period.

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1. Introduction

1.1 Background

The last quarter of the twentieth century has been a significant period for Europe's environment and its management during which major steps were taken by the international community to halt, and ultimately reverse, acidification. This report is intended to contribute to evaluation of how well the issue was addressed during this period through review of the observed trends in acidifying and eutrophying atmospheric pollution across Europe between 1978 and 1998.

In 1976, in response to the observed acidification of a growing region of Europe, the Co-operative Programme for the Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe – EMEP – was established. The programme included coordinated background measurements of acidifying air pollutants to be performed by countries themselves, with data assembled by the Chemical Coordinating Centre of EMEP, hosted by NILU. Beginning on 1st January 1978, the first measurement phase monitored acidity and sulphur compounds in air and precipitation across 46 stations and 14 countries. Since then, a total of over 150 stations across 35 countries covering the whole of the European continent have produced data at various times as part of the acidification/ eutrophication network. The acidification programme itself has extended beyond sulphur to include oxidised and reduced nitrogen compounds in air and precipitation, as well as base cations. In addition to acidification, ozone, VOC, and trace contaminant programmes have also been established. Extensive quality control procedures have been put in place, field sampling and laboratory analysis intercomparisons between countries conducted, techniques developed and Standard Operating Procedures (SOPs) established. Countries have been strongly encouraged to harmonise their methodologies to ensure comparability over time and space.

Information from this monitoring programme has been employed closely in the development of several international Protocols on reduction of acidifying and eutrophying emissions. Formulated within the framework of the 1979 Geneva Convention on Long Range Transboundary Air Pollution (CLRTAP), the first of these was the *1985 Protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes by 30%.* However, whilst sulphur was believed to be the principal perpetrator of observed acidification of rainfall and the European environment, the contribution made by atmospheric nitrogen compounds was not overlooked. In 1988 a *Protocol Concerning the Control of Nitrogen Oxides or* *their Transboundary Fluxes* was agreed which sought to stabilise emissions. Upon expiry of first Sulphur agreement the *1994 Protocol on Further Reduction of Sulphur Emissions* was negotiated. These protocols have stipulated that EMEP should use measurement data to inform about levels and depositions of relevant compounds across Europe, and to assist in the calculation of transboundary fluxes. At the end of the 20th century, in 1999, a further agreement was signed by many countries in which acidification was no longer to be dealt with in isolation but in relation to photochemical problems, the so-called "multi-pollutant, multi-effect" Protocol.

1.2 Purposes of trend review

The EMEP monitoring programme provides a long term record of atmospheric conditions unique in its extent, consistency and quality. In this report the opportunity is taken to utilise this long term record to review the changing state-of-the-acidifying-environment in Europe at the close of the twentieth century. Observed state-of-the-environment analyses play a fundamental part in scientific and political progress. Thus, although the description of past trends can be a straightforward objective it is also one of great value which can assist evaluation of whether basic desires to steadily improve the condition of the environment are being satisfied. The establishment of observed relationships between air quality and emissions is one such aspect of this.

Obvious amongst such issues is the degree to which the intentions of the various agreements under CLRTAP have been achieved. These have reflected the capabilities of the time, the characteristics of the pollutants themselves, and the will to pay the costs of acidification and eutrophication abatement in Europe. From even a cursory review of such it is evident that control has developed considerably since the mid-1980s. Whilst initial agreements achieved a degree of acceptance for equal decreases of a nominal 30% in releases by signatories between 1980 and 1993 (some major polluters not being in agreement), the second Sulphur Protocol a decade later was able to stipulate differential reductions by up to 87% according to geography, impact and costs, again beginning from a 1980 base year. The stated purpose of these agreements developed simultaneously. In 1985 it was left to the preamble to suggest the justification behind the measure. Emission reductions were undertaken through concern "that the present emissions of air pollutants are causing widespread damage, in exposed parts of Europe and North America, to natural resources of vital environmental and economic importance" (First Sulphur Protocol, 1985, Preamble). The 1994 Protocol by comparison openly wished to reduce acidification from sulphur deposition, and indicated the quantifiable goal of an ultimate "no-harm" objective. Since this time emission levels can be seen to have proceeded as hoped. Figure 1.1 displays reported emissions of sulphur for the whole of Europe supplied from the EMEP emission database, together with those for nitrogen (Vestreng, pers. comm., July 2000; also Vestreng and Støren, 2000).

Thus, there is a promising basis from which to consider progress towards targets of environmental quality, and observations from the EMEP monitoring programme over the past two decades provides information from which the degree of such improvement can be estimated. Assessment is thus assisted as to whether the underlying intentions of the agreed emission reductions have been met.

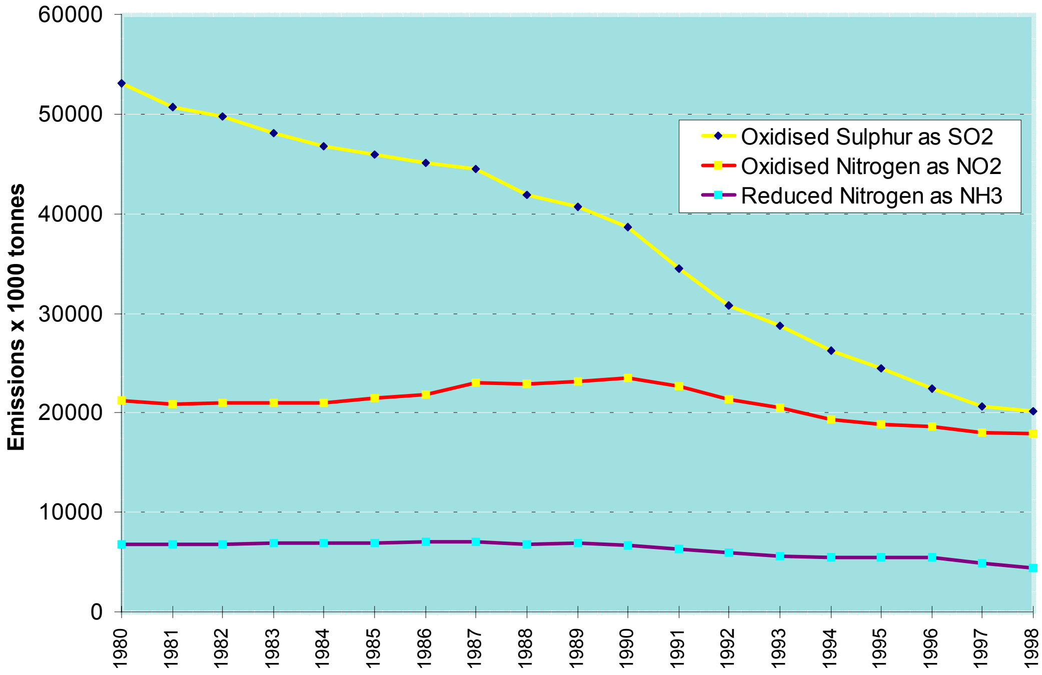


Figure 1.1: Emissions of sulphur dioxide, nitrogen dioxide, and of ammonia as reported to the UN ECE (Vestreng and Støren, 2000).

Regarding sulphur and the state of the environment since 1980, there has been a target of a 30% reduction in atmospheric sulphur release by the end of 1993. The monitoring network permits evaluation of the degree of change in atmospheric content and terrestrial sulphur supply between these dates. With the majority of atmospheric sulphur being anthropogenic, and an estimated lifetime of sulphur compounds in the atmosphere of a few days indicating a European source for much observed European sulphur, the change in content provides circumstantial evidence of changes in European emissions.

Commitments on nitrogen are also open to assessment. The 1988 Protocol intended that there should be no increase in emissions of nitrogen oxides between 1987 and the end of 1994. As with sulphur, the measurement programme cannot directly assess the achievement of this objective but can provide indirect evidence via estimating environmental loadings of nitrogen oxides.

1.3 Objectives

The last quarter of the twentieth century has been a significant period for the European environment and its management. Major steps have been taken to halt and ultimately reverse acidification. The coordinated and coherent EMEP monitoring programme over the last two decades can provide information on observed air quality and atmospheric pollutant supply to allow assessment of improvement in overall environmental quality in this period. This report considers the evolution of Europe's acidifying and eutrophying atmospheric environment throughout CLRTAP initiatives. The 18-year period from 1980 is reviewed, extending from the reference year for the first of the international abatement Protocols through to 1998, the latest year in which observations have been reported to the Steering Body of EMEP. A fact not to be forgotten, however, is that the monitoring data discussed in this report remains the property of the countries collecting it, and represents a fraction of the information available to them. This report can be no more than a contribution to more comprehensive assessment under their guidance. Objectives nevertheless include:

- *Establish the degree to which improved air quality is readily observable.*

- *Estimate the rates of change which have been monitored.*

- *Ascertain whether reported emission reductions of at least 30% in Europe's sulphur emissions since 1980 have been translated into similar reductions in terrestrial supply.*

- *Evaluate whether rates of oxidised nitrogen supply have remained consistent since 1987.*

- *To contribute to a review of the changing State of the Environment, and more specifically, to a review of trends in the acidification state of the environment.*

2. The EMEP Measurement Programme and co-ordinated monitoring data on acidifying compounds

2.1 Origins of the network

Coordinated international monitoring of acidifying air pollution in Europe developed steadily from the 1950's, when the Swedish precipitation monitoring network supervised by the Institute of Meteorology, Stockholm, was first extended to a number of other countries under the name of the European Air Chemistry Network (EACN). Around 100 sites were involved. By the 1960's observations indicated an expanding area of Europe subject to highly acidic precipitation (pH 3-4), and supported a link with observed riverine and lacustrine acidification with disappearance of fish (e.g. Odén, 1968). In the early 1970s, the Organisation for Economic Co-operation and Development (OECD) approved a Co-operative Technical Programme to Measure the Long Range Transport of Air Pollutants, and by 1974 fourteen countries were either active participants or otherwise assisting (A, BE, DK, FRG, FI, FR, IS, IT, NL, NO, SE, CH, UK, Can). Many sites from the EACN became a part of this programme, with co-ordination of measurements and of data analysis now carried out by the Central Co-ordinating Unit hosted by the Norwegian Institute for Air Research (NILU). The objective of the programme was "to determine the relative importance of local and distant source of sulphur compounds in terms of their contribution to the air pollution over a region…". The *Measurements and Findings*, made public by the OECD in 1977, were instrumental in establishment of today's Co-operative Programme for the Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe - EMEP - initially with funding from UNEP and later transferred to the UN ECE. This programme has since served the technical requirements of international agreements under the 1979 Geneva Convention on Long Range Transboundary Air Pollution with effective reduction of transboundary air pollution as its aim. Renamed the Chemical Coordinating Centre (CCC), the measurement programme continued to be centrally coordinated whilst based firmly upon national and international programmes and conducted by countries themselves.

Emission reductions are expensive, and with observation and measurement of the environment underpinning the development of strategies, great importance has been attached to obtaining high quality, reliable, measurements. This has been a task requiring experience and commitment. Often sites were operational before EMEP's initiation, and from the outset there has been recognition of the dangers inherent in multinational networks from inconsistent measurement and of systematic differences between networks. A Manual for Sampling and Chemical Analysis has been produced and updated by the CCC since 1977. The intention has been to establish methods that are appropriate with respect to accuracy, which are as simple as possible, and which are thoroughly documented so as to allow comparability in measurements made across the width of the continent over periods of decades.

2.2 Monitoring station siting

Comparability in measurement site location is crucial as observed characteristics of air quality are quite different in close proximity to emission sources than they are after dispersion and transformation at some distance away. Given this and the EMEP programme's concern with transboundary transfers of pollutants, criteria for the siting of monitoring stations have been put forward from the outset. At the same time, harmonisation with other international activities has always been considered highly desirable, and the criteria of the World Meteorological Organisation (WMO) with regard to regional background stations have been employed, key to which is that local sources should not have undue influence. In general terms it requires depositions in the area to exceed emissions: for net source regions such as the United Kingdom and Germany it will still require that local emissions should be lower than those of adjacent areas. The stations should be located far away from local sources and be representative for a region. Although representativeness is a concept which is site and component specific, it is expressed in the Manual that the "region" should be "larger than the size resolution of the atmospheric dispersion models available" to EMEP, currently 50 km (thus linking the extensive measurement programme with EMEP's attempt to model dispersion and deposition across the continent). More recently the importance of regional, representativeness has been emphasised, rather than "background location". A sites representativeness may also have an expression dependent on time scale, e.g. characteristics on a daily basis, for seasonal averages, annual averages, etc. Clearly being a difficult criterion to measure, although technically possible e.g. for gas measurement using passive samplers, straightforward standards can be used as a surrogate. Having satisfied that emissions influencing a site should arise largely outside the area, attention should be given to "the effects of the immediate surroundings and emissions within the nearest 20 km. These local emissions should not be allowed to result in unrepresentative measured air concentrations or precipitation chemistry". Minimum distance requirements are specified, and are based on similar guidelines from North American programmes:

Table 2.1: Siting criteria for EMEP background monitoring stations.

Type	Minimum Distance	Comment
Large pollution sources (towns, power plants, major motorways)	50 km	Depending on prevailing wind direction
Small scale domestic heating with coal, fuel oil or wood	100 m	Only one emission source at minimum distance
Minor roads	100 m	up to 50 vehicles/day
Main roads	500 m	up to 500 vehicles/day
Application of manure, stabling of animals	2 km	Depending on the number of animals and size of fertilised field or pasture
Grazing by domestic animals on fertilised pasture	500 m	Depending on the number of animals and size of fertilised fields or pasture

Further than the immediate locality, representativeness should also be with respect to air mass. Valleys, etc. subject to stagnant air masses should be avoided, as should mountain tops. Sites should not be unduly sheltered. With respect to precipitation monitoring requirements, there should be conformity with WMO site requirements for precipitation gauges (WMO, 1971). Finally at the macro scale, consideration should be given to the distance between sites. The broad recommendation is for 150-200 km in central Europe, and about 300 km in areas subject to influence by emission sources over 500 km distant. Spatial covariance of annual average concentrations gives rather variable ranges of covariance for different components, regions and years, but usually in the range 300-600 km. Countries themselves have always decided the extent to which they are able to participate in the programme, and Table 2.2 lists the locations of all stations which have reported acidifying/eutrophying components to EMEP. The locations of these are shown in Figure 2.1 overlain on a map of SO_2 emissions at 50 km as used in current EMEP acid modelling (Olendrzynski, pers. comm., July 2000). It is quite evident from this diagram that stations have in general been located away from the emission areas in each country. Maps given labelled locations of individual stations are presented in Appendix A.

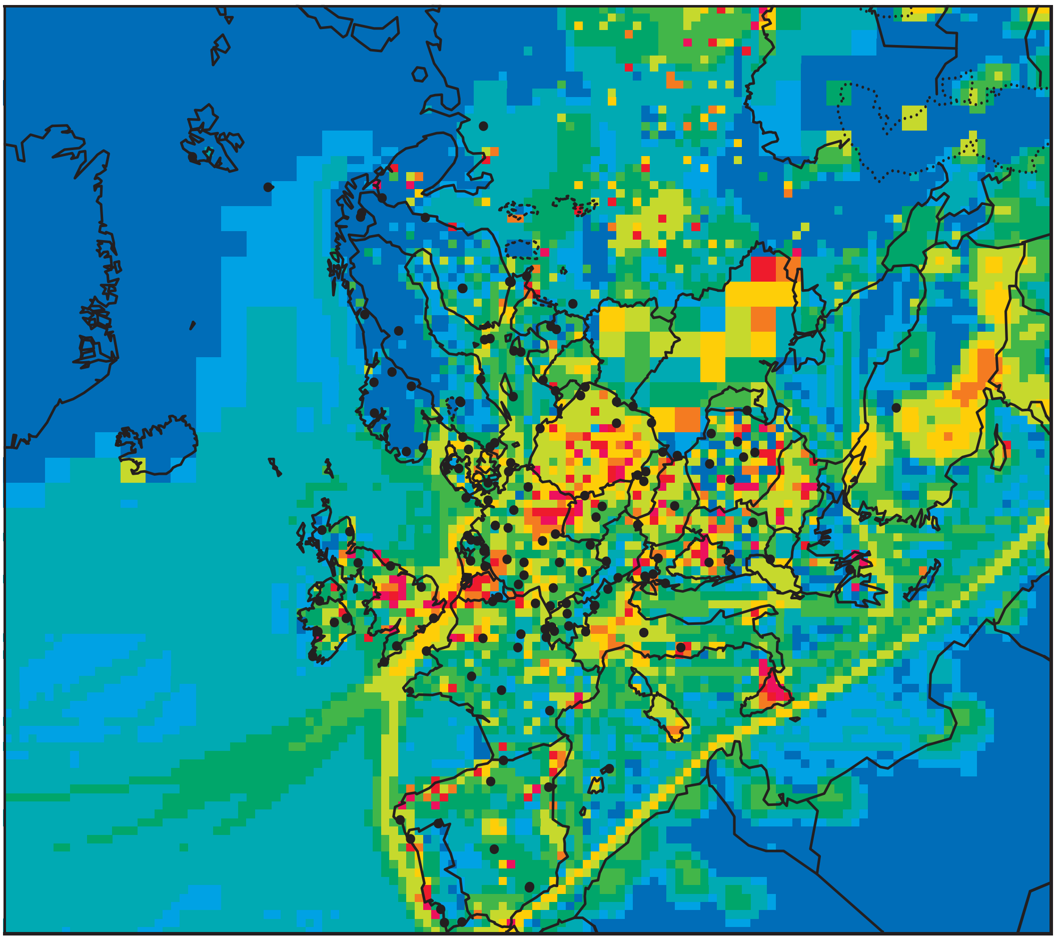


Figure 2.1: Location of all acid monitoring stations which have reported to EMEP, relative to emissions of sulphur dioxide (red = highest emission densities, dark blue = lowest).

Table 2.2: Stations which have reported acidifying/eutrophying compounds.

Country	Code, earlier code	Station name	Lat.	Long.	Alt.	precipitation S	precipitation ox-N	precipitation red-N	airborne S	airborne ox-N	airborne red-N	from	to
AUSTRIA	AT02	Illmitz	47 46 N	16 46 E	117	•	•	•	•	•		Jan-78	
	AT03	Achenkirch	47 33 N	11 43 E	960	•	•	•				Aug-83	Dec-95
	AT04	St. Koloman	47 39 N	13 12 E	851	•	•	•	•	•		Aug-83	
	AT05	Vorhegg	46 40 N	12 58 E	1020	•	•	•	•	•		Jan-96	
BELARUS	BY04, SU04	Vysokoe	52 20 N	23 26 E	163	•	•	•	•	•	•	Oct-79	Dec-91
BELGIUM	BE01	Offagne	49 53 N	5 12 E	420	•	•	•	•	•		Aug-78	Dec-91
BOSNIA	BA06, YU06	Ivan Sedlo	43 46 N	18 2 E	970	•	•	•	•	•		Jul-80	Feb-92
CROATIA	HR02, YU02	Puntijarka	45 54 N	15 58 E	988	•	•	•	•	•		Oct-77	
	HR04, YU04	Zavizan	44 49 N	14 59 E	1594	•	•	•	•	•		Sep-80	
CZECH R.	CZ01, CS01	Svratouch	49 44 N	16 2 E	737	•	•	•	•	•	•	Oct-77	
	CZ03, CS03	Kosetice	49 35 N	15 5 E	534	•	•	•	•	•	•	Jan-89	
DENMARK	DK01	Faeroerne	62 18 N	7 4 W	210	•	•	•				Feb-78	Oct-78
	DK03	Tange	56 21 N	9 36 E	13	•	•	•	•	•	•	Jan-78	
	DK05	Keldsnor	54 44 N	10 44 E	9	•	•	•	•	•	•	Jan-78	
	DK07	Faeroerne-Akbrg.	61 24 N	6 40W	90	•	•	•	•		•	Nov-78	Mar-91
	DK08	Anholt	56 43 N	11 31 E	40	•	•	•	•	•	•	Jan-90	
ESTONIA	EE02, SU02	Syrve	57 57 N	22 6 E	2	•	•	•			•	May-80	Dec-91
	EE09, SU09	Lahemaa	59 30 N	25 54 E	32	•	•	•	•	•	•	Jun-85	
	EE11, SU11	Vilsandy	58 23 N	21 49 E	6	•	•	•	•	•	•	Feb-89	
FINLAND	FI04	Ahtari	62 33 N	24 13 E	162	•	•	•	•	•	•	Oct-77	
	FI06	Kokar	59 55 N	20 55 E	10	•			•			Oct-77	Sep-79
	FI07	Virolahti	60 31 N	27 41 E	8	•	•	•	•			Oct-77	Jun-86
	FI09	Uto	59 47 N	21 23 E	7	•	•	•	•	•	•	Jan-80	
	FI17	Virolahti II	60 31 N	27 41 E	4	•	•	•	•	•	•	Jul-86	
	FI22	Oulanka	66 19 N	29 24 E	310	•	•	•	•	•	•	Jan-90	
	FI37	Ahtari II	62 35 N	24 11 E	180				•	•	•	May-97	
FRANCE	FR01	Vert-le-Petit	48 32 N	2 22 E	64	•	•	•	•			Jan-78	Jun-89
	FR03	La Crouzille	45 50 N	1 16 E	497	•	•	•	•			Jan-78	
	FR05	La Hague	49 37 N	1 50W	133	•	•	•	•			Jan-78	
	FR06	Valduc	47 35 N	4 52 E	470	•	•	•	•			Jan-78	Aug-84
	FR07	Lodeve	43 42 N	3 20 E	252	•	•	•	•			Jan-78	Feb-84
	FR08	Donon	48 30 N	7 8 E	775	•	•	•	•			Jan-90	
	FR09	Revin	49 54 N	4 38 E	390	•	•	•	•			Jan-90	
	FR10	Morvan	47 16 N	4 5 E	620	•	•	•	•			Jan-90	
	FR11	Bonnevaux	46 49 N	6 11 E	836	•	•	•	•			Jan-90	Mar-98
	FR12	Iraty	43 2 N	1 5 W	1300	•	•	•	•			Jan-90	
	FR13	Peyrusse Vieille	47 22 N	0 6 E	236	•	•	•	•			Jan-98	
	FR14	Montandon	47 11 N	6 30 E	746	•	•	•	•			Apr-98	
FYRM	MK07, YU07	Lazaropole	41 32 N	20 42 E	1332	•	•	•	•	•		Oct-77	Dec-91
GERMANY	DE01	Westerland	54 55 N	8 18 E	12	•	•	•	•	•		Oct-77	
	DE02	Langenbrugge	52 48 N	10 45 E	74	•	•	•	•	•		Oct-77	
	DE03	Schauinsland	47 55 N	7 54 E	1205	•	•	•	•	•		Oct-77	
	DE04	Deuselbach	49 46 N	7 3 E	480	•	•	•	•	•		Oct-77	
	DE05	Brotjacklriegel	48 49 N	13 13 E	1016	•	•	•	•	•		Oct-77	
	DE06, DD01	Arkona	54 41 N	13 26 E	42	•	•	•	•			Jan-81	Dec-90
	DE07, DD02	Neuglobsow	53 09 N	13 2 E	62	•	•	•	•	•		Jan-81	
	DE08	Schmucke	50 39 N	10 46 E	937	•	•	•	•	•		Jul-91	
	DE09	Zingst	54 26 N	12 44 E	1	•	•	•	•	•		Sep-92	
	DE11	Hohenwestedt	54 6 N	9 40 E	75				•			Oct-77	Jun-98
	DE12	Bassum	52 51 N	8 43 E	52				•			Oct-77	Dec-95
	DE13	Rodenberg	52 19 N	9 22 E	148				•			Oct-77	Apr-93
	DE14	Meinerzhagen	51 07 N	7 38 E	510				•			Oct-77	Aug-98
	DE15	Usingen	50 20 N	8 32 E	485				•			Oct-77	Dec-93
	DE16	Bad Kreuznach	49 50 N	7 52 E	230				•			Oct-77	Mar-90
	DE17	Ansbach	49 18 N	10 34 E	481				•			Oct-77	
	DE18	Rottenburg	48 29 N	8 56 E	427				•			Oct-77	Dec-98
	DE19	Starnberg	48 1 N	11 21 E	729				•			Oct-77	Nov-94
	DE20	Hof	50 19 N	11 53 E	568				•			Jul-80	Dec-93
GREAT	GB02	Eskdalemuir	55 19 N	3 12W	243	•	•	•	•	•	•	Dec-77	
BRITAIN	GB03	Goonhilly	50 3 N	5 11W	108	•	•	•	•	•		Aug-79	Apr-88
	GB04	Stoke Ferry	52 34 N	0 30 E	15	•	•	•	•			Sep-80	
	GB05	Ludlow	52 22 N	2 38 W	190	•	•	•	•			May-81	Dec-88
	GB06	Lough Navar	54 26 N	7 54 W	126	•	•	•	•		•	Jan-84	
	GB07	Barcombe Mills	50 52 N	0 2 W	8	•	•	•	•			Apr-85	
	GB13	Yarner Wood	50 36 N	3 43 W	119	•	•	•	•			Jan-87	
	GB14	High Muffles	54 20 N	0 48 W	267	•	•	•	•	•	•	Jan-87	
	GB15	Strath Vaich	57 44 N	4 46 W	270	•	•	•	•	•		Mar-87	
	GB16	Glen Dye	56 58 N	2 25 W	85	•	•	•	•			Feb-87	
	GB36	Harwell	51 34 N	1 19 W	137					•[a]		Jan-88	
	GB37	Ladybower	53 24 N	1 45 W	420					•[a]		Jan-88	
	GB38	Lullington Heath	50 48 N	0 11 E	120					•[a]		Jan-88	
	GB43	Narberth	51 47 N	4 42 W	160					•[a]		Jan-97	
	GB45	Wicken Fen	52 18 N	0 18 W	5					•[a]		Aug-97	
GREECE	GR01	Aliartos	38 22 N	23 5 E	110	•[b]	•[b]	•[b]	•	•		Oct-77	
HUNGARY	HU02, HU01	K-puszta	46 58 N	19 35 E	125	•	•	•	•	•	•	Oct-77	
ICELAND	IS01	Rjupnahed	64 5 N	21 51W	120	•			•			Sep-78	Dec-79
	IS02	Irafoss	64 5 N	21 1 W	61	•			•			Jan-80	
IRELAND	IE01	Valentina Obs.	51 56 N	10 15W	9	•	•	•	•	•		Feb-80	
	IE02	Turlough Hill	53 2 N	6 24W	420	•	•	•	•			Jan-91	
	IE03	The Burren	53 0 N	9 6 W	90	•	•	•	•			Jan-97	
	IE04	Ridge of Capard	53 7 N	27 7 W	340	•	•	•	•			Jan-97	

a: only NO2 b: not reported for many years

Table 2.2, cont.

Country	Code, earlier code	Station name	Lat.	Long.	Alt.	precipitation S	precipitation ox-N	precipitation red-N	airborne S	airborne ox-N	airborne red-N	from	to
ITALY	IT01	Montelibretti	42 6 N	12 38 E	48	•	•	•	•	•	•	Oct-83	
	IT02	Stelvio	46 21 N	10 23 E	1415	•	•	•	•	•	•	Sep-84	May-89
	IT03	Vallombrosa	43 44 N	11 33 E	1000	•	•	•	•		•	Jul-84	Mar-85
	IT04	Ispra	45 48 N	8 38 E	209	•	•	•	•	•	•	Nov-85	
	IT05	Arabba	46 31 N	11 53 E	2030	•	•	•	•	•		Mar-86	

LATVIA	LV10, SU10	Rucava	56 13 N	21 13 E	18	•	•	•	•	•	•	Jun-85	
	LV16	Zoseni	57 8 N	25 55 E	183	•	•	•	•	•	•	Jun-94	
LITHUAN.	LT15, LT03,SU03	Preila (Nida)	55 21 N	21 4 E	5	•	•	•	•	•	•	May-80	
MOLDOVA	MD12, SU12	Leovo	46 30 N	28 16 E	156	•	•	•	•	•	•	Nov-87	Oct-91
NETHERL.	NL02	Witteveen	52 49 N	6 40 E	18	•	•	•	•	•	•	Oct-77	Jun-93
	NL05	Rekken	52 6 N	6 43 E	25	•	•	•	•	•		Oct-77	Sep-83
	NL06	Appelscha	52 57 N	6 18 E	10	•	•	•	•	•		Oct-77	Mar-81
	NL07	Eibergen	52 5 N	6 34 E	20	•	•	•	•	•		Oct-83	Aug-87
	NL08	Bilthoven	52 7 N	5 12 E	5	•	•	•	•	•	•	Sep-87	Dec-92
	NL09	Kollumerwaard	53 20 N	6 17 E	0	•	•	•	•	•	•	Jan-93	
	NL10	Vreedepeel	51 32 N	5 51 E	28				•	•	•	Jan-93	
NORWAY	NO01	Birkenes	58 23 N	8 15 E	190	•	•	•	•	•	•	Oct-77	
	NO08	Skreadalen	58 49 N	6 43 E	475	•	•	•	•	•	•	Oct-77	
	NO15	Tustervatn	65 50 N	13 55 E	439	•	•	•	•	•	•	Oct-77	
	NO30	Jergul	69 24 N	24 36 E	255	•	•	•	•	•	•	Oct-77	Mar-97
	NO35	Narbuvoll	62 21 N	11 28 E	768	•	•	•				Oct-77	Dec-87
	NO36	Hummelfjell	62 27 N	11 16 E	1539				•			Oct-77	Dec-87
	NO37	Bjornoya	74 31 N	19 1 E	20	•	•	•	•			Oct-77	Jul-89
	NO39	Karvatn	62 47 N	8 53 E	210	•	•	•	•	•	•	Feb-78	
	NO41	Osen	61 15 N	11 47 E	440	•	•	•	•	•	•	Sep-87	
	NO42	Spitzbergen	78 54 N	11 53 E	474				•	•	•	Jan-90	
	NO55	Karasjok	69 28 N	25 13 E	333	•	•	•	•	•	•	Apr-97	
POLAND	PL01	Suwalki	54 8 N	22 57 E	184	•	•	•	•	•	•	May-78	Dec-93
	PL02	Jarczew	51 19 N	21 59 E	180	•	•	•	•	•	•	Jan-85	
	PL03	Sniezka	50 44 N	15 44 E	1604	•	•	•	•	•	•	Jan-91	
	PL04	Leba	54 45 N	17 32 E	2	•	•	•	•	•	•	Jan-93	
	PL05	Diabla Gora	54 9 N	22 4 E	157	•	•	•	•	•	•	Jul-92	
PORTUGAL	PT01	Braganca	41 49 N	6 46 W	691	•	•	•	•	•	•	Aug-79	
	PT02	Faro	37 1 N	7 58 W	8	•	•	•	•			Aug-79	Dec-86
	PT03	V. d. Castelo	41 42 N	8 48 W	16	•	•	•	•			Jun-87	
	PT04	Monte Velho	38 5 N	8 48 W	43	•	•	•	•	•	•	Jan-88	
	PT05	Foia	37 19 N	8 54 W	902				•			Jul-90	Jun-93
ROMANIA	RO01	Rarau	47 27 N	25 27 E	1536	•	•	•	•			Jan-80	Dec-87
	RO02	Stina de Vale	46 41 N	23 32 E	1111	•	•	•	•			Jan-80	Dec-87
	RO03	Semenic	45 7 N	25 58 E	1432	•	•	•	•			Feb-80	Dec-87
	RO04	Paring	45 23 N	23 28 E	1585	•	•	•	•			Mar-80	Dec-87
	RO05	Fundata	45 28 N	25 18 E	1371	•	•	•	•			Jan-80	Dec-87
	RO06	Turia	46 7 N	25 59 E	1008	•	•	•	•			Jan-80	Dec-87
RUSSIAN F	RU01, SU01	Janiskoski	68 56 N	28 51 E	118	•	•	•	•	•	•	Nov-79	
	RU08, SU08	Lesogorsky	61 0 N	28 58 E	39			•			•	Oct-79	Dec-88
	RU13, SU13	Pinega	64 42 N	43 24 E	28	•	•	•	•	•	•	Oct-89	
	RU14, SU14	Pushkinskie G.	57 0 N	28 54 E	103	•	•	•	•	•	•	May-90	Nov-95
	RU16	Shepeljovo	59 58 N	29 7 E	4	•	•	•	•	•	•	Nov-94	
SLOVAKIA	SK02, CS02	Chopok	48 56 N	19 35 E	2008	•	•	•	•	•		Jan-78	
	SK04	Stara Lesna	49 9 N	20 17 E	808	•	•	•	•	•		Jan-92	
	SK05	Liesek	49 22 N	19 41 E	892	•	•	•	•	•		Jan-92	
	SK06	Starina	49 3 N	22 16 E	345	•	•	•	•	•		Mar-94	
SLOVENIA	SI01, YU01	Masun	45 39 N	14 22 E	1026	•	•	•	•			Nov-80	Dec-91
	SI08	Iskrba	45 34 N	14 52 E	520				•	•		May-96	
SPAIN	ES01	Toledo	39 33 N	4 21 W	917	•	•	•	•	•	•	Nov-84	
	ES02	La Cartuja	37 12 N	3 36 W	720	•	•	•	•		•	Jan-87	Nov-95
	ES03	Roquetas	40 49 N	0 30 W	50	•	•	•	•	•	•	Jun-87	
	ES04	Logrono	42 27 N	2 2 W	370	•	•	•	•	•	•	Jan-88	
	ES05	Noia	42 44 N	8 55 W	685	•	•	•	•	•	•	Jan-93	
	ES06	Mahon	39 54 N	4 15 E	-	•	•	•	•	•	•	Jan-95	
	ES07	Viznar	37 14 N	3 32W	1265	•	•	•	•	•	•	Nov-95	
SWEDEN	SE01	Ekerod	55 54 N	13 43 E	140	•	•	•	•	•		Jul-79	Sep-84
	SE02	Rorvik	57 25 N	11 56 E	10	•	•	•	•	•	•	Nov-77	
	SE03	Velen	58 47 N	14 18 E	127		•	•	•	•	•	Aug-79	Jul-90
	SE05	Bredkalen	63 51 N	15 20 E	404	•	•	•	•	•	•	Aug-79	
	SE08	Hoburg	56 55 N	18 9 E	58	•	•	•	•	•	•	Sep-78	
	SE11	Vavihill	56 1 N	13 9 E	172	•	•	•	•	•	•	Sep-84	
	SE12	Aspvreten	58 48 N	17 23 E	20	•	•	•	•	•	•	May-84	
	SE13	Esrange	67 53 N	21 4 E	475	•	•	•	•	•	•	Oct-90	
SWITZERL	CH01	Jungfraujoch	46 33 N	7 59 E	3573	•	•	•	•	•		Sep-80	
	CH02	Payerne	46 48 N	6 57 E	510	•	•	•	•	•	•	Apr-79	
	CH03	Taenikon	47 29 N	8 54 E	540	•	•	•	•	•		Jan-88	
	CH04	Chaumont	47 3 N	6 58 E	1130	•	•	•	•	•		Jan-92	
	CH05	Rigi	47 4 N	8 27 E	1028	•	•	•	•	•		Jan-92	
TURKEY	TR01	Cubuk II	40 30 N	33 0 E	1169	•	•	•	•	•	•	Mar-93	
UKRAINE	UA05, SU05	Svityaz	51 31 N	23 53 E	164	•	•	•	•	•	•	Nov-79	Oct-91
	UA06, SU06	Rava-Russkaya	50 15 N	23 38 E	249	•	•	•	•	•	•	Nov-79	Oct-91
	UA07, SU07	Beregovo	48 15 N	22 41 E	112			•				Nov-79	Oct-89
YUGOSL.	YU05	Kamenicki vis	43 24 N	21 57 E	813	•	•	•	•	•		Jan-84	
	YU08	Zabljak	43 9 N	19 8 E	1450	•	•	•	•	•		Mar-93	

Whilst a large number of stations have participated in the EMEP programme, the table shows that stations have operated for dissimilar periods. This is one aspect of the difficulties and dangers inherent in multinational networks, and is another reason for determined promotion of comparable documented methodologies which have proven operational reliability. Two important reasons for fluctuations in monitoring activity over the past two decades have been: 1) development of agreements concerning air pollution; 2) major political changes. In Figure 2.2 the snapshot number of station monitoring given components at points in time are displayed, along with the total numbers of stations to have monitored those components by that time, and the snapshot number of countries actively monitoring. The two influences can be clearly seen.

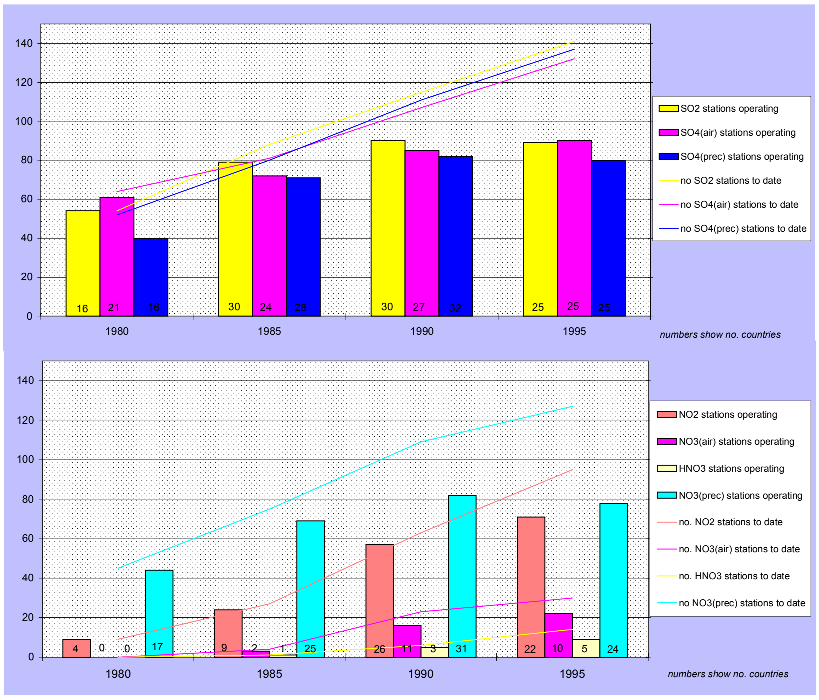


Figure 2.2: Numbers of stations monitoring and reporting given components in 1980, -85, -90 and -95, plus total numbers of stations to have monitored those components by the said date. Also lists nos. of monitoring countries.

Firstly, there is a notable difference between sulphur monitoring effort and that for oxidised nitrogen. The number of sulphur stations rapidly achieved high numbers as early focus was on this substance. Overall effort has been reasonably consistent, although some turnover in stations opens the danger of inconsistencies in time. For nitrogen, precipitation monitoring has slowly crept up towards sulphur levels, but airborne monitoring has been quite limited. Some components were not monitored at all for a period, and adoption of monitoring for the most commonly observed airborne compound, nitrogen dioxide, really only occurred with the imminence of the first nitrogen protocol. Negotiated agreements appear to influence effort here. The other influence is political change and emergence of newly independent states. A jump in countries participating in the early 1990s has fallen back slightly as some of these rapidly ceased monitoring. These features stress the point that coordinated monitoring has been fundamental in maintaining reliable and consistent surveillance. In subsequent sections illustrations are given of changes in station location having limited consequence on observed trends. This is a matter which requires care and a case-by-case approach to assess, but that reliable temporal information can be observed from a monitoring network forever in transition is an indication of the effectiveness of quality management over the years.

2.3 Measurement, analysis, and quality assurance

Initial concern with acidification focused on sulphur compounds. Reflecting the stated "desirability of Contracting Parties joining in and fully implementing EMEP which, as a first step, is based on the monitoring of sulphur dioxide and related substances" (CLRTAP art. 9(a)), a "minimum activity" was established which comprised 24-hourly measurements of sulphur dioxide, of sulphate aerosol, of sulphate in precipitation, and of acidity in precipitation (pH). Hence, the programme has employed daily observations from the beginning, these being reported without aggregation to coarser resolution. Since this time the role of nitrogen compounds in acidification has been recognised, and eutrophication (specifically anthropogenic reinforcement of adequate nitrogen supply, or reduction in limitation of that supply) via atmospheric transport pathways has joined the agenda. Although always listed as part of an "extended activity", nitrogen and base cations in precipitation joined the mainstream of the programme from 1987. The recommendations for the acidification/eutrophication elements to the monitoring programme as it now stands are given in Table 2.3.

Quite correctly, methodologies have improved during the period. These have been recommended as appropriate once both their benefits and their comparability with earlier methods were understood. For example, the replacement of absorbing sampling solutions for monitoring of SO_2 and NO_2 with impregnated filter packs, a shift from bulk precipitation samplers to wet-only samplers with defined sensitivity for opening of the lid, adoption of Ion Chromatography for analysis of sulphate rather than X-Ray Fluorescence or the Thorin method, and so on. Careful cooperation and coordination between countries has always been sought in these matters, e.g. through a series of workshops and expert meetings on data quality and chemical matters. Hence, for both field sampling and analytical techniques methodological recommendations have always been given in consultation with the countries themselves. CLRTAP itself recognised "the need to use comparable or standardised procedures for monitoring wherever possible" (art. 9(b)). Inevitably, however, it has not always been possible for countries to replace familiar methods with a single common approach as recommended. The detailed record of which stations undertook which measurements for which periods may be found in Appendix B along with all other station/country specific technical information. To manage these problems alternative methods are suggested in the programme, such as indophenol blue spectrophotometry for ammonium ion determination.

Table 2.3: Monitoring and Analytical Techniques recommended for the EMEP acidification/eutrophication programme, plus data quality objectives (DQO's).

	Measurement period/ frequency	***Field technique***	***Analytical technique***	***Analytical accuracy***
Gases				
SO_2	24 hours/daily	3-filter pack	IC	$^{(1)}$
NO_2		impreg. glass frit	Griess	0.01 mg N $l^{-1(2)}$
HNO_3		denuder	IC / Griess	
NH_3		denuder	IC / Indophenol	
Particles				
$SO_4^=$	24 hours/daily	3-filter pack	IC	$^{(1)}$
NO_3^-		denuder	IC / Griess	
NH_4^+		denuder	IC / Indophenol	
Gas + Particles				
HNO_3+NO_3^-	24 hours/daily	3-filter pack	IC / Griess	$^{(1)}$
NH_3+NH_4^+		3-filter pack	IC / Indophenol	
Precipitation				
amount	24 hours/daily	rain gauge	by weight	
$SO_4^=$	24 hours/daily	wet only sampler	IC	1µmol S l^{-1}
NO_3^-			IC / Griess	1µmol N l^{-1}
NH_4^+			IC / Indophenol	2µmol N l^{-1}
pH/H^+,	24 hours/daily	wet only sampler	potentiometry	0.1 units
Cl^-,			IC / Thiocyanate	0.3µmol Cl l^{-1}
Na^+, K^+,			AAS / IC	0.3µmol Na/K l^{-1}
Mg^{++}, Ca^{++}			IC / AES	0.3µmol Mg/Ca l^{-1}
conductivity			conductivity cell	

IC: Ion chromotography. AAS: Atomic Absorption Spectrophotometry. AES Atomic Emission Spectrophotometry
$^{(1)}$ DQO for wet analysis of samples extracted from air filters as for precipitation $^{(2)}$ For NO_2 as NO_2^- in solution

Remaining DQO's:
-) 10% accuracy or better for ox-S and N in single analysis.
-) 15% accuracy or better for remaining components.
-) 15-25% uncertainty for combined sampling and analysis.
-) 90% data completeness of daily valves.

The approach has been to focus on Quality Assurance, with harmonisation recognising the limits to national capabilities. Stemming from the experience of the EACN a number of QA activities have been in place from the start for every stage in measurement, analysis and reporting, and when faced with variability in techniques it has been considered fundamental to effective management to establish the quantitative comparability between methods. Comparative standards of analysis between collaborating laboratories is a part of this. Between 1980 and 1998 a total of sixteen laboratory intercomparisons were undertaken with results openly distributed since 1986. In this report we present for the first time attributed performance for earlier year (Appendix A). Such intercomparisons both establish the relative quality of performance, and improve the analytical skills of laboratories. The latest of these, in 1997, involved 37 laboratories from 32 countries. Samples were distributed to collaborating laboratories, analysed, and results returned to CCC for evaluation. In Figure 2.3 an example of the quality of analysis and of the improvements which have been seen is given. By 1997 virtually all laboratories were within 5% in determination of SO_2 and SO_4 in air, and SO_4, NO_3, and NH_4 in precipitation. This represents a steady improvement with time. Analysis within 10% accuracy has always been achieved by the majority, with over 90% of laboratories achieving this standard on occasions.

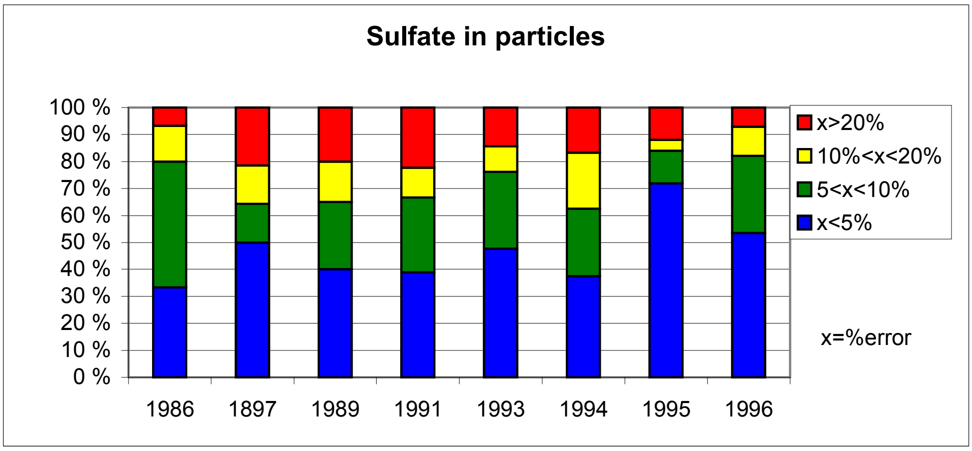


Figure 2.3: Quality evaluation of laboratory analysis in successive laboratory intercomparisons. Percentage of laboratories.

Steady improvements with time have allowed high standards of analysis to be defined as part of the programme. Table 2.3 which gave recommended methods, also listed the targets for analytical accuracy asked. These are standards for the lowest concentrations monitored, and accord with the WMO GAW recommendations for regional stations.

Such exercises have provided an encouragement to achieve and maintain defined standards. This has been supplemented by an Expert Consultation programme from 1988 in which experts from the CCC visited each of the collaborating laboratories in order to become familiar with operation of sites and laboratories, to give guidance, and to provide information on the quality of the measurement programme. The general impression was that sites are generally well chosen, in some countries significant improvements were made on account of the programme, but that in a few cases limited resources restricted availability of instrumentation and qualified personnel. In Table 2.4 a summary table of impressions gained of laboratories visited is given. This table represents the impressions gained at the time of visit. Subsequently there were improvements at several laboratories, as reported in Schaug *et al.* (1996), and since this time some laboratories have ceased to operate. However, the impressions of the laboratories given at time of visit better indicates laboratory quality during the time period which is the subject of this report. Whilst such impressions give an expectation as to the quality of data from each country, they are nevertheless to a degree subjective. There are in place recognised accreditation mechanisms for ascertaining the quality of work undertaken by laboratories, such as EN-45001

Table 2.4: Impressions gained of laboratories visited during the Expert Consultation programme, 1988-94.

Country	Laboratory	Status	Equipment	Personnel
Austria	Umweltbundesamt, Vienna	Good	Good	Good
Belgium	Institute of Hygiene, Brussels	Good	Good	Good
Bulgaria	Scientific Information Centre		Not adequate	
Czech Republic	Hydrometeorological Institute, Prague	Good	Adequate	Good
Denmark	National Environmental Research Institute, Roskilde	Good	Good	Good
Estonia	Estonian Environmental Laboratory, Tallin	Not satisfactory	Adequate	Adequate
Finland	Air Quality Department, FMI	Good	Good	Good
France	Laboratoires Wolff, Clichy	Good	Good	Adequate
Germany	Umweltbundesamt, Messtelle Schauinsland	Good	Good	Good
Greece	Ministry of Environment, Physical Planning and Public Works, Environ. Division.	Not satisfactory	Not adequate	Good
Hungary	Institute of Atmospheric Physics, Budapest	Not satisfactory	Not adequate	Not adequate
Ireland	Meteorological Service, Dublin	Good	Adequate	Good
Italy	Istituto sull'Inquinamente Atmospherico, Rome	Good	Good	Good
Latvia	Hydrometeorological Institute, Air and Water Control Laboratory, Leipaja	Not satisfactory	Not adequate	Good
Netherlands	Institute of Public Health and Environment, Bilthoven	Good	Good	Good
Norway	Norwegian Institute for Air Research	Good	Good	Good
Poland	Institute for Meteorology and Water Management, Warsaw	Good	Poor	Good
Portugal	Lab. for Air and Water Pollution Control, Sines	Not Satisfactory	Not adequate	Not adequate
Romania	Hydrometeorological Institute, Bucharest	Not satisfactory	Not adequate	Adequate
Russian Fed.	Institute of Global Climate and Ecology, Moscow	Good	Good	Good
Slovak Republic	Hydrometeorological Institute, Bratislava	Good	Adequate	Good
Slovenia	Hydrometeorological Institute		Adequate	Adequate
Spain	Institute Carlos III	Good	Good	Good
Switzerland	EMPA, Zurich	Good	Good	Good
Turkey	Refik Saydam Hygiene Centre	Good	Good	Adequate
United Kingdom	Warren Spring Laboratory, Stevenage	Good	Good	Good
Yugoslavia	Federal Hydromet. Institute	Not satisfactory	Not adequate	Good

"General Criteria for the Operation of Testing Laboratories", ISO/IEC Guide 25 "General Requirements for the technical competence of testing laboratories", and ISO 9000 concerning certification of quality systems. A new standard for testing and calibration laboratories, EN ISO/IEC 17025, will replace earlier ones. Many of the national laboratories conducting analysis within the EMEP programme achieved the earlier standards.

Field intercomparisons have been an equally important part of achieving and maintaining quality measurements. Field comparisons have been organised both as large-scale exercises with parallel measurements using different equipment from different organisations at one location over 4-6 weeks, e.g. as held in Sweden and Germany, and as comparisons between individual national methods and the EMEP reference methods at sites in various respective countries during the year. Such comparisons of air quality measurements of SO_2, SO_4 NO_3, HNO_3 and NO_2 have been undertaken, and comparisons completed in Ireland, United Kingdom, Portugal, Poland, France, Germany, and the Czech Republic. These exercises have provided clear recommendations, such as confirmation that filter pack measurement is most clearly the method which can provide reliable results at such low levels as 0.1-0.2 $\mu g\ SO_2\text{-}S\ m^{-3}$ as encountered at EMEP background stations.

Such measures as outlined above all refer to Quality Assurance procedures to be applied at the points of data origin. Part of this includes that submitting laboratories should conduct quality checks upon their final data prior to submission to the CCC. To aid this, software is supplied to participating institutes to support calculation of ion balance, conductivity and sea salt ratios, to compare data with statistical calculations on historical data, and to support adding or removing warning flags to the data (Hjellbrekke, 1997). An extensive list of data flags is utilised, and this is constantly being revised and updated.

The quality of data is also validated and flagged by the CCC before entry to the database. Uniformity in data submission aids quality control, and the EMEP programme now uses the NASA/Ames 1001 format for data submission which allows rapid and consistent checks to be conducted upon data quality. During the recent past all historical data submitted has been transferred to NASA/Ames format at the CCC, and has been subject to the same range of quality control checks as is new data. One of the arguments for having a complete precipitation programme was to enable comparisons between measured and calculated conductivities, and to make use of ion balances in precipitation data validation. These are strong tools for data checking and have given a large improvement from the first years. For gas and aerosol data validation is based on statistics and graphic display, as has always been the case. Any validation procedure cannot guarantee to exclude data with serious errors from the database, but that currently used should go a considerable way towards this.

For comparative purposes it is worth noting that the Steering Body of EMEP has recently requested that both monitoring and modelled data should search to achieve 30% accuracy. Comparisons suggest that many laboratories are less than 5% away from theoretical values in tests, and that most achieve better than the 10 and 15% Data Quality Objectives listed in Table 2.3. Constant assessment is undertaken so as to note e.g. from field intercomparisons, where measurement data does not always comply with the DQO (Aas *et al.*, 2000). However, monitoring data provided to EMEP is essentially within these requirements, and is an indication that the QA system is effective. Finally, to aid use, annual average data is now further classified by 4 categories on the basis of quality control checks, field intercomparisons and laboratory intercomparisons, such that class:

A	has expected error of 10% or better
B	has expected error of 25% or better
C	has expected error of 30% or better
D	has expected error of worse than 30% / unknown / not documented

Whilst this is a new procedure which is not applied retrospectively to the historical data which is the subject of this report on observed trends, the classifications can suggest the quality of past performance, at least in recent years. The majority of stations are submitting data in classes A and B. A list of classifications for 1997 and 1998 data is given in CCC data quality reports (Aas *et al*., 1999; Aas *et al*., 2000).

3. Regional trend review

The network described in chapter two provides a consistent observation-based foundation for analysis of the trends in acidifying air pollution in Europe between 1980 and the present day, thus permitting a description of changes in the state of the atmospheric environment during this period. As a starting point summary of emission changes underlying air quality is given simply for convenient reference. This is followed by a brief overview of the literature on atmospheric trend analysis is given in order to illustrate some particular points relevant to interpreting observed trends in the European environment. Finally the methodology adopted in this report is given.

3.1 Overview of emission changes in Europe

This following section is intended only as a convenient summary, intended to provide relevant background information to the ensuing analysis of trends in observed air quality. For a thorough statement of emissions of acidifying compounds in Europe as held on the UN ECE database, EMEP Note 1/00 should be referred to (Vestreng and Støren, 2000). The information presented here has been taken solely from the UN ECE database and named reference. Data for emissions of sulphur is presented graphically divided according to the regions within Europe chosen for trend analysis as described in the following sections. For nitrogen, releases from selected countries and groups of countries are given as examples. A critical point is that emissions within a region may not represent the critical influences upon air quality in that region. Current estimates for the influences of countries upon each other may be found in EMEP Report 1/2000 (Tarrason and Schaug (eds.), 2000). By presenting emission data together at this point, rather than divided between regional sections in the following trend analysis, it is hoped that cross-referencing is assisted and that the potentially misleading association between regional air quality and its own emissions can be minimised. Emission trends for the whole of Europe have been presented in Figure 1.1. The following commentary provides a summary of the data in Figure 3.1.

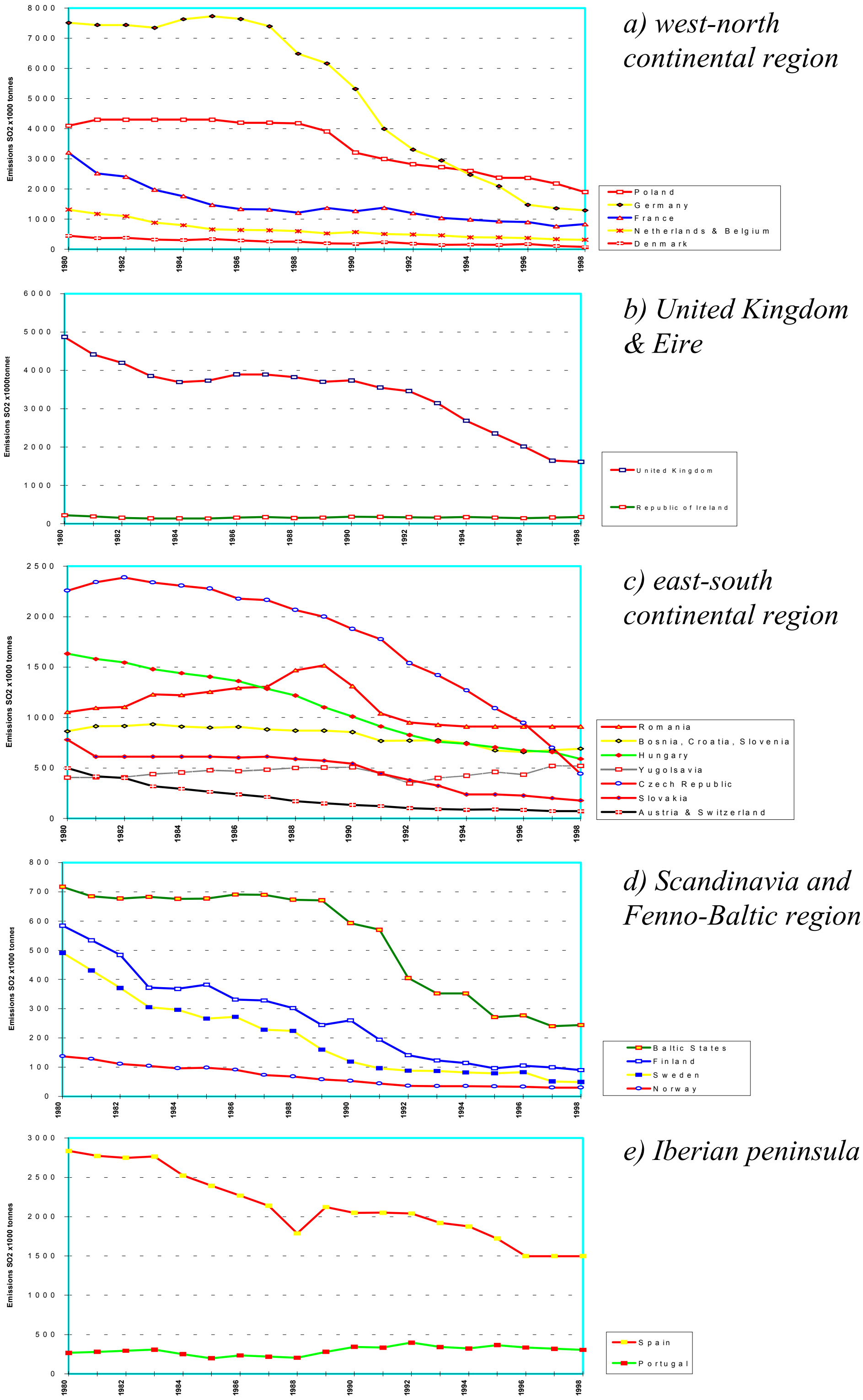
Striking in the west-north continental region is the rapid and consistent decline in emissions of sulphur dioxide from Germany since 1988. Despite having remained consistent before this date the decline was by approximately 60% of 1980 emission totals by conclusion of the first Sulphur Protocol. A similar progression is seen in Polish emissions to the east, although reductions were less stark. On the north and north-west margins of the continent the pattern seen in BeNeLux and Danish emissions is of steady decline throughout. Quite a different pattern was reported for France to the west. By the time Germany was reporting noticeable reductions France had already seen emission falls of approaching 60%. From 1988 emissions largely levelled off. To the north-west, combined sulphur emissions from the United Kingdom and Republic of Ireland in 1980 were approximately equal to the combined totals for neighbouring countries. After some decline, British and Irish emissions stabilised from the mid-1980s until the early 1990’s. Fresh decline in the 1990s meant that by expiry of the Helsinki Protocol at the end of 1993 the UK and Ireland had reduced emissions by approaching 30% although neither were signatories (35% and 27% respectively). By comparison eighbouring

France, Belgium and the Netherlands, all signatories, had each reduced by two thirds (67%, 64% and 66% respectively), and Europe as a whole reduced by 45%.

Developments in the east-south continental region can be divided into three groups. First there are those countries with steady declines in emission totals, namely the Czech Republic, Hungary, Austria and Slovakia. The second group are those with largely constant emissions throughout, namely the Balkan states of Croatia, Bosnia and Hercegovina, Slovenia and the Federal Republic of Yugoslavia. The final category has a single member, Romania, in which emissions underwent a dramatic step down between 1990 and 1992, followed by stability. The share of the first group to the regional total fell from over 2/3 in 1980 to approximately 1/3 in 1998. Accompanying this, the other two groups have become regionally more important although the overall picture is of steady decline by around 35% of 1980 levels by 1994 (continuing to around 50% by 1998). Changes in neighbouring countries can be important, for example Germany. Whereas in 1980 German emissions of sulphur dioxide exceeded those of the east-south continental region, by 1993 total region releases were 50% greater than in Germany, and by 1998 were over twice as great.

In northern Europe there is an evident difference between the steady decline in emissions from Scandinavia, and a clear step down in Baltic State emissions after 1989. Nevertheless, between 1980 and 1993 all countries reported emission reductions of 75%+. However, being relatively small in absolute terms and being located either in the westerly cyclone tract and/or subject to anticyclonic influence from the south, the emission patterns which are possibly most relevant may be those from the United Kingdom, and in the two continental regions. In the opposite direction, in Iberia Spanish emissions are dominant, these having seen a reported decrease of around 1/3 during the period of the first sulphur protocol. Thereafter there has been a continued steady decline at a rate approximating that beforehand. Portuguese emissions, on the other hand, are reported to have increased gently during the second half of the 1980s, and have declined marginally ever since. Overall, the picture may be summarised as one of gentle and continued decline, with stability to the west.

Nitrogen emissions have followed quite varied progressions across Europe. Whilst as a whole the continent has seen reported oxidised nitrogen emissions fall by a little over 15% between 1980 and 1998 (see Figure 1.1), the picture is far from homogenous. Marked declines have occurred in some countries, such as Germany (>45%), and the Czech Republic (>55%). Countries reporting increases include Spain (>20%), Greece (>20%), Ireland (>60%), and Portugal (>120%). Many countries have held emissions fairly constant, such as France, and Hungary. Developments in reduced nitrogen release also broadly follow geographical areas. The largest changes have occurred across the centre of the continent, from Germany through the central European countries, all of which have reported large reductions. Although not shown, the Balkan states have also seen large falls in ammonia release. Countries not undergoing large changes are those to the west and north-west. The UK and France are virtually unchanged in comparison to 1980, as is Sweden and Finland. Countries reporting rising emissions are on the western periphery, Ireland, Norway and Spain. Examination of nitrogen emission changes is also found in EMEP MSC-W Note 1/00 (Vestreng and Støren, 2000).



a) west-north continental region

b) United Kingdom & Eire

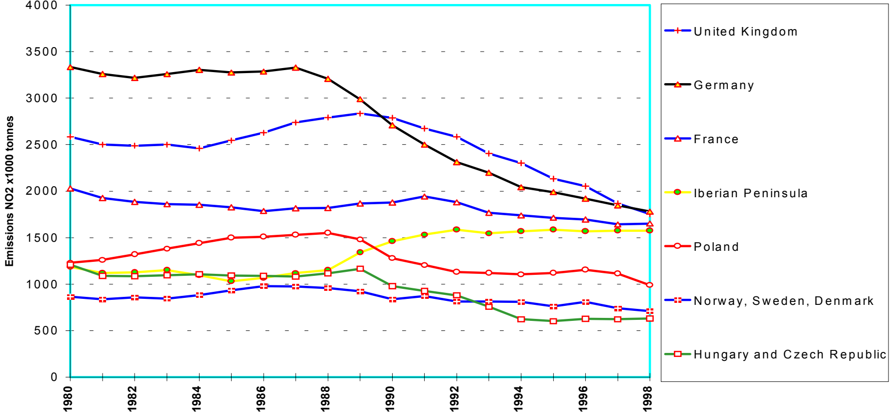
c) east-south continental region

d) Scandinavia and Fenno-Baltic region

e) Iberian peninsula

Figure 3.1: Reported emissions of sulphur dioxide in regions of Europe. Totals from UN ECE emission database (Vestreng and Støren, 2000).

a) nitrogen oxides



b) reduced nitrogen

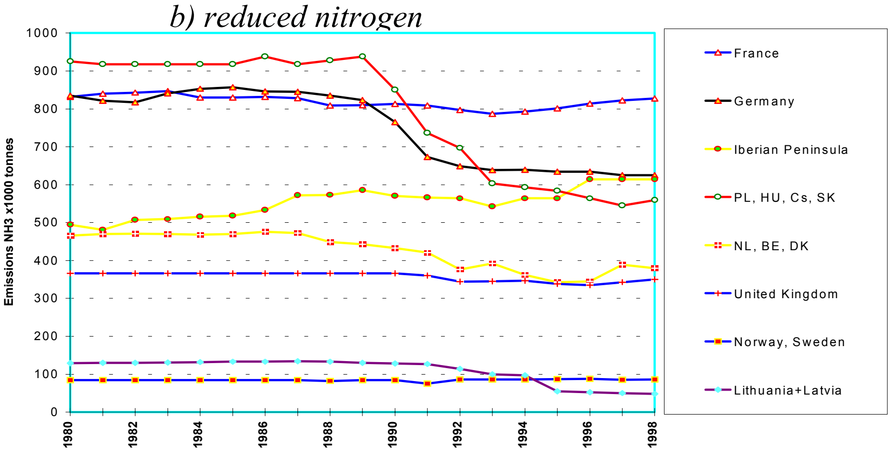


Figure 3.2: Reported emissions of nitrogen in selected European countries. Totals from UN ECE emission database (Vestreng and Støren, 2000).

3.2 Overview of air quality trend analysis to date

Of particular interest in this report is the regional patterns which may be extracted from site monitoring data. This form of examination was undertaken by Shannon (1999) for 16 years of Canadian and US data from 1980, and for 13 years of NADP data by Lynch *et al.* (1995) both using regression analysis. Both studies recognised considerable inter- and intra- regional variability, even in small regions with multiple sites. Obtaining statistically significant estimates of trends at the individual station level does not automatically lead to equivalent significance at the regional scale, although regional averaging can remove small scale variability in data. This may be expected to have special relevance in a geographically diverse region such as Europe, making the description of regional trends an inexact science.

There has been proper interest in the correspondence between emission changes resulting from policy, and the observed quality of the atmosphere. Such studies include Holland *et al.* (1999) and Lynch *et al.* (2000). The former found good comparison between reported emission changes (-35%) and changing sulphur dioxide concentrations calculated from regression techniques (-32%), whilst the latter working with a three year data set found that overall changes in air quality were of the order expected, but that at such obviously short time scales deviations in meteorology can be particularly important, notably in mountainous areas subject to considerable fluctuations in precipitation. Holland *et al.* (1999) also examined both trends at individual sites and those for aggregated regions, finding it more problematic to assign regional descriptors to complex terrain. Butler and Likens (1991) listed similar difficulties to both of these studies in their comparison between observed conditions and reported emission changes, including meteorological variability influencing short records, and difficulty in defining regions.

The question of time period and of the size of network appropriate for revealing changes in air quality was taken up by Blanchard *et al.* (1996) and by Sirois *et al.* (1996). Keeping mind of the fact that such studies are to a degree site-specific, in areas subject to higher levels of deposition (>20kg S ha^{-1} yr^{-1}) the power to detect trends could be expected to reach 90% within around two years, whilst monitoring in regions with below this level of deposition may take twice as long to identify such a likelihood. The time taken to quantify that trend, however, would likely take an additional 6-7 years even in the higher deposition zone. In a similar way the studies also revealed that whilst identification of a trend may be possible with a limited monitoring network, defining isopleths for given deposition criteria then becomes quite uncertain. This can have relevance e.g. to critical load exceedance, and to the period of consistent widespread monitoring necessary to step from recognising change to estimating its scale.

Of particular interest to this study are reported trends from observations made across Europe. Klemm and Lange (1999) examined 13 years of data from city and from forest monitoring sites in **Bavaria**. They found good comparison between the reported emission changes for 1985-94 of -61% in SO_2, and changes in observed forest SO_2 95-percentile concentrations also of -61%. They noted a strong decline in city-forest differences, and a particularly large decline overall between 1987 and 1988 which they attribute to enforcement of air pollution control strategies in western Germany. The reduction in emissions caused by breakdown of the East German economy in 1990-91 is not reflected in the Bavarian dataset. Similarly, the reported decline in nitrogen emissions of 29% were not reflected in the dataset.

Also in **Germany** during approximately the same period, 1982-92, Fricke and Beilke (1993) report a decline in precipitation sulphate of around 50%. This is in agreement with observations in the former **East Germany.** Precipitation sampling for the period 1983-1994 examined by Marquardt and Brüggemann (1995) revealed over 50% decreases in sulphate concentrations. Further to this, on account of short-period monitoring (4-hour samples) back-trajectory analysis distinguished comparative declines in precipitation concentration according to whether air masses had traversed eastern or western Germany. The impact of economic change from 1991 was not marked. What is marked, however, was a sharp rise in acidity of precipitation in air masses arriving from eastern Germany, notably in 1993-94. They comment on falling calcium precipitation content likely with closure of old plants and improved particulate removal in emissions from remaining industry, but also on the closure of KCl mining and the end of firing of salt-coal which corresponds to the sharp fall in chloride concentrations in precipitation from eastern German air masses.

In the Tyrol area of **western Austria** regression analysis by Puxbaum *et al.* (1998) upon data from five sites in the national network showed a 36% decline in wet sulphur deposition. They suggested from consideration of precipitation chemistry that this may reflect changes in SO_2 emissions both within and beyond Austria. The data set also revealed that decline in H^+ concentrations could not be fully explained by this, but did correspond well with an increase in NH_4 wet deposition of 17%.

Analysis of monitoring at Arnhem in the **Netherlands** (Ruijgrok and Römer, 1993) indicated approximately a 20% decline in sulphate wet deposition between 1984 and 1991, with a large part of this decrease occurring in the first three years. Whilst this was in line with Dutch sulphur emission changes, actually only 30% of monitored sulphur was believed due to national emissions. Back trajectory analysis suggested emission sources in neighbouring countries were important. Significant trends were not observed for nitrogen species.

Observations of both airborne and precipitation components in **Denmark** examined by Hovmand and Andersen (1995) for the years 1985-94 indicated rather surprisingly no significant trend in airborne SO_4 concentrations. A decline was observed in SO_2 concentrations, but this was less than the 50% reduction they report for Danish sulphur emissions. Precipitation concentrations of sulphate do decrease, as do observed throughfall concentrations. The magnitude of these declines is not expressly given, but appears from data displayed to be below 50% in both cases. For nitrogen compounds they report no significant trend in either airborne or precipitation concentrations.

A comparison of dry and wet deposition of sulphur in the **United Kingdom** between 1978 and 1993 has been provided by Downing *et al.* (1995). They also constructed mapped wet deposition for 1978-80 to compare with equivalent maps for 1989-93 for the whole of mainland Britain. Wet deposition of sulphur for the UK as a whole declined by 43% whilst UK emissions fell by 32%. During the same period decline in SO_2 concentrations and dry deposition in remote areas reached as much as 70%. This indicates that UK emissions alone could not account for the changes in British air quality. This picture is comparable with a study of urban air quality in the UK by Egglestone *et al.* (1992) indicating over 70% decreases in some urban SO_2 levels between the early 1960's and early 1990's. One consequence is then that external sources of sulphur dioxide constitute a rising proportion of rural ambient concentrations compared to urban sources.

For **Sweden**, Kindbom *et al.* (1994) evaluated the five stations reporting to EMEP using linear regression analysis. In general the trends of SO_2 and airborne SO_4 displayed a similar decline in the region of 40–50%. Interestingly, concentrations of sulphate in precipitation were downwards at 4 of 5 stations, but only statistically significant at two of them (-25–30%). Still further, no stations showed statistically significant trends in sulphur wet deposition. In a similar way, airborne nitrate concentrations underwent a significant decline of 25–40% at stations with sufficient records, whilst concentrations in precipitation and wet deposition had no significant trend. The decline in airborne concentrations compares with analysis of Swedish urban NO_2 concentrations by Sjödin *et al.* (1996) who described an average decline of around 40% for 1986–1994.

An extensive analysis of monitoring data from **Finland** has been presented by Kulmala *et al.* (1998). The individual trends observed at 15 locations were analysed using Mann-Kendall and seasonal Kendall tests. Sulphur wet deposition was found to have decreased by up to 60% at most stations between 1981 and 1996, and in some cases over a longer period, the greater declines more recently. This was also the case for SO_2 for which the fall has been slightly stronger, at 60-80%. Trends were also found in nitrogen compounds. Deposition trends were not statistically significant in the central and northern areas, but in the south approximated 35% for nitrate and 60% for ammonium.

The national monitoring network in **Norway** has revealed a decline in sulphate concentrations in precipitation of typically 50-60% between 1980 and 1999 (Aas *et al.*, 2000) . Changes in airborne concentrations are reported as higher than this, at 60-70% for sulphate, and 70-99% for SO_2. For nitrogen compounds a similar picture was seen as for Sweden, with no significant trends seen in oxidised nitrogen concentrations in precipitation. However, Tørseth *et al.* (2000) report reductions in ambient NO_2 of the order of 40-60% during 1985-96. Not unexpectedly, trends were found to vary in relation to air mass origin. The trends in ammonium concentrations at different sites have been found conflicting.

Across southern Europe patterns have also been identified. For a background mountain site in NE **Spain**, Avila (1996) described time series of precipitation chemistry between 1983 and 1994. Regression analysis suggested a 39% decline in sulphur deposition. It is interesting to note that there was an apparent sharp rise in sulphur deposition from 1989 to 1991, and thereafter a decline back to the underlying linear regression decline. Reported measurements made in **Greece** tend to concern urban environments, e.g. Paliatsos (1997) who suggested decreases of 40-50% in Athens SO_2 concentrations between 1971 and the mid-1980's, and Kelessis *et al.* (1996) who pointed towards a decline of similar order in Thessaloniki between 1989 and 1993. Trends in NO and NO_2 were not particularly apparent.

That there are unambiguous trends in observed atmospheric sulphur across Europe is evident in the correspondence between the various discrete studies assembled here. The picture for nitrogen is somewhat more equivocal, although patterns are suggested in some peripheral regions. These provide a viewpoint from which to examine the trends observed across Europe by the coordinated and consistent EMEP monitoring programme. A paucity of other co-ordinated programmes hinders such examination. However, one useful review and starting point is an examination of the data collected by the European Air Chemistry Network between 1955 and 1979 (Rodhe and Granat, 1984).

Consistency and quality of data were considered important problems by Rodhe and Granat (1984). The precipitation data was derived from monthly sampling periods using bulk collectors with analysis conducted by various laboratories. Difficulties arising from contaminated samples were managed using a filtering process in which those lying more than 3 standard deviations from the mean were rejected. Long term data series were utilised such that only stations contributing to at least 3 5-year periods were used. Regional analysis was attempted by grouping stations according to geography and according to laboratories undertaking sampling and analysis. Even then there were difficulties with inconsistent stations in different time periods, and so the examination accompanied regional descriptions with time series from selected stations. Ultimately, a statistical assessment was avoided. Review dealt with changes in observed precipitation concentrations of non-sea-salt sulphate represented as five-year average concentrations for the periods 1955-59, 1960-64, 1965-69, 1970-74, 1975-79. Data from over 80 stations was used, divided into 7 regions and 13 sub regions. The observed trends are summarised in Table 3.1.

As well as pointing towards typical trends (upward in the 1960, flattening or reducing thereafter), the summary also indicates some of the difficulties with data quality which EMEP-CCC could learn from in network management from the outset.

Table 3.1: Summary of trends in Europe, 1955-1979, from the EACN (extracted from Rodhe and Granat, 1984).

Region: subregions	**Characteristics**
Continental Europe: Austria, France, BeNeLux	Increased concentrations from late 1950s to early 1970s, from +40% (Austria) to +60% (France)
United Kingdom and Ireland: Atlantic coast, North, South	Suggested 1960s decrease for Atlantic coast and North. South is variable. Data likely inadequate for detection of long-term trends.
Southernmost Scandinavia: Denmark, South Sweden	Danish upward tendencies at start and end of period. Swedish stations decline at end of period. Some suspicion of local influences.
Central Scandinavia: Coastal, Non-coastal	Increase of 20-50% late-1950s to early-1960s, further slight increase to early-1970s, 20-30% decrease to late-1970s. Datagroup which inspires greatest confidence.
Northern Scandinavia	Trends resemble central Scandinavia. Lower concentrations.
Finland	Resemble Scandinavian data to early 1970s. No data from 1975.
Iceland	Uniform pattern with no obvious trend.

3.3 Methodology for describing trends

This report employs a range of approaches in order to contribute to our knowledge and understanding of the developments in atmospheric quality across Europe which the EMEP network is capable of revealing. On the one hand, simple time series display alone is somewhat of a restricted approach to trend analysis. On the other, blank application of statistical techniques is liable to mislead, although valuable information can be derived from appropriate statistical tools. The approaches used are:

- time series review and non-parametric statistical trend detection, and
- cartographic display.

Initially, time series review and statistical description of observed trends is undertaken. Data is then aggregated and re-presented in cartographic form. Comment includes comparison with recognised quantitative objectives for environmental quality. Finally regression analysis is undertaken to comment on the relationship between observed changes in air quality and reported emission changes.

An important first step in trend analysis is simple time-series review. This allows both characteristics of the data to be understood (missing data, outliers, tendencies, distribution, etc), which assists correct application of techniques (Sirois, 1999), and assists particularly in the current study when analysis of trends in 'regions' of Europe was desired. The review of literature indicated that complex geography could generate problems of inhomogeneity between sites. This problem was also encountered by the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Waters) in their "Nine-year report" (Lükewille *et al.*, 1997). Comment was made on the large differences between countries and that variation between sites within a country was often sufficiently large that country-by-country analysis was not felt a good presentation of results. A crucial part in definition of sub-regions was time series review to judge whether patterns and observed variables were similar between adjacent sites.

From this point an assessment of the significance and magnitude of trends could be made. Straightforward common means of detecting and estimating trends include linear regression and such as the Mann-Kendall Test, often along with Sen's slope estimator. However, much environmental data, including air quality observations, is seasonal. Averaging is then required. Aggregating from daily samples to annual averages in the case of EMEP data, for example, risks losing information, as skewed distributions can lead to misleading averaged values which may exaggerate tendencies. Missing data can also lead to bias in time-aggregated data. The advice of Sirois (1999) is that aggregating, e.g. to annual averages, introduces bias and hence should be a restricted means of overcoming problems of temporal variability. One widely used technique for handling such problems is application of the non-parametric Seasonal Kendall Test (SKT). The test has no difficulty with non-normality, missing, or seasonal data. In brief terms, the test compares the ranked value of individual observations within a season with subsequent observations in the same season. If trends are found to be homogenous across seasons, the Z-statistics calculated for each can be combined to give an overall result. Slope estimates (i.e. the magnitude of the trend) is usually calculated from the Sen’s slope estimator on the basis of seasonal data, i.e. the median of between year differences for each season is calculated, combing these as required to an annual estimate. This way each season is given equal weight, restricting bias from long period averaging.

This report seeks to describe as far as possible regional patterns to trends monitored through the EMEP programme. Trend analysis results for individual sites must therefore be combined into an overall spatial statistic, which can be achieved from SKT results in much the same way that annual estimates can be derived from seasonal. Fully satisfactory combination of seasonal data depends on homogeneity in trends between the constituent seasons; in the same way derivation of regional statistics on the basis of combined site measurements is preferred with homogeneity between sites. Should this not be so then the trends at different stations could be judged inconsistent. The technique can be found in various texts: we have utilised the description given by Gilbert, 1987. In Appendix B we describe the methodology employed.

Given Europe’s great geographical variability, the sub-regions described in this study were often of limited extent. The process was an informal one, and to some extent iterative, relying on comparison of time series and summary data, exploratory calculation of trend in/homogeneity, and consideration of expected patterns. In essence this is a form of representativity analysis, albeit without formal criteria, in which stations should be judged to demonstrate sufficient equivalence or difference. The final list of regions and associated subregions considered was as follows:

West-north continental Europe:

France
BeNeLux
Jutland Peninsula
Germany-north
Germany-south
East European plain north

Great Britain and the Republic of Ireland:

West coast
Scotland
East coast north
East coast south
South east
South west

East-south continental Europe:

Czech Basin
Hungarian plain
North-East Balkans
High Alps and Carpathians

Scandinavia and Fenno-Baltic region:

South Norway
South Sweden
East Sweden
Central Scandinavia
Baltic States
South Finland
the North

Iberian peninsula:

Portugal
Spain

Sections 3.4 and 3.5 of this report deal with trends in sulphur and in nitrogen respectively. Within the sulphur section the regions are separately discussed in terms of the observed time series in airborne sulphur at selected stations before statistical analysis of the aggregated stations in each sub-region is presented. At this point, changes in concentrations of sulphur in precipitation are also evaluated. With more limited monitoring data available, the discussion of nitrogen trends does not separately consider regions.

A short synthesis of the information behind the initial time series and statistical review is then presented in section 4. By means of cartographic display and summary tables the degree and direction of temporal changes across Europe is presented, and changes in deposition considered. The spatial patterns observed in long-term averages are mapped. In addition, one intention of this report is to comment on the degree of achievement of political objectives which may be ascertained from monitoring data for the period available. The objectives for nitrogen were simply of stability whilst for sulphur marked changes are hoped for.

For each station across Europe which has monitored sulphur in air or in precipitation the 3-year average depositions have been calculated for 1980-82, 1985-87, 1990-92, and 1995-97. Precipitation estimates are a straightforward combination of reported precipitation sulphate concentrations and precipitation amounts. Stations are not monitoring precipitation without also analysing its sulphate concentration. Dry deposition estimates are estimated on the basis of reported SO_2 and SO_4 airborne concentrations aggregated to monthly resolution. A dry deposition velocity is applied to these as explained in section 4.2. The wet and the dry deposition estimates have then been kriged to provide mapped estimates of total S deposition across Europe in the same way that EMEP monitoring data has frequently been presented. The kriged estimates of each are then added to provide grid-square estimates of annual total sulphur deposition for each of the 3-year periods given, and these are mapped. Of interest is whether such information encourages confidence that intended objectives achieved during this period, although it should be noted that uncertainty in regions away from measurement sites may be considerable. Objectives for simple total sulphur supply have been implied, if not stated, from the first Protocol in 1985 in which signatories agreed to a 30% emission reduction. The degree of change in deposition since the 1980 base year for the protocol can be displayed.

3.4 Sulphur air quality trends in Europe

3.4.1 West-north Continental Europe

Monitoring network

Somewhat of an all-encompassing name, here this is taken as the EMEP region of continental Europe north of the Alps and Carpathian central mountains, south of the Baltic/North Sea coast, and extending across to the plains of east Europe. Figure 3.3 displays the region and its monitoring stations. The subregions dealt with are: i) France, ii) BeNeLux, iii) Jutland Peninsula, iv) northern Germany, v) southern Germany, vi) eastern European plain north.

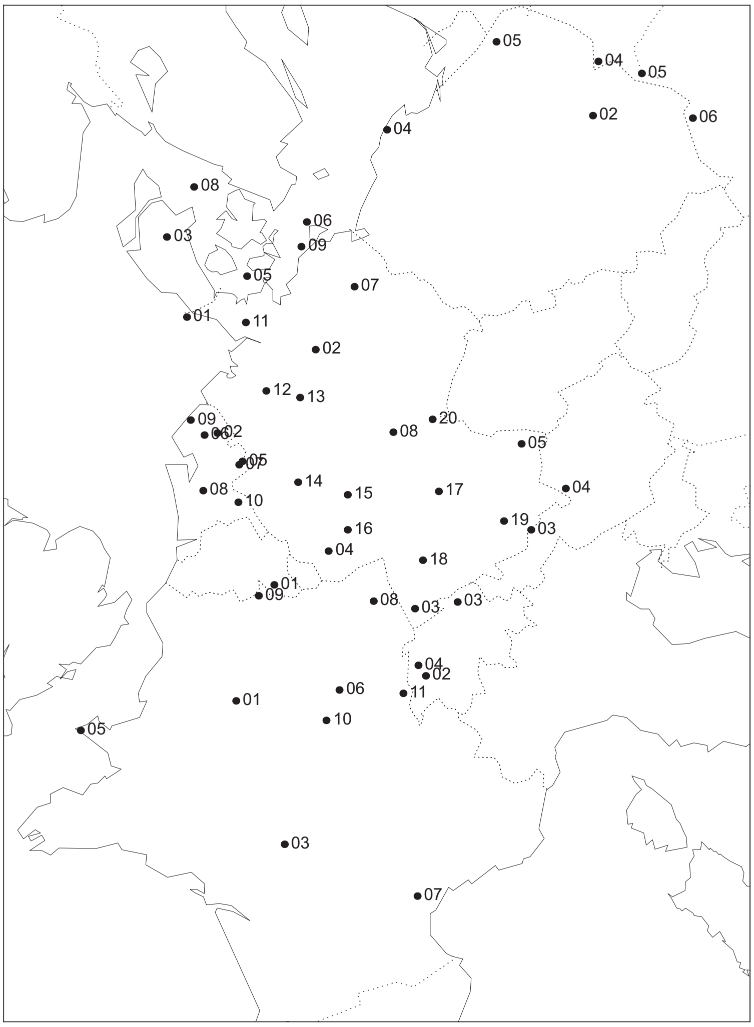


Figure 3.3: Central Continental Europe region and monitoring stations.

The periods and stations in the region from which quality controlled monthly monitored data for sulphur compounds in air and precipitation are available are shown in Figure 3.4. Reference may also be made to Appendix A containing details of methodological changes. Whilst in France two stations provide largely continuous coverage, the increase in number of monitoring stations across mid and eastern areas from 1990 is quite evident. Analysis of airborne components changed from 1988, with precipitation sampling changing from 1990. Notable in the Netherlands is the biannual shift in monitoring location. Furthermore, sampling and analysis methods have changed several times between 1983 and 1992, although have been consistent thereafter. For the Belgian site sulphate aerosol sampling and precipitation analysis methods changed in 1988. Long term coverage is available for several sites on the Jutland Peninsula, although methodologies have been less constant, most changes occurring between 1983 and 1990. Across Germany sulphate aerosol has been monitored widely, whilst available precipitation data is restricted for the north, with conversely less available sulphur dioxide data for the south. Sampling and analysis methods have been largely unchanged. Into Switzerland the density of monitoring increased in later years, precipitation sampling and analysis changed in 1984, and airborne compound sampling and analysis changed in 1988. Stretching from Germany the eastern plains is a very large area. Methods have been fairly constant in Poland save a sulphur dioxide sampling change in 1986, and were consistent in Belarus and Ukraine until 1988.

Time series review:
Sulphur dioxide
With long term records from several stations, the centre of this region is a convenient starting point. Located south-east of Hamburg and northeast of Hanover, Langenbrugge, DE0002, displays a steady decline in observed SO_2 concentrations since the later 1980s. Annual mean concentrations of around 10 µg S m^{-3} at the end of the 1970s declined from the last quarter of the 1980s to approximately 2 µg S m^{-3} by 1993, and have continued down to typically below a microgramme after 1996. These observations are broadly indicative for the **northern region of Germany** which has had generally higher concentrations in the past between the Rheinland in the west and Brandenburg in the east. Observations at Deuselbach, DE0004 in the west or at Neuglobsow, DE0007 in the east may also be considered characteristic. Other central sites with similar progressions include Usingen, DE0015, to the west and Ansbach, DE0017, to the south. In **southern Germany** concentrations have been notably lower, e.g. at Starnberg, DE0019, and Rottenburg, DE0018, where concentrations of around 5 µg S-SO_2 m^{-3} in 1980 fell to below 1 µg S-SO_2 m^{-3} by 1994.

Noticeable at all stations is a sharp decline in the magnitude of episodes, strong enough to have a profound influence on the monthly mean concentrations. Langenbrugge experienced a mean monthly concentration in excess of 60 µg SO_2-S m^{-3} in December 1994, whilst Hof, DE0020, in the east towards the Czech Republic reported a mean monthly concentration of over 130 µg m^{-3} as sulphur in February 1986 at which time 24hour concentrations reached several hundred microgrammes per cubic metre. The significance of these episodes to data interpretation can be seen if annual concentrations are represented as median rather than mean averages. Figure 3.6 reveals it was not unknown for there to be a factor of two difference between annual geometric and arithmetic mean concentrations. The last year when this was apparent, however, was 1987 since when reduced emissions and more benevolent meteorology have likely combined beneficially. Medians are commonly felt to be good for trend analysis by reducing bias to short term high values.

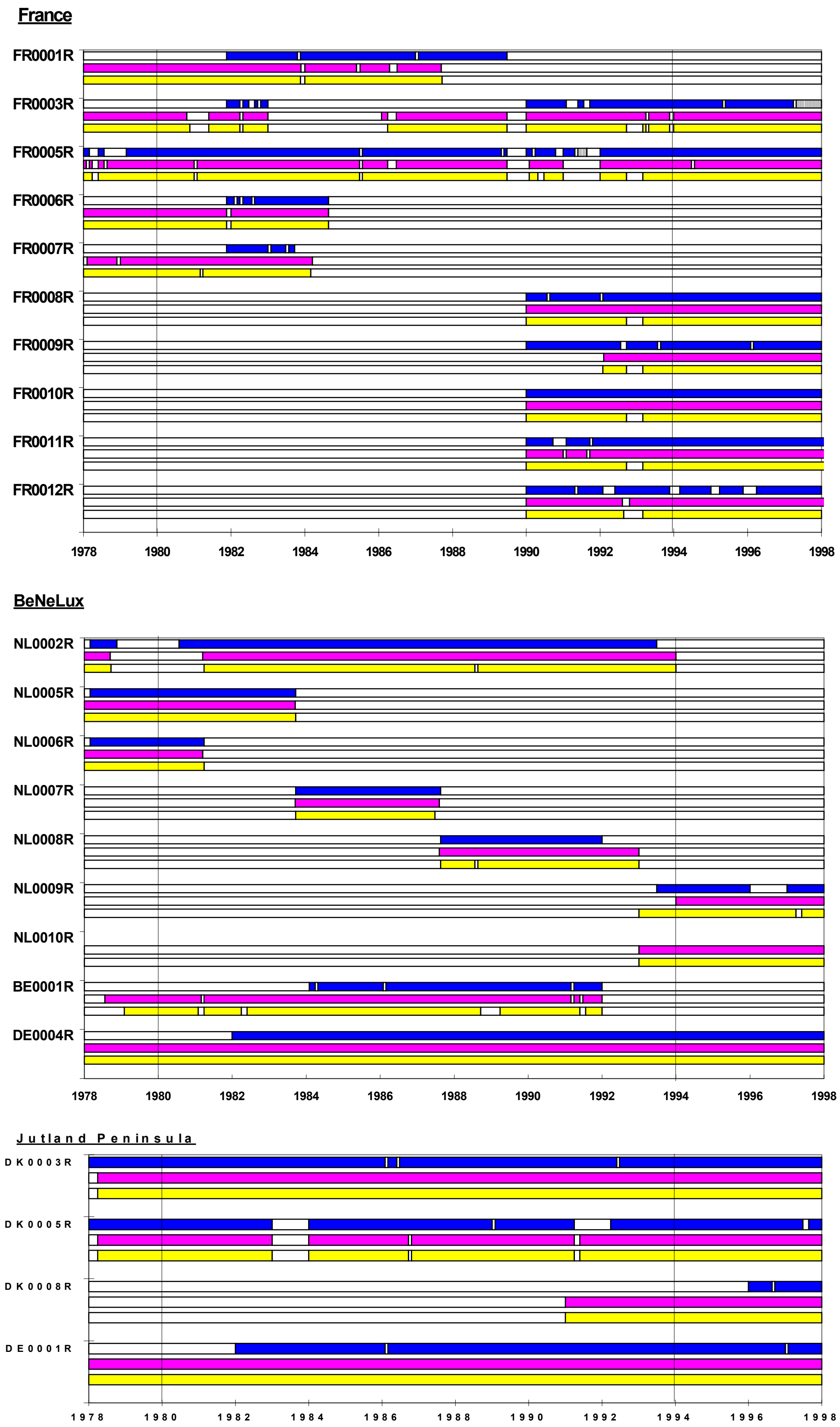


Figure 3.4: Sulphur monitoring records for west-north Continental region. Submitted to EMEP CCC, with monthly values available after quality control. Blue = sulphate in precipitation; red = sulphate aerosol; yellow = sulphur dioxide.

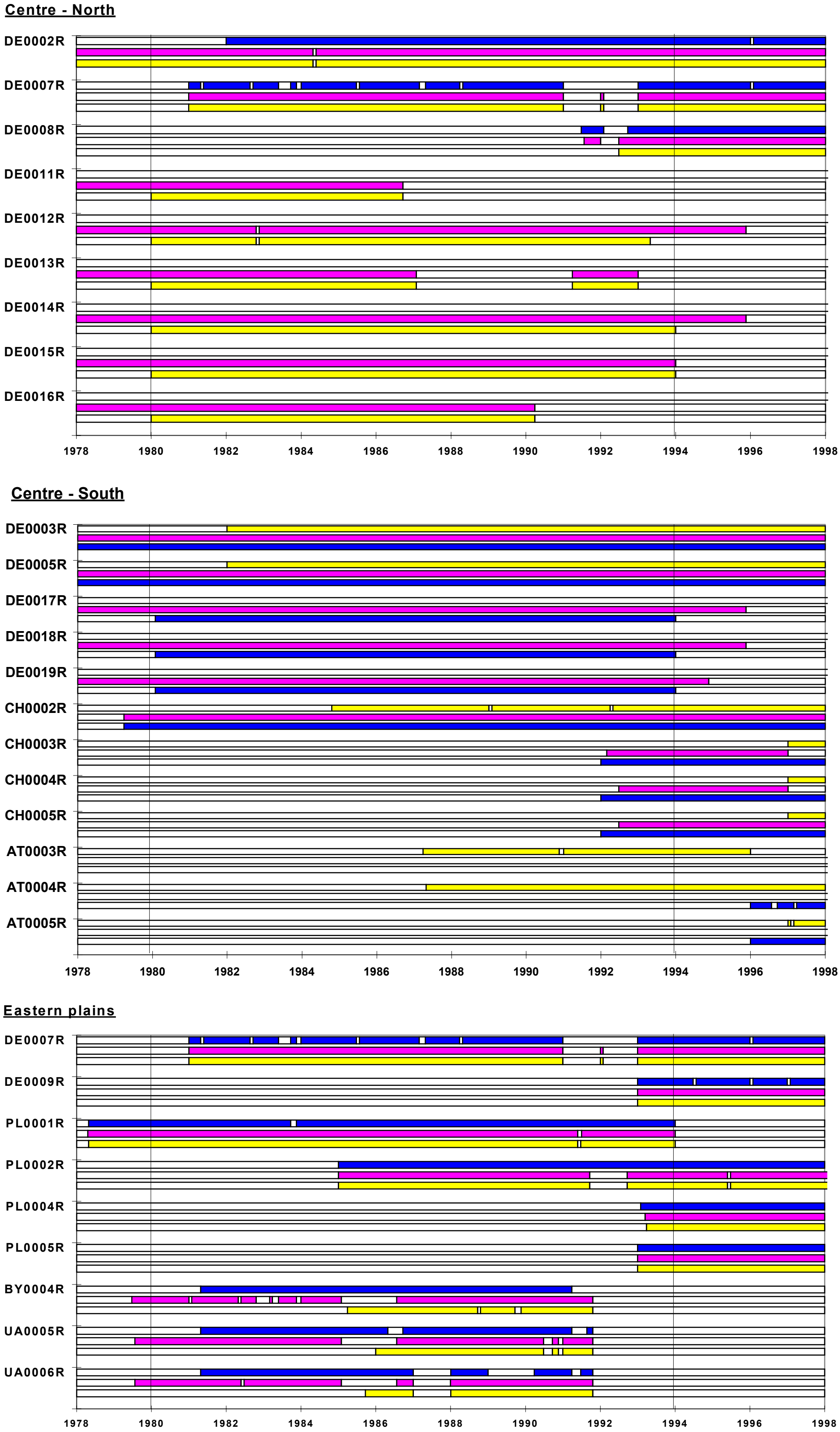


Figure 3.4 (cont): Sulphur monitoring records for west-north Continental region. Blank indicates no or insufficient data, or data not passing quality control. Blue = sulphate in precipitation; red = sulphate aerosol; yellow = sulphur dioxide.

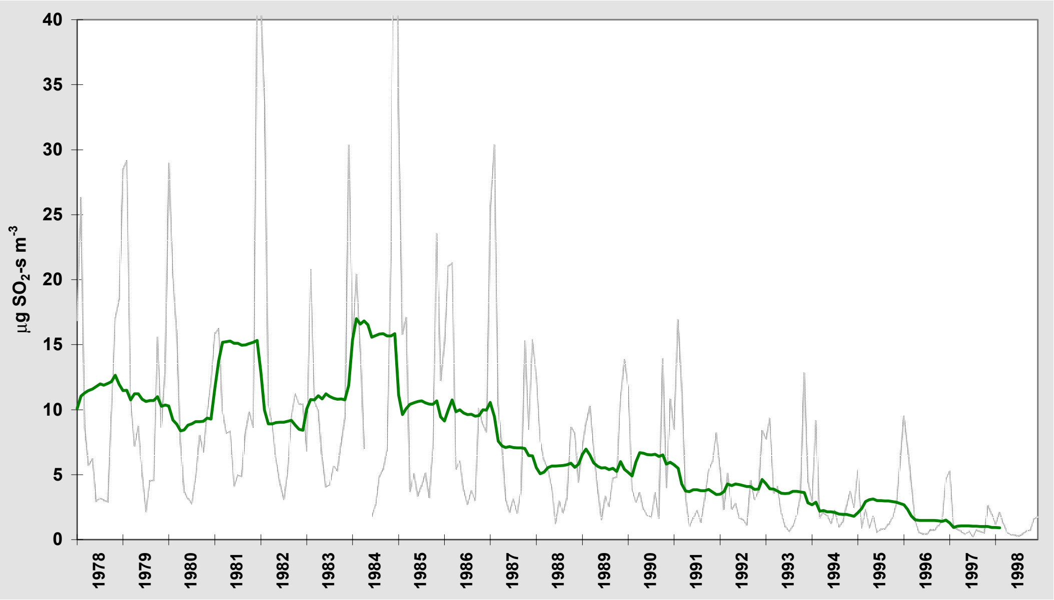


Figure 3.5: Example observed SO_2 time series for northern Germany. DE02, Langenbrugge. Monthly mean (fine line) and 12-month running mean (bold line) (µg S m^{-3}).

Moving north to the **Jutland Peninsula**, comprising Denmark and upper Schleswig-Holstein, measurements at Arkona, DD0001/DE0006, in the area of the former GDR and later not too distant at Zingst, DE0009, also show a clear downward progression, perhaps beginning slightly earlier from 1985. This earlier decline is also seen at DE0001, Westerland, close to Denmark, and at the Danish stations Tange, DK0003 (Figure 3.7), and Keldsnor, DK0005. Indeed, in Denmark there has been none of the apparent stability which characterised Germany during the first years of the 1980s, rather a steady decline throughout. Both stations observed around 6 µg SO_2-S as an annual mean in 1978, falling to just over 2 µg m^{-3} at Keldsnor, and to something over a microgramme by 1994 at DK0003.

Observations from the west of continental Europe indicate that the spatial extent of observed SO_2 decline was rather limited during the earlier period of reductions in sulphur dioxide emission reported by France. The **BeNeLux** region, as represented by Witteveen, NL0002 (Figure 3.8), shows steadily declining sulphur dioxide throughout the period, similar to that in Denmark. Measurements across France, however, at Vert-le-Petit, FR0001, south of Paris, and La Hague, FR0005, on the Channel coast (also Figure 3.8) show clear and steady declines from the late 1970s through to the later1980s, before a more modest decline thereafter. Observations to the mid-1980s in mid-eastern France at Valduc, FR0006, is in agreement with this.

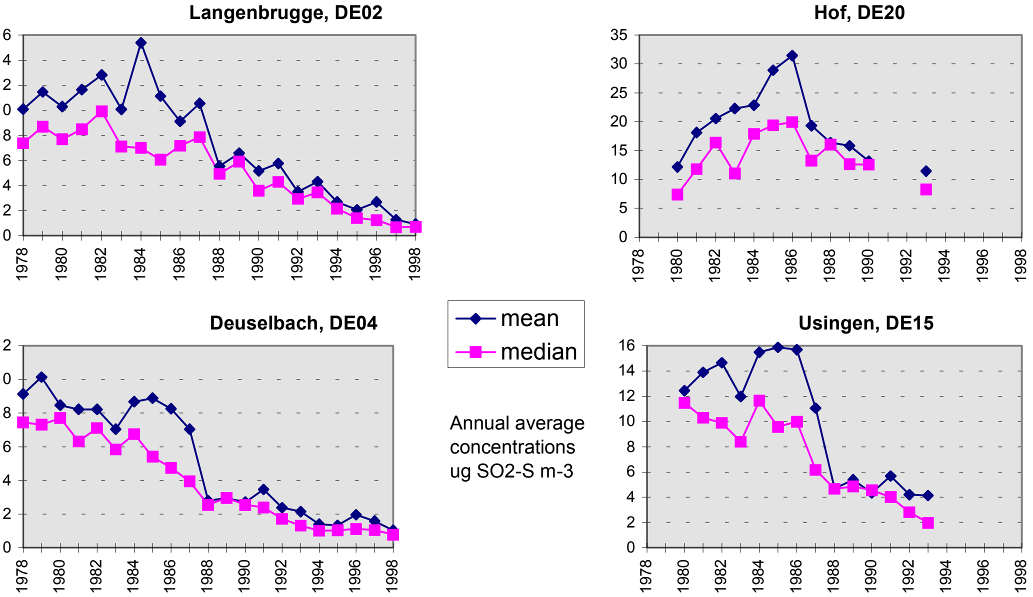


Figure 3.6: *Comparison of 12-month average concentrations measured at German stations when expressed either as mean and as median values.*

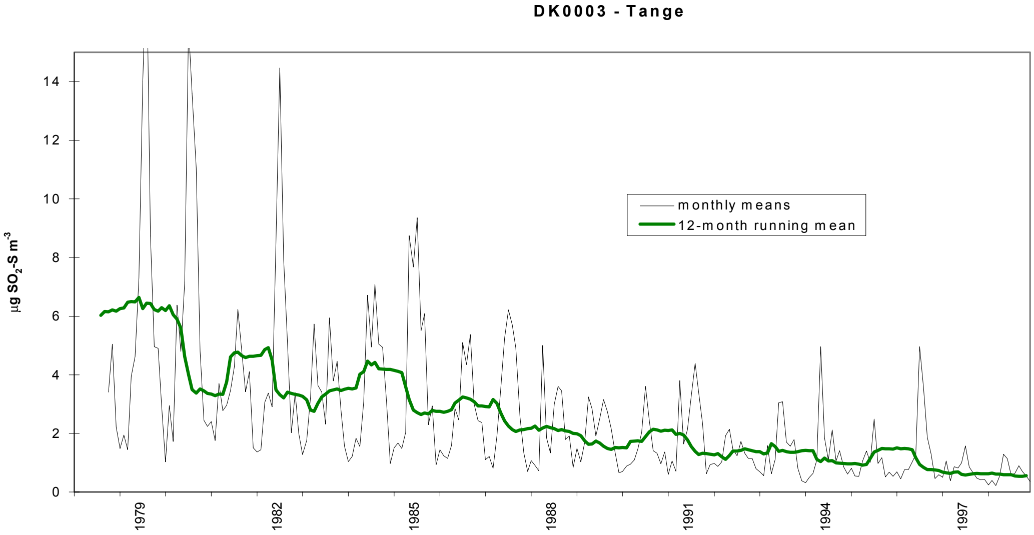


Figure 3.7: *Example of sulphur dioxide time series for the Jutland Peninsula. DK03 Tange.*

Moving across the **eastern plain** from Germany, the reasonably steady downward tendency at Arkona and Zingst in the north-east on the Polish border has been mentioned, as has the sharp decline in episodic concentrations at Hof. Elsewhere on the border the SO_2 concentration decline follows that of elsewhere in Germany, e.g. at Neuglobsow, DD0002/DE0007, a fall from ~8 to 2 µg S m^{-3} between 1980 and 1994, and to the south-east towards the Czech/Austrian border Brotjackriegel, DE0005, the same progression, albeit from a lower air concentration starting point. Given similar reported emission changes in the two countries, these progressions are not surprising. Nevertheless in Poland measurements reveal a more gentle decline, such as at PL0002, Jarcew, or in the east at Suwalki, PL0001, (and later not too distant at Diabla Gora, PL0005). The temporary increase at Suwalki between 1985 and 1988 is believed to reflect subregional changes in air quality related to urban expansion (Figure 3.8).

Sulphate air concentrations
In general the sulphate concentrations show a similar pattern but with greater similarity between subregions - little change until decline in the latter 1980s. The pattern seen at Deuselbach, DE0004 (Figure 3.9), is characteristic for much of the central region. From the Rheinland-Brandenburg the **northern German** zone for sulphate may be said to have extended as far as around Nurenburg, with concentrations of 2-3 μg SO_4-S m^{-3} through to 1987, thereafter falling by around a microgramme during the lifetime of the Protocol. The decline since has continued at a similar rate. In **Germany south** and towards the Alps a similar pattern has been followed from initial concentrations in the region of 1½–2 μg S m^{-3}. In **Jutland** on the continents northern edge all stations, e.g. Westerland (DE0001), reported a continued steady decline from the first years (mirroring SO_2), perhaps slowing later on, and all beginning from slightly elevated concentrations around 3 μg S m-3. Moving west into the **BeNeLux and French** regions the bulk of decline occurred earlier. At La Hague on the English Channel (FR0005), at Vert-le-Petit south of Paris (FR0001), and at Offagne in the Belgian Ardenne (BE0001) concentrations fell from around 3 to approximately 1 μg SO_4-S m^{-3} between 1980 and 1988. Information from the **eastern plains** is more sparse, but hints at a constant concentrations before 1988, or even a slight rise, before a noted fall thereafter.

The shift in ratios of SO_2 to SO_4 can indicate a decreased proportion of ‘younger’ sulphur emissions in the total sulphur burden. The central region has seen the ratio fall from 5-6 (e.g Langenbrugge, Deuselbach) to 2-3, whilst southwards ratios have fallen from around 4 to around 1½ (DE0019, Starnberg). Away from the central major emission region a lesser decline in ratio has been observed, perhaps indicative that the influence upon the total atmospheric sulphur loading of reductions in more local emissions do not outpace the influence of more distant reductions to such an extent. Danish ratios declined from around 2 to about 1, whilst at Westerland in northern Germany falls were from 2 to approximately 1½. Peripheral areas did not see even these changes, with French and Dutch ratios remaining of similar magnitude (2-3), Polish and eastern German ratios remaining at 1-2 and 2-3 respectively, and with ratios at Offagne (BE0001) actually revealing a strong increase in the proportion of SO_2 in total sulphur from 2 to 5.

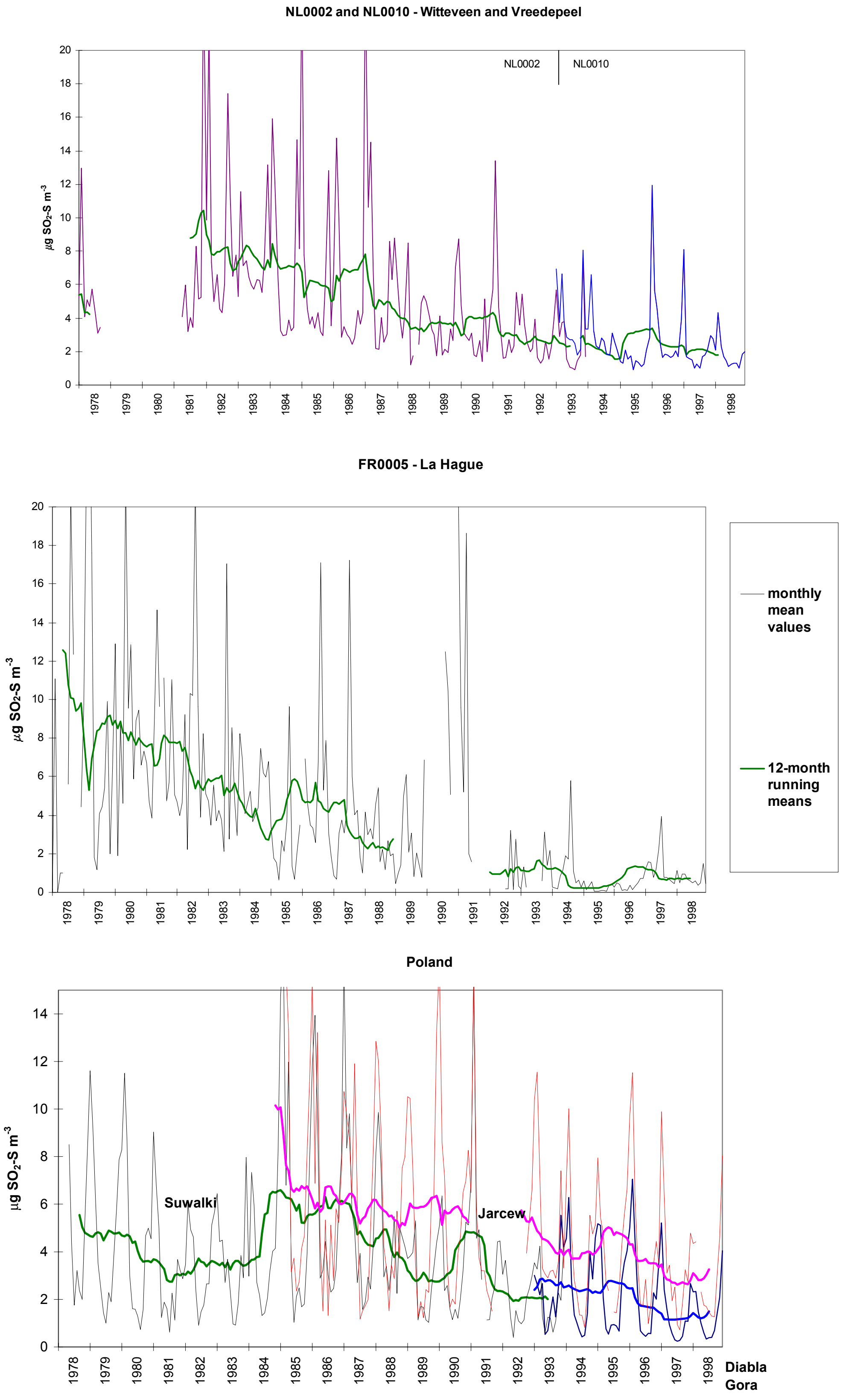


Figure 3.8: Example sulphur dioxide concentrations in the BeNeLux (top), French (centre) and Eastern plains (lower) regions.

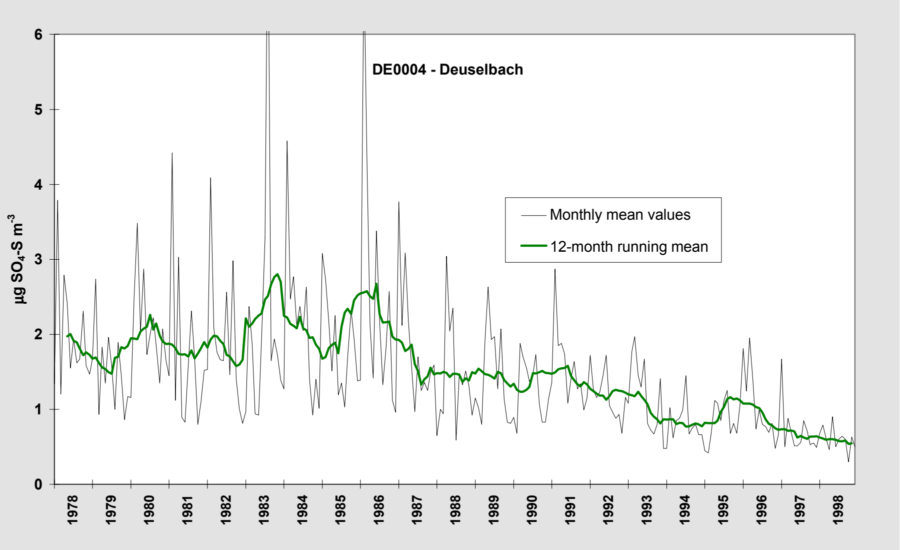


Figure 3.9: Example development in airborne sulphate concentrations for the continental Europe region. Deuselbach DE0004.

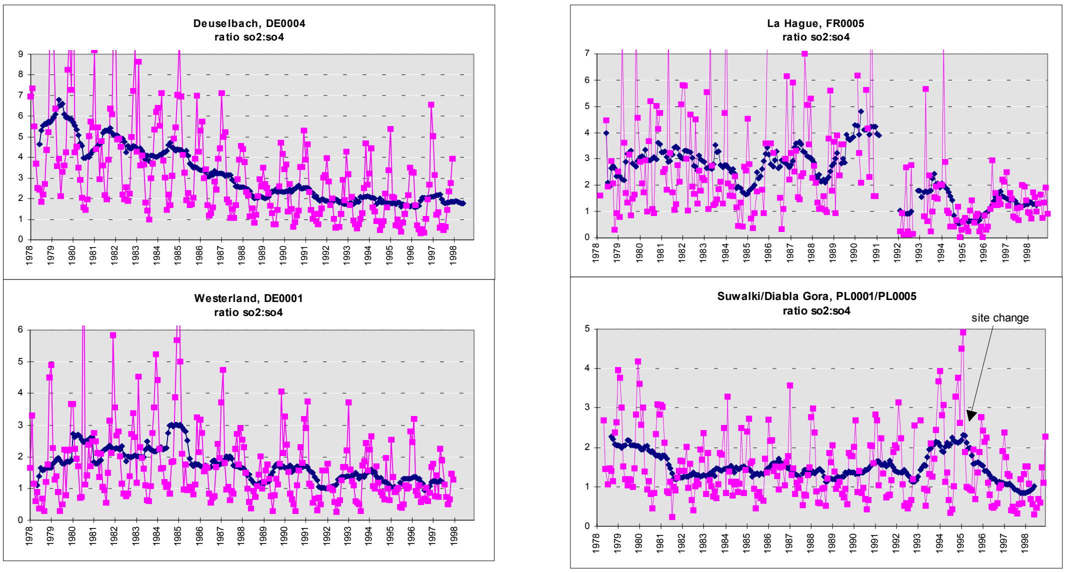


Figure 3.10: SO2:SO4(aerosol) ratios for selected continental European sites. Monthly means and running 12-month averages.

Statistical trend evaluation

Examination of time series suggests two periods of change in the atmospheric sulphur environment, the first to the mid-1980s, and the second thereafter. Emission levels in Germany, France and Poland reached an inflection point at this time, although being dissimilar in that German and Polish emissions began to decline, whilst French emissions slowed their rate of fall. Suggestion of difference is also seen in the plotted time series, both in French observations and to a lesser extent in German SO_2 and SO_4. A further indicator of change is the comparison of mean and median values for Germany, showing near similarity after the mid-1980s, and divergence before. Division of the period into two parts, 1980-87 and

1988-98, on the basis of time series review is reasonably supportable when considering method and location changes. For France the division accords well with station and method alterations. In BeNeLux the Belgian method change in 1988 is accommodated, whilst the regular changes in the Netherlands do not encourage selection of any particular time periods before the mid-1990s. The changes in methods in Denmark may indicate more reliable division at 1990, although given very good and consistent performance in laboratory precipitation analysis intercomparisons since 1979 and no apparent time series changes this is not considered sufficient a problem to warrant action. The two periods are happily accommodated by the consistency in methods and laboratory performance in Germany from 1980. Changes in Swiss airborne components methods in 1988 make a time division at that point acceptable, whilst for precipitation the earlier changes may render the first period less comfortable, noting the change in laboratory performance which accompanied the change. For these reasons the period has been divided into 1980-87, and 1988 to 1998. The statistical tests employed offer determination of the simple existence of trends in both time periods, and of quantifying the rate of change in concentrations in each.

Statistically significant downward trends in sulphur dioxide concentrations were found in all subregions except the Eastern Plains in the first period, and in all subregions in the second. This is in broad agreement with previous studies (section 3.1). From 1980-87 trends were most substantial in the west and north-west of the mainland continent which agrees with the early decline in French sulphur emissions. What is interesting is the existence of significant trends across these parts of Germany. Whilst East German emissions increased to the mid-1980s and then stabilised, West German emissions declined throughout. Both declined in the 1990s. Further to the east this is not found. There is also the suggestion that French developments to the west may have contributed to a positive influence on the German atmospheric environment. Post 1988 the curious feature is that whilst significant trends are found everywhere, the rate of change in Germany is little different than before. In the eastern plains there is a marked downturn in concentrations, whilst in France the rate of decline eases. What may have happened is that in the early period French emission changes to some extent counteracted some German increases, and in the latter period German reductions have taken this role. It is interesting also that stations representing the central subregion show greater heterogeneity than those in other regions. Of the three measures of homogeneity (site difference, season difference and site-season interaction) the centre-north subregion is the only district to satisfy only one in both periods.

The patterns in airborne sulphate are also quite distinct. Central areas show no significant trend before 1988, and those in the east whilst significant are estimated to be very slight indeed. The largest trends are found respectively in France, BeNeLux and Jutland. This contrasts with the assessment by Hovmand and Andersen (1995) for Denmark. From then and into the 1990s the rates of decline decrease in the west, and pick up eastwards. Greatest similarity between stations is again found in the far west and in the far east. The quite different emission patterns in these subregions which unlike central regions are well separated by distance may contribute, quite alongside meteorological difference.

Precipitation changes have much in common with airborne sulphate changes, central and eastern subregions have no trend, or trends with very broad and equivocal confidence limits. The lack of trend in France is curious, and may well be related to the meteorological circumstances which contribute most to precipitation. This has not been evaluated here. The contrast with the second period is notable. All subregions display significant downward trends, these becoming stronger moving eastwards.

Table 3.2: Summary statistics for trends in west-north continental Europe.

	SO_2		**SO_4 airborne**		**SO_4 in precip.**	
	% Change (best est)	*hom*	% Change best est.	*hom*	%Change best est.	*hom*
subregion	slope ±90% $\mu gS\ m^3yr^{-1}$		slope ±90% μgSm^3yr^{-1}		slope ±90% $mgSl^{-1}yr^{-1}$	
1980-87						
France	**-50** -0.112 -0.412	(*=3)	**-62** -0.111 -0.287	(+*=3)	**–** +0.050 -0.108	(+*=3)
BeNeLux	**-25** -0.050 -0.408	(+*=3)	**-30** -0.022 -0.171	(=3)	**-43** -0.041 -0.161	(*=3)
Jutland Peninsula	**-34** -0.087 -0.266	(*=3)	**-27** -0.014 -0.146	(+ =3)	**-20** -0.005 -0.086	(+*=3)
Centre north	**-23** -0.113 -0.351	(=3)	**–** +0.066 -0.055	(+ =3)	+ +0.078 -0.079	(*=3)
Centre south	**-27** -0.033 -0.232	(+=5)	**+** +0.071 -0.054	(+ =5)	**-24** -0.024 -0.106	(*=3)
Eastern plains	– +0.080 -0.964	(*=3)	– +0.333 -0.306	(* =3)	**–** +0.059 -0.271	(*=3)
1988-93						
France	**-47** -0.026 -0.119	(+*=2)	**-42** -0.023 -0.077	(+*=2)	**-42** -0.009 - 0.036	(+*=2)
BeNeLux	**-22** -0.056 -0.203	(*=3)	**+** +0.126 -0.041	(=3)	**-64** -0.034 -0.224	(* 3)
Jutland Peninsula	**-58** -0.091 -0.196	(*=3)	**-44** -0.055 -0.090	(+*=3)	**-45** -0.035 -0.067	(+*=3)
Centre north	**-72** -0.158 -0.328	(* 3)	**-67** -0.061 -0.111	(*=3)	**-71** -0.077 -0.124	(* 3)
Centre south	**-54** -0.040 -0.168	(*=5)	**-73** -0.082 -0.143	(=5)	**-47** -0.024 -0.046	(* 3)
Eastern plains	**-62** -0.194 -0.369	(+*=3)	**-84** -0.170 -0.317	(+*=3)	**-73** -0.080 -0.157	(* 3)

Key:

'Best est.' indicates best estimate decrease in the initial concentration, expressed in percent, calculated from best fit in annual decrease multiplied over whole period. Those given and in bold face are statistically significant at p=0.1. Direction only (+/-) indicates not statistically significant.

'slope ±90%' indicates upper and lower annual slope confidence limits at p=0.1.

'hom' indicates regional homogeneity measures significant at p=0.1. Full homogeneity given as *(+*=[num])* where:

+ indicates station homogeneity,
* indicates seasonal homogeneity,
= indicates homogenous season-station interaction,
[num] indicates no. stations used.

Absence of symbol indicates characteristic dissimilar at p=0.1. Refer to text and Appendix B.

Subregion definition:

France:	FR01, FR03, FR05.
BeNeLux:	BE01, NL02, DE04
Jutland Peninsula:	DE01, DK03, DK05
centre north:	DE02, DE12, DE08 (88-98), DE13 (80-87)
centre south:	DE03, DE05 (precip.), DE17 (air), DE18 (air), DE19 (air), CH02
Eastern plain:	DE07, PL01, PLO2
centre:	DE02, DE03, DE04, DE05, DE07, DE08, CH02 (for summary statistics Table 4.1).

3.4.2 Great Britain and Republic of Ireland

Monitoring network

These Atlantic island states are a natural regional grouping. Their location relative to predominant weather patterns and to distributions of emissions and environmental sensitivity also render them of notable importance to the European air pollution environment. Figure 3.11 shows this region and the monitoring sites therein which have submitted data to EMEP.

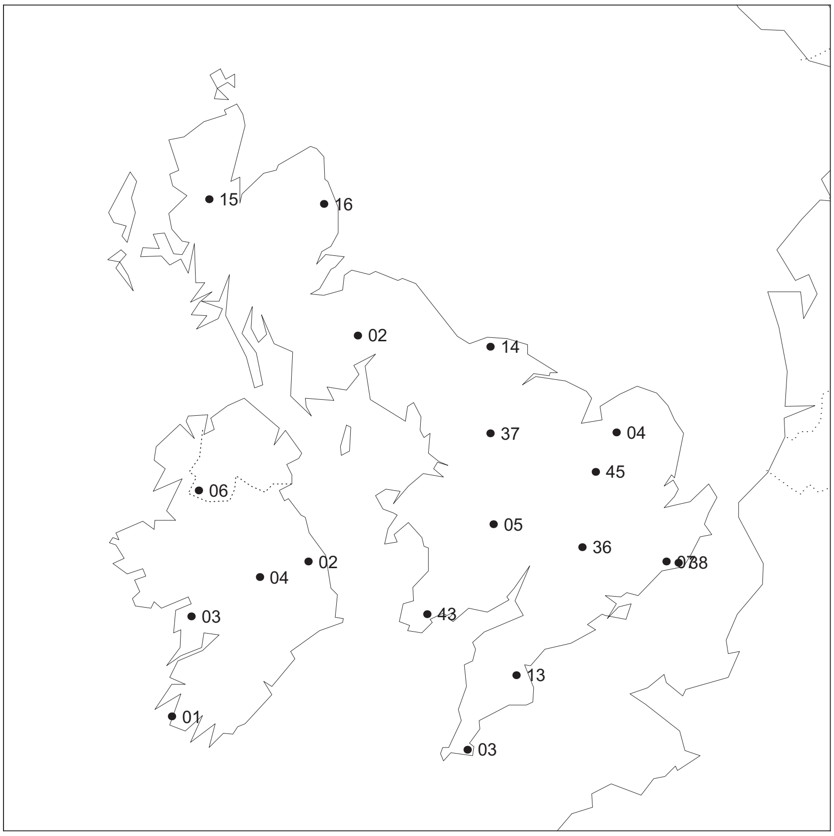


Figure 3.11: Monitoring sites in Great Britain and the Republic of Ireland.

Monitoring reported to EMEP was notably more extensive from 1987, although sulphur monitoring in the centre of mainland Britain has been restricted. Most of the early sites, however, continued in use into the later period, with a reasonably good comparison in observations between GB0003 and GB0013 (see Figure 3.12) despite a site change of some distance further strengthening these long term records. Method changes are have been limited - some changes to precipitation sampling in 1986 and again in 1992, and otherwise analysis of sulphate in air changing in the latter 1990s. Laboratory performance for precipitation has been consistent since the early 1980s. In the Republic of Ireland there has been long term monitoring at one site. Some changes were made to measurement techniques, mostly before 1992, and the laboratory intercomparisons have been a little variable in quality. Further observations from central and eastern Ireland have been reported only more recently.

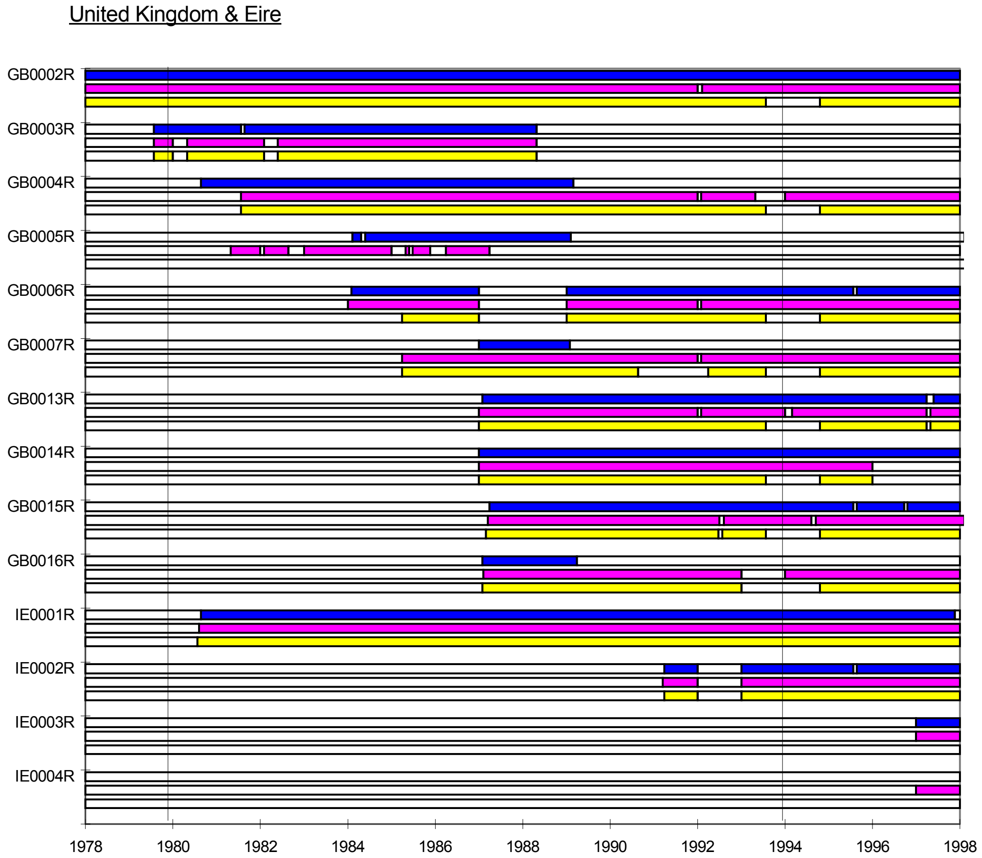


Figure 3.12: Sulphur monitoring records for Great Britain and the Republic of Ireland. Submitted to EMEP CCC, with monthly values available after quality control. Blank indicates no or insufficient data, or data not passing quality control. Blue = sulphate in precipitation; red = sulphate aerosol; yellow = sulphur dioxide.

Time series review

Sulphur dioxide

Long and relatively complete reporting of observed sulphur dioxide levels has been made for the north (Eskdalemuir - GB0002), east (Stoke Ferry - GB0004), west (Valentia Island - IE0001), and the south west (Goonhilly Down plus Yarner Wood - GB0003 and GB0013) of the region. The **south-west and western sites** would appear from reported concentrations to more reflect peripheral conditions. Lowest concentrations have been observed at Valentia (Figure 3.13) where the running 12-month average has remained at and below 1 µg SO_2-S m^{-3} since 1980. This station is located in the far south-west of Ireland facing the open Atlantic Ocean. There is a weak tendency to a falling 12-month average during this period, but with no evident changes in slope. There is an evident seasonal pattern, with elevated winter month concentrations (not displayed). The other 'western periphery' site is the combined record of Goonhilly Down (1979-88) and of Yarner Wood (1987-present) on the south-west peninsula of England (Figure 3.13). Goonhilly was a coastal station on the Lizard virtually at the southernmost point in the UK and some 40 km from the westernmost point. Yarner Wood lies around 120 km further east on the Dartmoor massif. No particular change in the running average occurs between these sites despite the later being within some tens of kilometres of the cities of Plymouth, Torquay and Exeter. Running annual SO_2 concentrations have steadily declined from around 2.5 to 1.5 µg S m^{-3} and below by the late 1990s. Concentrations now approximate those at Valentia. Evidence of greater past exposure to more contaminated air masses away from these subregions is seen with a far more obvious decline in concentrations in **southern Scotland**. Eskdalemuir, GB0002, declined from 1978 average concentrations in the region of 4 µg S m^{-3} down to around 1.5 µg S m^{-3} by 1986. Thereafter further decline has been slight and steady. Whilst in itself a relatively remote location, emissions from Belfast downwind to the south-west, and from the major conurbations of Newcastle to the east and Glasgow to the north (each ~100 km distant) can be expected to influence subregional air quality. However, the site with long records which appears most reflective of subregional contamination is Stoke Ferry, GB0004, in **east England**. Running annual concentrations of 6-8 µg S m^{-3} in 1982 at least in part reflects London to the south-west, and regional towns within tens of kilometres. Initial concentrations have fallen steadily to around 2 µg S m^{-3} in 1998. Other sites reporting to EMEP largely operated during the latter period. These tend to confirm steady/slow declines in SO_2 concentrations in more central districts in later years, or low and consistent concentrations at remote coastal sites. Appendix A gives summary data.

Sulphate air concentrations

The temporal development of observed airborne sulphate concentrations has somewhat different characteristics. Elevated absolute sulphate levels or a seasonal pattern in concentrations is a tell tale for greater influence of contaminated air masses. At the remote sites seasonal patterns are not striking, and none of the coastal sites show particularly elevated levels of airborne SO_4, suggesting limited influence by distant sources. In the remote **west**, Valentia Island shows much the same pattern as for SO_2 – low and steady/slightly declining concentrations, typically of below 0.8 µg S m^{-3} throughout. Similar levels are observed further north at Lough Navar, GB0006, in Co. Fermanagh. In contrast to SO_2, the only other subregion which may readily be categorised as ‘remote’ is northern **Scotland**. The reported data series from the latter 1980s show observed running 12-month mean levels below 1 µg S m^{-3}, with peak monthly means reaching only around 2 µg m^{-3}. In **SW England** the running 12-month mean sulphate concentration observed at Goonhilly Down was in the region of a microgramme sulphur per cubic metre until monitoring ceased in the late 1980s, whilst at Yarner Wood at this time levels of around 1.5 µg S m^{-3} were slightly elevated. That this elevation was not observed for sulphur dioxide suggests slight difference in the relative remoteness of these adjacent locations. Yarner wood concentrations have declined during the 1990s to around 1 µg S m^{-3} and below, similar to those in remote western Ireland, suggesting decline in distant sources.

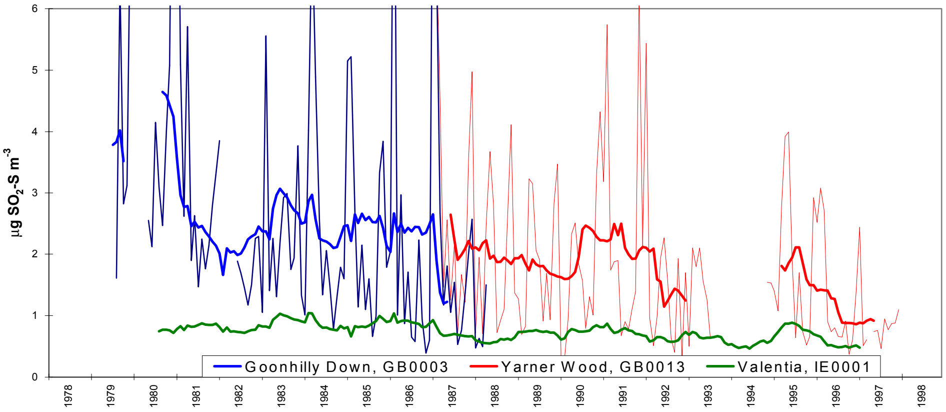


Figure 3.13: Observed SO$_2$ concentrations at Goonhilly Down, GB0003, Yarner Wood, GB0013, and Valentia Island, IE0001. Running annual means, and monthly means (not IE0001), µg S m^{-3}.

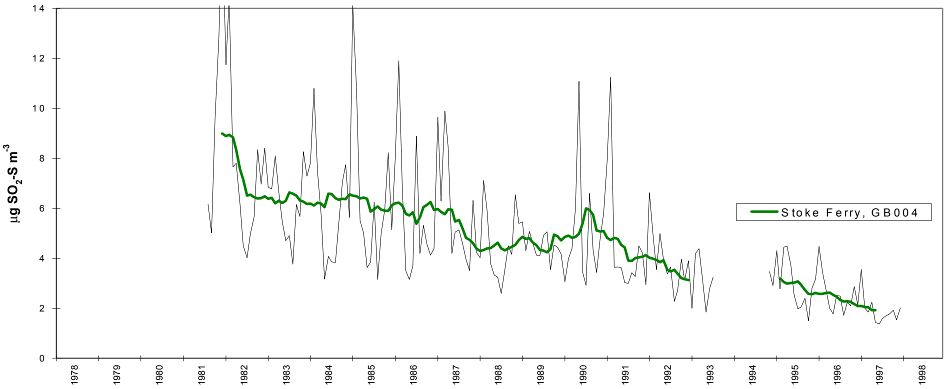


Figure 3.14: Observed SO$_2$ concentrations at Stoke Ferry, GB0004. Running annual means and monthly means, µg S m^{-3}.

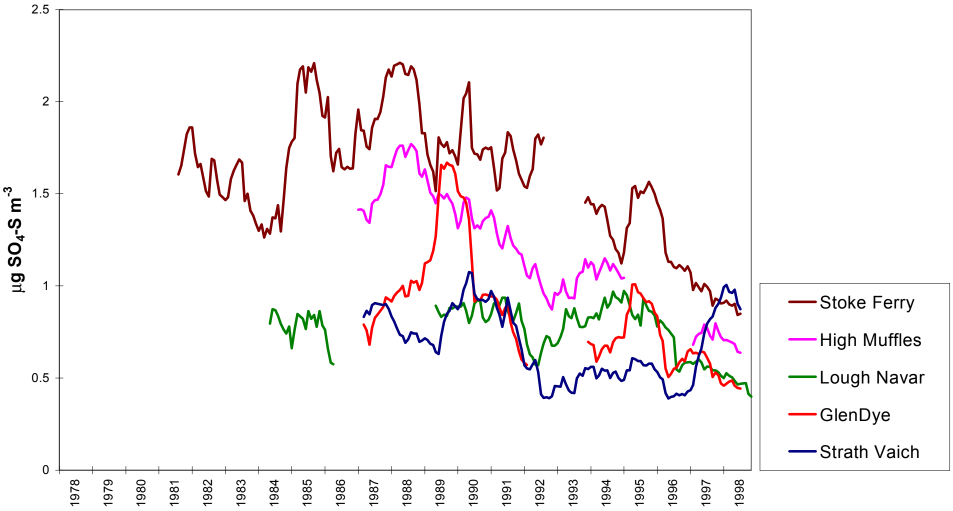


Figure 3.15: Sulphate particulate concentrations across the UK. Running annual mean concentrations; µg S m^{-3}.

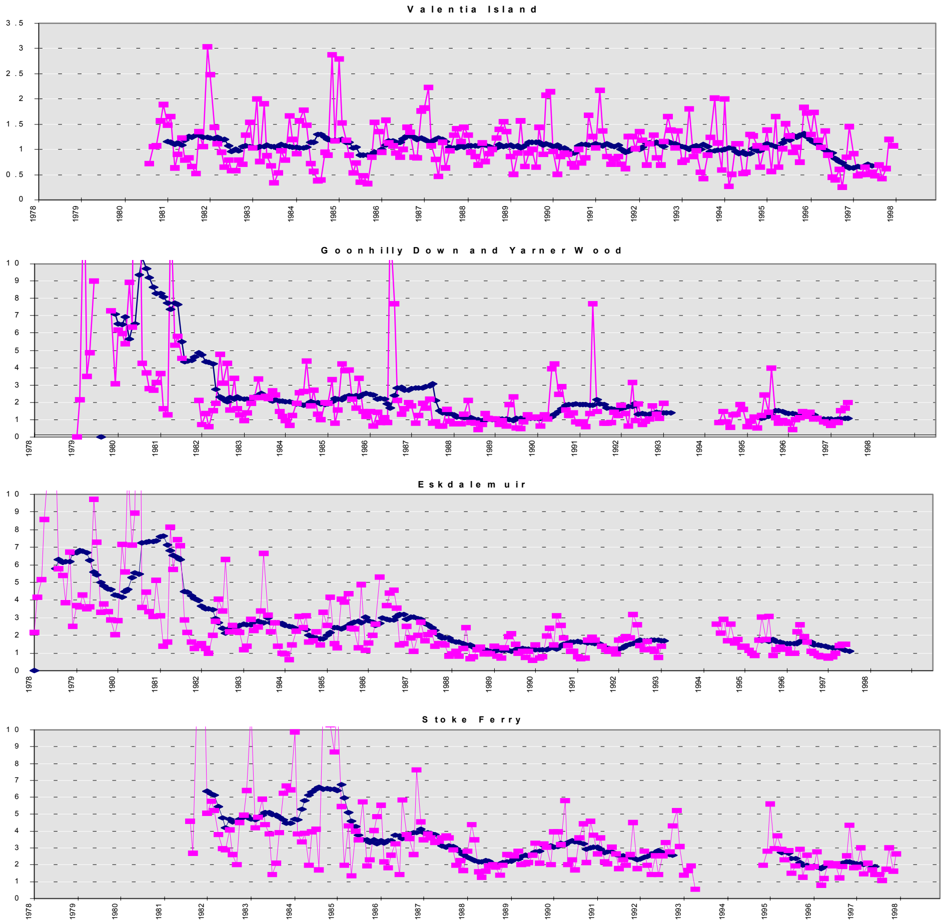


Figure 3.16: Observed ratios of SO_2:SO_4 at Irish and British sites. Monthly means and running 12-months averages.

At Eskdalemuir on the northern British mainland observed concentrations are not strongly elevated (typically < 1 µg S m^{-3}), but a strong seasonal signal gives away the influence of contaminated air masses. Wintertime running 12-month average concentrations of sulphate-sulphur exceed a microgramme per m^3, falling by up to 50% during the summer. Concentrations see gentle and constant decline from 1978. In the south-east subregion there is combined seasonality with raised overall concentrations, indicating the importance of contaminated air masses. Both GB0004, Stoke Ferry, and GB0007, Barcombe Mills show similar time series' and similar concentrations. The downward progression was continued and steady as seen further north, and as seen at High Muffles, GB0014, approaching the North Sea in the north east.

The approximate 1:1 sulphur ratio between sulphate in air and sulphur dioxide at Valentia indicates, along with the absolute concentrations themselves, that air is not purely 'aged' air from Atlantic sources. A lower ratio would be expected in this case. Limited power generation and smaller settlements in the immediate region may lie behind this. On the scale of long range transport, it must also be remembered that the UK is affected not only by westerly air masses. Sulphate and sulphur dioxide from the continent will be oserved at times. However, unlike other sites there has been no apparent change in this ratio, indicating little change in background sources. At Lough Navar further north on the Atlantic coast, a decline to equivalency in ratios to late 1989, with further decline to around 0.5 in the 1990s suggests the decline of subregion sulphur emissions in the absence of sulphate trends. The similar relative remoteness of the far north subregion is indicated by ratios down to 0.5 in the early 1990s at Strath Vaich, GB0015, in the far north-west of Britain. Across much of Britain, however, initial mean annual ratios of around 7 declined sharply so that by 1983 ratios were 2-3, and by the latter 1980s approached equity. This pattern corresponds in time to initial reductions in reported sulphur dioxide emissions. The influence of neighbouring countries is not widely evident in the ratios at this temporal resolution. One site which may do so is High Muffles in north-east England with relative proximity to the eastern seaboard. An initial decline from 5 to 3 was followed by a climb back to 5 and beyond. This can suggest initial declines in sulphur releases from sources closer at hand, with later falls in emissions from sources more distant.

Statistical trend evaluation
The time series review of observations encouraged dividing statistical analysis into two time periods, 1980-86, and 1987-98. Visual inspection of time series confirms that tendencies are monotonic in both time periods, i.e. proceed in a single direction, satisfying statistical requirements. As well as observed circumstances, the development of the EMEP network gives support to this approach. In the earlier period analysis of subregional trends must be made on the basis of a single site in each subregion. The sites were widely spread, and combination of the records of those sites which were in operation to give an overall evaluation for the islands faces the difficulties of homogeneity commented in section 3.3 on account of the enormous variability in weather and climate experienced in the region. During the second period more sites were reporting, largely permitting two or more to be combined for different subregions. Changes made to precipitation sampling are not anticipated to have particular influence on estimated wet sulphur concentrations given the consistent quality of precipitation analysis intercomparison.

All subregions showed statistically significant trends in sulphur dioxide concentrations in both time periods. The rate of decline was not consistent, however, either across time or in space. For the early period although significant, trends in the west on the Atlantic coast were very weak as to be expected. More unexpectedly was a clear downward trend found in SW England. However, the major trends were found on the British mainland, and were of like strength in both southern Scotland and the south-east. It is interesting to speculate on the emission changes which contributed to these changes. Whilst it seems highly likely that those in southern Scotland had largely a national British origin, the non-homogeneity in behaviour of trends across seasons at Stoke Ferry in south-east England should be noted. This may imply differing sources of contaminated air at different times of year, hence disturbance of seasonal homogeneity in air concentrations. From 1987 the downward trends tend to weaken at most locations, as did the decline in both British and Irish and in Franco-Dutch Belgian sulphur releases. However, again the south-east does not fully conform, its rate of decline not being substantially different than pre-1987. Whether emission changes in the regional vicinity, or continental changes, such as those in Germany, were of principal influence cannot be judged.

The picture for airborne sulphate is quite different. Up to the mid-1980s most subregions enjoyed no significant trend in concentrations. From 1987 all subregions have significant declines, with the greatest downturn seen across southern subregions, and the weakest in Scotland and western Ireland. These tendencies are only partly reflected in observations of the sulphate concentrations in precipitation, in that early period changes are weak and equivocal. Later period changes tended to negative but were uncertain. The match is quite imperfect, with large parts of the south not experiencing significant trends at all. As commented for France, it may be speculated that the meteorology of precipitation and of more contaminated air masses is dissimilar.

Table 3.3: Summary statistics for trends in Great Britain and Eire.

	SO_2		**SO_4 airborne**		**SO_4 in precip.**	
	% Change (best est)	*hom*	% Change best est.	*hom*	%Change best est.	*hom*
subregion	slope ±90% µgS m^3yr^{-1}		slope ±90% μgSm^3yr^{-1}		slope ±90% μgSm^3yr^{-1}	
1980-86						
West Coast	–	*(* 1)*	**–**	*(* 1)*	**-24**	*(* 1)*
	+0.025 -0.038		+0.039 -0.186		-0.002 -0.024	
Scotland	**-72**	*(*1)*	**+**	*(* 1)*	**–**	*(* 1)*
	-0.326 -0.498		+0.176 -0.009		+0.006 -0.050	
South-East	**-47**	*(1)*	**–**	*(* 1)*	+	*(* 1)*
	-0.310 -0.778		+0.345 -0.406		+0.080 -0.016	
South-West	**-62**	*(*1)*	**+52**	*(* 1)*	**+**	*(* 1)*
	-0.204 -0.422		+0.105 +0.020		+0.050 -0.042	
1987-98						
West Coast	**-26**	*(+*=2)*	**-31**	*(+ =2)*	**-21**	*(*=2)*
	-0.006 -0.028		-0.004 -0.033		-0.001 -0.011	
East Coast sth.	**-64**	*(*=2)*	**-56**	*(+*=2)*	–	*(+*=2)*
	-0.262 -0.361		-0.067 -0.106		+0.286 -0.249	
East Coast nth.	**-59**	*(* 2)*	**-56**	*(* 2)*	–	*(* 2)*
	-0.154 -0.246		-0.044 -0.078		+0.089 -0.079	
South-east	**-68**	*(* 2)*	**-49**	*(* 2)*	**–**	*(* 2)*
	-0.209 -0.295		-0.065 -0.104		+0.378 -0.519	
South-west	**-61**	*(* 1)*	**-47**	*(* 1)*	**–**	*(* 1)*
	-0.076 -0.159		-0.032 -0.018		+0.003 -0.014	
Scotland and north west	**-50**	*(*=3)*	**-47**	*(=3)*	–	*(*=2)*
	-0.042 -0.083		-0.023 -0.055		+0.061 -0.050	

Key:

'Best est.' indicates best estimate decrease in the initial concentration, expressed in percent, calculated from best fit in annual decrease multiplied over whole period. Those given and in bold face are statistically significant at p=0.1. Direction only (+/-) indicates not statistically significant.

'slope ±90%' indicates upper and lower annual slope confidence limits at p=0.1.

'*hom'* indicates regional homogeneity measures significant at p=0.1. Full homogeneity given as *(+*=[num])* where:
- + indicates station homogeneity,
- * indicates seasonal homogeneity,
- = indicates homogenous season-station interaction,
- [num] indicates no. stations used.

Absence of symbol indicates characteristic dissimilar at p=0.1. Refer to text and Appendix B.

Subregion definition:	1980-86	1987-98
West coast:	IE01	IE01, GB06
Scotland + north-west:	GB02	GB02, GB06, GB16
South-west:	GB03	GB13
South-east:	GB04	GB04, GB07
East coast (nth.):		GB14, GB16
East coast (sth.):		GB04, GB14

3.4.3 East-South Continental Europe

Monitoring network

The East-south region is taken here to mean the region south of the Carpathian-Alp mountain chain, and east of the Adriatic. It is dealt with here in four subregions: i) Czech basin, within the Sudeten highlands and including the Danube valley through the Carpathians; ii) Hungarian plain; iii) NE Balkans, i.e. region of the former Yugoslavia; iv) Mountains: High Alps and Carpathians. South-east Europe itself has seen much less extensive and intensive monitoring than other regions. It is not, therefore, possible to provide description of regional scale long term trends for such areas.

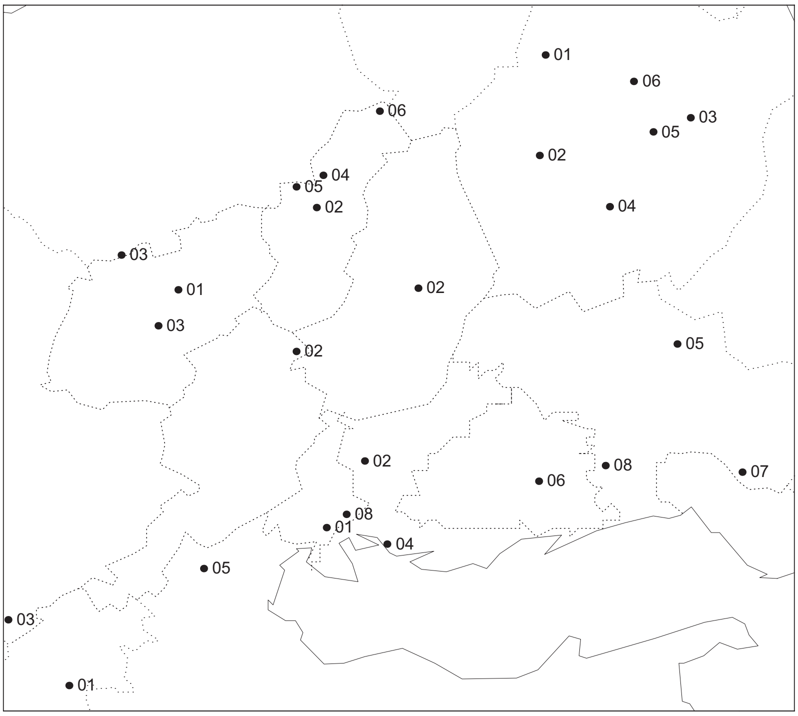


Figure 3.17: East-South Continental Region and monitoring stations.

The record across the east-south continental region is irregular both in time and space (Figure 3.18). For the Czech basin there is one long term record, and this at the neck of the basin, AT0002. Analysis of airborne components changed in 1988, and sampling of precipitation earlier in 1983. Analysis quality remained consistently good for precipitation sulphate from 1981. Additional monitoring in the basin proper was reported only from the end of the 1980s since when methodologies have been unchanged and precipitation analysis intercomparisons have performed consistently well. In Slovakia observations were reported at lower altitudes (i.e. the bulk of the country) not before the 1990s since when methods of precipitation sampling and SO_2 analysis have nevertheless changed (1994). Similarly, only limited reported observations are available for the Hungarian plain. A single record for all three components has been maintained at HU0002. Whilst methods of precipitation sampling and analysis have been consistent until very recent years performance in laboratory intercomparisons has been somewhat below average (see Appendix A). In the Transylvanian hills of Romania intermittent records of precipitation and sulphur dioxide are available for the 1980s. It is to be noted that laboratory intercomparison of precipitation sulphate analysis at this time for Romania supplied the largest relative error (>50%) of the participants. Across the Balkan countries there has been no reported monitoring of airborne sulphate until 1996. Analysis methods have been unchanged for Yugoslavia and Slovenia and FYRM during the period, Croatia reporting changed sulphate in precipitation methods from 1992, and precipitation sampling changing across the region between 1988 and 1992. The large relative error in precipitation sulphate analysis during laboratory intercomparisons should be noted for the former Yugoslavia. Mountainous areas supply the final ‘sub-region’ considered in this section. Given the great variability anticipated in pollutant loading to mountainous sites, the very limited coverage over large distances is a clear restriction. No reported precipitation sampling at all for the Balkan and Transylvanian uplands compounds the picture. Methodological changes have been commented earlier under each country save Italy, for which methods were minimally reported before the 1990s.

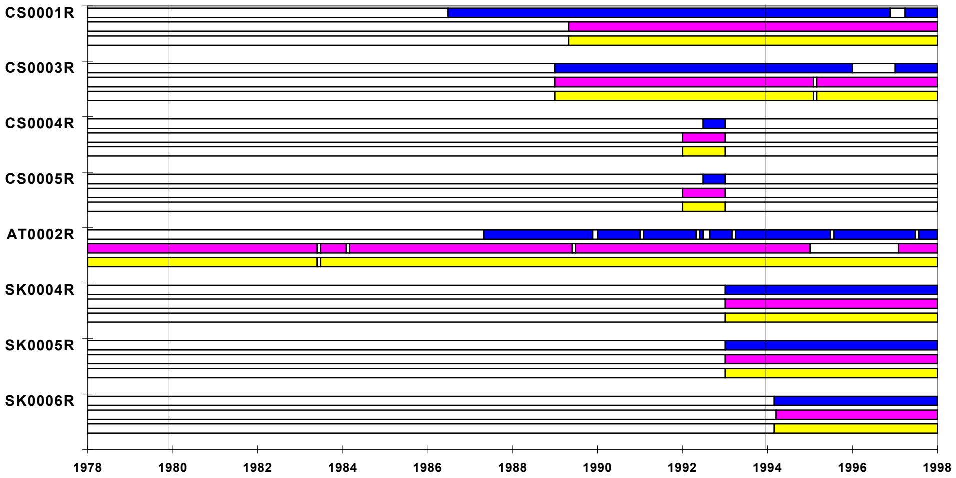
Time series review

Sulphur dioxide

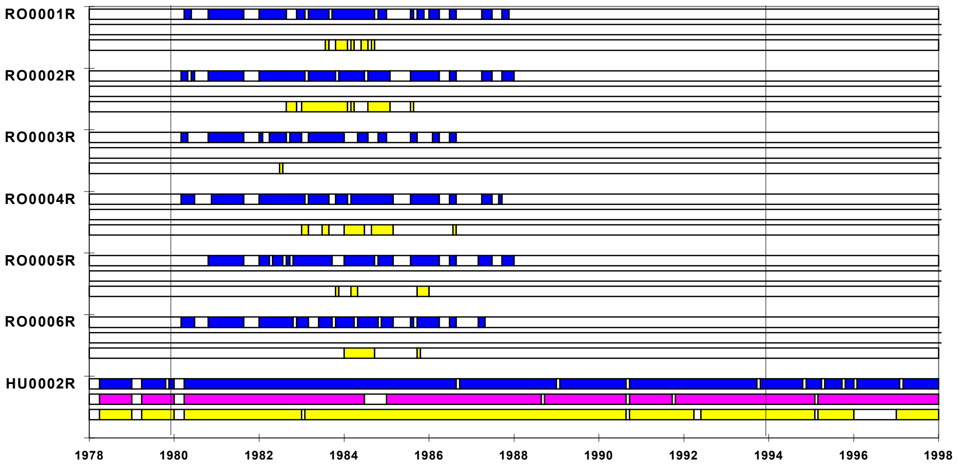
The subregions with greatest emissions, and with the clearest trends, are the Czech basin and the Hungarian plains. Whilst the number of stations with long records is limited, Figure 3.19 suggests good similarity between the **Czech basin** proper and its southern opening onto the Danube valley, justifying its definition as a common sub-region. The long records of observed SO_2 at Illmitz, AT0002, does not indicate any obvious decline prior to the 1990s despite the bulk of Austrian decreases in emission occurring earlier, and rather seems to mirror developments in Czech sulphur emissions. The similar pattern seen high in the Tatras at SK0002, Chopok, with relative stability before decline from the 1990s, the mirroring of the declines thereafter at these stations in observations made in the centre of the basin at Košetice, CS0002, and the correspondence with Czech emission changes suggests a consistent sub-regional phenomena. Observations of changes across the **Hungarian plain** are limited to those from Kecskemet/ K-Puszta, HU0001/2, south of Budapest. Levels are slightly lower than in the Czech basin, and the downward turn begins a few years earlier. Interestingly, comparison with reported emission data indicates better correspondence with declining Czech emissions than did the pattern of Czech SO_2 concentrations. Decline in Hungarian and Slovak national totals began earlier than the fall in their air concentrations of SO_2, these seeing a downturn at the time Czech emissions are reported to decline below 1980 levels. The fall in running mean concentrations between their peak and 1994 was of the order of at least 50% in both subregions.

Moving south into the **NE Balkans** there is also little long term data for the period of the first Sulphur Protocol. Yet patterns seen at quite opposite sides of the subregion, from Croatia to Serbia, are similar (Figure 3.20). At such distance this may be simple coincidence, and indeed, there is little in reported national emission totals of these countries or immediate neighbours to correspond with the pattern. Whatever the causative factor, major distant sources or subregional changes, the apparent decrease in annual concentrations of SO_2 from the start of records (early-mid 1980s) and the conclusion of the Helsinki Protocol was also 50% and above.

Czech Basin -Slovakia



Hungarian plain - Romania



Balkans

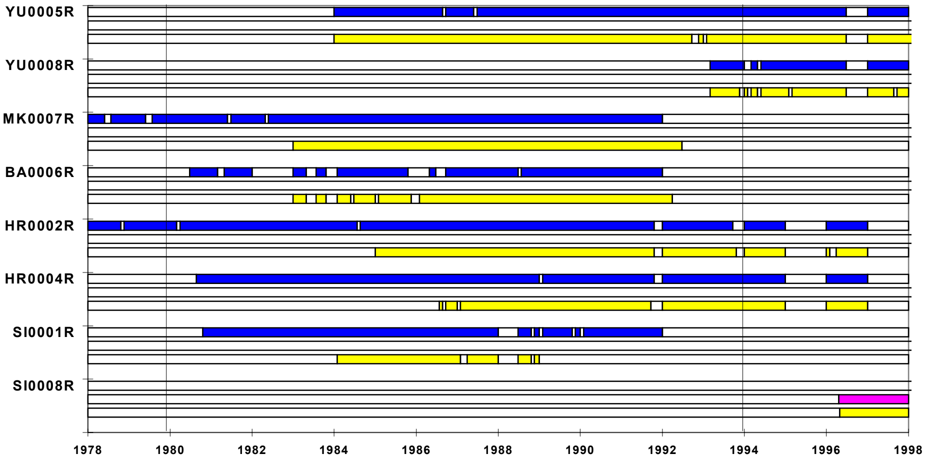


Figure 3.18: Sulphur monitoring records for the east-south Continental region. Submitted to EMEP CCC, with monthly values available after quality control. Blank indicates no or insufficient data, or data not passing quality control. Blue = sulphate in precipitation; red = sulphate aerosol; yellow = sulphur dioxide.

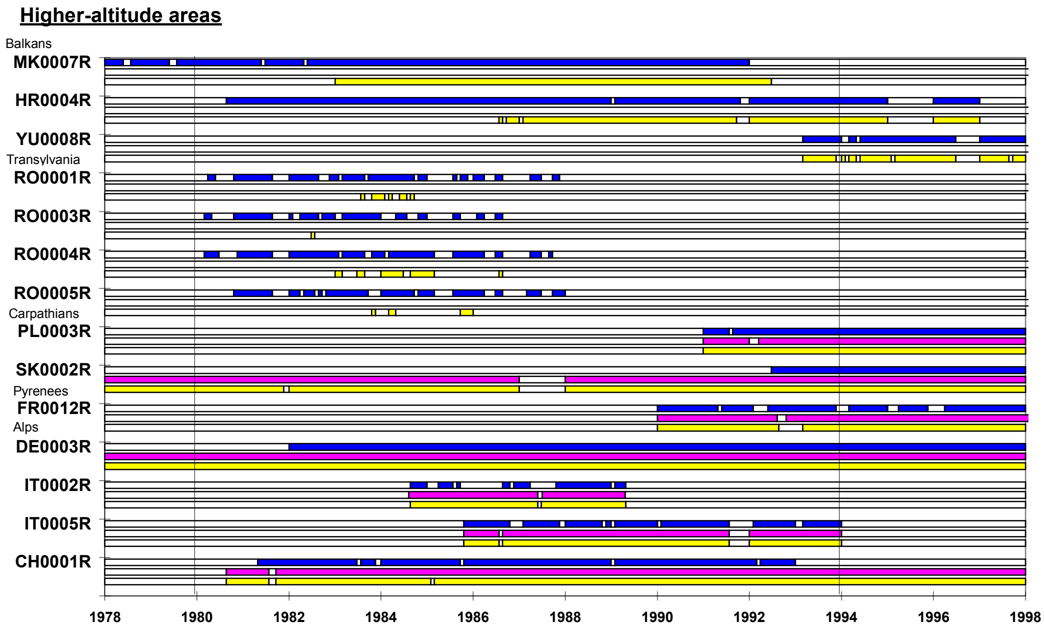


Figure 3.18 (cont.) Sulphur monitoring records for east-south Continental region. Submitted to EMEP CCC, with monthly values available after quality control. Blank indicates no or insufficient data, or data not passing quality control. Blue = sulphate in precipitation; red = sulphate aerosol; yellow = sulphur dioxide.

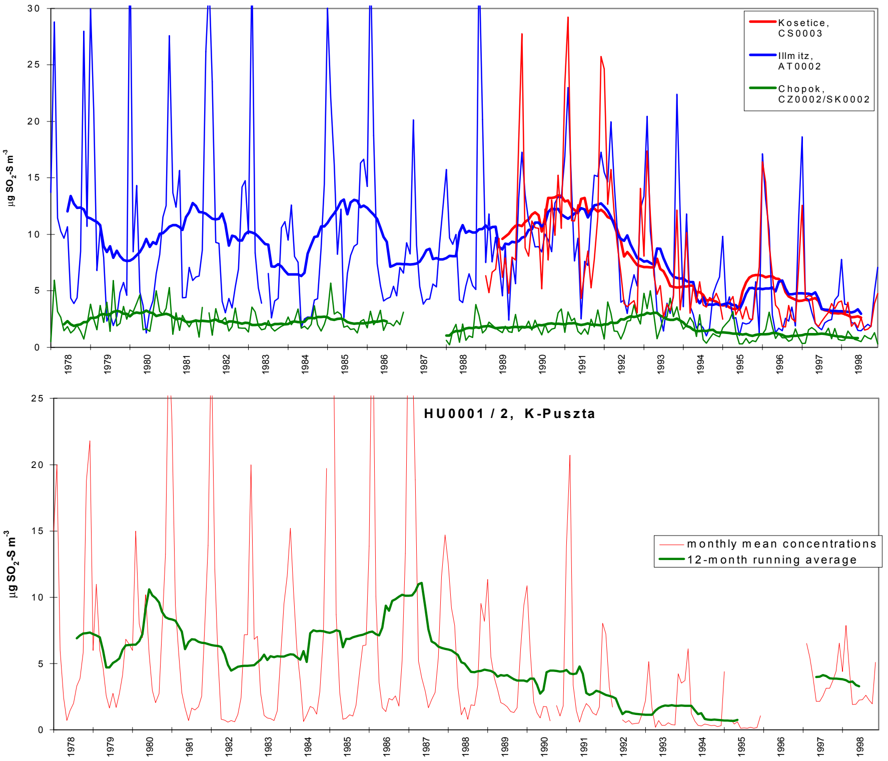


Figure 3.19: Observed SO_2 concentrations: Czech Basin/Hungarian plain. Monthly mean values and running 12-month averages.

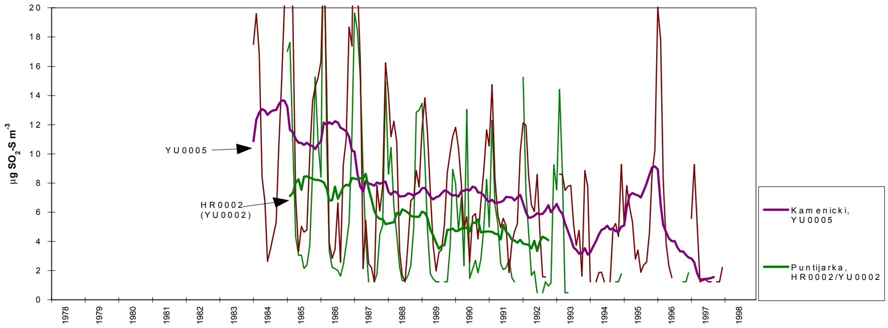


Figure 3.20: Sulphur dioxide concentrations (monthly means and running 12-month averages) in Serbia and Croatia.

The final 'subregion' to be considered in the East-South region is the assembly of **mountain** monitoring sites. These are located across the breadth of the mountain areas, yet have similarity in that they are often high above adjacent emission zones, some can frequently be above the boundary layer which was the previous regime of EMEP's acid modelling, and as mountain sites represent some quite ecologically sensitive locations. This is held of sufficient interest to outweigh their contradiction of spatial grouping as employed in the rest of this report.

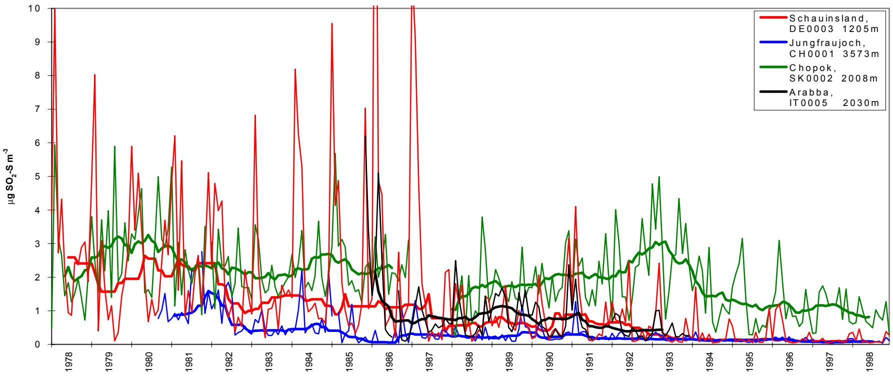


Figure 3.21: Observed SO_2 concentrations in continental mountains. $\mu g\ SO_2\text{-}S\ m^{-3}$, mean monthly and 12-month running averages.

Alpine stations are seen to all exhibit similar patterns (accepting the "foothills" status of DE003, rather than true Alpine). Whilst concentrations at the beginning of the period were quite different, there has been convergence at mean concentrations of well below 0.5 $\mu g\ SO_2\text{-}S\ m^{-3}$. The Slovak station high in the Carpathians, however, has seen a large percentage decrease but still remains far above the others. Across the sites the only regular pattern is one of steady decline.

Sulphate air concentrations

The progression of annual average air concentrations of SO_4 for the **Czech basin** and the **Hungarian plain** suggest that the influences upon these separate subregions have become much more similar. Whilst the late 1970s-early 1980s indicated that the Hungarian plain was exposed to a greater degree to oxidised emissions, these sources have diminished to approximate those affecting the Czech basin, in which subregion the decrease has been less though nonetheless clear (maybe 50%). Of note is that whilst for the period of the first sulphur Protocol both regions exhibit similar development, observations from the years immediately prior reveal that the atmospheric environment of these is actually different.

As may be expected, the **mountain** sites provide an indication of the broader background in long-range transported sulphur. Figure 3.21 gives the running 12-month average concentrations of airborne sulphate observed at Jungfraujoch and Schauinsland in the Alps, and Chopok in the Carpathians. Referring back to Figure 3.20 in which sulphur dioxide concentrations were seen to have been consistently elevated in the Carpathians, there is much greater similarity in exposure of the mid-altitude Alps and Carpathians to airborne SO_4 (SK0002 2008m, DE003 1205m). At greater altitudes (CH0001, 3573m) concentrations have always been around 50% lower. As with the lowland subregions, the temporal change has been rather constant throughout.

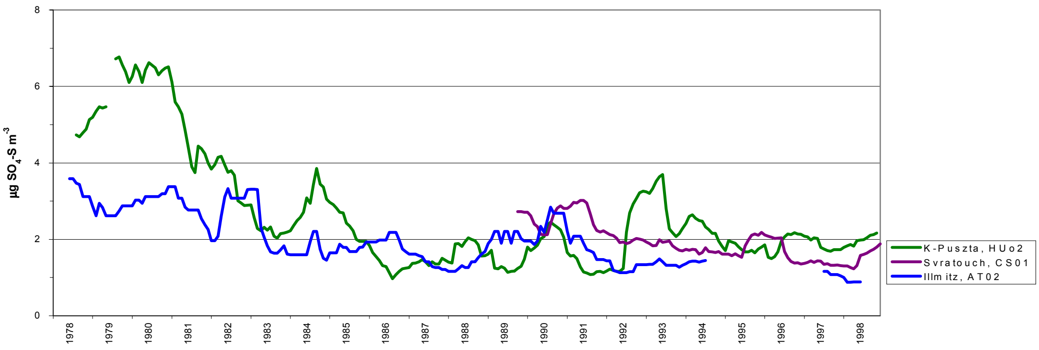


Figure 3.22: Twelve-month running average airborne sulphate concentrations: Czech Basin and Hungarian plain: µg SO_4-S m^{-3}.

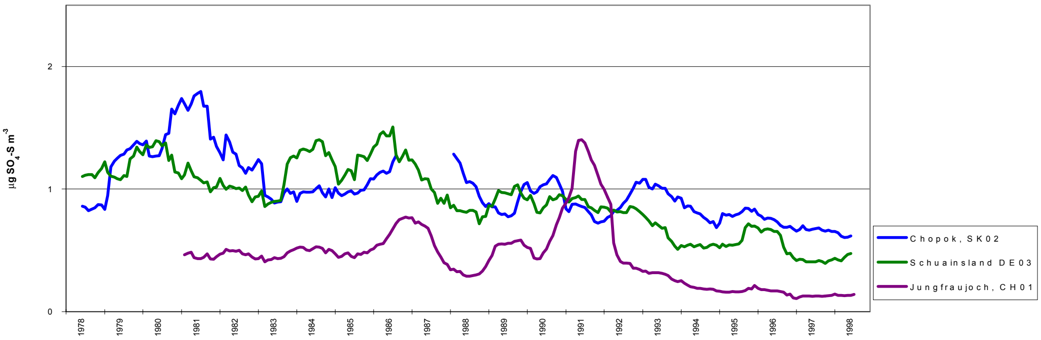


Figure 3.23: Airborne sulphate concentrations in the Alps and Carpathians. Running 12-month averages: µg SO_4-S m^{-3}.

To the end of the '80s SO_2:SO_4 aerosol ratios increased, which as local emissions were not increasing likely reflects falling emissions at distance. Into the 1990s this situation was more than reversed, ratios declining down to values typical for much of Europe. During this period sub-regional emission reductions continued whilst distant reductions slowed. Ratios have remained slightly higher in and adjacent to the Czech basin whose topography may entrap a degree of local emissions. One clear cause of high ratios is SO_2 episodes, e.g. at K-Puszta as shown by the comparative running mean and median concentration curves, and at Illmitz by periodic mean concentration elevation.

Although mid-altitude ratios have decreased on mountains, at high elevations (CH0001) the opposite has occurred. By 1994 at Jungfraujoch (3573m) annual running average aerosol sulphate concentrations had declined by around 60% from 1980. Meanwhile, SO_2 concentrations had fallen by around 80%, with most (60%) occurring by 1985. The comparison with French emission changes in the early 1980s is good, but the continued fall shows that this high altitude location is influenced by wider sources than this.

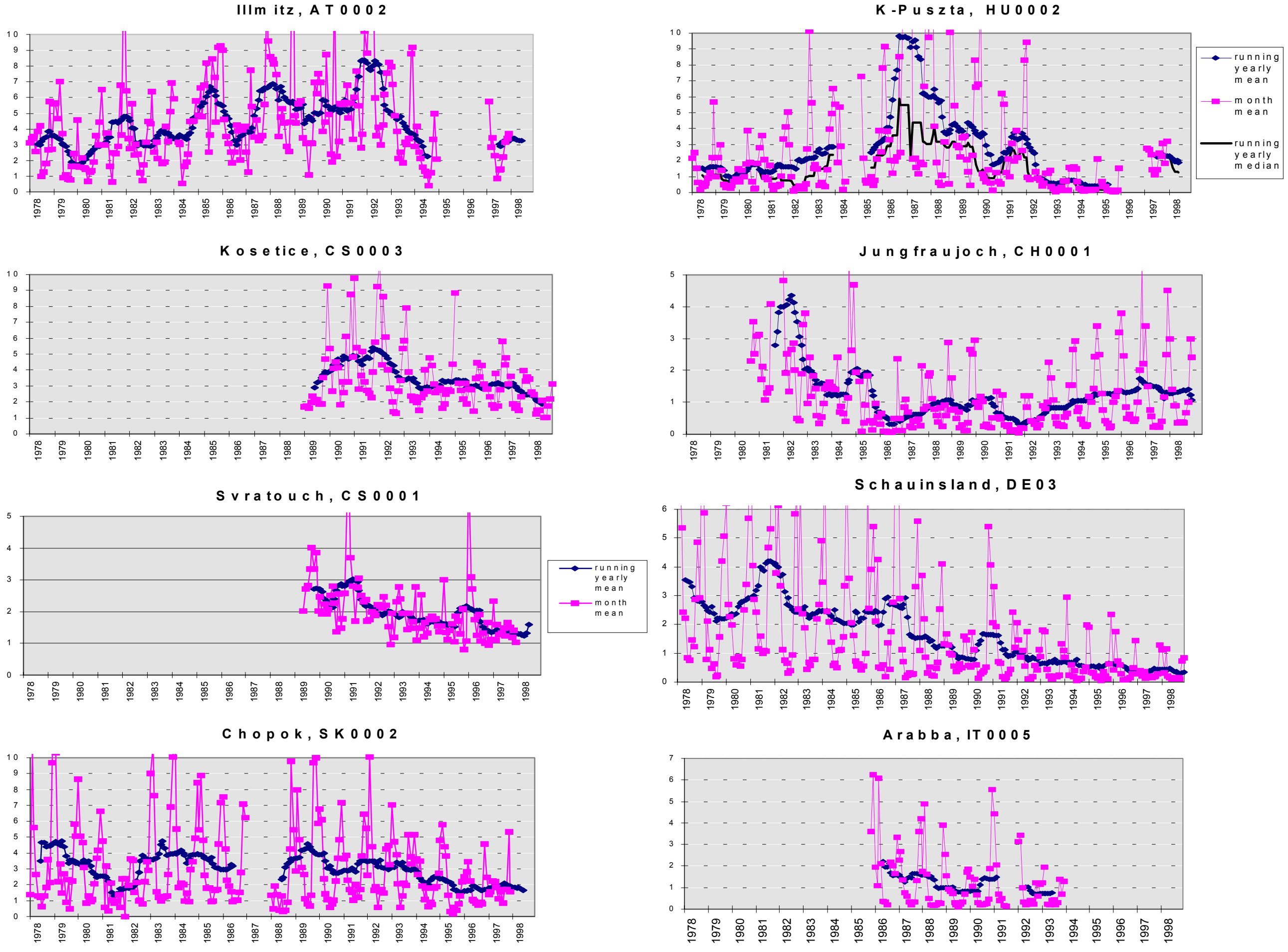


Figure 3.24: SO_2:SO_4 aerosol ratios for the Czech basin, Hungarian plain, and mountain sites. Running annual mean, monthly mean, and running annual median (K-Puszta).

Statistical trend evaluation
Regional statistical analysis of the East-South region suffers from relatively few stations with long records. There is also difficulty from intermittent periods of monitoring which may dictate the periods analysed. For the Hungarian plain it is possible from the long record to divide examination into pre- and post- 1986 on account of the time series review. Review of the monitoring regimes does not indicate distinct periods for trend analysis. Consistency in methods in Balkan areas up to the 1990s, with limited change thereafter provides flexibility, and the paucity of records for most areas requires a pragmatic definition of time periods and choice of stations according to time series review and record availability.

There are obvious limitations which must be understood. Description of the Czech basin during the 1980s on the basis of AT0002 at the basin neck reflects the absence of other stations during this period and relies on the good comparison with CS0003 in the 1990s seen in Figure 3.19. Similarly, using HU0002 to reflect conditions on the Hungarian plain suffers from the relatively poor performance in laboratory intercomparisons, reflects the absence of further data, and relies both on the reasonable comparison in absolute quantities with other regional stations found during review of time series and on the geographical homogeneity of the plain. Examination of trends in the Romania suffers from lack of data, and whilst the Balkans are better served, the size and diversity of the region and still limited observations is a restriction. Finally, with the high-altitude areas the extreme variability encountered in such environments and the paucity of stations (one in the Pyrenees, two in the Carpathians, etc.) means caution should be exercised in interpreting results. On the benefit side these stations will spend lengthy periods above the mixing layer, and as such will be less influenced by sub-regional sources. Thus they may be able to give some indication of the scale of the overall trend in continental scale air quality changes.

Evaluation of the early period indicates no statistical trends in sulphur dioxide concentrations across either the Hungarian plain or the Czech basin. This is in agreement with time series which despite some fluctuations could not be said to show directional tendency. In contrast, the decline in concentrations into the second periods was both significant and strong. Greatest falls were in the Czech basin where concentrations decreased at around twice the rate of Hungarian levels. Overall, however, the total proportional decline 1980-98 was of similar magnitude between these two (70-80%), and quite consistent with trends elsewhere in the region, e.g. the NE Balkans, and on mid-altitude Alpine mountains. Monitoring in the Carpathians, on the rim of the Czech basin observed a slightly weaker decline of 60%.

The changes in airborne sulphate invites questions. The decline in first period Hungarian SO_4 observations is quite strong, and appears somewhat stronger than neighbouring emission changes. Overall European emissions have declined less still. Yet, when the trend for the whole period is estimated the decline is in accordance with national emission changes, and broadly in agreement with European total releases. As with SO_2, Czech basin sulphate declines at a more marked overall rate. Sulphate concentrations in precipitation show very close agreement between the basin and plain, both declining by 60% between 1980 and 1998.

It is interesting that mountain sites do not follow these developments well. The proportional decreases in SO_2 concentrations were slightly higher in the Alps, but lower in the Carpathians. In contrast, the decline is airborne and aqueous sulphate concentrations have been much weaker than in lower lying regions. However, for all developments it should be remembered that with limited numbers of stations description of regional trends must be made with caution. It is, for example, the case that time series review showed restricted agreement between the Czech basin and Hungarian plain, but that statistical analysis indicates greater commonality.

Table 3.4: Summary statistics for trends in east-south Europe.

	SO_2		SO_4 in air		SO_4 in precip.	
	% Change (best est)	*hom*	% Change best est.	*hom*	%Change best est.	*hom*
subregion	slope ±90% $\mu gS\ m^3yr^{-1}$		slope ±90% μgSm^3yr^{-1}		slope ±90% $mgSl^{-1}yr^{-1}$	
Hungarian plain						
1980-1986	ns +0.100 -0.240		-ve -0.417 -0.733	(*1)		
1987-1993	**-ve** -0.440 -0.813	(*1)	-ve -0.130 -0.051	(*1)		
1980-1998	**-71** -0.110 -0.201	(*1)	**-50** -0.042 -0.103	(*1)	**-59** -0.049 -0.082	(*1)
Czech Basin						
1980-1990	ns +0.129 -0.061					
1991-1995	**-ve** -0.896 -1.997					
1980-1998	**-79** -0.518 -0.771	(*3)	**-72** -0.117 -0.174	(+*=3)	**-68** -0.065 -0.110	(*=3)
Slovakia						
1993-1998	**-17** -0.018 -0.189	(+*=3)	**-41** -0.096 -0.180	(+=3)	**-22** -0.072 -0.194	(+*=3)
Romania						
1980-1988					– +0.025 -0.026	(+*=4)
N.E. Balkans						
1980-1994	– +0.445 -0.466	(*=4)			**-35** -0.004 -0.094	(+=4)
High altitudes						
IT/DE Alps 1980-98	**-81** -0.052 -0.099	(*=2)	**-36** -0.009 -0.046	(*2)	– +0.021 -0.042	(2)
High Alps 1980-98	**-83** -0.022 -0.030	(*1)	**-62** -0.017 -0.025	(*1)	**-37** -0.000 -0.017	(*1)
Carpathians 1990-98	**-61** -0.128 -0.243	(*2)	**-47** -0.053 -0.115	(+*=2)	**-41** -0.046 -0.134	(+*=2)
Pyrenees 1990-98	**-79** -0.119 -0.255	(*1)	**-38** -0.019 -0.067	(*1)	**-26** -0.004 -0.049	(*1)
Balkan Uplands 1980-94	+ +0.175 -0.564	(*4)			**-44** -0.026 -0.086	(*=2)

Key:

'Best est.' indicates best estimate decrease in the initial concentration, expressed in percent, calculated from best fit in annual decrease multiplied over whole period. Those given and in bold face are statistically significant at p=0.1. Direction only (+/-) indicates not statistically significant.

'slope ±90%' indicates upper and lower annual slope confidence limits at p=0.1.

'hom' indicates regional homogeneity measures significant at p=0.1. Full homogeneity given as *(+*=[num])* where:

+ indicates station homogeneity,
* indicates seasonal homogeneity,
= indicates homogenous season-station interaction,
[num] indicates no. stations used.

Absence of symbol indicates characteristic dissimilar at p=0.1. Refer to text and Appendix B.

-ve statistically significant negative trend at 90% confidence.
ns trend not significant at 90% confidence.

Subregion definition:

Czech basin: CS01, CS03, AT02, SK02 (not 1991-95, 1980-98)
Slovakia: SK04, SK05, SK06
Hungarian plain: HU02
Romania: R01, R03, R04, R05
High Alps: CH01
IT/DE Alps: DE03, IT05
NE Balkans: HR02, YU05, BA06,, SI01
Carpathians: SK02
Pyrenees: FR12
Balkan Uplands: SK04, SK05, SK06

3.4.4 Nordic and Fenno-Baltic Region

Monitoring network

The region is taken to mean Sweden, Norway, Finland, the Baltic States and immediately adjacent territory of Russia. On the basis of geography and some experiment it has been divided into the following subregions for review and analysis: i) S. Norway, ii) S. Sweden, iii) E. Sweden, iv) Central Scandinavia, v) Baltic States, vi) S. Finland, vii) the North

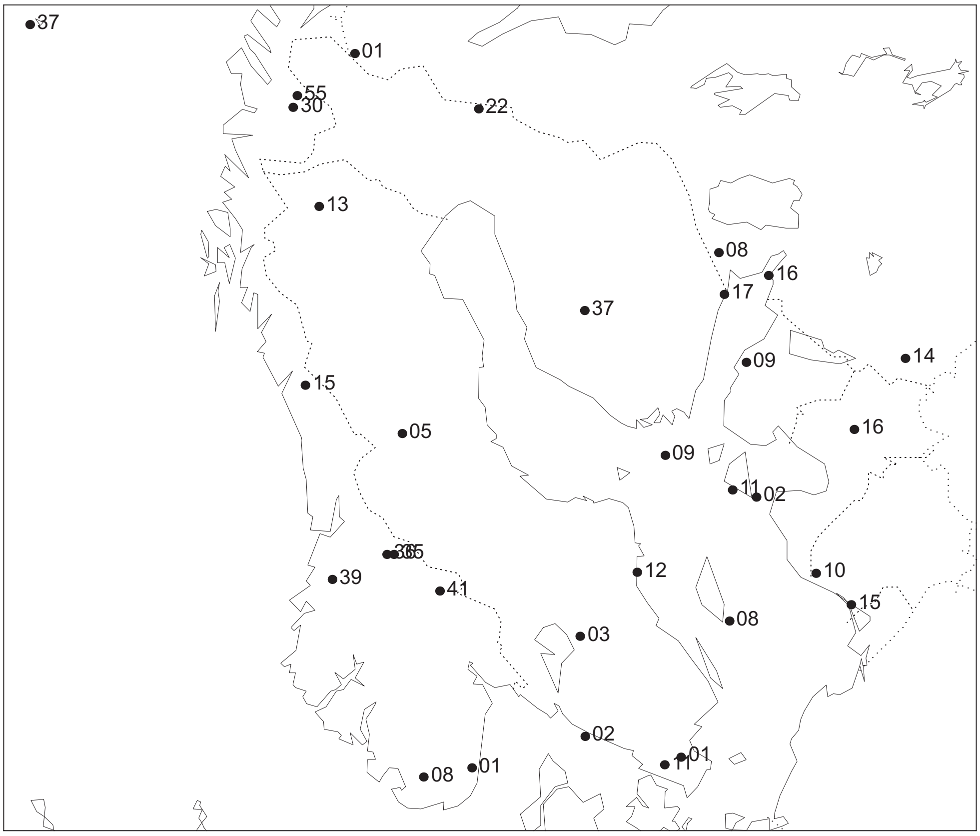


Figure 3.25: The Scandinavian region and monitoring sites.

The southern parts of both Sweden and Norway have been each served by two stations throughout the period. In Sweden a shift of some 10 km occurred in site location for one of these in 1984 (SE0001 to SE0011). In central Scandinavia there was a switch in stations in 1988, and an end to reporting from another in 1990. Otherwise have three stations continued throughout. In northern arctic areas reported observations are spread in time and space. The longest observation records continued until 1997 at NO0030 but were in proximity to major metal smelters. Also in some proximity to these, long records exist from Russia (RU0001). Remaining records from Sweden and Finland did not begin until the 1990s excepting island observations off the north coast, themselves moving further north from 1990. Long records are available for all components from several sites on the Swedish east coast and Finnish south coast of the Baltic. Station site changes have been localised, meaning that the region was served by five-six stations throughout. To the east of the Baltic Sea continuous records are available from dispersed sites since 1988, before which the picture was a little intermittent.

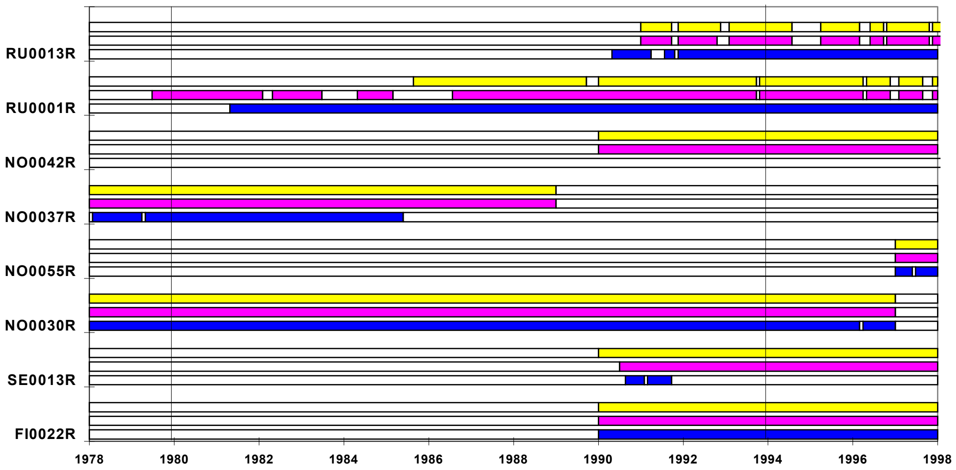
Analytical methods for sulphate in air were changed in Sweden in 1988, and for sulphur dioxide in Norway in 1986. Otherwise changes have been in sampling methodology, although not for precipitation in Norway, or since 1983 in Sweden. All Finnish changes have occurred in 1984 and 1989-90. Intercomparison between laboratories indicate a steady improvement in Swedish performance, albeit with some aberration simultaneous with a switch in precipitation sulphate analysis methodology in 1988. Norwegian performance has remained similar throughout, whilst Finnish performance has been of high quality since the 1980s.

Time series review

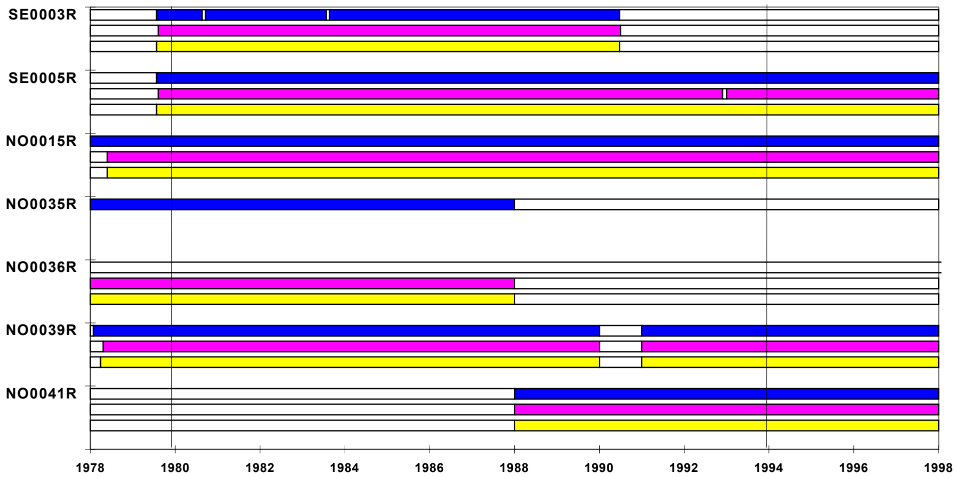
Sulphur dioxide

Figure 3.27 displays example time series for observations of sulphur dioxide made at sites across the subregions of Scandinavia. It is apparent that in general the progression with time has been steady at all sites, and that absolute values for concentrations are one of the chief differences between subregions. For **southern Norway**, NO0008 displays a curve similar to that found for Birkenes, NO0001, with concentrations always typically below a microgramme m^{-3}. Into **southern Sweden**, Rörvik (SE0002) has only recently seen concentrations fall this low. In the early 1980s values were 3-4 times greater than this. This is seen at other southern Swedish sites, e.g. Vavihill, SE0011. The centre of Scandinavia is here dealt with in two groups, being Central Scandinavia to the west, and Eastern Sweden to the east. The two subregions display a decrease in concentrations as compared to the previous two more southerly subregions. For **mid-western Scandinavia**, Kårvatn, NO0039, towards the Norwegian west coast has typically experienced concentrations around 50% lower than in southern Norway. But even if concentrations have been low, a steady and readily observable downward trend has been observed throughout the past two decades. Moving eastwards concentrations have been higher, so that at Hoburg, SE0005, on the **Swedish east coast** concentrations are several times higher. There remains a decrease as compared to the southern Swedish subregion, although at around 30% lower the fall is not as sharp as was seen for mid-Scandinavia. Into the **northern region** and to **Finland**, concentrations are seen to have been higher than seen elsewhere in Scandinavia. The station FI0009 at Utö in Finland is an isolated island site in the northern Baltic, but is still within the south of the country where the bulk of Finnish activity occurs. There is an apparent increase in rate of decline of SO_2 in the later 1980s, although reported national emission totals do not inform as to any possible association. The observations at Jergul, NO0030, are much lower, but are higher than seen in mid-Scandinavia. There is a tendency to falling air concentrations, but this is not so strong as seen elsewhere. Mineral production and processing occurs in various locations in Arctic Scandinavia (particulary the Kola Peninsula) and elevated SO_2 concentrations, such as at Svanvik, is associated with this subregional economic activity. It is important in this time series inspection simply to note that there is a steady downward tendency.

Northern Nordic region



Central Scandinavia



Southern Norway / southern Sweden

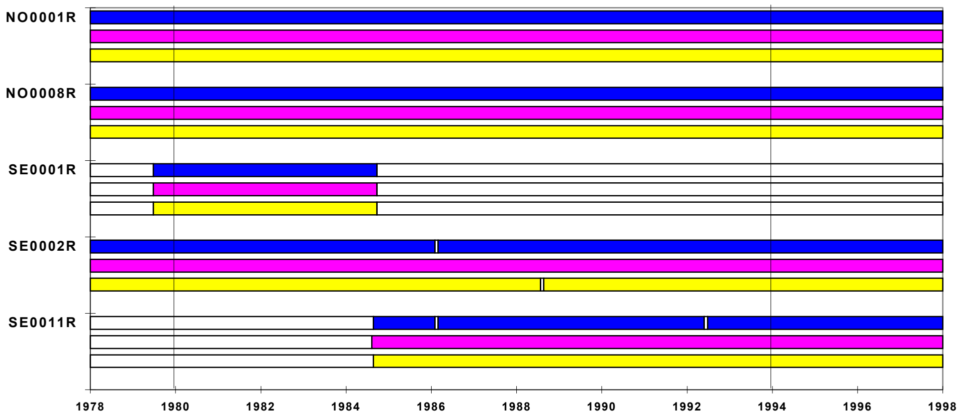
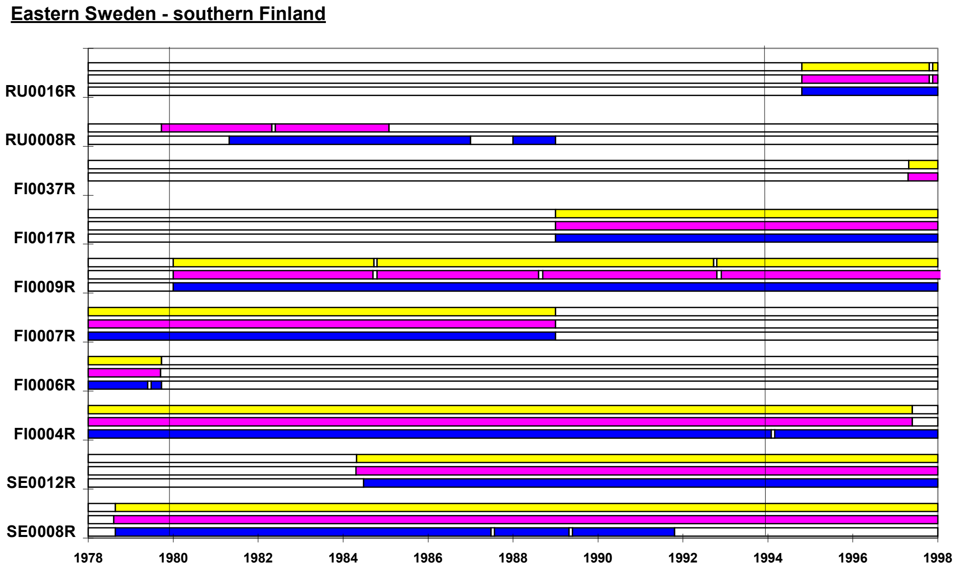


Figure 3.26: Sulphur monitoring records for Nordic and Fenno-Baltic region. Submitted to EMEP CCC, with monthly values available after quality control. Blank indicates no or insufficient data, or data not passing quality control. Blue = sulphate in precipitation; red = sulphate aerosol; yellow = sulphur dioxide.



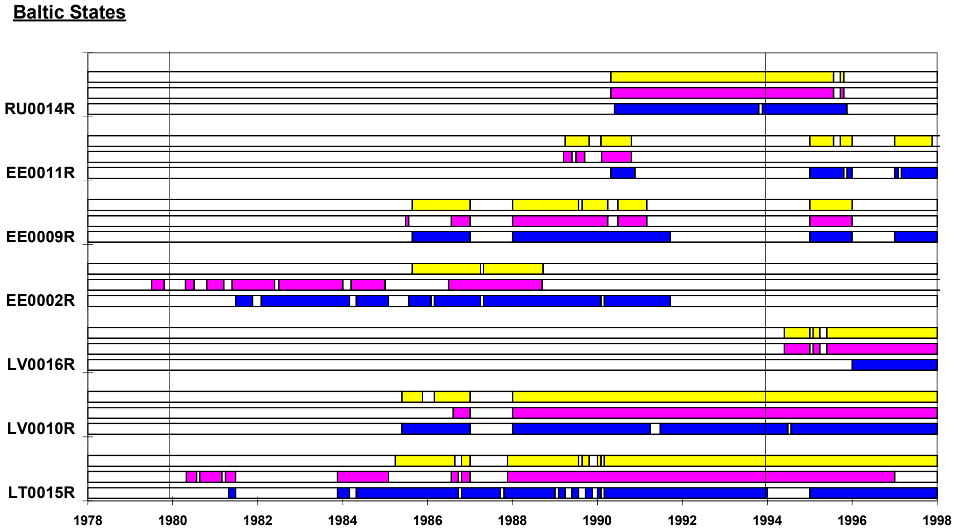


Figure 3.26 (cont.) Sulphur monitoring records for Nordic and Fenno-Baltic region. Submitted to EMEP CCC, with monthly values available after quality control. Blank indicates no or insufficient data, or data not passing quality control. Blue = sulphate in precipitation; red = sulphate aerosol; yellow = sulphur dioxide.

Sulphate air concentrations

Figure 3.27 displays examples of the time series for airborne sulphate. There is some distraction between patterns in the centre and east, and those in the west and north. As was the case with SO_2, levels have been highest in southern Finland, followed by southern Sweden, central Scandinavia and finally the west and north. There is also a suggestion of increased rate of decline in the more affected regions between 1989 and 1992. A change in slope is not obvious in time series for the south and north.

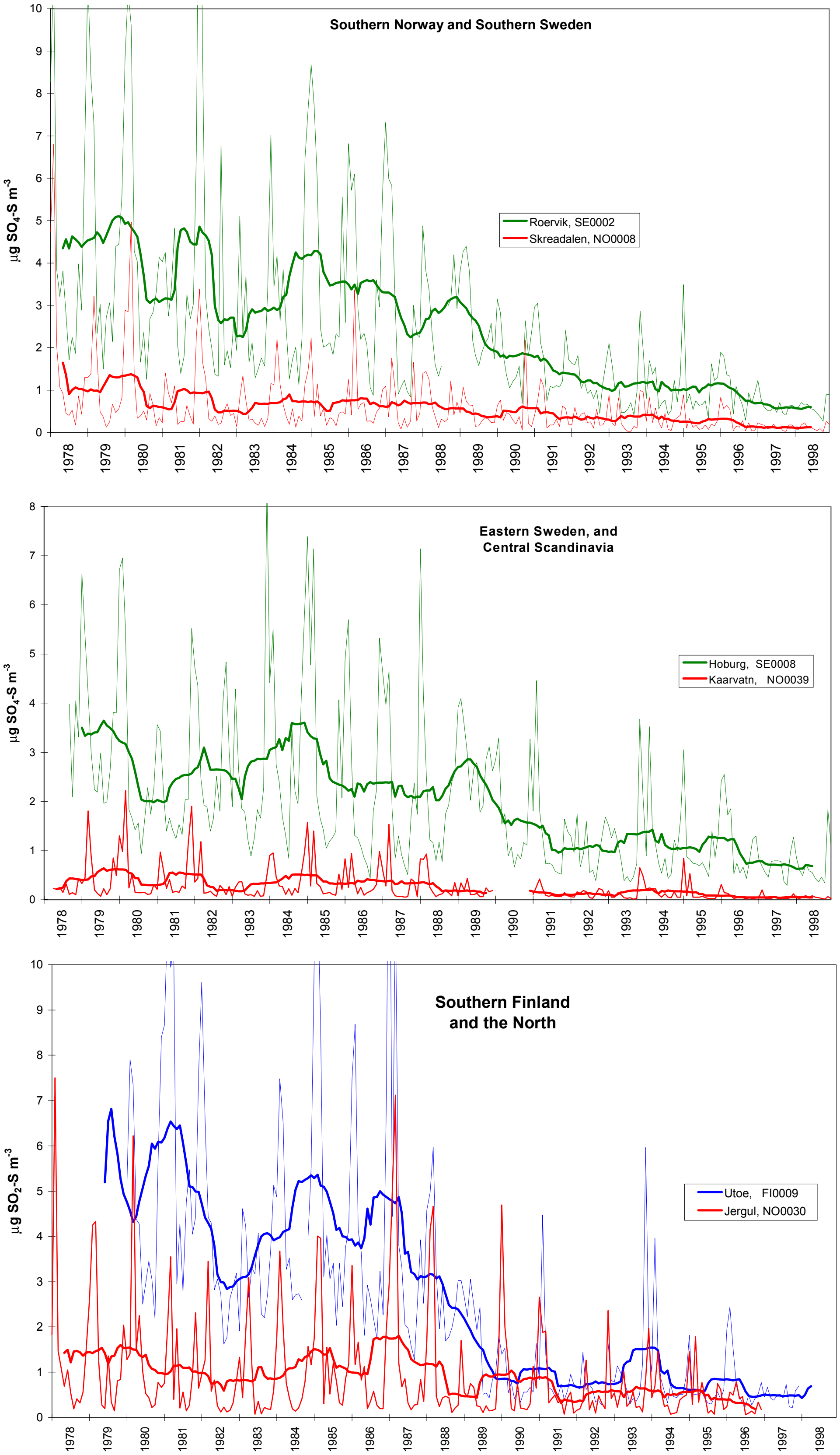


Figure 3.27: Example time series for sulphur dioxide across Scandinavia.

Sulphate air concentrations

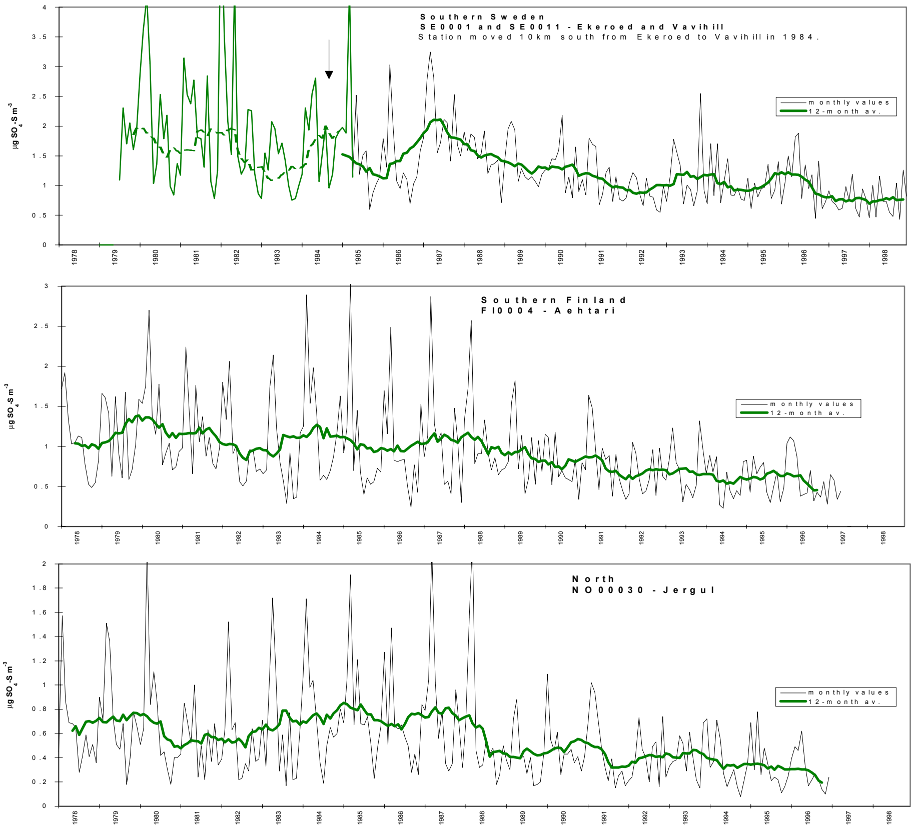


Figure 3.28: Observed sulphate concentrations (µg SO_4-S m^{-3}). S. Sweden, Southern Finland, and the North. Monthly means and running annual averages.

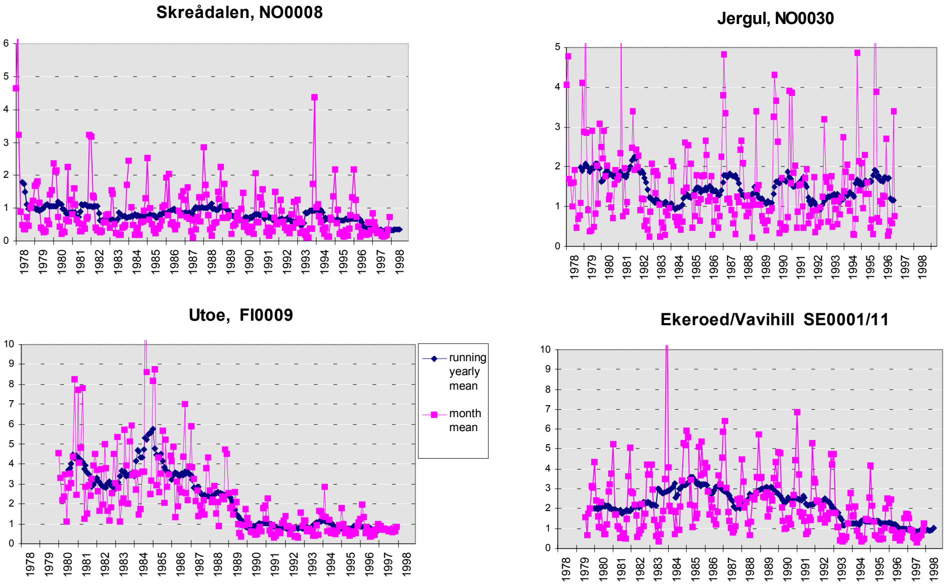


Figure 3.29: Ratios of SO2:SO4 (airborne) in southern Norway, Eastern Sweden, Southern Finland and the north.

Statistical trend evaluation

With time series review indicating not only monotonic, but steady downward tendencies in observed air concentrations throughout, trend significance testing and estimation is suggested for the whole period 1980-98. Review of monitoring and analysis regimes has indicated changes at different times throughout the 1980s with consistency thereafter. This can encourage division of the period into two parts. However, the uninterrupted downward tendencies do not suggest major problems from method changes, and so analysis of the whole period has been conducted. Sites have been combined as shown in Table 3.5 so that no subregion is represented by observations at only a single site. What have been found are stronger trends for SO_2 than airborne SO_4, weaker declines still for sulphate in precipitation, an apparent south-north progression in observed trends in airborne compounds, but a degree of variability in precipitation changes.

Table 3.5: Summary statistics for trends in Nordic and Fenno Baltic regions.

	SO_2		SO_4 in air		SO_4 in precip.	
	% Change (best est)	*hom*	% Change best est.	*hom*	%Change best est.	*hom*
subregion	slope ±90% µgS m^{3}yr^{-1}		slope ±90% µgSm^{3}yr^{-1}		slope ±90% mgSl^{-1}yr^{-1}	
South Norway	**-66**	*(+*=2)*	**-54**	*(+*=2)*	**-46**	*(+*=2)*
	-0.017 -0.028		-0.024 -0.037		-0.017 -0.028	
South Sweden	**-82**	*(*=3)*	**-82**	*(*=3)*	–	*(*=3)*
	-0.114 -0.251		-0.053 -0.143		+0.017 -0.069	
Central Scan.	**-79**	*(*3)*	**-61**	*(*=5)*	**-62**	*(*=4)*
	-0.011 -0.018		-0.012 -0.025		-0.009 -0.019	
East Sweden	**-71**	*(* 2)*	**-59**	*(* 2)*	**-33**	*(*2)*
	-0.066 -0.094		-0.039 -0.060		-0.008 -0.051	
South Finland	**-77**	*(* 4)*	**-51**	*(* 4)*	**-62**	*(*4)*
	-0.105 -0.162		-0.027 -0.060		-0.033 -0.061	
North	**-50**	*(+*=3)*	**-51**	*(*5)*	**-52**	*(*4)*
	-0.008 -0.024		-0.010 -0.026		-0.008 -0.021	
Baltic States	–	*(*=4)*	**-78**	*(+*=4)*	–	*(*=4)*
	+0.031 -0.048		-0.043 -0.155		+0.016 -0.042	

Key:

'Best est.' indicates best estimate decrease in the initial concentration, expressed in percent, calculated from best fit in annual decrease multiplied over whole period. Those given and in bold face are statistically significant at p=0.1. Direction only (+/-) indicates not statistically significant.

'slope ±90%' indicates upper and lower annual slope confidence limits at p=0.1.

'hom' indicates regional homogeneity measures significant at p=0.1. Full homogeneity given as *(+*=[num])* where:
- + indicates station homogeneity,
- * indicates seasonal homogeneity,
- = indicates homogenous season-station interaction,
- [num] indicates no. stations used.

Absence of symbol indicates characteristic dissimilar at p=0.1. Refer to text and Appendix B.

Subregion definition:

S.Norway:	NO01, NO08.
S.Sweden:	SE01, SE02, SE11 (not SO_2)
C.Scandinavia:	NO15, NO36, NO39, NO41, SE05.
E.Sweden:	SE08, SE12.
S.Finland:	FI04, FI07, FI09, FI17.
North:	RU01, NO30, NO37 (80-88), SE13 (SO_4 air), FI22 (89-93)
Baltic States:	RU14, EE02 (not SO_2 or SO_4p), EE09 (not SO_4 air), LT15, LV10

All subregions show significant downward trends for the period. Away from the west coast and far north, at the coarse scale considered here declines in SO_2 concentrations have been typically 70-80% across Scandinavia, and there is little to distinguish subregions. The slightly higher declines in Sweden and Finland may not be surprising given higher rates of emission reductions. More noticeable than the trend magnitudes themselves, however, is the degree of inhomogeneity between sites. Whilst southern Norway and the north displayed homogeneity across seasons, sites and their interaction, the sites of central Scandinavia do not display site or interaction homogeneity. A possible reason for this is the variable influences of westerly and of anticyclonic weather systems on the region during winter and summer, bringing contaminated air masses possessing differing temporal characteristics. Regions subject to consistent influence - the west and north - may thus reveal greater subregion homogeneity.

Decreases in airborne sulphate concentration have generally been slightly weaker. Southern and eastern Sweden have experienced the greater rates of decline, but in general rates across the whole region again do not show large variation, being 50-60% with the noted exception of higher rates of decline in southern Sweden. Alongside this apparent similarity, however, must be taken the statistical inhomogeneity between stations in subregions. On this occasion the least homogeneity is found amongst eastern subregions. Precisely this same station heterogeneity is observed in levels of sulphate in precipitation. As such, the reasonableness of combining trends from separate stations is open to evaluation. Such features as the relative consistency in absolute rates of change across subregions along with restricted geographical groupings will lend weight to the overall estimates of change.

3.4.5 *Iberian Peninsula*

Monitoring network

A natural geographic unit, the Iberian Peninsula is taken as the combined land mass of Portugal and Spain. As a consequence of the monitoring programme followed in each country, and of the air quality time series seen at individual sites, this region is divided into Portuguese and Spanish regions on occasions in this review, whilst at other times is dealt with as an entity.

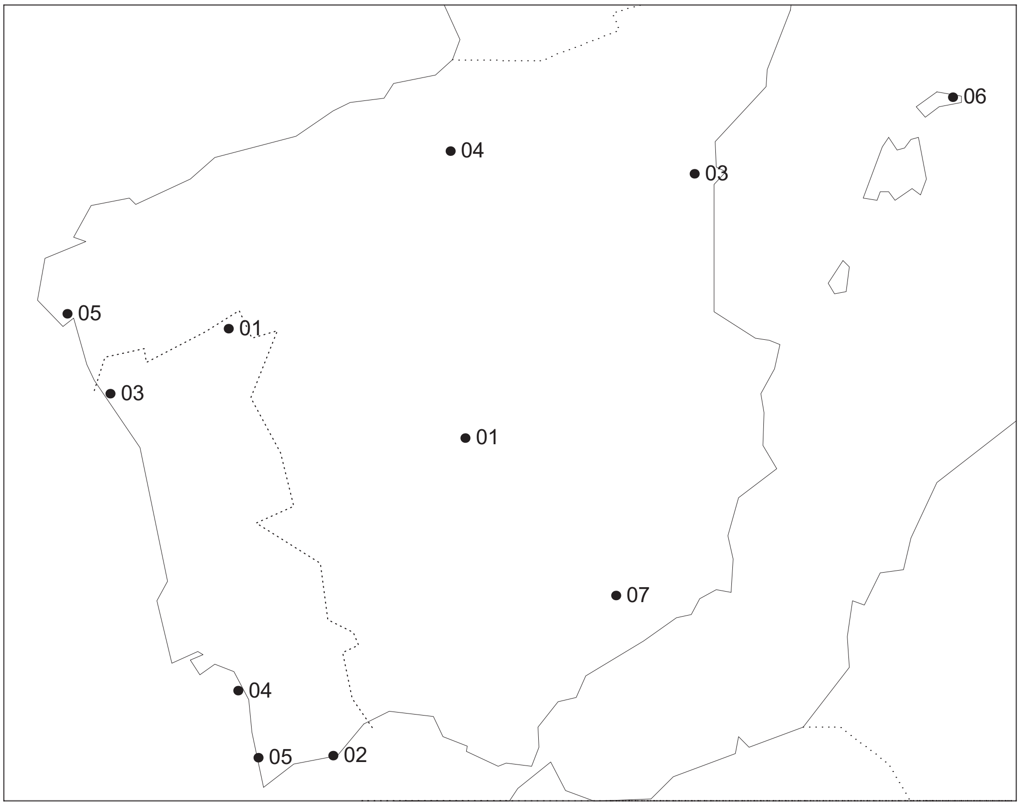


Figure 3.30: Monitoring stations on the Iberian Peninsula.

Reported observations on the Iberian peninsula appear divisible into two parts, before and after the latter 1980s. Long term monitoring, if a little intermittent, is available from one Portuguese station. Until 1986 a second reported, this being replaced by observations from two others in 1987. Neither are in immediate proximity to PT0002 which ceased to report. Further, from 1989 observed sulphate in precipitation data is available. Sampling methods for SO2 and for sulphate in precipitation changed in 1990 and 1991 respectively, with analysis for all three components changing in 1995. Before this analytical change the relative error during laboratory intercomparisons of sulphate in solution was found to be quite variable. In Spain four stations began to report measurements between 1985 and 1988. No data is available before this time. Since 1988 methods of sampling and of analysis have been constant for all components. The quality of aqueous sulphate analysis during laboratory intercomparison has generally given relative errors of within 10%, although 1991 and 1993 indicated greater uncertainty.

The observation record for the remaining Mediterranean is also shown in Figure 3.31. This confirms the paucity of records for the region, and their considerable intermittency. Methods in Greece have been virtually unchanging although the relative error of aqueous sulphate analysis has been consistently found to be moderate. Turkish methods have also been unchanging, and have been accompanied by low relative error in the analysis of sulphate in solution. Reported data from Italy has been somewhat irregular, information on methods used has only been supplied since the mid-1990s, and the relative error in sulphate in solution found to be somewhere between that for Turkey and Greece.

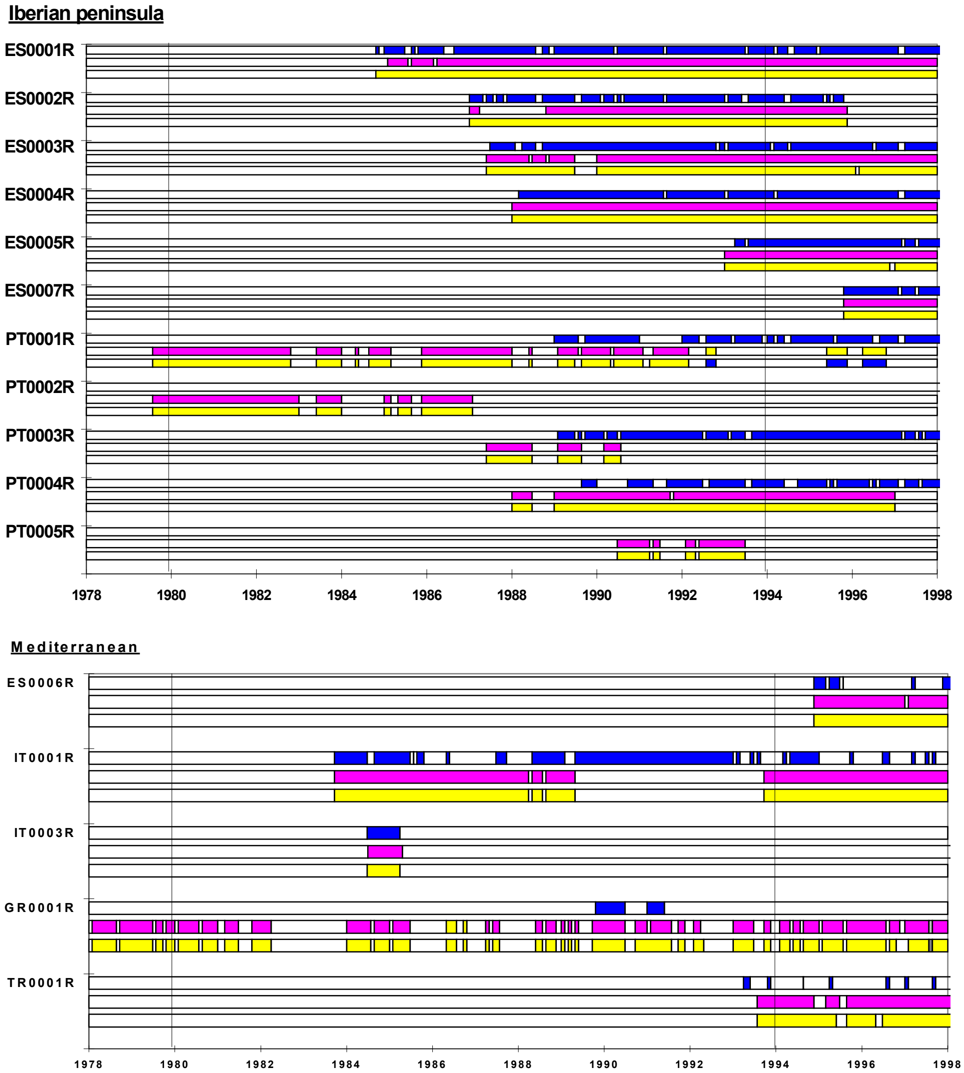


Figure 3.31: Sulphur monitoring records for the Iberian peninsula and Mediterranean. Submitted to EMEP CCC, with monthly values available after quality control. Blank indicates no or insufficient data, or data not passing quality control. Blue = sulphate in precipitation; red = sulphate aerosol; yellow = sulphur dioxide.

Time series review

Monitored data for sulphur dioxide is unfortunately limited for the Iberian Peninsula. Moreover it has rather unusual temporal characteristics. Figure 3.32 displays time series for sites located across the breadth of the peninsula. In eastern Spain near Barcelona is ES0003, Roquetas. In the centre at Toledo, south-west of Madrid, is station ES0001. On the Atlantic coast in Portugal south of Lisbon, is PT0004, Monte Velho. The pattern found is remarkably similar. Both the timing and magnitude of apparent peaks in concentration is quite uncanny. Sites are both coastal and inland, and cover the width of the peninsula. There is no correspondence with reported national emission changes. The scale of the peak means that any calculated trend value will be strongly determined by this, and with records only for a limited period and without further explanation it has been decided that statistical evaluation would not provide information of meaning. Trend analysis of Iberian SO_2 concentrations will here be limited to presentation of these time series.

Observed sulphate concentrations do offer the opportunity for further assessment. Although monitoring in Spain began later at most sites, these then do show consistency, and an apparent slight decline in monitored air concentrations. The one site with longer monitoring also is consistent with the newer sites from that time. This site, however, does show a different earlier trend, a steady rise in observed concentrations which ceased around 1989. It is curious that all sites show some correspondence in their peak with that seen for SO_2.

Sulphate aerosol observations in Portugal are somewhat more erratic in time (Figure 3.33). However, the length of the record and the capability of the SKT analysis to accept missing data mean that statistical analysis can be attempted. Quite inevitably, with data appearing slightly variable and incomplete it is quite proper to treat this with a degree of caution.

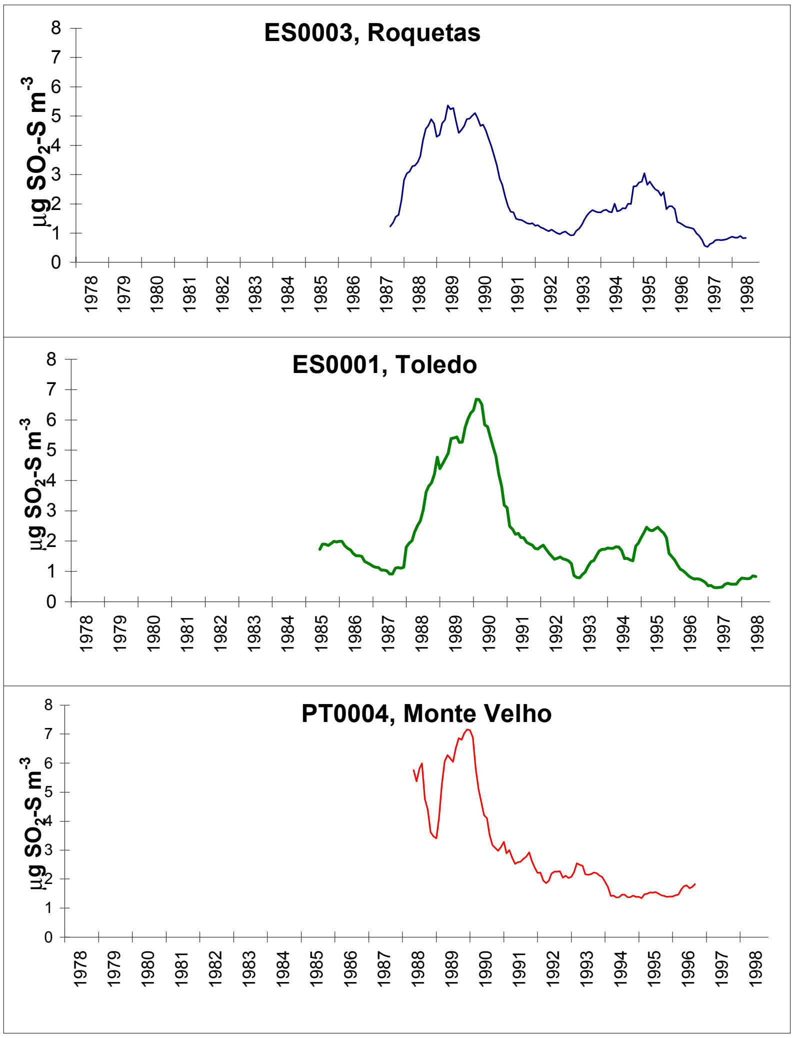


Figure 3.32: Example observed SO_2 concentrations across Iberia: Running annual mean, µg SO_2-S m^{-3}.

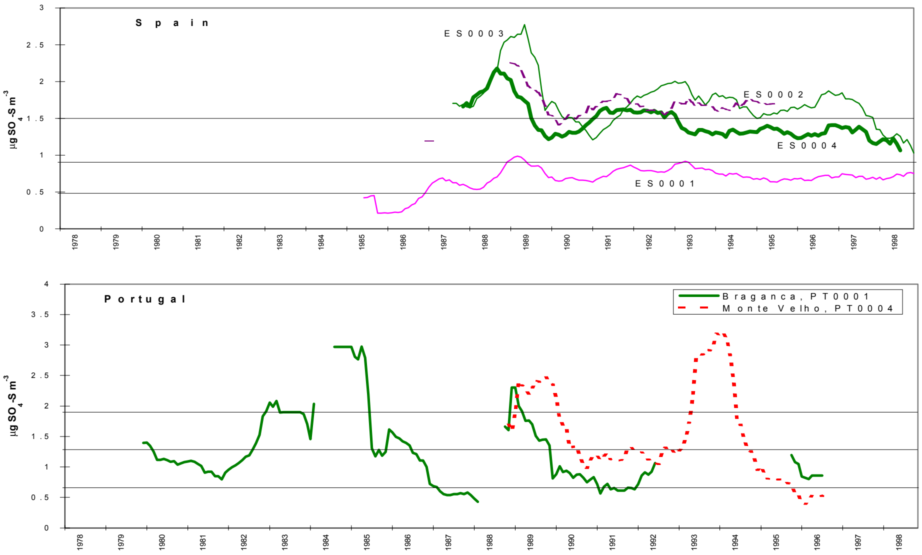


Figure 3.33: Sulphate aerosol in Iberia: running annual mean µg SO_4-S m^{-3}.

Statistical trend evaluation

As commented, statistical evaluation has been conducted only for sulphate, airborne and in precipitation. Division of the region into time periods and subregions has been dictated by data availability. Monitoring has been conducted at three sites in Portugal, allowing a single analysis of this data across the whole period. Nothing in time series review suggested subdivision of time. For Spain, the period from 1989-93 with several sites has been defined as a common unit, whilst the years from 1985-88 with monitoring at Toledo is considered alone.

An apparent decline in observed airborne sulphate concentrations across the peninsula indicated by the separate Spanish and Portuguese observations would initially appear rather undermined by the unusual sharp increases at Toledo in the latter 1980s. However, the use of single stations to describe regional trends must always be tentative, a data record of only four years is limited an thereby more open to spurious influences, and such an increase in sulphur was described by Avila, 1996 in NE Spain from 1989. Her study also suggested an overall decrease in sulphur depositions despite this rise. However, without detailed study little can be offered in explanation.

Table 3.6: Summary statistics for trends in Iberia.

	SO4 in air		**SO4 in precipitation**	
	% Change (best est)	hom	% Change (best est)	hom
subregion	slope ±90% $\mu gS\ m^3 yr^{-1}$		slope ±90% $mgSl^{-1}yr^{-1}$	
1980-93				
Portugal	**-47**	*(=3)*	**+**	*(*=3)*
	-0.014 -0.113		+0.023 -0.026	
1985-89				
Toledo, ES0001	**+353**	*(*1)*	**+**	*(*1)*
	+0.184 +0.117		(+0.074 -0.018)	
1989-1993				
Spain	**-19**	*(*4)*	**+**	*(*4)*
	-0.001 -0.056		+0.050 -0.027	

Key:

'Best est.' indicates best estimate decrease in the initial concentration, expressed in percent, calculated from best fit in annual decrease multiplied over whole period. Those given and in bold face are statistically significant at p=0.1. Direction only (+/-) indicates not statistically significant.

'slope ±90%' indicates upper and lower annual slope confidence limits at p=0.1.

'hom' indicates regional homogeneity measures significant at p=0.1. Full homogeneity given as *(+*=[num])* where:
+ indicates station homogeneity,
* indicates seasonal homogeneity,
= indicates homogenous season-station interaction,
[num] indicates no. stations used.

Absence of symbol indicates characteristic dissimilar at p=0.1. Refer to text adn Appendix B.

Subregion definition:

Portugal:	PT01, PT02, PT04
Spain:	ES01, ES02, ES03, ES04
Iberia:	ES01, ES02, ES03, ES04, PT01, PT02, PT04 (for summary statistics, Table 4.1)

The clear significant trends in airborne sulphate concentrations were not translated into the concentrations of sulphur in precipitation. No significant trends were found for the grouped sites in either Portugal or Spain, and were also not observed beside the dramatic rise in Toledo aerosol sulphate concentrations.

3.5 Nitrogen air quality trends in Europe

As a consequence of less extensive nitrogen monitoring than sulphur the examination of nitrogen trends will not be divided into regional units as was done for sulphur. Rather, this section will be divided into two, one dealing with oxidised and one with reduced nitrogen. Each section will devote discussion to emission patterns, to time series review, and to broad scale statistical assessment.

3.5.1 Oxidised nitrogen

Time series review

Whilst the monitoring of nitrate in precipitation has been as extensive as for sulphate in precipitation, monitoring of airborne nitrogen components has been more modest than for sulphur. As shown in Figure 2.2 the most widely monitored airborne component has been NO_2, and whilst by 1995 the numbers of stations in operation (71) were of similar order to those measuring sulphur (89 for SO_2, 90 for SO_4), this total had grown only during the previous decade from a very low number in 1980 (9), apparently corresponding to negotiations within the Convention for an oxidised nitrogen Protocol. The number of countries monitoring has also only risen to double figures in the last decade which is a further indication of the limitations to spatial discussion. Remaining components have been monitored less extensively and for a shorter period. Components better indicating the effects of long range transport (e.g. NO_3 + HNO_3 in air) have been less monitored than such as NO_2. Overall description of time series hampered by this limited temporal coverage. Given these restrictions to long term consistent transnational observations, comment here on trends is inevitably limited.

Nitrogen dioxide - Widespread long term monitoring of NO_2 has been undertaken by Germany since the 1970s, and Sweden and Norway since the 1980s. Finland operated several stations from the 1990s. A number of stations have operated in the Netherlands, beginning in 1978. Many countries, e.g. Austria, United Kingdom did not report from widespread monitoring until the mid-1990s.

What is noticeable in long term observations in **central continental Europe** is that NO_2 inconsistently reflects changes in national emissions of nitrogen oxides. A strong decline in emissions has been reported for Germany and for the Czech Republic since the late 1980s. Inspection of observed air concentration time series, however, gives a mixed impression. Stations with reasonable agreement include DE0002, Langenbrugge, and DE0004, Deuselbach towards the western border (Figure 3.34). Decline has been of similar order to emission changes, and did not begin until the second-half of the 1980s. In the Czech Republic similarly NO_2 measurements at Svratouch correspond well to reported emission change (see Figure 3.35). These patterns are not observed at other sites. For example, no clear tendencies are seen in the south at Schauinsland, DE0003, towards the Czech border at Brotjackriegel, DE0005, (Figure 3.34, even a suggestion of increase) or on the north coast at Langenbrugge, DE0001. Issues of data quality should not be forgotten. German NO_2 measurements overestimate at low concentrations, making decreasing trends difficult to determine, and Czech NO_2 measurements deviate considerably from reference measurements (Aas *et al.*, 2000). The southern **North**

Sea coast has experienced quite flat time series elsewhere, e.g. NL0002, Witteveen (Figure 3.35).

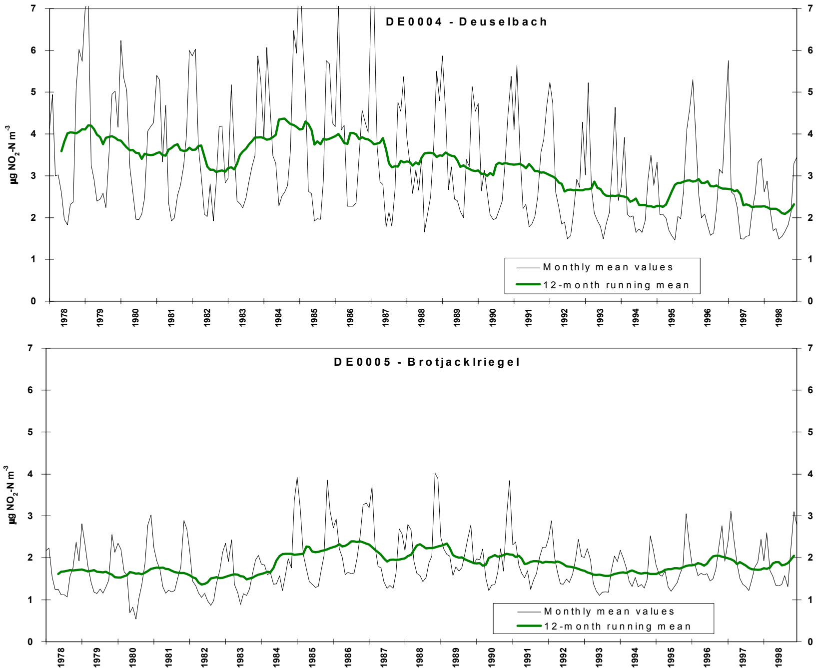


Figure 3.34: Monitored NO_2 concentrations in central continental Europe. Examples of apparent decline (top) and of limited change (bottom). µg N m^{-3}.

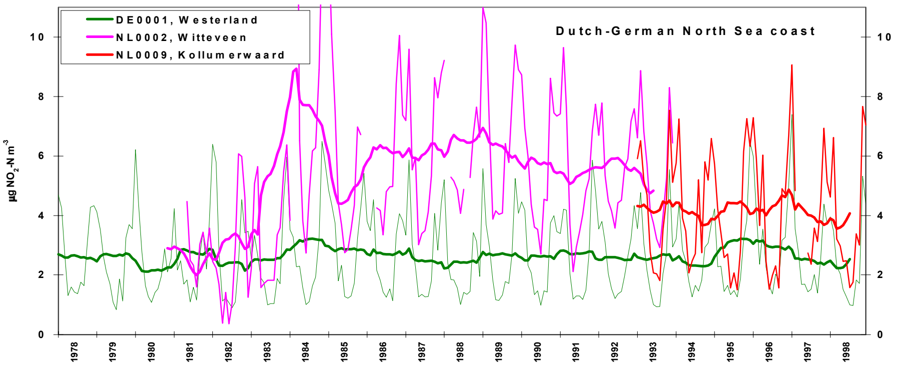


Figure 3.35: Observations of NO_2 along the southern North Sea coast. Monthly mean values and running 12-month averages.

Into the **eastern European plains** there are fewer sites with long records, although these do indicate good comparison with reported national emissions. Poland has reported releases of NO_2 declining by around 1/3 since the mid-late 1980s. In the east Jarcew, PL0002, does indicate a similar scale of decline over this time period. Encouraging comparison is also seen for the Hungarian plain where K-Puszta, HU0002, especially when taken alongside records for Kosetice, CS0003, and Svratouch in the Czech Republic (Figure 3.36). Together these show some of the benefits to be gained from coordinated international monitoring. Taken alone, the time series for K-Puszta indicates that values for 1992-94 are uncertain. When set alongside time series' from stations clearly subject to similar atmospheric conditions the apparent uncertainty appears reinforced, making it possible to propose alternative exposure for the period in question than reported. Such records also allow judgement as to spatial scales of regional similarity.

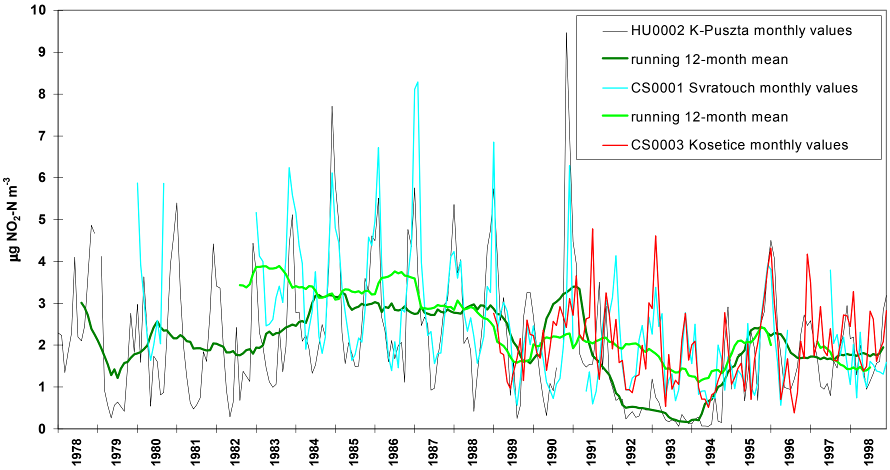


Figure 3.36: Comparison between NO_2 *concentrations observed on the Hungarian plain at K-Puszta (HU0002), and in the Czech basin at Košetice (CS0003) and Svratouch (CS0001). In addition to displaying observed concentrations, potential benefits of coordinated international monitoring are suggested. The comparison in monthly mean concentrations is good, and may indicate uncertainty with measurements made at HU0002 in 1992-4.*

Whilst from limited records there appears a degree of commonality in circumstances over the east European plains, in **Scandinavia** there is perhaps greater heterogeneity. There is also strong indication of strong transboundary influence. A very consistent picture is found in concentrations measured at Norwegian sites (Figure 3.37). Since the mid-1980s concentrations have declined by around 1/3 at all sites. Given the lack of correspondence with Norwegian nitrogen dioxide emissions (which between 1980 and 1998 have increased by approxiately one-fifth) there is clear influence by non-national sources. It may be recalled that UK and German emissions did not rise during this period, rather declining by around 35-45%. Swedish emissions also declined during this period by a similar order, although atmospheric concentrations observed throughout Sweden show a different picture. Certainly across southern regions the time series indicate between unchanging and increasing air concentrations (Figure 3.37). Observations have also been made in Finland, although only since the 1990s, and then with some intermittency in reliable results. Due to difficulties, observations from the 1980s at Utö are not employed for trend analysis (Kulmala *et al.*, 1998).

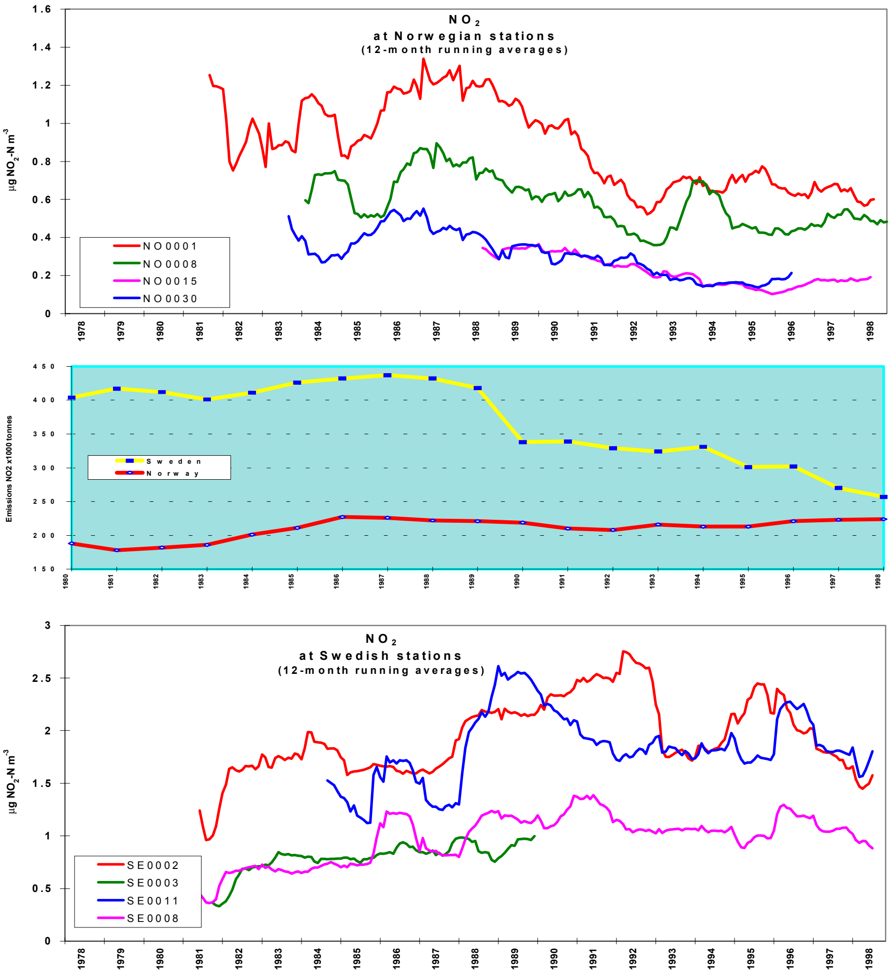


Figure 3.37: Comparison between observations of NO_2 concentrations at Norwegian and Swedish sites, and with reported emissions of NO_2 in those countries.

Widespread **Spanish** monitoring commenced in the 1980s, although results have been frequently found to be inconsistent with EMEP's modelled estimates (e.g. Barrett *et al*., 1995). Figure 3.38 displays a curious similarity in reported observations across stations. Without clear explanation for this characteristic, the Spanish NO_2 observations have not been employed further here for trend analysis.

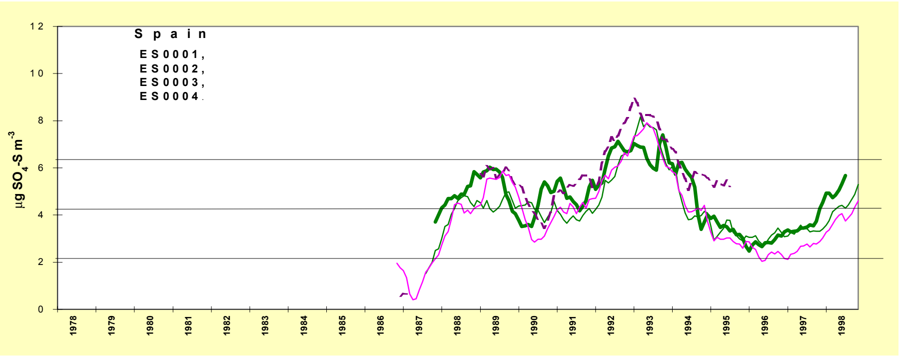


Figure 3.38: NO_2 concentrations across Spain. 12-month running means.

Nitrate in air - As mentioned, monitoring of HNO_3 + airborne NO_3 has been less extensive. In most places monitoring did not begin before the end of the 1980s. Observed changes over this shorter period in regions can merely be suggested by individual time series'. In Figure 3.39 some examples of monthly mean concentrations measured at points across the continent are displayed. Tendencies are not seen to be strong in any of these. In southern Sweden (SE0002) the suggestion is of a downward change, at least to the end of the 1980s. Further south in Poland there is little sign of any directional tendency. Also plotted on this figure is the running annual mean observed concentrations at Payerne in Switzerland. Again, no trend is discernible. Finally, examples are plotted from Spain, showing opposite tendencies at the two stations. Common to all of these is the similar absolute concentrations observed, and the strong seasonal changes.

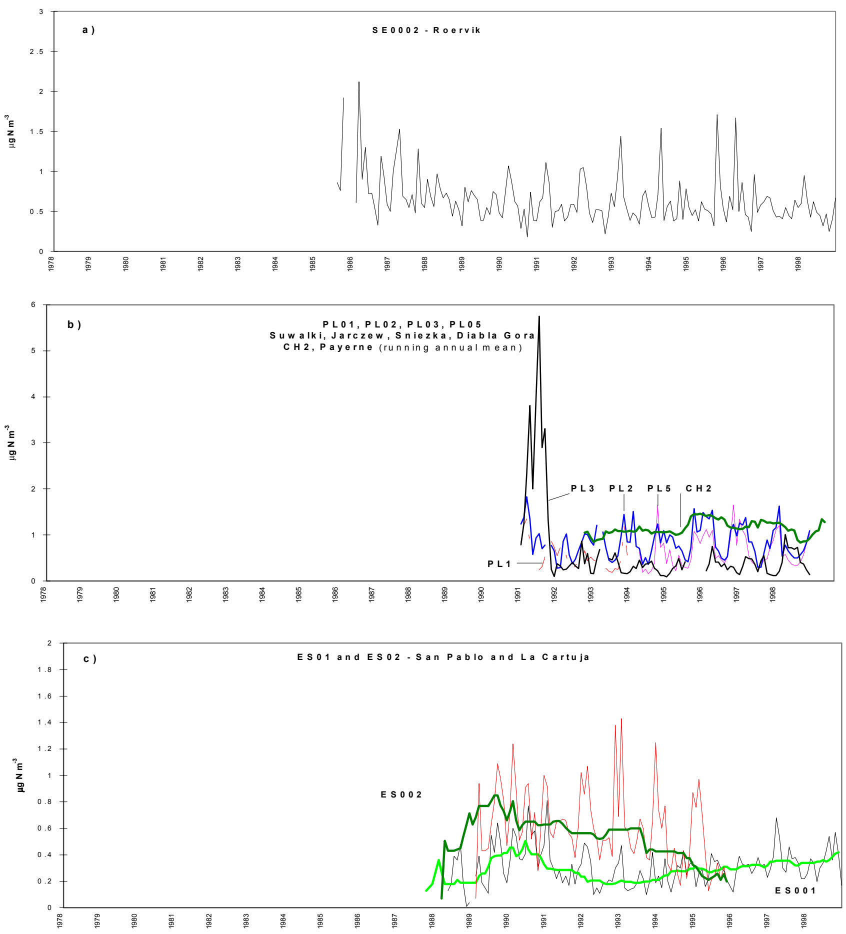


Figure 3.39: Examples of observed sum of HNO_3 + NO_3 airborne. Monthly and running annual means. $\mu g\ N\ m^{-3}$.
a) Southern Sweden   b) Poland and Switzerland   c) Spain.

Nitrate in precipitation - Not surprisingly, given the importance of secondary components to aqueous forms and the consequent roles of time and distance, time series of nitrate concentrations in precipitation show considerable similarity across Europe. In Figure 3.40 the observed monthly and running 12-month concentrations are displayed from 24 sites across the breadth and length of Europe.

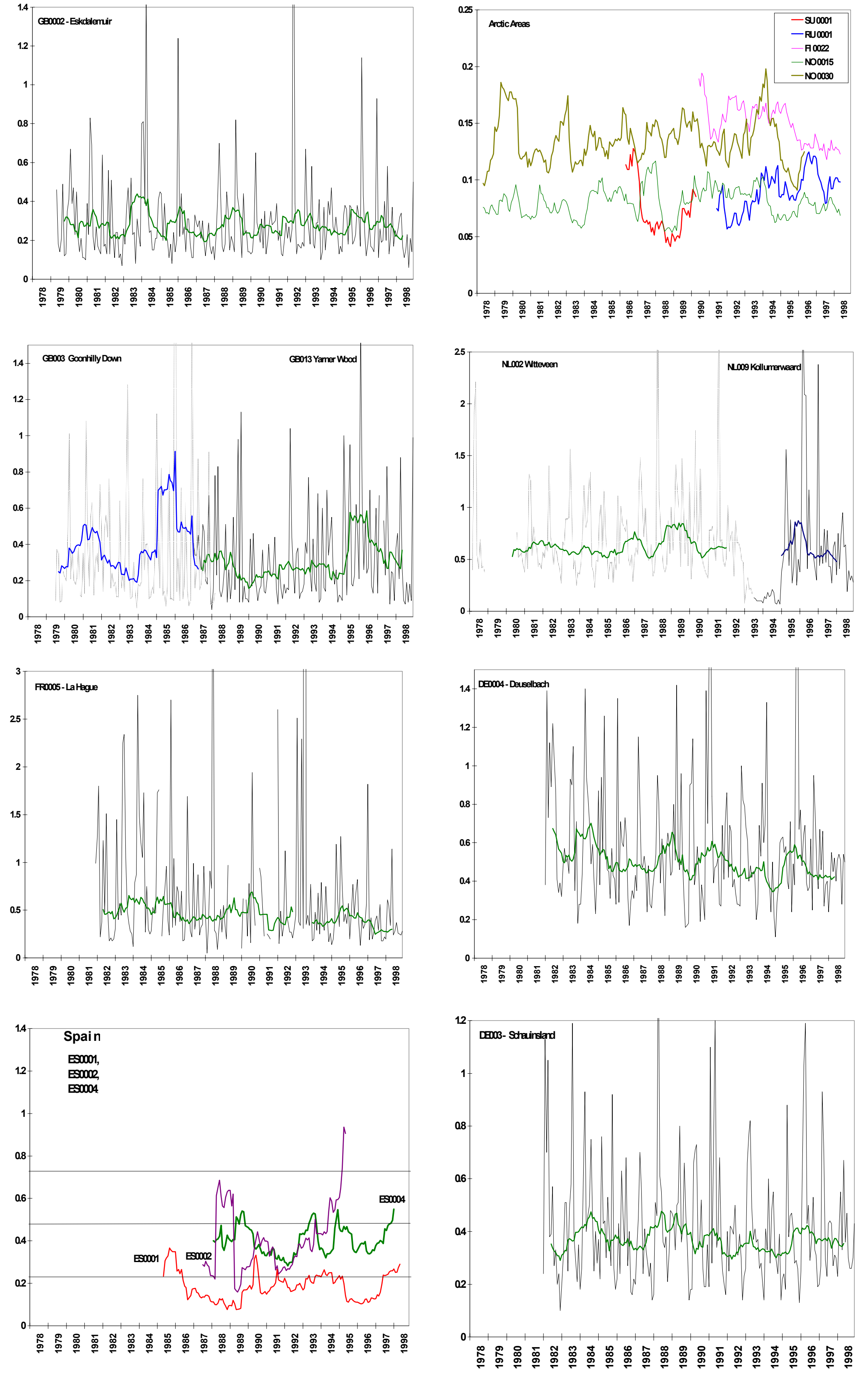


Figure 3.40: Nitrate in precipitation concentrations across Europe: mg N l^{-1}.

a) Scotland Eskdalemuir GB02	*e) Arctic SU01, RU01, FI22, NO15, NO30 (annual)*
b) SW England Goonhilly GB03 Yarner Wood GB13	*f) Netherlands Witteveen NL02 Kollumerwaard NL09*
c) N France La Hague FR05	*g) Germany-west Deuselbach DE04*
d) Spain (annual averages only) ES01, ES02, ES04	*h) Germany-south Schauinsland DE03*

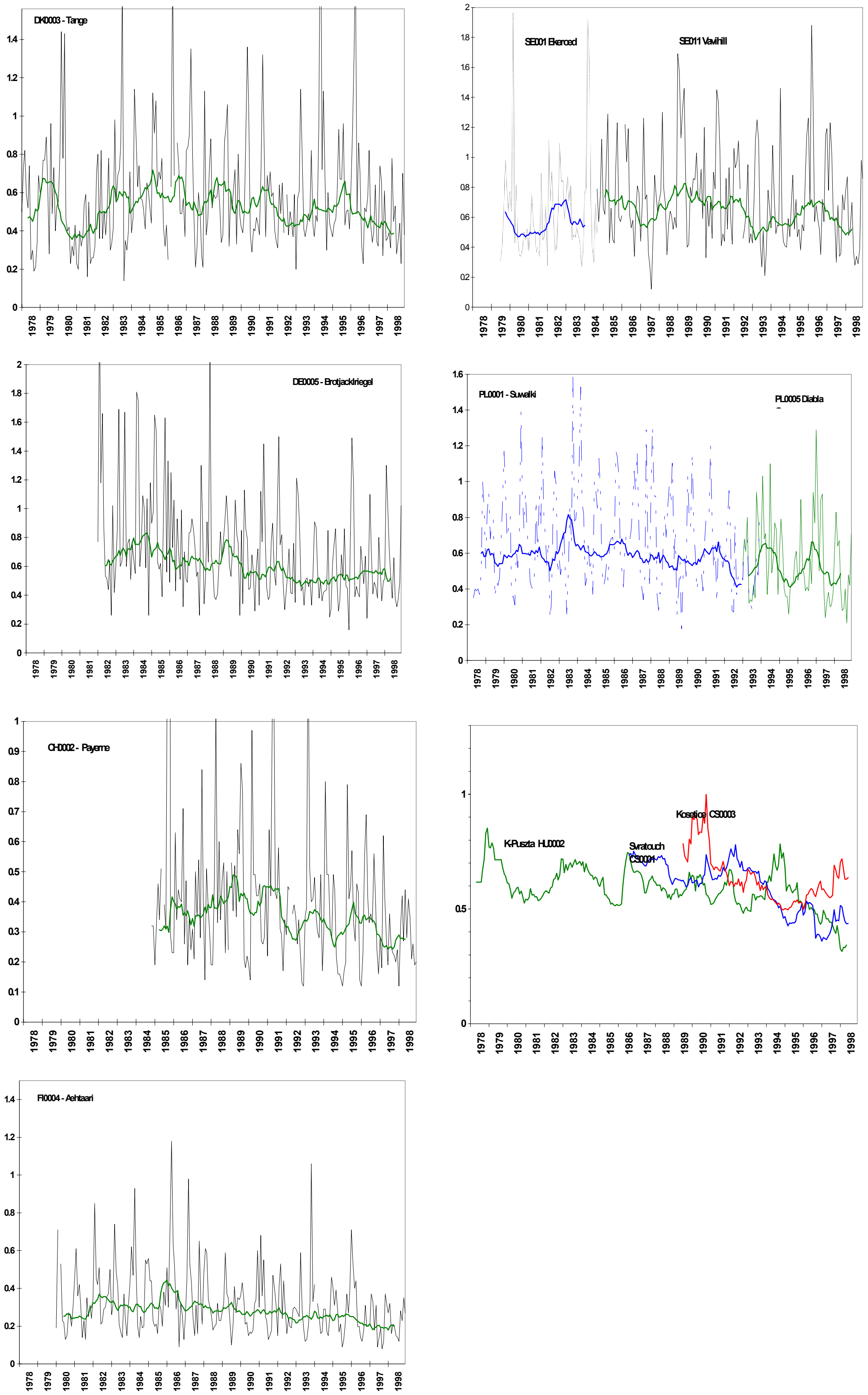


Figure 3.40 (cont): monthly and prec. wgtd. annual running mean concentrations.

i) Denmark Tange DK03
j) Germany-east/south Brotjacklriegel DE05
k) Switzerland Payerne CH02
l) South Finland Aehtaeri FI04

m) south Sweden Ekeroed SE01 Vavihill SE11
n) Poland Suwalki PL01 Diabla Gora PL05
o) central plains K-Puszta HU02 Svratouch CS01
Kosetice CS03 (annual only)

Tendencies upwards or downwards are not dramatic. This is also not surprising when reported emission reductions in nitrogen oxides for the whole of Europe of under 20% between 1980 and 1998 are considered (Figure 1.1). Decreases in the concentration of nitrate in precipitation by a similar proportion are seen to have occurred over large areas of continental Europe, from northern France, through Germany, to the northern and central plains of Eastern Europe. In more peripheral areas these decreases are less immediately evident, for example in northern and south-west Britain, Arctic regions, and even into Scandinavia. On the Iberian peninsula there is, to the contrary, a suggestion of rising concentrations.

Good comparison between adjacent sites is reason for confidence in the comparability of aqueous nitrate measurements, and for confidence that sites do offer regional representativity for this component. The closure of one site and opening of another at distance but within the same region has on various occasions not led to dramatic changes in observations. Several examples are given in Figure 3.40. Shifting from Goonhilly Down to Yarner Wood in SW England, from Ekeröd to Vavihill in southern Sweden, and from Suwalki to Diabla Gora in Poland all appear to have had limited influence. As was seen for NO_2, there is good comparison between sites in the Czech basin and on the Hungarian plain. Given the very low concentrations observed, similarities in trends in Arctic areas across Finnish, Norwegian, Soviet and Russian jurisdictions are encouraging. In summary, there has broadly been a downward tendency in observed nitrogen oxide concentrations in air and precipitation of similar scale to emission changes, the latter being more homogenous than the former. Air concentrations of NO_2 do appear to more reflect regional emission changes, as expected, but not necessarily of a country itself. The quality of precipitation with respect to nitrate away from the periphery suggests more of a common European environment.

3.5.2 Reduced Nitrogen

Attention here focuses on ammonium in precipitation. Monitoring of airborne reduced nitrogen concentrations is less comprehensive than for oxidised nitrogen making discussion of trends somewhat limited in the context of a review of European scale changes to air quality. However, even with precipitation concentrations care must be taken. In contrast to the emissions of oxidised sulphur and nitrogen, the ammonia sources are area sources. Originating from agricultural activities the reactive ammonia will often be released at ground level and relative short distances from measurement sites causing site representativeness problems for ammonia and ammonium. This can be seen from the spatial correlations which are much shorter for ammonium than for sulphate and nitrate in precipitation, suggesting that observed increased/decreased ammonium concentrations may be due to changes on a local, rather than regional scale.

Time series review

Ammonia+ammonium in air - A number of the available time series’ show some fluctuation. Both emission changes and local contamination may be the casue of this. Displayed in Figure 3.41 are examples of common patterns. Observations from Keldsnor in Denmark have been made broadly within what may be considered a source region of ammonia emissions. Two time series’ from peripheral regions accompany this, one from the north at Oulanka, Finland, and one from the west at Eskdalemuir, Scotland. Neither of the peripheral sites show the decline in air concentrations seen at the centre. This may indicate that much removal of reduced nitrogen occurs before transport over considerable distances, and may also reflect reduced production of ammonium as ammonium sulphate due to decreasing air concentrations of sulphur with emission abatement. Appendix B gives estimates for all time monitoring stations.

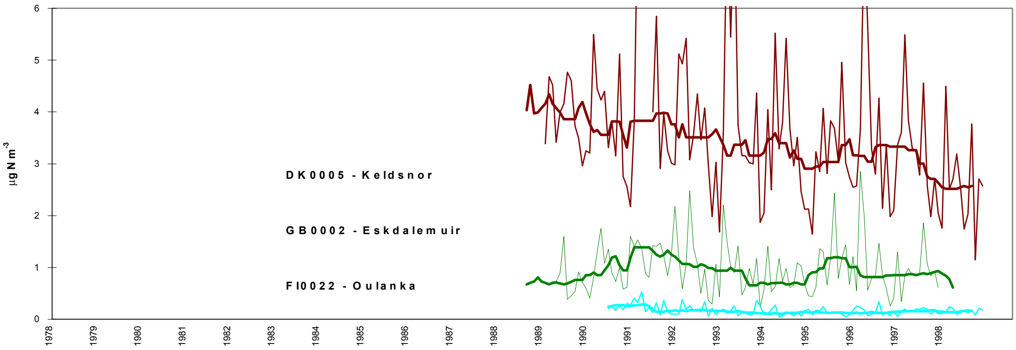


Figure 3.41: Examples of observed airborne ammonia+ammonium concentrations. Monthly and running annual means. µg N m^{-3}.

Monitoring of the separate reduced nitrogen airborne components has not been extensively undertaken. Indeed, the ammonia fraction is the least monitored nitrogen component. No stations were operating in 1980 or 1985, the total increasing somewhat reluctantly to 3 in 1990 and 6 in 1995. More effort has been given to ammonium aerosol, although having jumped from 5 stations in 1980 to 23 in 1985, the number has since fluctuated about this point, and the number of countries involved has fallen (comparison may be made with Figure 2.2 for comparison with engagement in monitoring of oxidised nitrogen and sulphur).

Observation of ammonium in precipitation, however, has been undertaken to a similar extent as for sulphur and oxidised nitrogen. With spatial and temporal coverage of this nature, discussion here on European trends in air quality will be limited to the wet component, ammonium in precipitation.

Ammonium in precipitation - In general there is more fluctuation in monthly mean concentrations on precipitation ammonium than of oxidised nitrogen or sulphur. This is to be expected given the solubility and the local emission quality of ammoniacal nitrogen. For review of time series', however, it adds a clumsy quality to visual presentation. Careful although somewhat subjective review of time series records, however, does permit commentary on apparent patterns across Europe. Throughout this discussion reference is made to Figure 3.42 where time series plots for several stations in each of a series of geographical areas are provided.

Quite clear downward tendencies are seen for the **eastern plains** (Figure 3.42g-h). As has been commented for other components, there is good agreement between several stations in the Czech-Hungarian area, indicating that the fall in concentrations of ammonium in precipitation has been of the order of 25-50% since the mid-1980s. This agrees with the review of emission totals, which observed the strong decline in these subregional emissions. The quality of agreement again points towards potential inconsistencies in records which have not been addressed earlier. On this occasion it is Košetice, CS0003, in 1992 which has unusual records. Earlier records are less extensive, restricting confidence in commenting on tendencies before this date, although on the basis of reported emissions it may well be that no trend existed earlier. Towards the **central continental** area the picture is more confused, despite strong falls in German emissions. To the east DE0005 displays the clearest downward tendency, whilst in contrast DE0004 to the west does not obviously display any trend (Figure 3.42c). It may be noted that French emissions have changed little during the period. The southern areas, exemplified by Payerne, CH0002, and central-northern parts represented by DE0002 show a downward progression, if somewhat faltering. Quantifying changes from visual inspection of running 12-month means is a little suspect. The south and centre-north may have seen concentrations of ammonium in precipitation decline by around 1/3, the east by more than this, and the west not at all. However, the variability in concentrations means that such numbers must be taken with caution. Going north there are a number of interesting trends and observed characteristics. The first of these falls into the latter category. Records for the **Netherlands** are somewhat intermittent. Of six sites displayed (Figure 3.42b) only one, NL0002, has operated for an extended period. This displays a upward tendency during the 1980s, with a possible decline into the 1990s. How to interpret the remaining sites in relation to this is a difficult question. On the one side they may be said to provide some support for the long term record. On the other side together they may be said to indicate relatively little change either way. Clearly, similar concentrations are being observed, and it is simply the limited long term monitoring at individual sites which is introducing some difficulty. North into **Scandinavia**, the Swedish sites, located in the east and south, all show marked downward trends of approaching 50%. Given virtually unchanging Swedish emissions, this may be a reflection of transboundary transport in which Sweden is benefiting from falling emissions elsewhere, or may reflect less formation of ammonium aerosol with falling European sulphur emission. The same is true for Norway, although sites displayed show lesser tendencies. Both are on the Atlantic coast. The northernmost has observed low and relatively consistent concentrations of reduced nitrogen in precipitation, whilst the southern site, NO0008, does reveal falling concentrations, despite Norwegian emissions haven risen by approaching 20% during the period. Another (undisplayed) site, NO0001, has a clearer decline.

Finland has also enjoyed a steady decline in precipitation concentrations at all sites, potentially by a greater amount than an approximate fall in national emissions of around 15% during the bulk of the period. Both FI0009 and FI0007/17 appear to have seen concentrations fall by up to 50%. An interesting and encouraging facet to data quality control in this case is the shift from site FI0007 to FI0017, which does not appear to have markedly interrupted the time series, support being lent by similar observations at FI0009. Such features owe a great deal to the coordinated nature of the whole monitoring programme. Going west, **Great Britain** shows patterns varying with location in an unsurprising way (Figure 3.42a). Sites exposed to the western and northern coasts do not immediately reveal trends in experienced precipitation quality, rather have consistently monitored low concentrations. On the other hand, sites to the east of the country indicate a possible sharp improvement in precipitation quality. This assessment is hampered by restricted periods of monitoring at different stations. Whilst locations subject to relatively homogenous environments show great similarity between monitoring sites (e.g. central plains), locations subject to enormous variability in weather and climate such as the United Kingdom cannot benefit from the same. The lack of consistent monitoring is a clear disadvantage in this case. Finally, comment may be made on trends at coastal sites. Not separately assembled, observations taken along the **Atlantic, North Sea and Baltic Sea** coasts are nevertheless displayed. There has been no overall visual trend at Atlantic coasts. Sites in Portugal, SW England, western Northern Ireland, northern Scotland and towards northern Norway do not indicate changes over the last two decades, and all have monitored ammonium concentrations in precipitation of 0.4 mg N l^{-1} and below. Around the North Sea there does appear to have been decline. Along the southern Norwegian coast there has been a fall of up to 1/3, the eastern English sites show clear falls of similar order although are difficult to quantify on site as explained, whilst German and Danish observations to the east (not displayed) suggest a decrease of around 25% in concentrations. Local variations may exist, as seen in the Dutch observations (Figure 3.42b). Whether there is decline, consistency, or even an increase is not altogether obvious here. The Baltic Sea has also seen a decline. Coastal observations in Sweden and Finland show notable decreases. Sites displayed monitored falls of ⅓ - ½ in ammonium concentrations. It is important to remember, however, that reduced nitrogen shows great local variability.

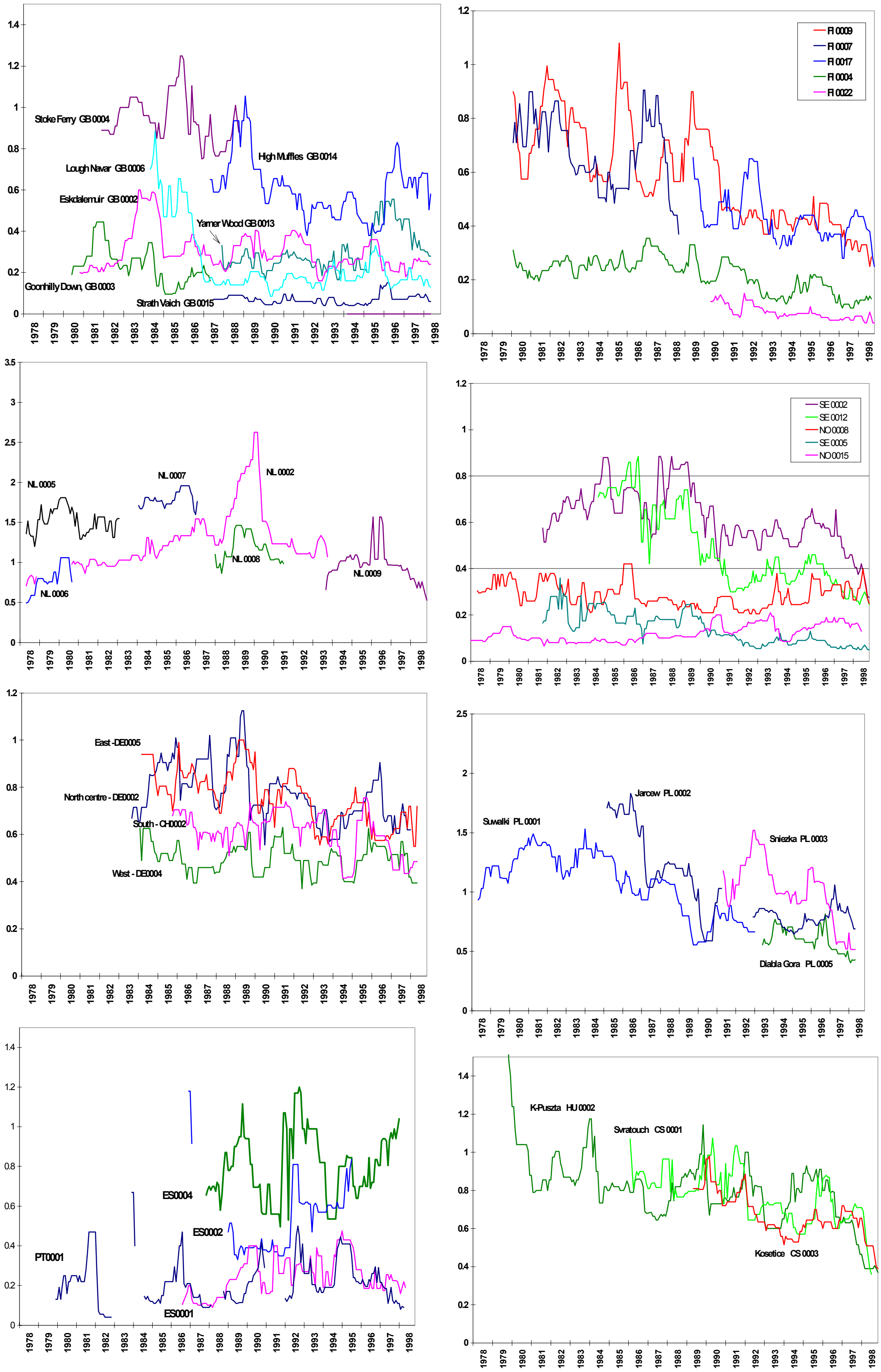


Figure 3.42: NH_4 in precip., mg N l^{-1}, running annual median concentrations.

a) United Kingdom GB02,03,04,06,13,14,15	*e) Finland FI04,07,09,17,22*
b) Netherlands NL02,05,06,07,08,09	*f) Scandinavia SE02,05,12,NO08,15*
c) Centre DE02,04,05,CH02	*g) Poland PL01,02,03,05*
d) Iberian peninsula ES01,02,04,PT01	*h) central plains HU02,CS01,03*

3.5.3 Statistical review

Of airborne components, monitoring of HNO_3+NO_3 and of NH_3+NH_4 was limited during the 1980s. For this reason each decade since 1980 has been considered separately, including for NO_2, purely for comparative purposes. There are no apparent changes in slop direction during these times. For nitrogen concentrations in precipitation, the lack of apparent changes in slope direction, and with no marked changes in slope magnitude the whole period has been subjected to statistical trend analysis using SKT and the Sen's slope estimator. These are explained in section 3.2 and Appendix B. As throughout this report, the analysis and slope estimates have been calculated for regions rather than single stations. Individual station results can be found in Appendix A. Confidence limits for the slope in concentrations have been calculated at p=0.1 (i.e. 90% confidence). Where statistically significant at 90% the best estimate of the slope has been converted to a percentage change from initial concentration for each region across the whole of the period 1980-98. The initial concentration has been calculated as the mean value regressed over the time, as explained in Appendix B.

The starting point for data used has been all data held on the monitoring database after quality control, expressed as monthly means. In consequence, where the number of data points submitted minus those removed at CCC during quality control failed to achieve 75% coverage for any month, no value was used. These procedures, plus quality control measures are explained in chapter 2 and in Appendix B. From this starting point, account was then taken of the observations regarding *time series review* above. Namely, the low NO_2 values at K-Puszta in 1992-94 were excluded, as were low values at Witteveen in 1981-82, low nitrate in precipitation values at Witteveen and at Kollumerwaard 1992-94, and high ammonium in precipitation values at Košetice 1992. Statistical analysis was then run for the various subregions listed in section 3.2 and results are presented in Table 3.7 and Table 3.8. Stations are listed after the table.

It is noticeable that there is restricted correspondence between trends in airborne concentrations and trends in precipitation concentrations. Trend direction is largely the same, but there is weak correspondence between regions with significant trends, and between regions with large magnitude trends. For oxidised nitrogen the regions experiencing significant declines in NO_2 concentrations are those at the geographical centre of the continent, from Germany eastwards. This is not readily observed in airborne nitrate levels. Moving away the picture remains heterogeneous. Southern Scandinavia saw initial increases during the 1980s in NO2 concentrations, and declines in the 1990s. The central and northern areas of Scandinavia have seen greatest proportional declines. Neither southern Norway nor southern Finland saw significant downward trends (Kulmala *et al.* (1998) also found a mixed picture for individual stations in Finland).

Over the whole period since 1980 the central European regions appear to have experienced the strongest downward trends in concentrations of nitrate in precipitation, with declines of 19-38%. The comparable picture across space lends some credence to the idea mentioned in time series review of homogeneity in much of continental Europe's nitrogen environment. As before, patterns are less distinct to the north and north-west, with an indication of increased concentrations in southern Finland and other northern regions. As most northern areas saw decreases in nitrogen air concentrations during one or other decade, the limited comparison between airborne and precipitation concentrations invites further analysis before clear explanation can be offered.

A rather similar picture is seen for reduced nitrogen. There have been somewhat equivocal changes in air concentrations during the 1990s. The Jutland peninsula, southern Norway, southern Finland and the United Kingdom demonstrate downward trends amongst the stations analysed, whilst central/eastern Europe and the north show no clear patterns. In precipitation, however, central and eastern Europe has seen significan falls in concentrations since 1980, whilst much of Scandinavia has not been found to reflect this.

Table 3.7: Summary statistics for airborne nitrogen trend analysis.

	NO$_2$				**NO$_3$ + HNO$_3$**		**NH$_3$ + NH$_4$**	
	1980-89		*1990-98*		*1990-98*		*1990-98*	
	% Change	*hom.*	% Change	*hom.*	% Change	*hom.*	% Change	*hom.*
	slope ±90% µg N m^{3}yr^{-1}		slope ±90% µg N m^{3}yr^{-1}		slope ±90% µg N m^{3}yr^{-1}		slope ±90% µg N m^{3}yr^{-1}	
BeNeLux	– +0.045	(+*=2) -0.340	**–** +0.115	(*=3) -0.196				
Jutland Peninsula					**-26** -0.014	(+*=3) -0.056	**-30** -0.063	(+*=3) -0.161
Centre	+ +0.093	(*=5) -0.017	**-17** -0.027	(*=7) -0.077				
Eastern plains	– +0.078	(*=3) -0.331	**-30** -0.010	(*=3) -0.189	– -0.003	(+*=4) -0.064	– +0.103	(+*=4) -0.604
Czech basin	**-35** -0.021	(+*=2) -0.165	**+** +0.266	(*=4) -0.127				
Hungarian plain	**+45** *+0.135*	(*1) *+0.048*	**–** +0.023	(*1) -0.070	**+** +0.014	(*1) -0.013	**–** -0.147	(*1) -0.340
South Norway	**+50** +0.051	(*=2) +0.002	**–** -0.003	(=2) -0.028	**–** +0.004	(+*=2) -0.008	**–** +0.012	(+=2) -0.023
South Sweden	+ +0.240	(*=3) -0.011	**-17** -0.014	(*3) -0.065	**-22** -0.006	(*=2) -0.026	**-31** -0.026	(*=2) -0.087
Mid-Scandinavia	+ +0.076	(*=5) -0.060	**-20** -0.003	(=5) -0.018	**–** -0.001	(=5) -0.005	**+** +0.014	(*=5) -0.008
North	– +0.019	(*1) -0.020	**-33** -0.005	(*=3) -0.018	+ +0.002	(=2) -0.003	**–** +0.002	(+*=2) -0.013
South Finland			– +0.031	(+*=3) -0.061	**-13** -0.000	(+*=3) -0.011	**-26** -0.005	(*=3) -0.037
United Kingdom					**-24** -0.002	(+*=2) -0.037	**-28** -0.007	(+*=2) -0.088
Spain					**-62** -0.031	(*=4) -0.063	**-94** -0.223	(*=4) -0.423

For Key, see Tables 3.2–3.6.
For Subregion definition, see Table 3.8.

Table 3.8: Summary statistics for precipitation nitrogen trend analysis.

subregion	NO₃ in precipitation		NH₄ in precipitation	
	% Change best est.	*hom*	% Change best est.	*hom*
	slope ±90% mg N l^{-1}		slope ±90% mg N l^{-1}	
1980-98				
France	**-38** -0.001 -0.025	*(+*=3)*	**-33** -0.004 -0.030	*(*=3)*
BeNeLux	**–** -0.008 -0.012	*(+*=3)*	**–** -0.006 -0.019	*(+ =3)*
Jutland Penin.	**-16** -0.000 -0.012	*(=3)*	**-21** -0.003 -0.017	*(+*=3)*
Eastern plains	**-26** -0.006 -0.019	*(*3)*	**-59** -0.031 -0.054	*(*=3)*
Czech basin/ Hungarian plain	**-19** -0.008 -0.024	*(* 5)*	**-20** -0.010 -0.032	*(+*=4)*
NE Balkans			– +0.024 -0.032	*(+*=3)*
South Norway	– +0.003 -0.004	*(+*=2)*	**-19** -0.001 -0.009	*(*=2)*
South Sweden	+ +0.015 -0.014	*(+*=3)*	– +0.020 -0.035	*(+*=3)*
Mid-Scandinavia	**-36** -0.003 -0.009	*(=5)*	– (-0.002 -0.009)	*(*=5)*
South Finland	**+7** +0.040 +0.007	*(+*=4)*	**+** +0.039 -0.008	*(*=4)*
North	+ +0.099 -0.009	*(*=2)*	+ +0.035 -0.006	*(*=2)*
W. Britain	– +0.004 -0.006	*(+*=5)*	**-6** -0.000 -0.015	*(*=5)*
E. Britain	– +0.015 -0.147	*(+*=3)*	– +0.064 -0.180	*(+*3)*
Scotland	+ +0.110 -0.049	*(+=3)*	– +0.010 -0.113	*(*=3)*
Iberian Peninsula	**+8** +0.031 +0.005	*(* 8)*	+ +0.020 -0.013	*(8)*

For Key, see Tables 3.2–3.6.

Subregion definition:

France:	FR1, FR3, FR5
BeNeLux:	BE1, NL2, DE4
Jutland Peninsula:	DE1, DK3, DK5, DK8 (not NO_2 or prec.)
Centre:	DE2, DE3, DE4, DE5, DE7 (90-98), DE8 (90-98), CH2
Eastern plains:	PL1, PL2, PL4 (not NO_2 or prec.), PL5 (not NO_2 or prec.), DE7 (not NO_2 or prec.)
Czech basin:	CS1, CS2 (90-98), AT2 (90-98), SK2
Hungarian plain:	HU2
N.E. Balkans:	YU5, YU8, MK7
South Norway:	NO1, NO8
South Sweden:	SE1, SE2, SE11
Mid-Scandinavia:	SE5, NO15, NO36, NO39, NO41
North:	SE13 (NO_2 90-98), NO30, FI22 (90-98)
South Finland:	FI4, FI7, FI9, FI17
United Kingdom:	GB2, GB14
Spain:	ES1, ES2, ES3, ES4
Iberia:	ES1, ES2, ES3, ES4, PT1, PT2, PT3, PT4
West Britain:	IE1, GB3, GB6, GB13, GB15
East Britain:	GB4, GB7, GB14
Scotland:	GB2, GB15, GB16

4. Europe's changing air quality: a synthesis of the continental picture

Chapter three has provided a regional and subregional review of monitored changes in air quality, and has provided quantitative estimates of the observed rates of change. The purpose of this current is to draw this information together and provide a continent-wide view of changes and their relation to environmental interests. The following approach is taken:

(1) Collated summary of regional statistical analysis, and extension to deposition of acidifying sulphur components
(2) Mapping of observed sulphur deposition changes

4.1 Summary regional air quality trend analysis, and extension to deposition

Thus far the analysis has concerned monitored concentrations of pollutants in air and precipitation, and region-by-region across Europe has described the observed subregional changes in these. In accordance with one of the intentions of this report, namely to provide analytical comment on achievements related to the first Sulphur Protocol, this information is collected together and presented in summary for the period 1980-93 in Table 4.1. In addition, SKT trend analysis has been conducted for calculated wet deposition, and this is presented in the table. This has been done in light of the objectives of Protocols, although these trends can be more influenced by meteorological differences than with other components.

To achieve consistent time-period estimates of total percentage change, the quantified regional trend estimates for periods of monitoring have been extended across the whole period. The conclusions of the regional review has been borne in mind. Where monitoring began late, or ceased early, extension of trends has only been applied where observations from surrounding sites and reported emission changes suggest this may be reasonable. Otherwise, no trend was assumed outside the monitored period. A good example of the latter is Spain, where much monitoring began several years into the 1980s, and where there is little reason from reported emission data to assume retro-extension of observed trends. On this same basis no value has been entered for the Carpathians. The site SK0002 began monitoring too short a period before 1993 to determine trends, and time series review plus statistical assessment did not point towards earlier trends.

The summary data in Table 4.1 is rather self-explanatory. The only regions not having seen statistically significant trends in sulphur during the lifetime of the first sulphur Protocol were western and north-western Britain, the Balkans and Iberia. Throughout the rest of the continent significant downward trends were observed, and the level of deposition, wet plus dry, is anticipated to have exceeded 30%, which was the level of emission reductions which signatories to the Protocol agreed to.

Table 4.1: Summary of trend analysis (SKT and Sen's estimator) atmospheric sulphur in European subregions, 1980-93.

	SO$_2$		**SO$_4$ airborne**		**SO$_4$ wet deposition**	
	% Change (best est)	*hom*	% Change best est.	*hom*	%Change best est.	*hom*
subregion	slope ±90% µgS m^{3}yr^{-1}		slope ±90% µgSm^{3}yr^{-1}		slope ±90% mgSm^{-2}yr^{-1}	
France	**-78** -0.148 -0.342	*(*=3)*	**-81** -0.091 -0.187	*(+*=3)*	**-79** -1 -102	*(*=2)*
BeNeLux	**-56** -0.222 -0.354	*(* 3)*	**-52** -0.070 -0.126	*(* 3)*	**-60** -33 -54	*(+*=2)*
Centre	**-60** -0.204 -0.327	*(* 7)*	**-45** -0.029 -0.148	*(7)*	**-61** -18 -56	*(=5)*
Eastern plains	**-38** -0.103 -0.291	*(* 3)*	**-45** -0.088 -0.193	*(*=3)*	**-59** -27 -76	*(*=3)*
Czech basin	**-42** -0.048 -0.677	*(*=4)*	**-56** -0.087 -0.238	*(* 4)*	**-78** -25 -40	*(+*=3)*
Hungarian plain	**-66** -0.144 -0.310	*(*1)*	**-73** -0.130 -0.224	*(* 1)*	**-74** -41 -95	*(*1)*
NE Balkans	**-62** -0.281 -0.616	*(+ =2)*			– +41 -143	*(+*=6)*
Jutland Peninsula	**-58** -0.122 -0.201	*(+*=3)*	**-35** -0.038 -0.076	*(+ =3)*	**-38** -10 -39	*(+=3)*
South Norway	**-41** -0.011 -0.028	*(+*=2)*	**-43** -0.021 -0.044	*(+*=2)*	**-33** -2 -61	*(+=2)*
South Sweden	**-62** -0.117 -0.296	*(*=3)*	**-67** -0.060 -0.169	*(*=3)*	**-31** -12 -36	*(*=3)*
Central Scan.	**-72** -0.021 -0.038	*(=5)*	**-51** -0.012 -0.034	*(+ =5)*	**-58** -6 -22	*(+=4)*
East Sweden	**-53** -0.063 -0.112	*(* 2)*	**-53** -0.043 -0.083	*(* 2)*	**-53** -10 -36	*(*=2)*
Baltic States	+ +0.119 -0.046	*(*=4)*	**-49** -0.014 -0.162	*(*=5)*	– +10 -27	
South Finland	**-64** -0.123 -0.210	*(* 4)*	**-34** -0.001 -0.070	*(* 4)*	**-60** -18 -56	*(+*=4)*
Iberia			– +0.043 -0.084	*(=7)*	+ +77 -50	*(+ 7)*
North-west Britain	**-55** -0.037 -0.131	*(*=3)*	**–** +0.022 -0.035	*(+*=3)*	-27 -5 -25	*(*=3)*
East and South England	**-56** -0.163 -0.366	*(* 3)*	**-31** -0.002 -0.078	*(* 3)*	**-64** -2 -79	*(+*=2)*
West Britain	**-36** -0.003 -0.048	*(+*=2)*	**–** -0.019 -0.016	*(+*=2)*	**–** +5 -15	*(+*=3)*

For Key, see Tables 3.2–3.6.

Subregion definition:
France: FR1, FR3 (not dep.), FR5
BeNeLux: BE1, NL2 (not dep.), DE4
Centre: DE2, DE3, DE4, DE5, DE7 (not dep.), DE8 (not dep.), CH2
Eastern plains: PL1, PL2, DE7
Czech basin: CS1, CS3, AT2, SK2 (not dep.)
Hungarian plain: HU2
N.E. Balkans: SI1 (dep.), HR2, HR4 (dep.), YU5, BA6 (dep.), MK7 (dep.)
Jutland Peninsula: DE1, DK3, DK5
South Norway: NO1, NO8
South Sweden: SE1, SE2, SE11
Central Scandinavia: SE5, NO15, NO36 (not dep.), NO39, NO41
East Sweden: SE8, SE12
Baltic States: EE2 (SO$_4$), EE9 (not dep.), LT15, LV10, RU14
South Finland: FI4, FI7, FI9, FI17
Iberia: PT1, PT3, PT4, ES1, ES2, ES3, ES4
North Britain: GB2, GB6, GB15
East and South Britain: GB4, GB14
West Britain: IE1, GB6, GB13

4.2 Mapping changes in sulphur deposition

The observation data assembled by EMEP has frequently been displayed cartographically using the technique of kriging. Originally developed for geostatistical purposes, the technique can be used to estimate unknown data from neighbouring values, e.g. to evaluate deposition fields from point measurements. It is assumed that the variable to be estimated has a value at every point in space, and that it can be described by a random function *Z(x)*. This function has the properties of a random variable with a distribution in all points in space. The correlations which exist between the variable at any two points can be expressed through *Z(x)*, i.e. the difference between deterministic model estimates and annual averages of measured values. This approach to describing measured spatial distributions has also been the basis for evaluation of spatial variations in EMEP's modelling capability in the past, e.g. Schaug *et al.* (1993), Tuovinen *et al.* (1994). The potential limitations of describing the European air quality field on the basis of sometimes a limited density of observations are known. Combination of measured and calculated values is one possible mean of addressing this. However, the desire here, as a point of departure and debate alone, is to describe purely what can be observed from the field observations made for EMEP. Therefore, as a complement to the tabulated statistical assessment given in section 4.1, the kriging technique is employed here as a valuable means of visualising the continental picture of changing air quality. Clearer patterns have been described for sulphur than nitrogen and temporally and spatially more extensive data is available, hence sulphur is considered in this section.

The difficulty of dealing with natural temporal variation is always present in environmental assessment. We have elected to address this in a simple manner by averaging across years, taking lead from both the review of trends in the former European Air Chemistry Network by Rodhe and Granat (1984) and from earlier presentations from the CCC (e.g. Schaug *et al.*, 1996). The period of averaging is a matter of judgment, and we have elected to provide a series of three-year averages at five-year intervals as a reasonable means of capturing rather than averaging temporal change through the lifetime of EMEP whilst reducing the influence of meteorological variability.

Sulphur has been monitored as airborne and as deposited components, and assessment has already been presented of the changes in each of these separately. What is intriguing is to combine these into estimates of total deposition. This has direct relevance to environmental concerns and the objectives set out in such as the first two sulphur Protocols. As wet deposition but not dry deposition is directly monitored, to obtain estimates at the latter we have to infer rates of deposition from air concentrations of depositing compounds. We have approximated this via a technique used traditionally in Lagrangian acid deposition modelling at EMEP MSC-W. Monthly mean concentrations at each station of sulphur dioxide and of sulphate have been multiplied by a deposition velocity and subject to seasonal and geographical scaling. Account was not taken of landuse in these approximations. The method is given in previous reports from MSC-W (e.g. Barrett *et al.*, 1995; Barrett and Berge, 1996). Sulphate concentrations multiplied by precipitation has been used for station wet deposition. The wet deposition estimate is believed reasonable when employing simply the EMEP network as stations measuring precipitation quantity also report sulphate concentrations. The monthly mean values of wet-deposited sulphate, of dry sulphur dioxide and of dry sulphate particulate deposition were then summed to give annual deposition estimates of each for those stations reporting data. Three consecutive years were then averaged, and the 3-year mean values of each of the three components were then kriged between stations with data. These three kriged maps (3-year averages of wet deposited sulphate, of dry deposited SO_2, and of dry deposited SO_4) were then summed to give total sulphur deposition as a three year average. This was done for the years 1980-82, 1985-87, 1990-92, and 1995-97. The resulting maps are displayed in Figures 4–4.4.

A specific measure can be estimated from the mapped data. Firstly, the first sulphur Protocol intended a reduction in sulphur emissions, and whilst did not specify deposition targets assessment of the changes in sulphur deposition during the relevant period would provide an indication of how well the spirit of the Protocol was achieved, provide one assessment of satisfaction that desired emission abatement was actual. Figure 4.5 displays the decrease in estimated observed sulphur deposition over the 15 years 1980-82 to 1995-97 as a percentage of monitored deposition in 1980-82. What is seen is that most of Europe has seen a decrease of at least 50% in annual sulphur deposition, for 1995-97 compared to 1980-82, except for the Czech and Slovak Republics, Poland, eastern England, central France, northern Italy and western Iberia. The latter three are the only areas not to achieve a 30% decrease.

Importantly, improved information may be available from the combination of measured and calculated data, as is commonly undertaken by EMEP. The display here is simply intended as an insight to the information available from the monitoring programme alone with respect to past agreed objectives.

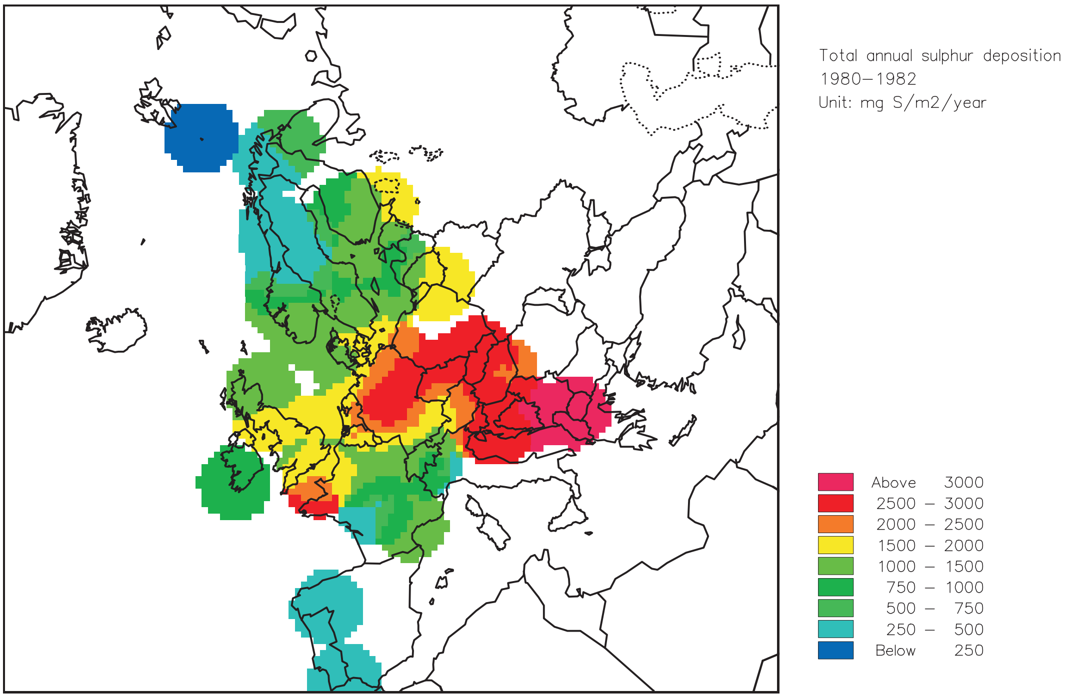


Figure 4.1: Annual total sulphur deposition 1980-82, mg S m^{-2} a^{-1}. *3-year mean measurements alone.*

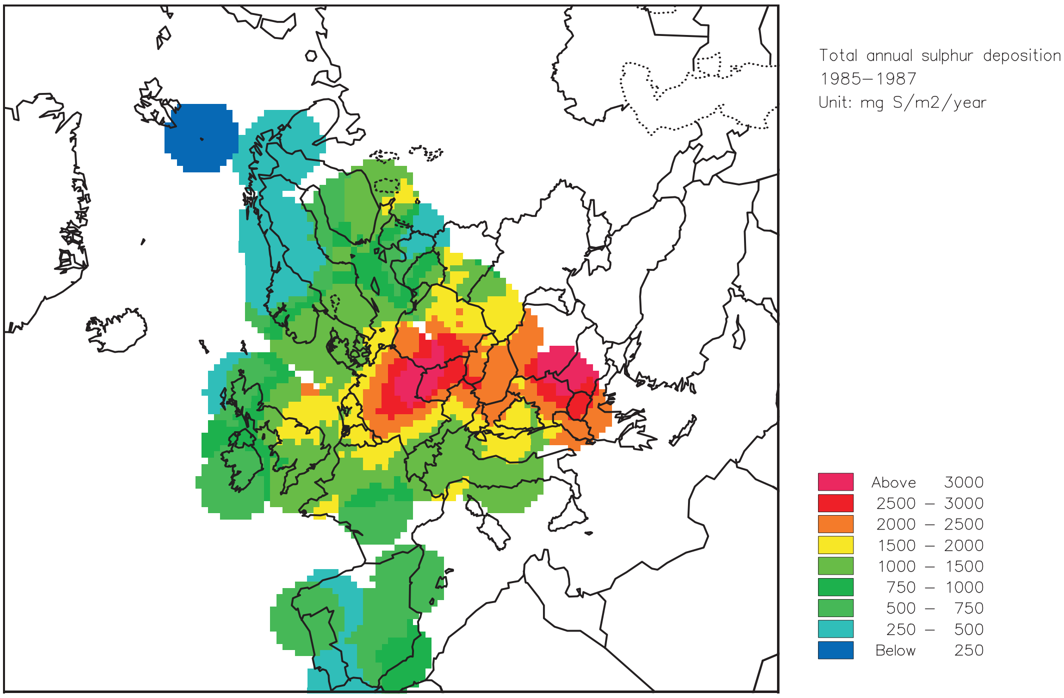


Figure 4.2: Annual total sulphur deposition 1985-87, mg S m^{-2} a^{-1}. *3-year mean measurements alone.*

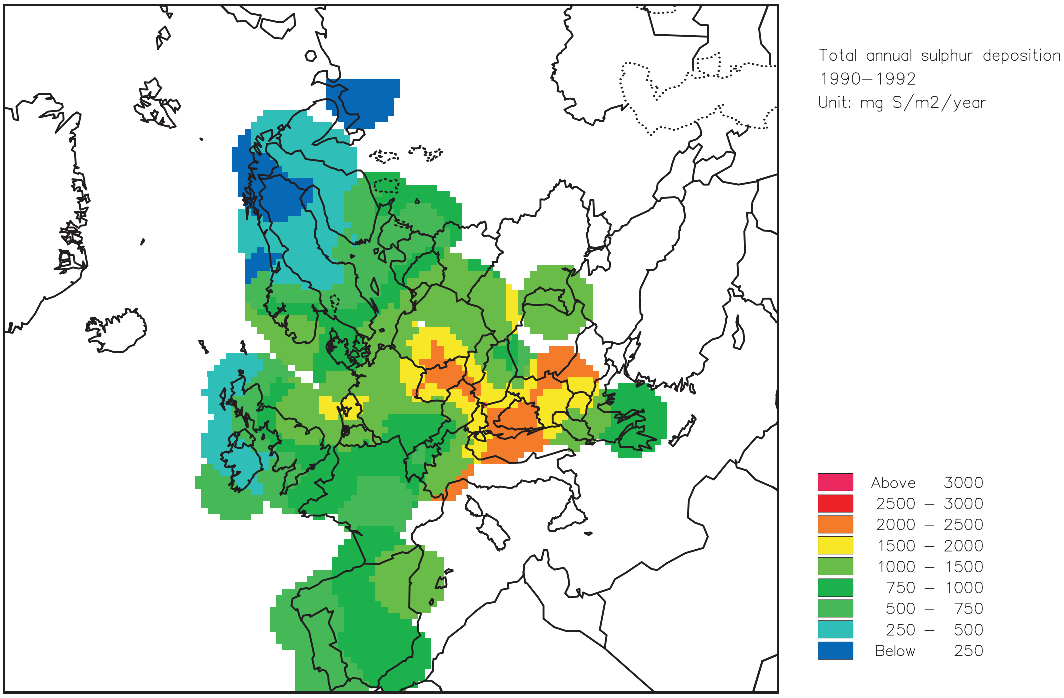


Figure 4.3: Annual total sulphur deposition 1990-92, mg S m^{-2} a^{-1}. 3-year mean measurements alone.

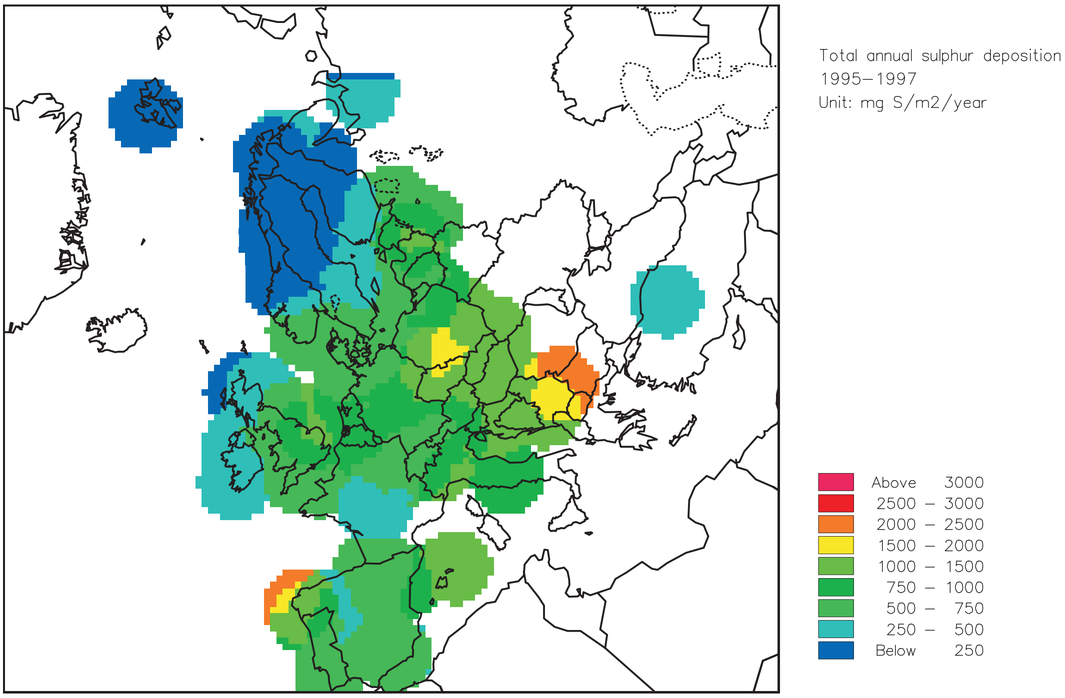


Figure 4.4: Annual total sulphur deposition 1995-97, mg S m^{-2} a^{-1}. 3-year mean measurements alone.

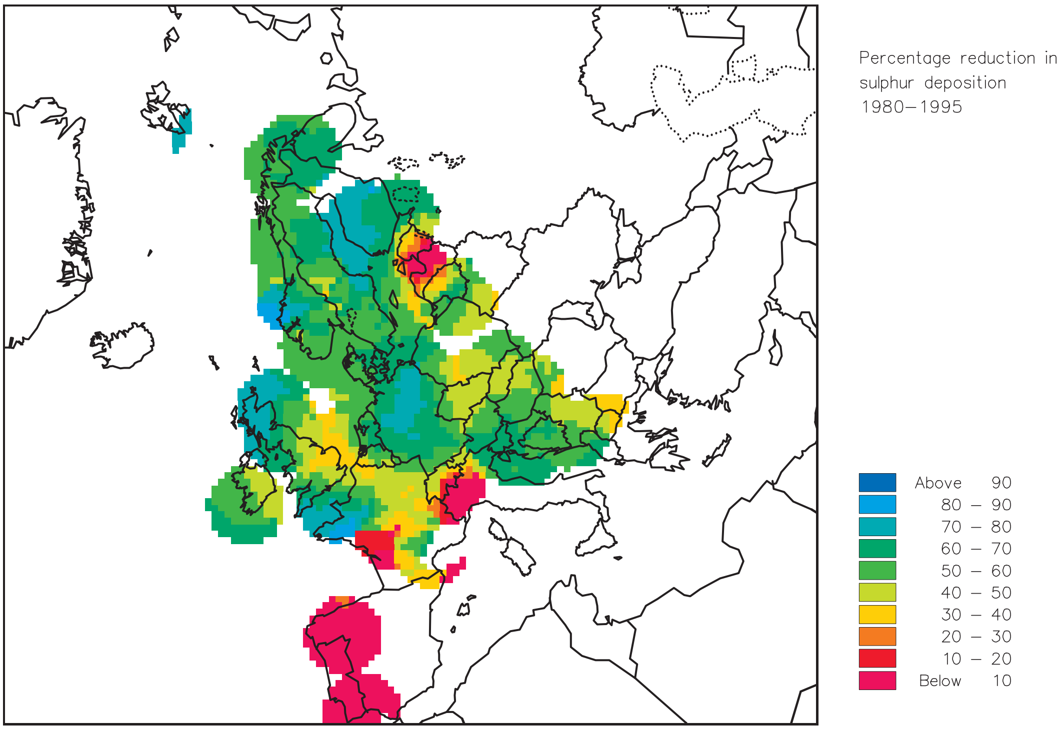


Figure 4.5: Percentage reductions in deposition of sulphur, 1980-82 to 1995-97.

5. Concluding remarks

Since the end of the 1970s, EMEP has organised airborne and precipitation monitoring of acidifying compounds across Europe. This has been managed by the Chemical Co-ordinating Centre with great focus on maintaining both comparability and quality. Comparability is needed across space and time, and quality required in all stages from monitoring site selection to acceptance of observed values into the database. Information from the monitoring network has been used for surveillance and for verification of computational tools, and has thus been employed closely in the development of international agreements within the framework of the 1979 Geneva Convention on Long Range Transboundary Air Pollution. Indeed, the last decades of the twentieth century have seen major coordinated efforts to overcome problems of transnational air pollution. This report takes the opportunity to use the observational data across Europe in this period to review the changing state-of-the-environment with respect to acidification, and to evaluate the observed trends in acidifying air pollution. Only from observation can changes in the environment be confirmed.

Examination of the time series of observations indicates marked declines in air and precipitation concentrations of sulphur across Europe. In the centre of Europe and in Scandinavia the apparent changes have been large. Only at the most remote peripheral stations on the north-west Atlantic coast may change be more equivocal. Statistical quantification of changes confirms these developments. Between 1980 and the end of 1993 sulphur concentrations in air were estimated to have declined by typically 40-80% according to location. Statistically significant trends are observed all across the continent. Table 4.1 has listed the observed changes. Thus, on the basis of observations there appears to be a clear downward trend in atmospheric sulphur concentrations which broadly corresponds changes in reported emissions, sulphur dioxide releases falling by over 40% on average across Europe during the same time period.

Rates of deposition of sulphur have similarly been seen to fall. Parts of north-central and northern Europe are estimated to have received around 80% less sulphur deposition per year by 1995 than they received annually in 1980. Across central Europe and western areas lesser decline has been observed, but is still estimated at in excess of 30-40%. Only very small regions have experienced lesser changes. The observed data offers an important degree of verification of improvements in environmental quality are anticipated to have occurred. This broad scale evaluation from EMEP importantly allows regional interconnections to be observed. However, the spatial scale of analysis is somewhat coarse and would benefit from complementary localised and computational assessment.

Nitrogen monitoring has been more limited than sulphur. Trends can be discerned in ambient NO_2, although are quite varied. Some regions have seen increased concentrations, some decreased, and others no observable trend. Airborne nitrate and reduced nitrogen trends have been broadly downward and less varied, but as of yet have been found to be uncertain over large areas of continental Europe. Nitrogen concentrations in precipitation are similarly geographically heterogeneous, being between no trend and a downward tendency. For these components continental Europe has seen the clearest decrease.

An attempt has been made in this report to comment on whether changes have been observed in air quality, whether they accord with reported emission changes, and whether environmental objectives have been met. The answer is positive on all counts, thus confirming the benefits of long term coordinated international monitoring.

6. Acknowledgement

National representatives from several countries have provided valued comment and clarification of data from their stations in the course of preparation of this report. We thank them for their assistance and are greatly appreciative of the diligence shown. We also thank our own staff for the considerable backup necessary to produce this report.

7. References

Aas, W., Hjellbrekke, A.G., Semb, A. and Schaug, J. (1999) Data quality 1997, quality assurance, and field comparisons. Kjeller, Norwegian Institute for Air Research (EMEP CCC Report No. 6/99).

Aas, W., Hjellbrekke, A.G. and Schaug, J. (2000) Data quality 1998, quality assurance, and field comparisons. Kjeller, Norwegian Institute for Air Research (EMEP CCC Report No. 6/2000).

Aas, W., Tørseth, K., Solberg, S., Berg, T. and Manø, S. (2000) Overvåking av langtransportert forurenset luft og nedbør. Atmosfærisk tilførsel, 1999. (Monitoring of long-range transported polluted air and precipitation. Atmospheric supply, 1999). Kjeller, Norwegian Institute for Air Research (NILU OR 23/2000). In Norwegian.

Avila, A. (1996) Time trends in the precipitation chemistry at a mountain site in northeastern Spain for the period 1983-94. *Atmos. Environ., 30*, 1363-1373.

Barrett, K.J., Seland, Ø., Foss, A., Mylona, S., Sandnes, H., Styve, H. and Tarrason, L. (1995) European transboundary acidifying air pollution. Ten years calculated fields and budgets to the end of the first Sulphur Protocol. Oslo, Norwegian Meteorological Institute Research (EMEP MSC-W Report 1/95) (DNMI Research Report 17).

Barrett, K.J. and Berge, E. (1996) Transboundary air pollution in Europe. Estimated dispersion of acidifying agents and of near surface ozone. Parts one and two. Oslo, Norwegian Meteorological Institute Research (EMEP MSC-W Report 1/96) (DNMI Research Report 32).

Blanchard, C.L., Sirois, A., Whelpdale, D.M., Brook, J. and Michaels, H.M (1996) Evaluation of the capabilities of deposition networks to resolve regional trends and spatial patterns. *Atmos. Environ., 30*, 2539-2549.

Butler, T.J. and Likens, G.E. (1991) The impact of changing regional emissions on precipitation chemistry in the Eastern United States. *Atmos. Environ., 25A*, 305-315.

CEN (2000) General requirements for the competence of testing and calibration laboratories. Comité Européen de Normalisation EN ISO/IEC 17025:1999. Bruxelles.

Downing, C.E.H., Vincent, K.J., Campbell, G.W., Fowler, D. and Smith, R.I. (1995) Trends in wet and dry deposition of sulphur in the United Kingdom. *Water, Air, Soil Poll., 85,* 659-664.

Egglestone, S., Hackman, M.P., Heyes, C.A., Irwin, J.G., Timmis, R.J. and Williams, M.L. (1992) Trends in urban air pollution in the United Kingdom during recent decades. *Atmos. Environ., 26B*, 227-239.

Fricke, W. and Bielke, S. (1993) Changing concentrations and deposition of sulfur and nitrogen compounds in Central Europe between 1980 and 1992. In: *General assessment of biogenic emissions and deposition of nitrogen compounds, sulphur compounds and oxidants in Europe. Proceedings of the joint workshop CEC/BIATEX of EUROTRAC, Aveiro, Portugal, 1993*, ed. by. J. Slanina, G. Angeletti and S. Beile. Brussels (Air Pollution Research Report 47). pp. 9-30.

Gilbert, R.O. (1987) Statistical methods for environmental pollution monitoring. New York, Van Nostrand Reinhold.

Hirsch, R.M., Slack, J.R. and Smith, R.A. (1982) Techniques of trend analysis for monthly water quality analysis. *Water Resources Res., 18,* 107-121.

Hjellbrekke, A.-G. (1997) User's guide for EDC 1.1. EMEP Data Check. Software for quality control of EMEP data. Kjeller, Norwegian Institute for Air Research (EMEP/CCC Report 1/97).

Hjellbrekke, A-G., Schaug, J., Hanssen, J.E. and Skjelmoen, J.E. (1997) Data Report 1995 Part 1: Annual summaries. Kjeller, Norwegian Institute for Air Research (EMEP/CCC Report 4/97).

Holland, D.M., Principe, P.P. and Sickles, J.E. (1999) Trends in atmospheric sulfur and nitrogen species in the eastern United States for 1989-1995. *Atmos. Environ., 33,* 37-49.

Hovmand, M.F. and Andersen, H.V. (1995) Nine years of measurements of atmospheric nitrogen and sulphur deposition to Danish forest. *Water, Air, Soil Poll., 85*, 2205-2210.

Jonson, J.E., Tarrason, L. and Bartnicki, J. (2000) Effects of international shipping on European pollution levels. Oslo, Norwegian Meteorological Institute (EMEP MSC-W Note 5/2000).

Kelessis, A.G., Zoumakis, N., Petrakis, M. and Vosnikos, F. (1996) Air pollutants concentration levels from a monitoring network in Thessaloniki, Greece. *Fresenius Envir. Bull., 5*, 637-642.

Kindbom, K., Lövblad, G. and Sjöberg, K. (1994) Sulphur and nitrogen compounds in air and precipitation in Sweden 1980-1992. Gothenburg (Swedish Environmental Research Institute Report B1144).

Klemm, O. and Lange, H. (1999) Trends of air pollution in the Fichtelgebirge mountains, Bavaria. *Environ. Sci. Pollut. Res., 6,* 193-199.

Kulmala, A., Leinonem, L., Ruoho-Airola, T., Salmi, T. and Walden, J. (1998) Air quality trends in Finland. Helsinki, Finnish Meteorological Institute.

Lükewille, A., Jeffries, D., Johannessen, M., Raddum, G., Stoddard, J. and Tråen, T. (1997) The nine year report: acidification of surface water in Europe and North America. Long-term developments (1980s and 1990s). Oslo, Norwegian Institute for Water Research (NIVA report 3637).

Lynch, J.A., Grimm, J.W. and Bowersox, V.C. (1995) Trends in precipitation chemistry in the United States: A national perspective, 1980-1992. *Atmos. Environ., 29*, 1231-1246

Lynch, J.A., Bowersox, V.C. and Grimm, J.W. (2000) Changes in sulfate deposition in eastern USA following implementation of Phase I of Title IV of the Clean Air Act Amendments of 1990. *Atmos. Environ., 34*, 1665-1680.

Marquardt, W. and Brüggemann, E. (1995) Long-term trends in chemistry of precipitation after longscale transport - effects of atmospheric rehabilitation in East Germany. *Water, Air, Soil Poll., 85*, 665-670.

Odén, S. (1968) Nederbördens och luftens försurning, dess orsaker, förlopp og verkan i olika miljöer. (Acidification of precipitation and air, its causes, development and effects in different environments). Stockholm, Statens naturvetenskapliga forskningsråd, Ekologikommittéen (Bulletin/Ecological Research Committee 1). In Swedish.

OECD (1978) The OECD Programme on Long Range Transport of Air Pollution. Measurements and findings. Paris, Organization for Economic Cooperation and Development.

Olendrzynski, K. (2000) Supply of spatial emission data used in EMEP acid modelling. Pers. comm.

Paliatsos, A.G. (1997) Twenty years of regular SO_2 measurements in Athens, Greece. *Fresenius Envir. Bull., 6*, 655-660.

Posch, M. (2000) Supply of critical load data and discussion. Pers. comm.

Puxbaum, H., Simeonov, V. and Kalina, M.F. (1998) Ten years trends (1984-1993) in the precipitation chemistry in central Austria. *Atmos. Environ., 32*, 193-202.

Rodhe, H. and Granat, L. (1984) An evaluation of sulfate in European precipitation 1955-1982. *Atmos. Environ., 18,* 2627-2639.

Ruijgrok, W. and Römer, F.G. (1993) Aspects of wet acidifying deposition in Arnhem: source regions, correlations and trends (1984-1991). *Atmos. Environ., 27A*, 637-653.

Schaug, J., Iversen, T. and Pedersen, U. (1993) Comparison of measurements and model results for airborne sulphur and nitrogen components with kriging. *Atmos. Environ., 27A*, 831-844.

Schaug. J., Semb, A., Solberg, S., Hanssen, J.E., Pacyna, J.M. and Hjellbrekke, A.-G. (1996) Summary report from the Chemical Co-ordinating Centre for the Fifth Phase of EMEP. Kjeller, Norwegian Institute for Air Research (EMEP/CCC Report 7/96).

Shannon, J.D. (1999) Regional trends in wet deposition of sulfate in the United States and SO_2 emissions from 1980 through 1985. *Atmos. Environ., 33*, 807-816.

Sirois, A., Blanchard, C.L. Whelpdale, D.M. and Michaels, H.M. (1996) The future monitoring capabilities of four network configurations in Eastern Canada. *Atmos. Environ., 30*, 4115-4124.

Sirois, A. (1999) A brief and biased overview of time series analysis, or How to find that evasive trend. Quebec, Environment Canada, Air Quality Research Branch, Atmospheric Environment Service (Applied statistics in atmospheric chemistry series 1).

Sjödin, Å., Sjöberg, K., Svanberg, P.A. and Backström, H. (1996) Verification of expected trends in urban traffic NO_x emissions from long term measurements of ambient NO_2 concentrations in urban air. *Sci. Total Environ., 189/90*, 213-220.

Tarrason, L. and Schaug, J. (2000) Transboundary acidification and eutrophication in Europe. EMEP Summary Report CCC and MSCW. Oslo (EMEP Report 1/2000).

Tørseth, K., Aas, W. and Solberg, S. (2000) Trends in airborne sulphur and nitrogen compounds in Norway during 1985-1996 in relation to air mass origin. Conference on Acidic Deposition, Tsukuba, Japan, 10–16/12/2000. Accepted.

Tuovinen, JP, Barrett, K. and Styve, H. (1994) Transboundary acidifying pollution in Europe: Calculated fields and budgets 1985-93. Oslo, Norwegian Meteorological Institute (EMEP MSC-W Report 1/94) (DNMI Technical Report 129).

van Belle, G. and Hughes, J.P. (1984) Nonparametric tests for trend in water quality. *Water Resources Res., 20*, 127-136.

Vestreng, V. (2000) Reported emission totals extracted from the UN ECE/EMEP emission database. Pers. comm.

Vestreng, V. and Støren, E. (2000) Analysis of UN ECE/EMEP emission data. MSC-W Status Report 2000. Oslo, Norwegian Meteorological Institute (EMEP MSC-W Note 1/00) (DNMI Research Note 37).

WMO (1971) Guide to meteorological instrument and observing practices. Geneva, World Meteorological Organization (WMO No. 8 TP3).

Appendix A

Country-by-country measured trend summary data

In this Appendix we provide summary data and supporting information for observed trends in each component at each station across the EMEP network for 1978-98. The following is provided on a country-by-country basis:

a) Map of monitoring locations with accompanying list of site names and code numbers
b) Table with trend sigmificance and magnitude calculated from SKT and Sen’s estimator across the whole period of measurement
c) Table showing measurement and analytical methods used for each year of operation
d) Bar chart showing laboratory performance over time in nalaysis of sulphate in precipitation during EMEP laboratory intercalibrations.

The intention is to both supply estimated trend information, and to provide relevant interpretive information regarding methods and quality. Present performance is considered in detail in the annual Data Quality Report (Aas et al., 2000).

Station map and list
The map shows locations of stations which have partaken in the EMEP acid monitoring programme. The station altitude and geographical coordinates can be found in table 2.3.

Trend summary table
From SKT analysis, the following information is given for each site and component, listed in columns:

station code	as listed in the station list
component	possible list: SO_2, SO_4 in air, SO_4 aqeuous (in precip.), NO_2, NO3 in air, HNO_3, NO_3 aqeuous (in precip.), NH_3, NH_4 in air, NH_3+NH_4, NH_4 aqeuous (in precip.)
start year	first year of monitoring and trend analysis
end year	last year of monitoring and trend analysis
trend significance and direction	results of SKT and Sen’s slope estimation. indicates if trend is negative, positive, not observed, and magnitude of significant trends plus confidence limits. Possible labels: NEG95 negative trend, statistically significant at 95% NEG90 negative trend, statistically significant at 90% NOT trend not statistically different from zero POS90 positive trend, statistically significant at 90% POS95 positive trend, statistically significant at 95%
seasonal homogeneity	whether or not the season trends were found to be not statistically dissimilar from each other, i.e. were homogenous. Possible labels: homog seasons were homogenous not seasons were not homogenous
+90% slope estimate	Sens slope estimator at the +90% confidence limit
best estimate slope	The best estimate of the Sen’s slope
-90% slope estimate	Sens slope estimator at the -90% confidence limit

List of measurement and analytical methods

Shows principal sampling and analytical techniques used over time. Mnemonics are used for many analytical techniques and sampling methods. Many of these are standard chemical terminology (e.g. AAS for Atomic Absorption Spectroscopy, IC for Ion chromatography) and are also found in the annual Data Reports from the CCC. In addition, mnemonics are used here with respect to particulate sampling, and these are:

Ca	Cellulose acetate filter
Cf	Cellulose filter
GZ	GZ Gelman Zefluor, teflon filter
MM	Millipore RAWP, mixed cellulose nitrate and acetate filter, 1.2 um
P	Petrianov AFA-XP-20
S	Scleicher & Schuell 589/4, cellulose filter
STE	Scleicher & Schuell TE36 membrane filter
S2L	Scleicher & Schuell 589/2L, cellulose filter
ST	Scleicher & Schuell ST-69, cellulose acetate
TS	Scleicher & Schuell, teflon filter
T	Teflon filter
W40	Whatman40
W41	Whatman41
W42	Whatman42
WGF/A	Whatman GF/A, glass fiber filter
KP	Kipszer Paraplan
GN6	Gelman GN-6 Metricel
TN	Nulepore - FN MEMB, teflon
SA	Sartorius 0.45 u, cellulose acetate
FN11	FN11, cellulose filter
BI	Binderless glass fiber filter
SY	Synpor 6, membane filter
MA	Machery-Nagel NM 85/89, glass fiber filter
MMF	Millipore MF filter
FL	Flowpore FA, cellulose acetate, 0.8 um

Performance in EMEP laboratory intercalibrations

An assessment of the performance of the analysing laboratory in each land is given as a bar chart against time. The quality of analysis of sulphate in precipitation during regular EMEP laboratory intercalibrations is plotted, using absolute percentage relative error as the measure of performance.

The political changes in Europe must be taken into account when reviewing the laboratory performance as countries newly independent have sometimes changed laboratories. For analytical quality prior to 1991, the performance of Bosnia & Hercegovina, Croatia, FYROM, and Slovenia is indicated by Jugoslavia, and of Belarus, the Ukraine, Latvia, Lithuania, Estonia and the Russian Federation by a separate table for the USSR within that for Russia.

AUSTRIA

AT02 Illmitz
AT03 Achenkirch
AT04 St. Koloman
AT05 Vorhegg

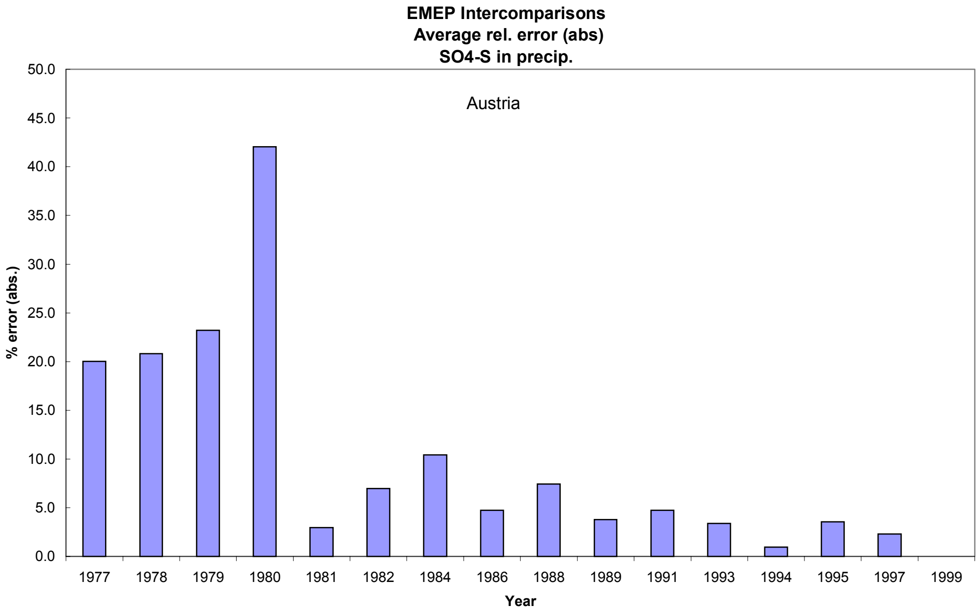
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
AT0002	SO2air	1978	1998	NEG99	homog	-0.152	-0.207	-0.264
AT0004	SO2air	1996	1998	NOT	not	0.036	-0.105	-0.21
AT0005	SO2air	1996	1998	NOT	homog	0.057	-0.172	-0.37
AT0002	SO4air	1978	1998	NEG99	homog	-0.08	-0.097	-0.114
AT0002	SO4aq.	1987	1998	NEG99	homog	-0.047	-0.077	-0.108
AT0003	SO4aq.	1987	1995	NEG99	homog	-0.017	-0.028	-0.04
AT0004	SO4aq.	1987	1998	NEG99	homog	-0.02	-0.03	-0.04
AT0005	SO4aq.	1997	1998	Insuf				
AT0002	NO2	1996	1998	NOT	homog	1.043	0.522	-0.293
AT0004	NO2	1996	1998	NEG95	homog	-0.033	-0.238	-0.457
AT0005	NO2	1996	1998	NOT	homog	0.06	-0.08	-0.277
AT0002	NO3aq.	1978	1998	NEG99	homog	-0.005	-0.01	-0.016
AT0003	NO3aq.	1983	1995	NOT	homog	0.01	0.004	-0.004
AT0004	NO3aq.	1983	1998	NOT	homog	0.004	0	-0.005
AT0005	NO3aq.	1997	1998	NOT	homog	0	0	0
AT0002	NH4aq.	1978	1998	NEG99	homog	-0.004	-0.012	-0.02
AT0003	NH4aq.	1983	1995	NEG95	not	-0.003	-0.011	-0.02
AT0004	NH4aq.	1983	1998	NEG95	not	-0.002	-0.007	-0.013
AT0005	NH4aq.	1997	1998	Insuf				

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin	Cd red., Griess	bulk
1980	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin	Cd red., Griess	bulk
1981	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin	Cd red., Griess	bulk
1982	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin	Cd red., Griess	bulk
1983	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin	Cd red., Griess	wet-only
1984	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin	Cd red., Griess	wet-only
1985	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin	Cd red., Griess	wet-only
1986	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin	Cd red., Griess	wet-only
1987	Abs., H2O2, 3	Thorin(IC)	W40, 3	XRF	Thorin(IC)	Cd red./IC	wet-only
1988	Abs., H2O2, 3	IC	W40, 3	XRF	IC	Cd red./IC	wet-only
1989	Abs., H2O2, 3	IC	W41, 4	XRF	IC	IC	wet-only
1990	Abs., H2O2, 3	IC	W41, 4	XRF	IC	IC	wet-only
1991	Abs., H2O2, 3	IC	W41, 4	XRF	IC		wet-only
1992	Abs., H2O2, 3	IC	W41, 4	XRF	IC	IC	wet-only
1993	Abs., H2O2, 3	IC	W41, 4	XRF	IC	IC	wet-only
1994	Abs., H2O2, 3	IC	W41, 4	XRF	IC	IC	wet-only
1995	DOAS	DOAS	W41, 4	XRF	IC	IC	wet-only
1996	DOAS	DOAS	W41, 4	XRF	IC	IC	wet-only
1997	DOAS	DOAS	STE, 0.45 u, 3	IC	IC	IC	wet-only
1998	DOAS	DOAS	STE, 0.45 u, 3	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



BELARUS

BY04 Vysokoe

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
BY0004	SO2air	1985	1991	POS95	homog	0.154	0.089	0.022
BY0004	SO4air	1979	1991	NEG99	homog	-0.105	-0.152	-0.188
BY0004	SO4aq.	1981	1991	NOT	homog	0.066	0.02	-0.01
BY0004	NO2	1986	1991	POS99	homog	1.005	0.467	0.27
BY0004	NO3aq.	1984	1991	NOT	homog	0.028	-0.002	-0.024
BY0004	NH4air	1982	1991	NOT	homog	0.024	-0.014	-0.055
BY0004	NH4aq.	1981	1991	NEG90	not	0.006	-0.028	-0.067

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1980			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1981			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1982			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1983			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1984			W40, 3 / 17	Thorin	Thorin	Cd red., Griess	bulk
1985			W40, 17	Thorin	Thorin	Cd red., Griess	bulk
1986			W40, 17	Thorin	Thorin	Cd red., Griess	bulk
1987			W40, 17	Thorin	Thorin	Cd red., Griess	bulk
1988	Abs. tubes, TCM, 3	IC	W40, 15	Thorin	Thorin(IC)	Cd red., Griess	bulk
1989	Abs. tubes, TCM, 3	Pararosanilin	W40, 15	Thorin	Thorin(IC)	Cd red., Griess	bulk
1990	NaOH, 15	Pararosanilin	W40, 15	Thorin	Thorin(IC)	Cd red., Griess	bulk
1991	NaOH, 15	Pararosanilin	W40, 15	Thorin	Thorin(IC)		

BELGIUM

BE01 Offagne

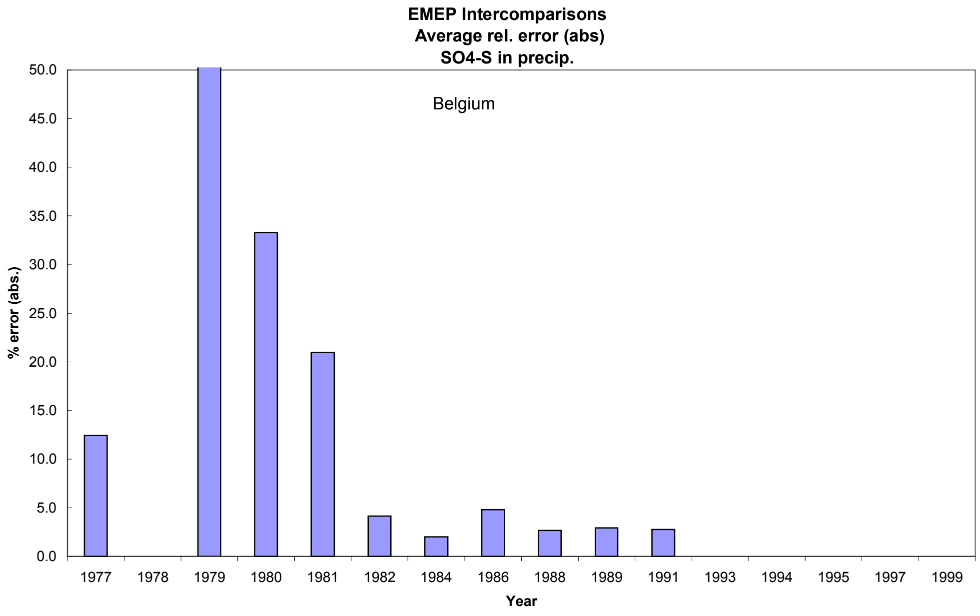
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
BE0001	SO2air	1979	1991	NEG95	homog	-0.004	-0.051	-0.102
BE0001	SO4air	1978	1991	NEG99	homog	-0.158	-0.192	-0.23
BE0001	SO4aq.	1984	1991	NEG99	homog	-0.098	-0.13	-0.168
BE0001	NO2	1986	1991	POS95	homog	0.56	0.257	-0.032
BE0001	NO3aq.	1978	1991	NEG95	homog	-0.003	-0.015	-0.028

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Monitor, flame phot..		Ca, 20		Thorin	IC	wet-only
1980	Monitor, flame phot..		Ca, 20	XRF	Thorin	IC	wet-only
1981	Monitor, flame phot..	Flame photometry	Ca, 20	XRF	Thorin	IC	wet-only
1982	Monitor, flame phot..	Flame photometry	Ca, 20	XRF	Thorin	IC	wet-only
1983	Monitor, flame phot..	Flame photometry	Ca, 20	XRF	Thorin	IC	wet-only
1984	Monitor, flame phot..	Flame photometry	Ca, 20	XRF	Thorin	IC	wet-only
1985	Monitor, flame phot..	Flame photometry	Ca, 20	XRF	Thorin	IC	wet-only
1986	Monitor, flame phot..	Flame photometry	Ca, 20	XRF	Thorin	IC	wet-only
1987	Monitor, flame phot..	Flame photometry	Ca, 20	XRF	Thorin	IC	wet-only
1988	Monitor, flame phot..	Flame photometry	SA, 0.45 u, 120	XRF	Thorin(IC)	IC	wet-only
1989	Monitor, flame phot..	Flame photometry	SA, 0.45 u, 120	XRF	Thorin(IC)	IC	wet-only
1990	Monitor, flame phot..	Flame photometry	SA, 0.45 u, 120	XRF	Thorin(IC)	IC	wet-only
1991	Monitor, flame phot..	Flame photometry	SA, 0.45 u, 120	XRF	Thorin(IC)	IC	wet-only
1992							
1993							
1994							
1995							
1996							
1997							
1998							

Performance in laboratory intercalibrations for sulphate in solution



BOSNIA HERCEGOVINA

BA06 Ivan Sedlo

SKT trend analysis and estimates of magnitude

Site	*Component*	*From*	*To*	*trend & significance*	*seasonal homogeneity*	*+90%*	*best est.*	*-90%*
BA0006	SO2air	1983	1992	POS95	homog	0.293	0.125	0
BA0006	SO4aq.	1980	1991	NEG95	homog	-0.009	-0.049	-0.093
BA0006	NO2	1990	1992	NOT	homog	0.387	-0.58	-2.594
BA0006	NO3aq.	1980	1991	POS99	homog	0.023	0.015	0.01
BA0006	NH4aq.	1980	1991	NOT	homog	0.016	0.002	-0.012

CROATIA

HR02 Puntijarka
HR04 Zavizan

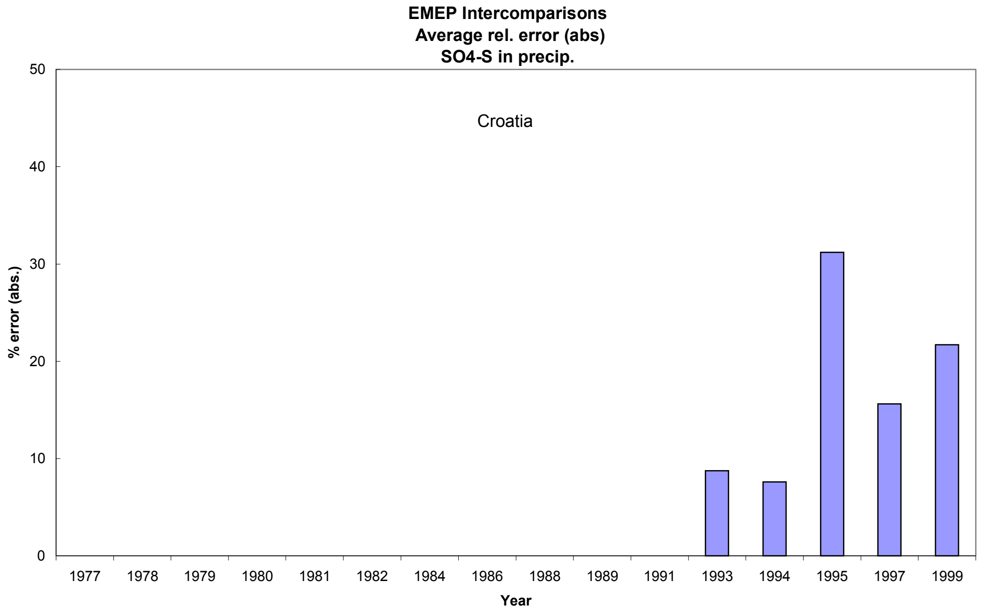
SKT trend analysis and estimates of magnitude

Site	*Component*	*From*	*To*	*trend & significance*	*seasonal homogeneity*	*+90%*	*best est.*	*-90%*
HR0002	SO2air	1985	1996	NEG99	homog	-0.226	-0.282	-0.372
HR0004	SO2air	1986	1996	NEG99	not	0	0	-0.019
HR0002	SO4aq.	1978	1996	NEG99	homog	-0.036	-0.056	-0.076
HR0004	SO4aq.	1980	1996	NEG99	homog	-0.029	-0.046	-0.064
HR0002	NO2	1990	1996	NEG99	homog	-0.37	-0.521	-0.67
HR0004	NO2	1990	1996	NEG99	homog	-0.078	-0.195	-0.285
HR0002	NO3aq.	1978	1996	POS99	homog	0.025	0.021	0.017
HR0004	NO3aq.	1980	1996	POS99	homog	0.017	0.012	0.009
HR0002	NH4aq.	1978	1996	POS95	homog	0.017	0.01	0.002
HR0004	NH4aq.	1980	1996	POS95	homog	0.015	0.008	0.001

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1991	Abs., TCM, 2						bulk
1992	Abs., TCM, 2				BaSO4 nephel.	UV spect.	bulk
1993	Abs., TCM, 2				BaSO4 nephel.	UV spect.	bulk
1994	Abs., TCM, 2				BaSO4 nephel.	UV spect.	bulk
1995	Abs., TCM, 2	Pararosanilin			BaSO4 nephel.	UV spect.	bulk
1996	Abs., TCM, 2	Pararosanilin			BaSO4 nephel.	UV spect.	bulk
1997	Abs., TCM, 2	Pararosanilin			BaSO4 nephel.	UV spect.	bulk
1998	Abs., TCM, 2	Pararosanilin			BaSO4 nephel.	UV spect.	bulk

Performance in laboratory intercalibrations for sulphate in solution



CZECH REPUBLIC

CZ01 Svratouch
CZ03 Kosetice

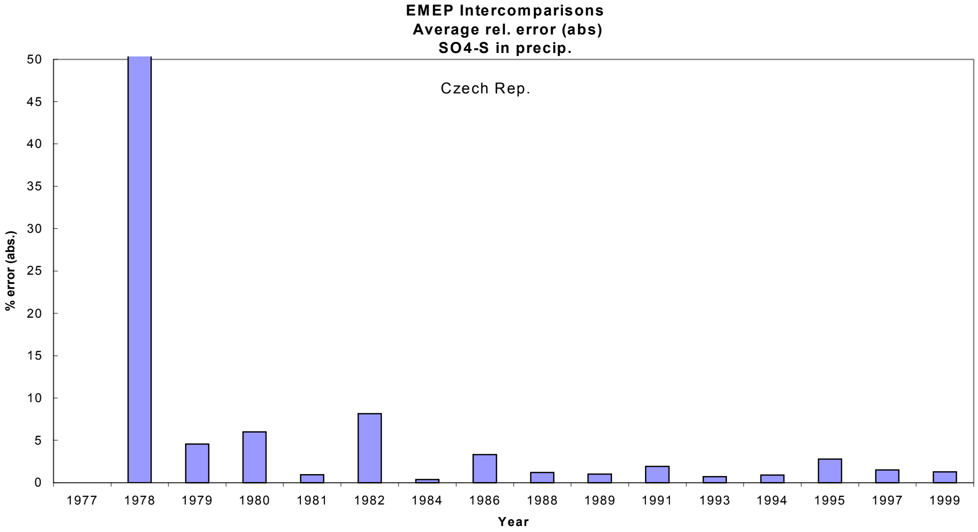
SKT trend analysis and estimates of magnitude

Site	*Component*	*From*	*To*	*trend & significance*	*seasonal homogeneity*	*+90%*	*best est.*	*-90%*
CS0001	SO2air	1989	1998	NEG99	homog	-0.765	-0.896	-1.084
CS0003	SO2air	1989	1998	NEG99	homog	-0.6	-0.752	-0.936
CS0001	SO4air	1989	1998	NEG99	homog	-0.12	-0.152	-0.185
CS0003	SO4air	1989	1998	NEG99	homog	-0.165	-0.195	-0.233
CS0001	SO4aq.	1986	1998	NEG99	homog	-0.084	-0.099	-0.113
CS0003	SO4aq.	1989	1998	NEG99	homog	-0.063	-0.085	-0.11
CS0001	NO2	1980	1998	NEG99	homog	-0.109	-0.13	-0.158
CS0003	NO2	1989	1998	NOT	homog	0.025	-0.017	-0.053
CS0001	NO3air	1989	1998	POS99	homog	0.045	0.031	0.021
CS0003	NO3air	1990	1998	NOT	homog	0.026	0.011	-0.014
CS0001	HNO3	1989	1998	POS99	homog	0.139	0.119	0.095
CS0003	HNO3	1990	1998	POS99	homog	0.125	0.1	0.074
CS0001	NO3aq.	1986	1998	NEG99	homog	-0.018	-0.023	-0.03
CS0003	NO3aq.	1989	1998	NEG99	homog	-0.014	-0.023	-0.039
CS0001	NH3	1989	1998	NEG99	homog	-0.082	-0.163	-0.23
CS0003	NH3	1990	1998	NEG99	homog	-0.21	-0.293	-0.371
CS0001	NH4air	1989	1998	NEG99	homog	-0.054	-0.095	-0.15
CS0003	NH4air	1990	1998	NEG90	homog	0.012	-0.033	-0.077
CS0001	NH4aq.	1986	1998	NEG99	homog	-0.018	-0.028	-0.04
CS0003	NH4aq.	1989	1998	NEG99	homog	-0.01	-0.025	-0.04

Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	KOH, 24	Thorin	W40, 25	Thorin	Thorin		bulk
1980	KOH, 24	Thorin	W40, 25	Thorin	Thorin		bulk
1981	KOH, 24	Thorin	W40, 25	Thorin	Thorin		bulk
1982	KOH, 24	Thorin	W40, 25	Thorin	Thorin		bulk
1983	KOH, 8	Thorin	W40, 10	Thorin	Thorin		bulk
1984	KOH, 8	Thorin	W40, 10	Thorin	Thorin		bulk
1985	KOH, 8	Thorin	W40, 10	Thorin	Thorin		bulk
1986	KOH, 8	Thorin	W40, 10	Thorin	Thorin	UV spect.	bulk
1987	KOH, 8	Thorin	W40, 10	Thorin	Thorin	UV spect.	bulk
1988	KOH, 8	Thorin	W40, 8	XRF	Thorin/IC	UV spect./IC	bulk
1989	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk
1990	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk
1991	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk
1992	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk
1993	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk
1994	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk
1995	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk
1996	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk
1997	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk/wet-only
1998	KOH, 8	Thorin	W40, 8	XRF	IC	IC	bulk/wet-only

Performance in laboratory intercalibrations for sulphate in solution



DENMARK

DK01 Færøerne
DK03 Tange
DK05 Keldsnor
DK07 Færøerne-Akraber
DK08 Anholt

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
DK0003	SO2air	1978	1998	NEG99	homog	-0.139	-0.161	-0.179
DK0005	SO2air	1978	1998	NEG99	homog	-0.155	-0.185	-0.215
DK0007	SO2air	1978	1991	NEG99	homog	-0.008	-0.014	-0.021
DK0008	SO2air	1991	1998	NEG99	homog	-0.112	-0.149	-0.187
DK0003	SO4air	1978	1998	NEG99	homog	-0.067	-0.076	-0.087
DK0005	SO4air	1978	1998	NEG99	homog	-0.078	-0.091	-0.105
DK0007	SO4air	1978	1990	NOT	homog	0.006	-0.02	-0.036
DK0008	SO4air	1991	1998	NEG99	homog	-0.103	-0.127	-0.16
DK0001	SO4aq.	1978	1978	Insuf				
DK0003	SO4aq.	1978	1998	NEG99	homog	-0.027	-0.034	-0.04
DK0005	SO4aq.	1978	1998	NEG99	homog	-0.05	-0.06	-0.072
DK0007	SO4aq.	1978	1991	NOT	homog	0.007	-0.013	-0.03
DK0008	SO4aq.	1996	1998	NEG95	homog	-0.04	-0.213	-0.491
DK0003	NO2	1990	1991	Insuf				
DK0005	NO2	1990	1991	Insuf				
DK0008	NO2	1991	1998	NOT	homog	0.076	0.011	-0.049
DK0003	NO3HNO3	1989	1998	NEG99	homog	-0.014	-0.024	-0.04
DK0005	NO3HNO3	1985	1998	NEG99	homog	-0.024	-0.044	-0.06
DK0007	NO3HNO3	1990	1991	Insuf				
DK0008	NO3HNO3	1991	1998	NEG99	homog	-0.011	-0.033	-0.055
DK0001	NO3aq.	1978	1978	Insuf				
DK0003	NO3aq.	1978	1998	NOT	homog	0.005	0.001	-0.003
DK0005	NO3aq.	1978	1998	NEG99	homog	-0.013	-0.02	-0.027
DK0007	NO3aq.	1978	1991	POS90	homog	0.01	0.005	0
DK0008	NO3aq.	1996	1998	NEG95	homog	-0.016	-0.225	-0.393

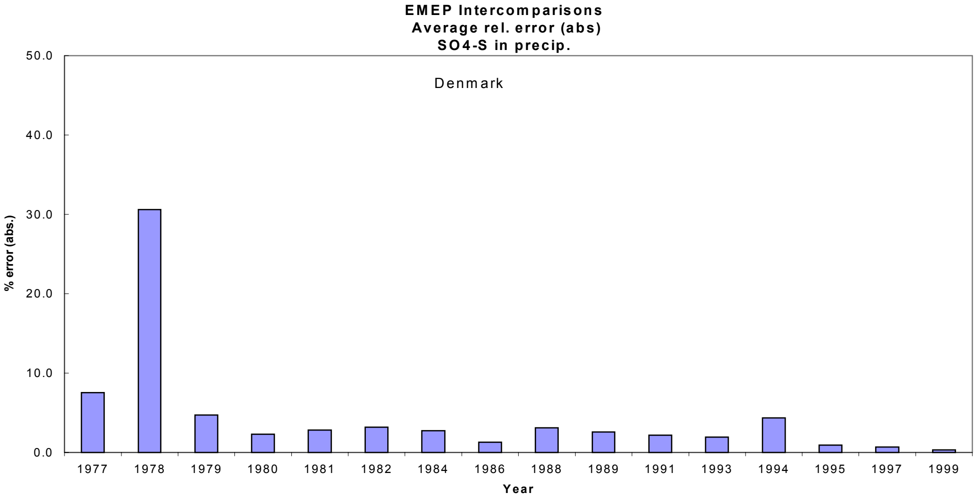
SKT trend analysis and estimates of magnitude(cont)

Site	*Component*	*From*	*To*	*trend & significance*	*seasonal homogeneity*	*+90%*	*best est.*	*-90%*
DK0003	NH4air	1978	1989	NOT	not	0.006	-0.033	-0.074
DK0005	NH4air	1978	1989	NEG95	homog	0	-0.038	-0.09
DK0007	NH4air	1978	1989	POS95	homog	0.02	0.01	0.003
DK0003	NH3+4	1989	1998	NEG99	homog	-0.09	-0.141	-0.188
DK0005	NH3+4	1985	1998	NEG99	homog	-0.06	-0.099	-0.154
DK0007	NH3+4	1990	1991	Insuf	not			
DK0008	NH3+4	1991	1998	NEG99	homog	-0.045	-0.08	-0.115
DK0001	NH4aq.	1978	1978	Insuf	not			
DK0003	NH4aq.	1978	1998	NEG95	homog	-0.001	-0.007	-0.013
DK0005	NH4aq.	1978	1998	NEG99	homog	-0.015	-0.022	-0.031
DK0007	NH4aq.	1978	1991	NOT	homog	0.006	0	-0.007
DK0008	NH4aq.	1996	1998	NEG90	homog	0.047	-0.078	-0.232

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	KOH, 58	Thorin	ST, 60	Thorin	Thorin aut.	NH2NH2 red., Griess	bulk
1980	KOH, 58	Thorin	ST, 60	Thorin	Thorin aut.	NH2NH2 red., Griess	bulk
1981	KOH, 58	Thorin	ST, 60	Thorin	Thorin aut.	NH2NH2 red., Griess	bulk
1982	KOH, 58	Thorin	ST, 60	Thorin	Thorin aut.	NH2NH2 red., Griess	bulk
1983	KOH, 58	Sulfonazo III, aut.	ST, 60	Sulfonazo III, aut.	Sulphonazo III, aut/IC	NH2NH2/IC	wet-only/bulk
1984	KOH, 58	Sulfonazo III, aut.	ST, 60	Sulfonazo III, aut.	IC	IC	wet-only/bulk
1985	KOH, 58	Sulfonazo III, aut.	ST, 60	Sulfonazo III, aut.	IC	IC	wet-only/bulk
1986	KOH, 58	Sulfonazo III, aut.	ST, 60	Sulfonazo III, aut.	IC	IC	wet-only/bulk
1987	KOH, 58	Sulfonazo III, aut.	ST/ MM, 58	Sulfonazo III, aut.	IC	IC	wet-only/bulk
1988	KOH, 58	Sulfonazo III, aut.	MM, 1.2 u, 58	Sulfonazo III, aut.	IC	IC	wet-only/bulk
1989	KOH, 58	Sulfonazo III, aut./IC	MM, 1.2 u, 58	Sulfonazo III, aut./PIXE	IC	IC	wet-only/bulk
1990	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only/bulk
1991	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only/bulk
1992	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only
1993	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only
1994	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only
1995	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only
1996	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only
1997	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only
1998	NaF + KOH, 58	IC	MM, 1.2 u, 58	PIXE	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



European Community

IT04 Ispra

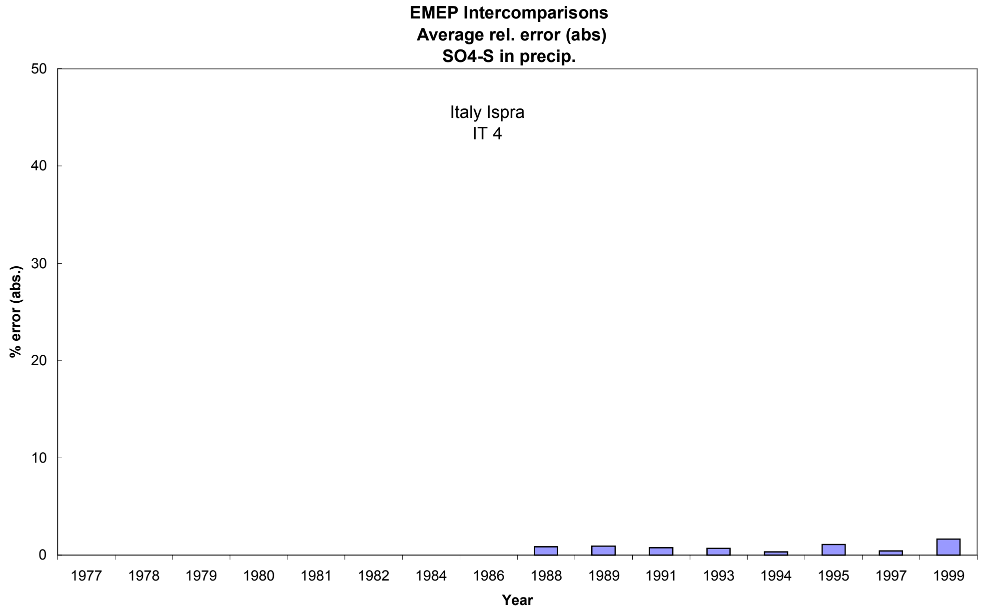
SKT trend analysis and estimates of magnitude

Site	*Component*	*From*	*To*	*trend & significance*	*seasonal homogeneity*	*+90%*	*best est.*	*-90%*
IT0004	SO2air	1985	1998	NEG99	homog	-0.194	-0.219	-0.258
IT0004	SO4air	1985	1998	NEG99	homog	-0.118	-0.14	-0.164
IT0004	SO4aq.	1985	1998	NEG99	homog	-0.035	-0.052	-0.07
IT0004	NO2	1985	1998	NEG99	homog	-0.03	-0.071	-0.115
IT0004	NO3air	1985	1998	NEG99	homog	-0.018	-0.032	-0.045
IT0004	NO3HNO3	1985	1994	NEG99	homog	-0.018	-0.049	-0.087
IT0004	HNO3	1985	1994	POS99	homog	0.216	0.129	0.014
IT0004	NO3aq.	1985	1998	NEG99	homog	-0.01	-0.022	-0.035
IT0004	NH3	1994	1994	Insuf				
IT0004	NH4air	1985	1998	NEG99	homog	-0.084	-0.116	-0.146
IT0004	NH3+4	1994	1994	Insuf				
IT0004	NH4aq.	1985	1998	NEG95	homog	-0.006	-0.022	-0.036

Sampling and analytical methods

	SO2		SO4 in air		SO4 prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1984							
1985			Ca, 12				
1986	KOH, 12	IC	Ca, 12	IC	IC	IC	wet-only
1987	KOH, 12	IC	Ca, 12	IC	IC	IC	wet-only
1988	Monitor, UV-fluor.	IC	FL, 0.8 u, 12	IC	IC	IC	wet-only
1989	Monitor, UV-fluor.	IC	FL, 0.8 u, 12	IC	IC	IC	wet-only
1990	Monitor, UV-fluor.	UV-fluores.	FL, 0.8 u, 12	IC	IC	IC	wet-only
1991	Monitor, UV-fluor.	IC	FL, 0.8 u, 12	IC	IC	IC	wet-only
1992	Monitor, UV-fluor.	IC(UV-fluores.)	FL, 0.8 u, 12	IC	IC	IC	wet-only
1993	Monitor, UV-fluor.	IC(UV-fluores.)	FL, 0.8 u, 12	IC	IC	IC	wet-only
1994	Monitor, UV-fluor.	IC(UV-fluores.)	FL, 0.8 u, 12	IC	IC	IC	wet-only
1995	Monitor, UV-fluor.	UV-fluores.	FL, 0.8 u, 12	IC	IC	IC	wet-only
1996	Monitor, UV-fluor.	UV-fluores.	FL, 0.8 u, 12	IC	IC	IC	wet-only
1997	Monitor, UV-fluor.	UV-fluores.	FL, 0.8 u, 12	IC	IC	IC	wet-only
1998	Monitor, UV-fluor.	UV-fluores.	FL, 0.8 u, 12	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



ESTONIA

EE02 Syrve
EE09 Lahemaa
EE11 Vilsandy

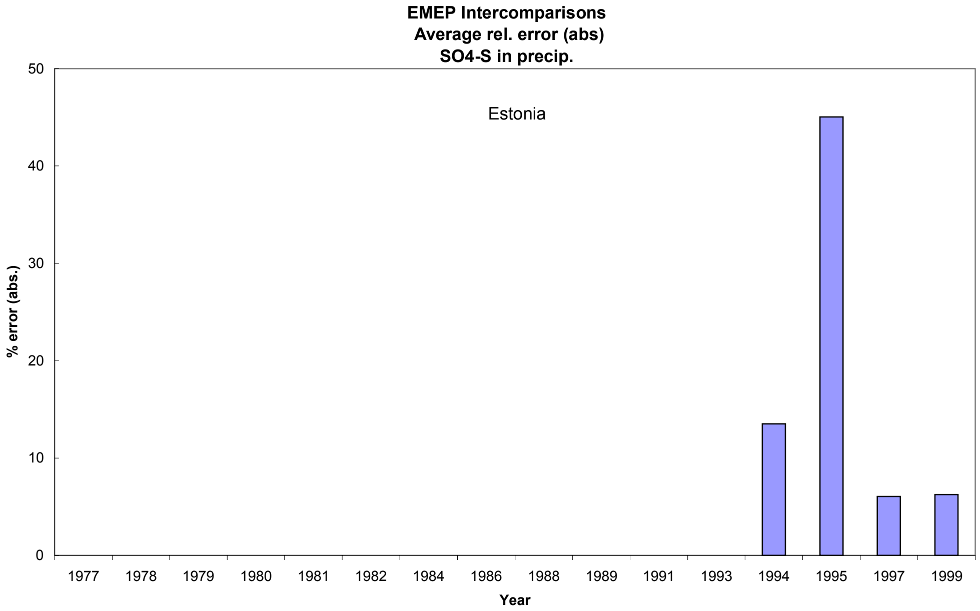
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
EE0002	SO2air	1985	1988	NOT	homog	0.02	0.002	-0.01
EE0009	SO2air	1985	1995	NEG99	homog	-0.025	-0.049	-0.075
EE0011	SO2air	1989	1998	POS90	homog	0.038	0.019	-0.001
EE0002	SO4air	1979	1988	NEG99	homog	-0.165	-0.271	-0.484
EE0009	SO4air	1985	1995	NEG99	homog	-0.057	-0.08	-0.105
EE0011	SO4air	1989	1990	Insuf				
EE0002	SO4aq.	1981	1991	NOT	homog	0.051	0.019	-0.017
EE0009	SO4aq.	1985	1998	NOT	homog	0.025	0.008	-0.026
EE0011	SO4aq.	1990	1998	NOT	homog	0.026	-0.019	-0.131
EE0002	NO2	1986	1988	NEG95	homog	-0.047	-0.382	-0.833
EE0009	NO2	1986	1998	NEG95	homog	-0.005	-0.03	-0.057
EE0011	NO2	1989	1998	POS99	homog	0.066	0.051	0.034
EE0002	NO3air	1986	1988	NEG90	homog	-0.004	-0.03	-0.067
EE0009	NO3air	1986	1991	NEG95	homog	0	-0.01	-0.029
EE0011	NO3air	1989	1990	Insuf				
EE0002	NO3aq.	1984	1991	NOT	homog	0.057	0.016	-0.021
EE0009	NO3aq.	1985	1998	NOT	homog	0.002	-0.003	-0.009
EE0011	NO3aq.	1990	1998	NOT	homog	0.043	0.014	-0.031
EE0002	NH4air	1982	1988	NEG99	homog	-0.06	-0.102	-0.145
EE0009	NH4air	1985	1991	NOT	homog	0.051	0.005	-0.116
EE0011	NH4air	1989	1990	Insuf				
EE0002	NH4aq.	1982	1991	NOT	homog	0.02	0.001	-0.023
EE0009	NH4aq.	1985	1998	NOT	homog	0.003	-0.008	-0.017
EE0011	NH4aq.	1990	1998	NOT	homog	0.04	-0.001	-0.04

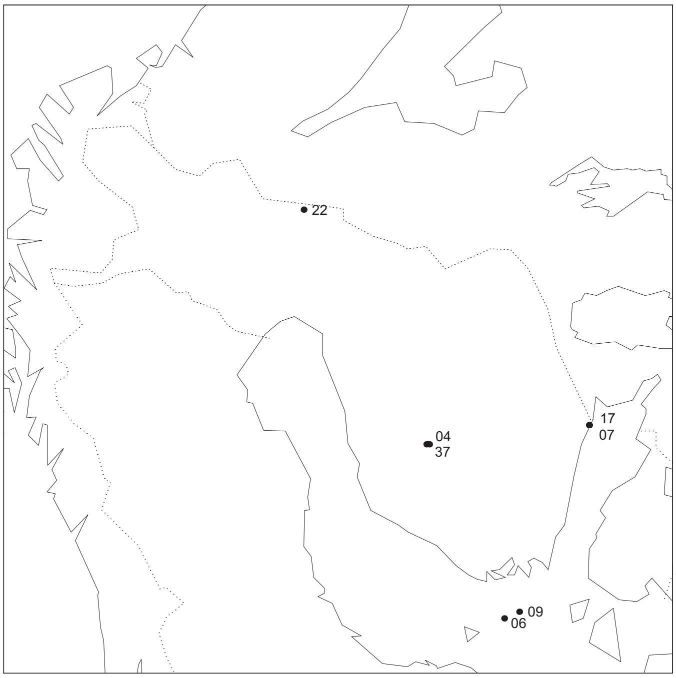
Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979							
1980							
1981							
1982							
1983							
1984							
1985							
1986							
1987							
1988							
1989							
1990							
1991	NaOH, 15		W40, 15	Thorin		IC	
1992							
1993							
1994							
1995							
1996							
1997	Monitor, UV-fluor.	IC, UV-fluores.	W40, 5	IC		IC	bulk
1998	NaOH, 5/ Monitor, UV-fluor	IC, UV-fluores.	W40, 5	IC	IC	IC	bulk

Performance in laboratory intercalibrations for sulphate in solution



FINLAND



FI04 Ahtari
FI06 Kokar
FI07 Virolahti
FI09 Utø
FI17 Virolahti II
FI22 Oulanka
FI37 Ahtari II

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
FI0004	SO2air	1978	1997	NEG99	homog	-0.152	-0.17	-0.188
FI0006	SO2air	1978	1979	Insuf				
FI0007	SO2air	1978	1988	NEG99	homog	-0.126	-0.166	-0.228
FI0009	SO2air	1980	1998	NEG99	homog	-0.206	-0.229	-0.25
FI0017	SO2air	1989	1998	NEG99	homog	-0.05	-0.073	-0.103
FI0022	SO2air	1990	1998	NEG99	homog	-0.013	-0.025	-0.035
FI0037	SO2air	1997	1998	Insuf				
FI0004	SO4air	1978	1997	NEG99	homog	-0.025	-0.032	-0.038
FI0006	SO4air	1978	1979	Insuf				
FI0007	SO4air	1978	1988	NOT	homog	0.018	-0.007	-0.03
FI0009	SO4air	1980	1998	NEG99	homog	-0.029	-0.04	-0.05
FI0017	SO4air	1989	1998	NEG99	homog	-0.037	-0.05	-0.07
FI0022	SO4air	1990	1998	NEG99	homog	-0.015	-0.024	-0.033
FI0037	SO4air	1997	1998	Insuf				
FI0004	SO4aq.	1978	1998	NEG99	homog	-0.022	-0.026	-0.03
FI0006	SO4aq.	1978	1979	Insuf				
FI0007	SO4aq.	1978	1988	NEG95	homog	-0.007	-0.022	-0.05
FI0009	SO4aq.	1980	1998	NEG99	homog	-0.05	-0.06	-0.07
FI0017	SO4aq.	1989	1998	NEG99	homog	-0.06	-0.08	-0.094
FI0022	SO4aq.	1990	1998	NEG99	homog	-0.017	-0.025	-0.032
FI0004	NO2	1990	1997	NOT	homog	0.034	-0.022	-0.09
FI0009	NO2	1990	1998	NOT	homog	0.045	0.003	-0.03
FI0017	NO2	1990	1998	NOT	homog	0.013	-0.028	-0.064
FI0022	NO2	1990	1998	NOT	homog	0.012	0.002	-0.005
FI0037	NO2	1997	1998	Insuf				

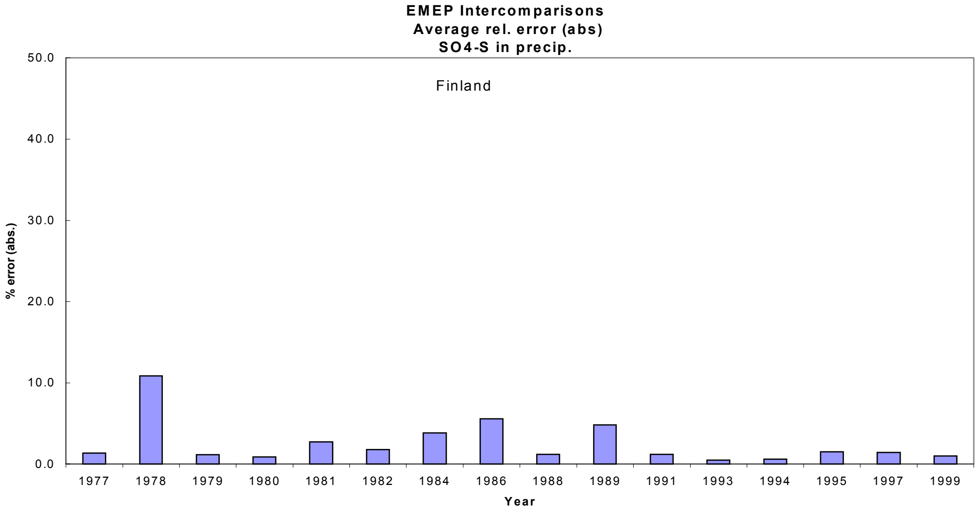
SKT trend analysis and estimates of magnitude(cont)

Site	Component	From	To	trend significance	& seasonal homogeneity	+90%	best est.	-90%
FI0004	NO3HNO3	1989	1997	NEG99	homog	-0.003	-0.006	-0.01
FI0009	NO3HNO3	1985	1998	NOT	homog	0.006	-0.004	-0.011
FI0017	NO3HNO3	1989	1998	NEG99	homog	-0.006	-0.01	-0.015
FI0022	NO3HNO3	1990	1998	NEG99	not	-0.002	-0.003	-0.005
FI0037	NO3HNO3	1997	1998	Insuf				
FI0004	NO3aq.	1980	1998	POS95	homog	0.008	0.004	0
FI0007	NO3aq.	1980	1988	POS99	homog	0.026	0.015	0.007
FI0009	NO3aq.	1980	1998	POS90	homog	0.02	0.008	0
FI0017	NO3aq.	1989	1998	POS99	homog	0.105	0.055	0.02
FI0022	NO3aq.	1990	1998	POS99	homog	0.096	0.038	0.02
FI0004	NH3+4	1989	1997	NEG99	homog	-0.02	-0.029	-0.044
FI0009	NH3+4	1985	1998	NEG95	homog	-0.006	-0.016	-0.027
FI0017	NH3+4	1989	1998	NEG95	homog	-0.002	-0.016	-0.031
FI0022	NH3+4	1990	1998	NEG95	homog	0	-0.007	-0.013
FI0037	NH3+4	1997	1998	Insuf				
FI0004	NH4aq.	1980	1998	POS90	homog	0.009	0.004	0
FI0007	NH4aq.	1980	1988	NEG99	homog	-0.01	-0.025	-0.04
FI0009	NH4aq.	1980	1998	NOT	homog	0.008	-0.001	-0.01
FI0017	NH4aq.	1989	1998	POS99	homog	0.15	0.07	0.017
FI0022	NH4aq.	1990	1998	POS99	homog	0.071	0.03	0.013

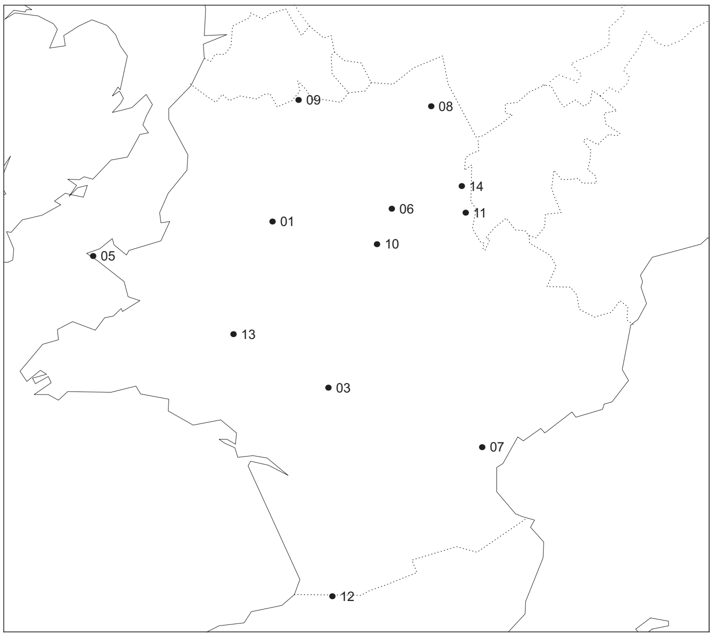
Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							bulk
1979	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin aut.	Cd red., Griess	bulk
1980	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin aut.	Cd red., Griess	bulk
1981	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin aut.	Cd red., Griess	bulk
1982	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin aut.	Cd red., Griess	bulk
1983	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin aut.	Cd red., Griess	bulk
1984	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1985	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1986	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1987	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1988	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1989	NaOH, 24	Thorin(IC)	W40 24	XRF(IC)	IC	IC	bulk
1990	NaOH, 24	IC	W40 24	IC	IC	IC	bulk
1991	NaOH, 24	IC	W40 24	IC	IC	IC	bulk
1992	NaOH, 24	IC	W40 24	IC	IC	IC	bulk
1993	NaOH, 24	IC	W40 24	IC	IC	IC	bulk
1994	NaOH, 24	IC	W40 24	IC	IC	IC	bulk
1995	NaOH, 24	IC	W40 24	IC	IC	IC	bulk
1996	NaOH, 24	IC	W40 24	IC	IC	IC	bulk
1997	NaOH, 24	IC	W40 24	IC	IC	IC	bulk
1998	NaOH, 24	IC	W40 24	IC	IC	IC	bulk

Performance in laboratory intercalibrations for sulphate in solution



FRANCE



FR01 Vert-le-Petit
FR03 La Crouzille
FR05 La Hague
FR06 Valduc
FR07 Lodeve
FR08 Donon
FR09 Revin
FR10 Morvan
FR11 Bonnevaux
FR12 Iraty
FR13 Peyrusse Vielle
FR14 Montandon

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
FR0001	SO2air	1978	1987	NEG99	homog	-0.178	-0.275	-0.392
FR0003	SO2air	1978	1998	NEG99	homog	-0.028	-0.04	-0.051
FR0005	SO2air	1978	1998	NEG99	homog	-0.282	-0.315	-0.36
FR0006	SO2air	1978	1984	NEG99	homog	-0.12	-0.23	-0.472
FR0007	SO2air	1978	1984	NOT	homog	0.223	0.046	-0.129
FR0008	SO2air	1990	1998	NEG99	homog	-0.087	-0.138	-0.225
FR0009	SO2air	1992	1998	NOT	homog	0.036	-0.022	-0.109
FR0010	SO2air	1990	1998	NEG99	homog	-0.032	-0.075	-0.134
FR0011	SO2air	1990	1998	NEG99	homog	-0.038	-0.1	-0.174
FR0012	SO2air	1990	1998	NEG99	homog	-0.119	-0.184	-0.255
FR0013	SO2air	1998	1998	Insuf				
FR0014	SO2air	1998	1998	Insuf				
FR0001	SO4air	1978	1987	NEG99	homog	-0.175	-0.225	-0.321
FR0003	SO4air	1978	1998	NEG99	homog	-0.035	-0.047	-0.06
FR0005	SO4air	1978	1998	NEG99	homog	-0.105	-0.125	-0.147
FR0006	SO4air	1978	1984	NEG99	homog	-0.273	-0.451	-0.641
FR0007	SO4air	1978	1984	NEG95	homog	-0.056	-0.257	-0.4
FR0008	SO4air	1990	1998	NEG99	homog	-0.02	-0.041	-0.07
FR0009	SO4air	1992	1998	NOT	homog	0.044	0	-0.05
FR0010	SO4air	1990	1998	NEG99	homog	-0.03	-0.063	-0.09
FR0011	SO4air	1990	1998	NEG99	homog	-0.027	-0.047	-0.067
FR0012	SO4air	1990	1998	NEG99	homog	-0.019	-0.041	-0.067
FR0013	SO4air	1998	1998	Insuf				
FR0014	SO4air	1998	1998	Insuf				
FR0001	SO4aq.	1981	1989	NEG95	not	-0.014	-0.071	-0.137
FR0003	SO4aq.	1981	1998	NEG99	homog	-0.008	-0.018	-0.03
FR0005	SO4aq.	1978	1998	NEG99	homog	-0.04	-0.05	-0.06

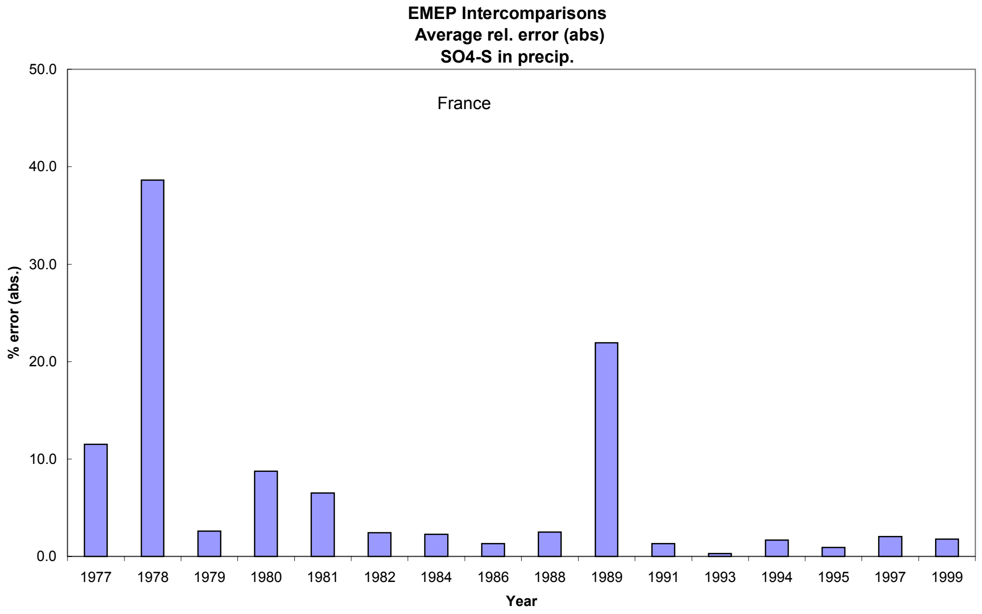
SKT trend analysis and estimates of magnitude(cont)

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
FR0006	SO4aq.	1981	1984	NOT	homog	0.424	0.145	-0.424
FR0007	SO4aq.	1981	1983	NOT	homog	1.164	-0.645	-1.858
FR0008	SO4aq.	1990	1998	NEG99	homog	-0.017	-0.03	-0.045
FR0009	SO4aq.	1990	1998	NEG99	homog	-0.01	-0.027	-0.04
FR0010	SO4aq.	1990	1998	NEG95	homog	0	-0.008	-0.023
FR0011	SO4aq.	1990	1998	NEG99	homog	-0.005	-0.013	-0.024
FR0012	SO4aq.	1990	1998	NEG95	homog	-0.004	-0.019	-0.049
FR0013	SO4aq.	1998	1998	Insuf				
FR0014	SO4aq.	1998	1998	Insuf				
FR0001	NO3aq.	1978	1989	NEG90	homog	0.003	-0.018	-0.031
FR0003	NO3aq.	1978	1998	NEG95	not	0	-0.004	-0.009
FR0005	NO3aq.	1981	1998	NEG99	homog	-0.002	-0.01	-0.016
FR0006	NO3aq.	1978	1984	NOT	homog	0.04	0.021	-0.015
FR0007	NO3aq.	1981	1983	NOT	homog	0.967	-0.13	-0.935
FR0008	NO3aq.	1990	1998	NOT	homog	0.002	-0.008	-0.02
FR0009	NO3aq.	1990	1998	NEG95	homog	-0.002	-0.01	-0.024
FR0010	NO3aq.	1990	1998	NOT	homog	0.008	0	-0.01
FR0011	NO3aq.	1990	1998	NOT	homog	0.005	-0.005	-0.013
FR0012	NO3aq.	1990	1998	NEG90	homog	0	-0.005	-0.016
FR0013	NO3aq.	1998	1998	Insuf				
FR0014	NO3aq.	1998	1998	Insuf				
FR0001	NH4aq.	1978	1989	NEG99	homog	-0.031	-0.07	-0.106
FR0003	NH4aq.	1978	1998	POS90	homog	0.013	0.007	-0.001
FR0005	NH4aq.	1981	1998	NOT	homog	0.004	-0.004	-0.013
FR0006	NH4aq.	1978	1984	NOT	homog	0.022	-0.052	-0.092
FR0007	NH4aq.	1981	1983	NOT	homog	0.637	0.09	-0.282
FR0008	NH4aq.	1990	1998	NEG99	homog	-0.04	-0.06	-0.077
FR0009	NH4aq.	1990	1998	NEG99	homog	-0.042	-0.068	-0.11
FR0010	NH4aq.	1990	1998	NEG99	homog	-0.038	-0.062	-0.083
FR0011	NH4aq.	1990	1998	NEG99	homog	-0.03	-0.053	-0.077
FR0012	NH4aq.	1990	1998	NEG99	homog	-0.049	-0.068	-0.09
FR0013	NH4aq.	1998	1998	Insuf				
FR0014	NH4aq.	1998	1998	Insuf				

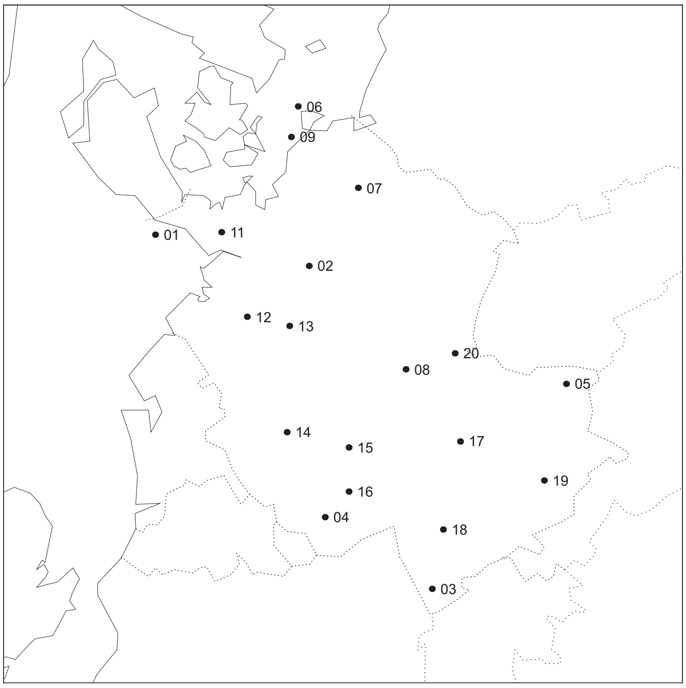
Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1980	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1981	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1982	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1983	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1984	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1985	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1986	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1987	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk
1988	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	bulk
1989	Abs., H2O2, 3	IC	W40, 3		IC		bulk
1990	Abs., H2O2, 3	IC	W40, 3		IC		wet-only
1991	Abs., H2O2, 3	IC	W40, 3	IC	IC		wet-only
1992	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	wet-only
1993	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	wet-only
1994	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	wet-only
1995	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	wet-only
1996	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	wet-only
1997	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	wet-only
1998	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



GERMANY



DE01 Westerland
DE02 Waldhof
DE03 Schauinsland
DE04 Deuselbach
DE05 Brotjacklriegel
DE06 Arkona
DE07 Neuglobsov
DE08 Schmucke
DE09 Zingst
DE11 Hohenwestedt
DE12 Bassum
DE13 Rodenberg
DE!4 Meinerzhagen
DE15 Usingen
DE16 Bad Kreuznach
DE17 Ansbach
DE18 Rottenburg
DE19 Starnberg
DE20 Hof

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
DD0001	SO2air	1981	1990	NEG99	homog	-0.027	-0.093	-0.199
DE0007	SO2air	1981	1998	NEG99	homog	-0.29	-0.338	-0.387
DE0001	SO2air	1978	1998	NEG99	homog	-0.08	-0.097	-0.118
DE0002	SO2air	1978	1998	NEG99	homog	-0.35	-0.388	-0.434
DE0003	SO2air	1978	1998	NEG99	homog	-0.08	-0.093	-0.106
DE0004	SO2air	1978	1998	NEG99	homog	-0.283	-0.315	-0.356
DE0005	SO2air	1978	1998	NEG99	homog	-0.183	-0.22	-0.255
DE0008	SO2air	1992	1998	NEG99	homog	-0.176	-0.274	-0.323
DE0009	SO2air	1993	1998	NEG99	homog	-0.02	-0.065	-0.16
DE0011	SO2air	1980	1986	NEG99	homog	-0.096	-0.186	-0.347
DE0012	SO2air	1980	1993	NEG99	homog	-0.401	-0.465	-0.549
DE0013	SO2air	1980	1992	NEG99	homog	-0.312	-0.402	-0.532
DE0014	SO2air	1980	1993	NEG99	homog	-0.61	-0.696	-0.816
DE0015	SO2air	1980	1993	NEG99	homog	-0.475	-0.557	-0.659
DE0016	SO2air	1980	1990	NEG99	homog	-0.515	-0.703	-0.86
DE0017	SO2air	1980	1993	NEG99	homog	-0.12	-0.199	-0.29
DE0018	SO2air	1980	1993	NEG99	homog	-0.161	-0.203	-0.26
DE0019	SO2air	1980	1993	NEG99	homog	-0.092	-0.13	-0.178
DE0020	SO2air	1980	1993	NOT	homog	0.123	-0.206	-0.523
DD0001	SO4air	1981	1990	NOT	homog	0.06	0.02	-0.014
DE0007	SO4air	1981	1998	NEG99	homog	-0.123	-0.138	-0.152
DE0001	SO4air	1978	1998	NEG99	homog	-0.032	-0.039	-0.046
DE0002	SO4air	1978	1998	NEG99	homog	-0.062	-0.074	-0.086
DE0003	SO4air	1978	1998	NEG99	homog	-0.025	-0.032	-0.041
DE0004	SO4air	1978	1998	NEG99	homog	-0.054	-0.064	-0.071
DE0005	SO4air	1978	1998	NEG99	homog	-0.038	-0.046	-0.054

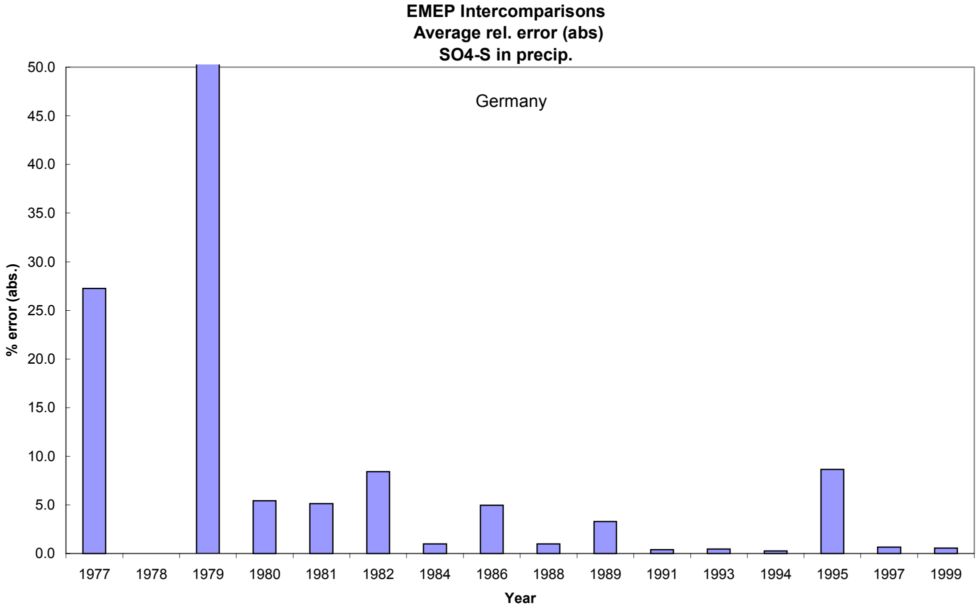
SKT trend analysis and estimates of magnitude(cont)

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
DE0008	SO4air	1991	1998	NEG99	homog	-0.049	-0.072	-0.114
DE0009	SO4air	1993	1998	NEG99	homog	-0.023	-0.054	-0.1
DE0011	SO4air	1978	1986	NEG95	homog	-0.01	-0.061	-0.12
DE0012	SO4air	1978	1995	NEG99	homog	-0.085	-0.1	-0.113
DE0013	SO4air	1978	1992	NEG99	homog	-0.038	-0.061	-0.09
DE0014	SO4air	1978	1995	NEG99	homog	-0.071	-0.081	-0.093
DE0015	SO4air	1978	1993	NEG99	homog	-0.059	-0.08	-0.096
DE0016	SO4air	1978	1990	NEG99	homog	-0.031	-0.054	-0.074
DE0017	SO4air	1978	1995	NEG99	homog	-0.08	-0.091	-0.105
DE0018	SO4air	1978	1995	NEG99	homog	-0.065	-0.08	-0.096
DE0019	SO4air	1978	1994	NEG99	homog	-0.047	-0.058	-0.072
DE0020	SO4air	1980	1993	NOT	not	0.044	0.009	-0.028
DD0001	SO4aq.	1985	1990	NEG99	homog	-0.064	-0.138	-0.281
DE0007	SO4aq.	1981	1998	NEG99	homog	-0.118	-0.129	-0.15
DE0001	SO4aq.	1982	1998	NEG99	homog	-0.024	-0.032	-0.041
DE0002	SO4aq.	1982	1998	NEG99	homog	-0.039	-0.049	-0.057
DE0003	SO4aq.	1982	1998	NEG99	homog	-0.009	-0.013	-0.018
DE0004	SO4aq.	1982	1998	NEG99	homog	-0.023	-0.031	-0.037
DE0005	SO4aq.	1982	1998	NEG99	homog	-0.044	-0.054	-0.062
DE0008	SO4aq.	1991	1998	NEG99	homog	-0.045	-0.071	-0.102
DE0009	SO4aq.	1993	1998	NOT	homog	0.034	-0.012	-0.035
DE0001	NO2	1978	1998	NOT	homog	0.013	0.005	-0.004
DE0002	NO2	1978	1998	NEG99	homog	-0.05	-0.06	-0.07
DE0003	NO2	1978	1998	NOT	homog	0.001	-0.002	-0.006
DE0004	NO2	1978	1998	NEG99	homog	-0.054	-0.062	-0.073
DE0005	NO2	1978	1998	POS99	homog	0.016	0.011	0.005
DE0007	NO2	1992	1998	NOT	homog	0.015	-0.009	-0.036
DE0008	NO2	1992	1998	NEG99	homog	-0.055	-0.08	-0.1
DE0009	NO2	1993	1998	NOT	homog	0.036	0.005	-0.03
DD0001	NO3aq.	1985	1990	NOT	homog	0.01	-0.024	-0.06
DE0007	NO3aq.	1981	1998	NOT	homog	0.001	-0.004	-0.009
DE0001	NO3aq.	1982	1998	NEG95	not	0	-0.007	-0.013
DE0002	NO3aq.	1982	1998	NEG99	homog	-0.004	-0.009	-0.014
DE0003	NO3aq.	1982	1998	NOT	homog	0.003	0	-0.003
DE0004	NO3aq.	1982	1998	NEG90	homog	0	-0.005	-0.01
DE0005	NO3aq.	1982	1998	NEG99	homog	-0.013	-0.018	-0.024
DE0008	NO3aq.	1991	1998	NEG90	homog	0.001	-0.015	-0.04
DE0009	NO3aq.	1993	1998	NOT	homog	0.03	0	-0.027
DD0001	NH4aq.	1985	1990	NEG90	homog	0.005	-0.034	-0.067
DE0007	NH4aq.	1981	1998	NEG95	homog	0	-0.007	-0.013
DE0001	NH4aq.	1982	1998	NEG99	homog	-0.004	-0.011	-0.018
DE0002	NH4aq.	1983	1998	NEG95	homog	0	-0.009	-0.015
DE0003	NH4aq.	1982	1998	NOT	homog	0.006	0.002	-0.001
DE0004	NH4aq.	1983	1998	NOT	homog	0.002	-0.002	-0.008
DE0005	NH4aq.	1983	1998	NEG99	homog	-0.013	-0.022	-0.03
DE0008	NH4aq.	1991	1998	NOT	homog	0.025	0.005	-0.02
DE0009	NH4aq.	1993	1998	NOT	homog	0.032	-0.002	-0.03

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip.	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC		bulk
1980	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC		bulk
1981	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	NH2NH2 red., Griess	bulk
1982	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	NH2NH2 red., Griess	bulk
1983	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1984	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1985	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1986	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1987	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1988	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1989	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	Isotope dilution	IC	bulk
1990	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1991	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1992	Abs., TCM, 1	Pararosanilin	S, 1	XRF	IC	IC	bulk
1993	Abs., TCM, 1	Pararosanilin	S, 1	XRF	IC	IC	bulk
1994	Abs., TCM, 1	Pararosanilin	S, 1	XRF	IC	IC	bulk
1995	Abs., TCM, 1	Pararosanilin	S, 1	XRF	IC	IC	bulk
1996	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1997	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk
1998	Abs., TCM, 1	Pararosanilin	S2L, 1	XRF	IC	IC	bulk

Performance in laboratory intercalibrations for sulphate in solution



GREECE

GR01 Aliartos

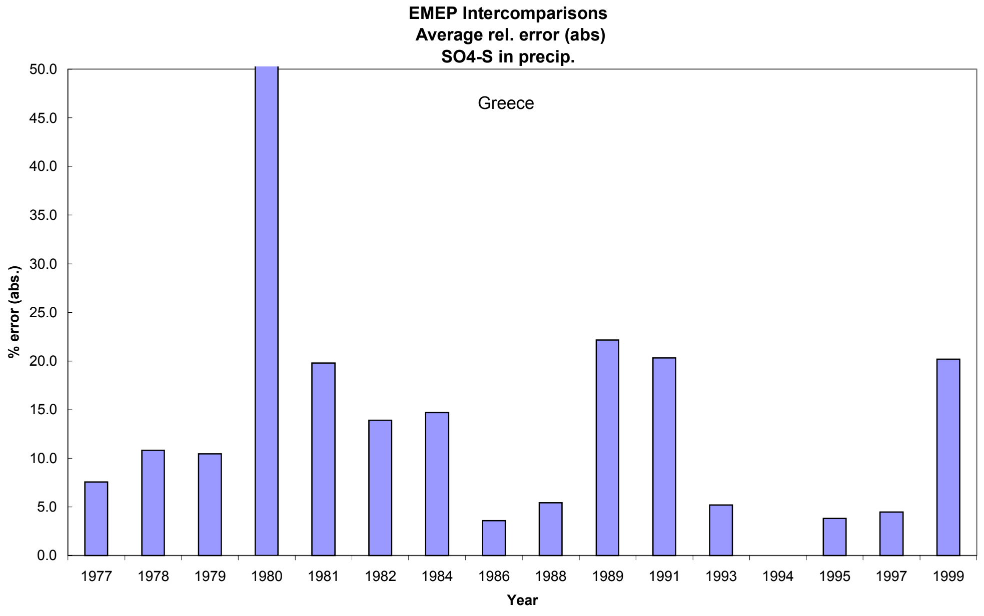
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
GR0001	SO2air	1978	1997	NOT	homog	0.063	0.005	-0.033
GR0001	SO4air	1978	1997	POS99	homog	0.158	0.115	0.067
GR0001	SO4aq.	1989	1991	Insuf				
GR0001	NO2	1987	1997	NOT	homog	0.09	-0.014	-0.089
GR0001	NO3aq.	1989	1991	Insuf				
GR0001	NH4aq.	1989	1991	Insuf				

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip.	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 1	Thorin	W40, 2	Thorin			
1980	Abs., H2O2, 1	Thorin	W40, 2	Thorin			
1981	Abs., H2O2, 1	Thorin	W40, 2	Thorin			
1982	Abs., H2O2, 1	Thorin	W40, 2	Thorin			
1983	Abs., H2O2, 1	Thorin	W40, 2	Thorin			
1984	Abs., H2O2, 1	Thorin	W40, 2	Thorin			
1985	Abs., H2O2, 1	Thorin	W40, 2	Thorin			
1986	Abs., H2O2, 1	Thorin	W41, 1	Thorin			
1987	Abs., H2O2, 1	Thorin	W41, 1	Thorin			
1988	Abs., H2O2, 1	Thorin	W41, 1	Thorin			
1989	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Thorin	Other spect.	wet-only
1990	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Thorin	Other spect.	wet-only
1991	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Thorin	Other spect.	wet-only
1992	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Thorin	Other spect.	wet-only
1993	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Thorin	Other spect.	wet-only
1994	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Thorin	Other spect.	wet-only
1995	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Thorin	Other spect.	wet-only
1996	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Isotope dilution	Other spect.	wet-only
1997	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Isotope dilution	Other spect.	wet-only
1998	Abs., H2O2, 1	Thorin	W41, 1	Thorin	Isotope dilution	Other spect.	wet-only

Performance in laboratory intercalibrations for sulphate in solution



HUNGARY

HU02 K-puszta

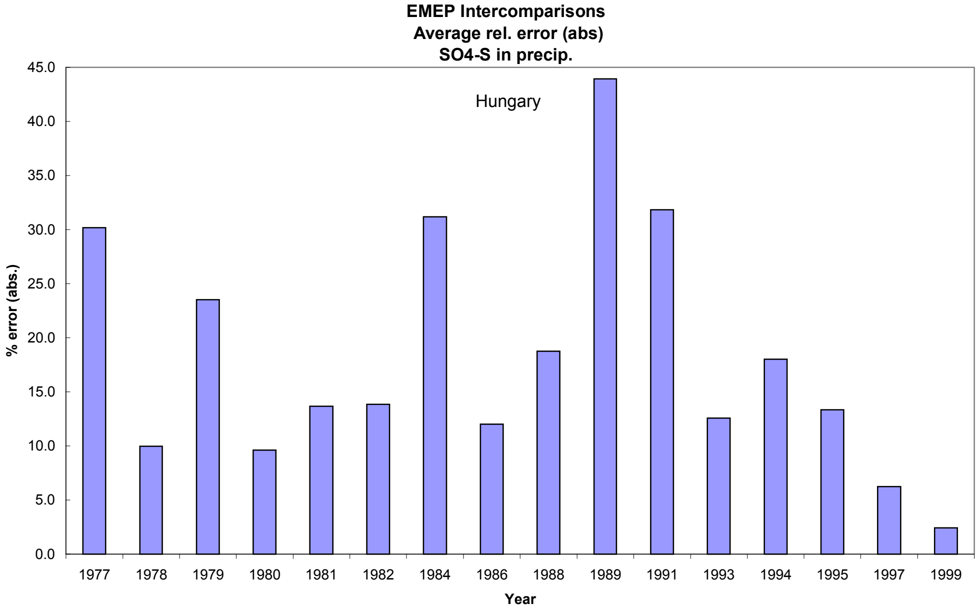
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
HU0002	SO2air	1978	1998	NEG99	homog	-0.11	-0.147	-0.186
HU0002	SO4air	1978	1998	NEG99	homog	-0.089	-0.114	-0.145
HU0002	SO4aq.	1978	1998	NEG99	homog	-0.052	-0.065	-0.082
HU0002	NO2	1978	1998	NEG90	homog	0.001	-0.017	-0.032
HU0002	NO3air	1986	1996	POS95	homog	0.017	0.01	0.002
HU0002	NO3HNO3	1990	1998	NOT	homog	0.014	0	-0.013
HU0002	HNO3	1986	1996	POS99	homog	0.025	0.016	0.009
HU0002	NO3aq.	1978	1998	NOT	homog	0.001	-0.003	-0.008
HU0002	NH3	1986	1998	POS99	homog	0.037	0.023	0.012
HU0002	NH4air	1978	1998	NOT	homog	0.016	0.002	-0.013
HU0002	NH3+4	1990	1993	NEG99	homog	-0.147	-0.235	-0.34
HU0002	NH4aq.	1978	1998	NEG99	homog	-0.008	-0.015	-0.023

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip.	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978			BI, 1000 / SY, 15				
1979	Abs., TCM, 1	Isotopic dilution	SY / BI, 15	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1980	Abs., TCM, 1	Isotopic dilution	BI, 15	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1981	Abs., TCM, 1	Pararosanilin	BI, 15	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1982	Abs., TCM, 1	Pararosanilin	BI, 15	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1983	Abs., TCM, 1	Pararosanilin	T, 20	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1984	Abs., TCM, 1	Pararosanilin	T, 20	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1985	Abs., TCM, 1	Pararosanilin	T, 20	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1986	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1987	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1988	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1989	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1990	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1991	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1992	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1993	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1994	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	Isotop dilution meth.	Isotope dilution	Nitr. of NaSal, spect.	wet-only
1995	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	IC	IC	IC	wet-only
1996	Abs., TCM, 1	Pararosanilin	T, KP, 0.45 u , 25	IC	IC	IC	wet-only
1997	KOH, 24	IC	TS, 1 u, 25	IC	IC	IC	wet-only
1998	KOH, 24	IC	TS, 1 u, 25	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



ICELAND

IS01 Rjupnahed
IS02 Irafoss

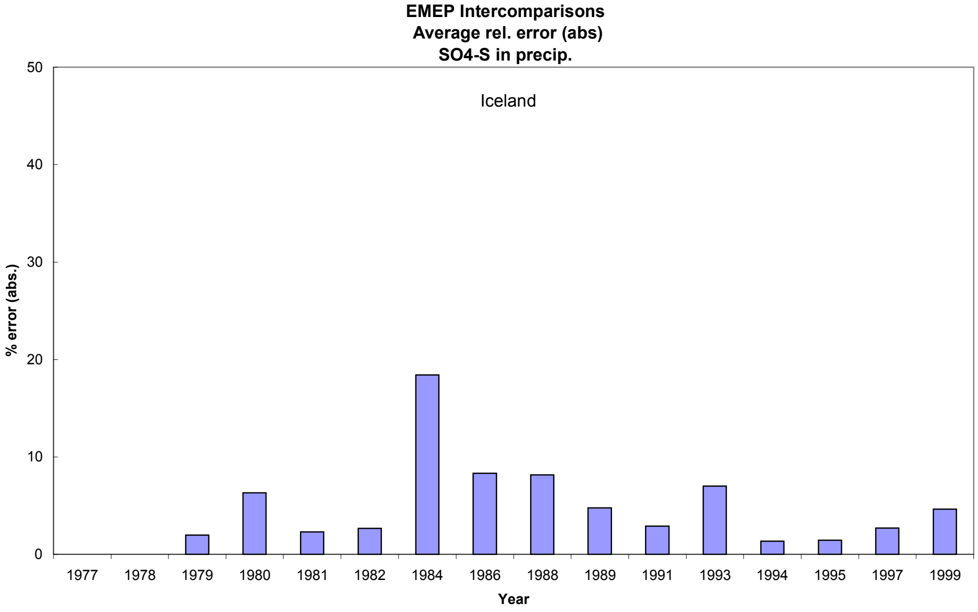
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
IS0001	SO4air	1978	1979	Insuf				
IS0002	SO4air	1980	1998	POS99	homog	0.005	0.003	0.001
IS0001	SO4aq.	1978	1979	Insuf				
IS0002	SO4aq.	1980	1998	NEG99	homog	-0.01	-0.013	-0.017

Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 4	Thorin		XRF	Thorin		bulk
1980	Abs., H2O2, 4	Thorin		XRF	Thorin		bulk
1981	Abs., H2O2, 4	Thorin		XRF	Thorin		bulk
1982	Abs., H2O2, 4	Thorin		XRF	Thorin		bulk / wet-only
1983	Abs., H2O2, 4	Thorin		XRF	Thorin		wet-only
1984	Abs., H2O2, 4	Thorin		XRF	Thorin		wet-only
1985	Abs., H2O2, 5	Thorin		XRF	Thorin		wet-only
1986	Abs., H2O2, 5	Thorin		XRF	Thorin		wet-only
1987	Abs., H2O2, 5	Thorin		XRF	Thorin		wet-only
1988	Abs., H2O2, 5	Thorin		XRF	Thorin		wet-only
1989	Abs., H2O2, 5	Thorin		XRF	Thorin		wet-only
1990	Abs., H2O2, 5	IC		XRF	IC	IC	wet-only
1991	Abs., H2O2, 5	IC		XRF	IC	IC	wet-only
1992	KOH, 25	IC	W40,25	IC	IC	IC	bulk
1993	KOH, 25	IC	W40,25	IC	IC	IC	bulk
1994	KOH, 25	IC	W40,25	IC	IC	IC	bulk
1995	KOH, 25	IC	W40,25	IC	IC	IC	bulk
1996	KOH, 25	IC	W40,25	IC	IC	IC	bulk
1997	KOH, 25	IC	W40,25	IC	IC	IC	bulk
1998	KOH, 30	IC	W40, 30	Plasma em. spectr.	IC	IC	bulk

Performance in laboratory intercalibrations for sulphate in solution



IRELAND

IE01 Valentia Obs.
IE02 Turlough Hill
IE03 The Burren
IE04 Ridge of Capard

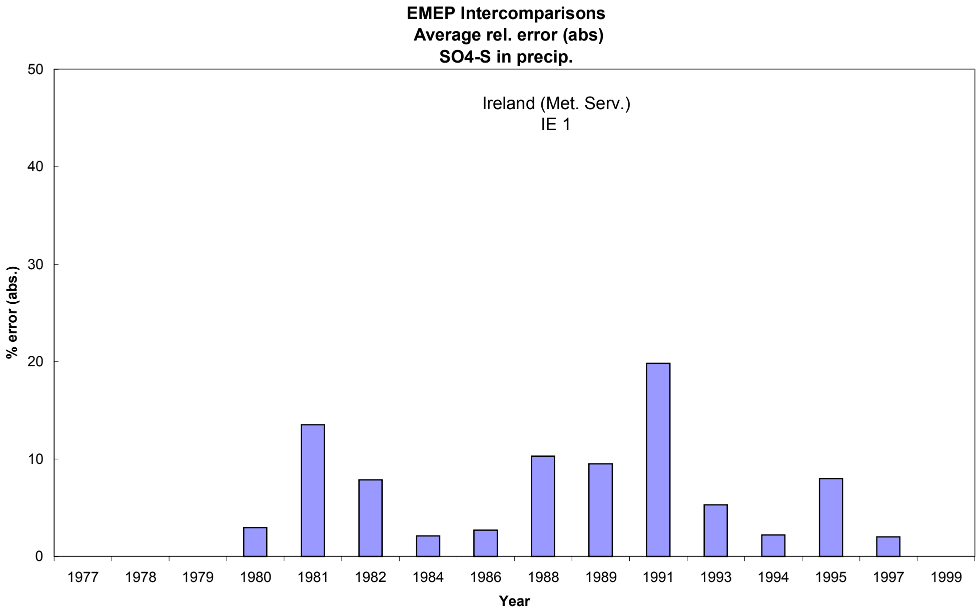
SKT trend analysis and estimates of magnitude

Site	*Component*	*From*	*To*	*trend & significance*	*seasonal homogeneity*	*+90%*	*best est.*	*-90%*
IE0001	SO2air	1980	1997	NEG99	not	-0.003	-0.009	-0.015
IE0002	SO2air	1991	1998	NOT	homog	0.026	-0.01	-0.04
IE0003	SO2air	1998	1998	Insuf				
IE0004	SO2air	1998	1998	Insuf				
IE0001	SO4air	1980	1997	NEG95	homog	0	-0.006	-0.01
IE0002	SO4air	1991	1998	POS99	homog	0.07	0.035	0.02
IE0003	SO4air	1997	1998	Insuf				
IE0004	SO4air	1997	1998	Insuf				
IE0001	SO4aq.	1980	1997	NEG99	homog	-0.005	-0.008	-0.01
IE0002	SO4aq.	1991	1998	NEG99	homog	-0.036	-0.06	-0.09
IE0003	SO4aq.	1997	1998	Insuf				
IE0004	SO4aq.	1998	1998	Insuf				
IE0001	NO2	1988	1997	NOT	homog	0.028	0.006	-0.01
IE0001	NO3aq.	1986	1997	NOT	homog	0.005	0.001	-0.002
IE0002	NO3aq.	1991	1998	NOT	homog	0.003	-0.007	-0.017
IE0003	NO3aq.	1997	1998	Insuf				
IE0004	NO3aq.	1997	1998	Insuf				
IE0001	NH4aq.	1986	1997	NOT	homog	0.002	-0.002	-0.005
IE0002	NH4aq.	1991	1998	NOT	homog	0.021	0.009	-0.007
IE0003	NH4aq.	1997	1998	Insuf				
IE0004	NH4aq.	1997	1998	Insuf				

Sampling and analytical methods

	SO2		SO4 in air		SO4 prec	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	KOH, 16	Thorin		Thorin	Thorin		bulk
1980	KOH, 16	Thorin		Thorin	Thorin		bulk
1981	KOH, 16	Thorin	MMF, 5	Thorin	Thorin		bulk
1982	KOH, 16	Thorin	MMF, 5	Thorin	Thorin		bulk
1983	KOH, 16	Thorin	W40, 18	Thorin	Thorin	Nesslers after red.	bulk/wet-only
1984	KOH, 16	Thorin	W40, 18	Thorin	Thorin	Nesslers after red.	wet-only
1985	KOH,18	Thorin	W40, 18	Thorin	Thorin	Nesslers after red.	wet-only
1986	KOH,18	Thorin	W40, 20	Thorin	Thorin	Nesslers after red.	bulk
1987	KOH,18	Thorin	W40, 20	Thorin	Thorin	Nesslers after red.	bulk
1988	KOH,18	Thorin	W40, 20	Thorin	Thorin	Nesslers after red.	bulk
1989	KOH,18	Thorin	W40, 20	Thorin	Thorin	Nesslers after red.	bulk
1990	KOH,18	Thorin	W40, 20	Thorin	Thorin	Nesslers after red.	bulk
1991	KOH, 25	Thorin	W40, 25	Thorin	Thorin	Nesslers after red.	bulk
1992	KOH, 25	IC	W40, 25	IC	IC	IC	bulk
1993	KOH, 25	IC	W40, 25	IC	IC	Nitr.NaSal, spect./IC	bulk/wet-only
1994	KOH, 25	IC	W40, 25	IC	IC	IC	bulk/wet-only
1995	KOH, 25	IC	W40, 25/GN6, 20	IC	IC	IC	bulk/wet-only
1996	KOH, 25	IC	W40, 25/GN6, 20	IC	IC	IC	bulk/wet-only
1997	KOH, 25	IC	W40, 25/GN6, 20	IC	IC	IC/FIA spect	bulk/wet-only
1998	KOH, 25	IC	W40, 25/GN6, 20	IC	IC	IC	bulk/wet-only

Performance in laboratory intercalibrations for sulphate in solution



ITALY

IT01 Montelibretti
IT02 Stelvio
IT03 Vallombrosa
IT05 Arabba

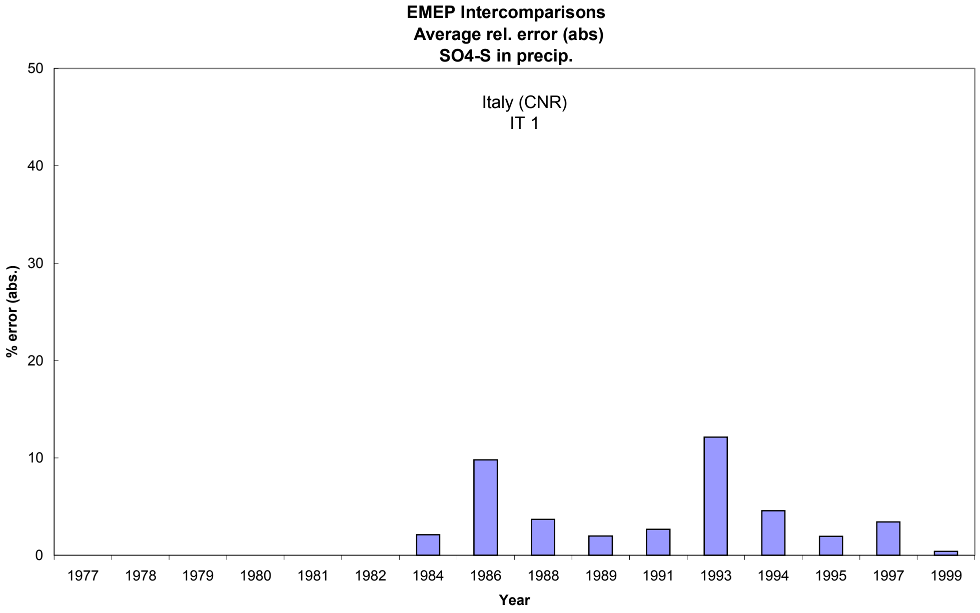
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
IT0001	SO2air	1983	1998	NEG99	homog	-0.088	-0.106	-0.125
IT0002	SO2air	1984	1989	NOT	homog	0.244	-0.013	-0.349
IT0003	SO2air	1984	1985	Insuf				
IT0005	SO2air	1985	1993	NEG99	homog	-0.028	-0.065	-0.095
IT0001	SO4air	1983	1998	NEG99	homog	-0.062	-0.079	-0.099
IT0002	SO4air	1984	1989	NOT	homog	0.226	0.025	-0.115
IT0003	SO4air	1984	1985	Insuf				
IT0005	SO4air	1985	1993	NOT	homog	0.01	-0.012	-0.046
IT0001	SO4aq.	1983	1998	NEG99	homog	-0.017	-0.029	-0.04
IT0002	SO4aq.	1984	1989	POS95	homog	0.659	0.33	0.025
IT0003	SO4aq.	1984	1985	Insuf				
IT0005	SO4aq.	1985	1993	NOT	not	0.052	-0.005	-0.056
IT0001	NO2	1984	1998	NOT	homog	0.314	-0.047	-0.681
IT0002	NO2	1984	1984	Insuf				
IT0001	NO3air	1987	1998	NOT	homog	0.011	-0.012	-0.046
IT0002	NO3air	1987	1987	Insuf				
IT0001	HNO3	1987	1998	NEG99	homog	-0.005	-0.01	-0.011
IT0002	HNO3	1987	1987	Insuf				
IT0001	NO3aq.	1983	1998	NOT	homog	0.008	0.003	-0.003
IT0002	NO3aq.	1984	1989	POS99	homog	0.366	0.202	0.063
IT0003	NO3aq.	1984	1985	Insuf				
IT0005	NO3aq.	1985	1993	NOT	homog	0.035	0.011	-0.01
IT0001	NH3	1996	1998	POS99	homog	0.351	0.3	0.184
IT0001	NH4air	1983	1998	NOT	not	0.035	0.021	-0.041
IT0002	NH4air	1984	1985	Insuf				
IT0003	NH4air	1984	1985	Insuf				
IT0001	NH4aq.	1983	1998	NOT	homog	0.005	-0.007	-0.02
IT0002	NH4aq.	1984	1984	Insuf				
IT0003	NH4aq.	1984	1985	Insuf				
IT0005	NH4aq.	1985	1993	NOT	homog	0.02	-0.001	-0.013

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip.	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979							
1980							
1981							
1982							
1983							
1984							
1985							
1986	KOH						
1987	KOH						
1988					IC		
1989							
1990							
1991							
1992							
1993	DN., NaCl, Na2CO3,17			IC	IC	IC	wet-only
1994	DN., NaCl, Na2CO3,17			IC	IC/Isotope dilution	Nitr. of NaSal, spect.	wet-only
1995	DN., NaCl, Na2CO3,17	IC	T,GZ, 1 u, 17	IC	IC/Isotope dilution	Nitr. of NaSal, spect.	wet-only
1996	DN., NaCl, Na2CO3,17	IC	T,GZ, 1 u, 17	IC	IC	IC	wet-only
1997	DN., NaCl, Na2CO3,17	IC	T,GZ, 1 u, 17	IC	IC	IC	wet-only
1998	DN., NaCl, Na2CO3,17	IC	T,GZ, 1 u, 17	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



LATVIA

LV10 Rucava
LV16 Zoseni

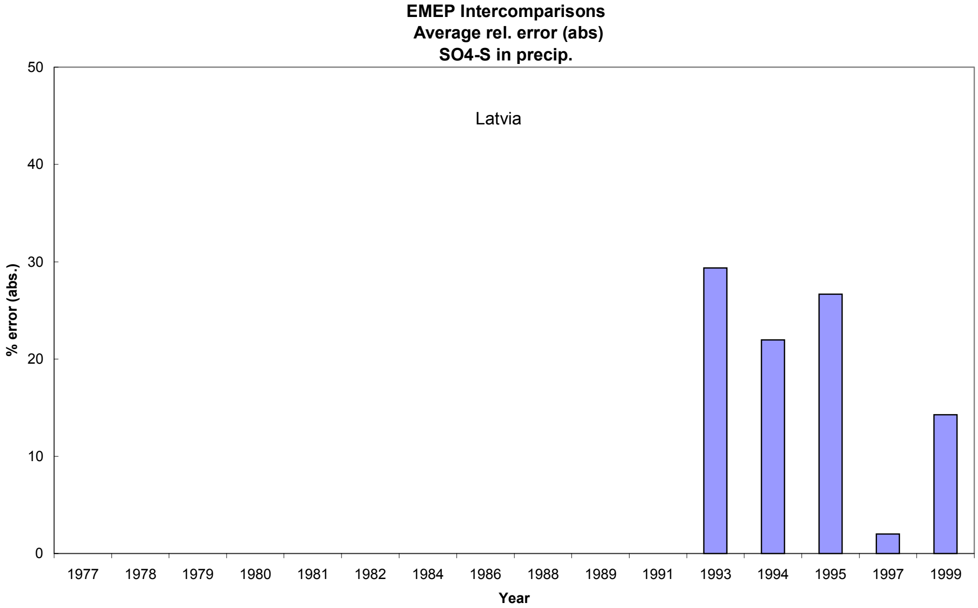
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
LV0010	SO2air	1985	1998	NOT	not	0.027	0.008	-0.007
LV0016	SO2air	1994	1998	NEG99	homog	-0.076	-0.127	-0.226
LV0010	SO4air	1986	1998	NEG95	homog	-0.005	-0.027	-0.048
LV0016	SO4air	1994	1998	NEG99	homog	-0.234	-0.315	-0.426
LV0010	SO4aq.	1985	1998	NEG99	homog	-0.04	-0.057	-0.074
LV0016	SO4aq.	1996	1998	NEG99	homog	-0.082	-0.173	-0.403
LV0010	NO2	1986	1998	NEG99	homog	-0.082	-0.103	-0.123
LV0016	NO2	1994	1998	NOT	homog	0.025	-0.017	-0.062
LV0010	NO3air	1986	1998	POS99	homog	0.039	0.03	0.02
LV0016	NO3air	1994	1998	NEG90	homog	0.003	-0.023	-0.044
LV0010	NO3HNO3	1994	1998	NOT	homog	0.045	-0.096	-0.14
LV0016	NO3HNO3	1996	1998	NEG99	homog	-0.077	-0.123	-0.18
LV0010	HNO3	1997	1997	Insuf				
LV0016	HNO3	1997	1997	Insuf				
LV0010	NO3aq.	1986	1998	NEG99	homog	-0.02	-0.029	-0.04
LV0016	NO3aq.	1996	1998	NOT	homog	0.01	-0.08	-0.165
LV0010	NH3	1997	1997	Insuf				
LV0016	NH3	1997	1997	Insuf				
LV0010	NH4air	1986	1998	NOT	homog	0.021	0.001	-0.016
LV0016	NH4air	1994	1998	NEG99	homog	-0.038	-0.091	-0.14
LV0010	NH3+4	1994	1998	NEG95	homog	-0.01	-0.151	-0.225
LV0016	NH3+4	1996	1998	NOT	homog	0.025	-0.072	-0.218
LV0010	NH4aq.	1985	1998	NOT	homog	0.005	-0.005	-0.017
LV0016	NH4aq.	1996	1998	NEG99	homog	-0.219	-0.387	-0.714

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip.	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979							
1980							
1981							
1982							
1983							
1984							
1985							
1986							
1987							
1988							
1989							
1990							
1991	NaOH, 20		W40, 22	Thorin		Cd red., Griess	bulk
1992	NaOH, 20	Thorin	W40, 20	Thorin	Thorin	Cd red., Griess	bulk
1993	NaOH, 20	Thorin	W40, 20	Thorin	Thorin	Cd red., Griess	bulk
1994	NaOH, 20	Thorin	W40, 20	Thorin	Thorin	Cd red., Griess	bulk
1995	NaOH, 20	Thorin	W40, 20	Thorin	Thorin/IC	Cd red., Griess/IC	bulk
1996	NaOH, 20	Thorin	W40, 20	Thorin	Thorin/IC	Cd red., Griess/IC	bulk/wet-only
1997	NaOH, 20	Thorin	W40, 20	Thorin	Thorin/IC	Cd red., Griess/IC	bulk/wet-only
1998	NaOH, 20	Thorin	W40, 20	Thorin	IC	IC	bulk/wet-only

Sampling and analytical methods



LITHUANIA

LT03 Lida
LT15 Preila

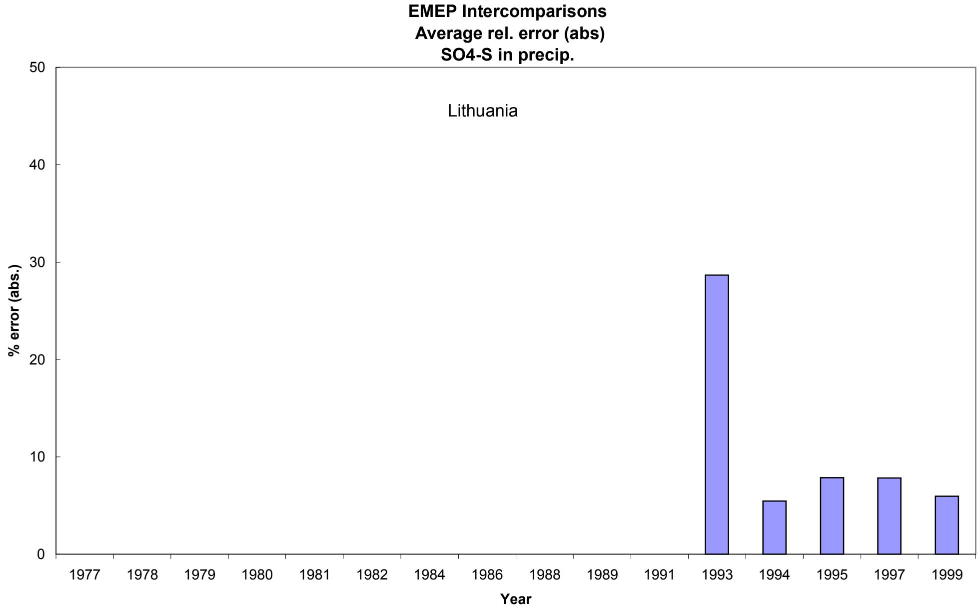
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
LT0015	SO2air	1985	1998	POS99	homog	0.113	0.077	0.048
LT0015	SO4air	1980	1998	NEG99	homog	-0.024	-0.057	-0.11
LT0015	SO4aq.	1981	1998	NEG95	homog	-0.005	-0.03	-0.053
LT0015	NO2	1986	1998	POS99	homog	0.267	0.215	0.168
LT0015	NO3air	1986	1998	POS99	homog	0.032	0.02	0.008
LT0015	NO3HNO3	1996	1998	NEG95	homog	-0.077	-0.18	-0.29
LT0015	HNO3	1992	1993	Insuf				
LT0015	NO3aq.	1984	1998	NEG99	homog	-0.01	-0.024	-0.04
LT0015	NH3	1991	1995	NOT	homog	0.174	-0.081	-0.193
LT0015	NH4air	1983	1998	POS90	homog	0.03	0.018	-0.003
LT0015	NH3+4	1996	1998	NEG90	homog	0.096	-0.4	-0.997
LT0015	NH4aq.	1983	1998	NOT	homog	0.024	0.007	-0.011

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip.	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979							
1980							
1981							
1982							
1983							
1984							
1985							
1986							
1987							
1988							
1989		Nephelometry					
1990		Nephelometry					
1991	DN,NaHCO3, 4	Nephelometry	P, 96	Nephelometry	BaSO4 nephelomtry	Cd red., Griess	bulk
1992	DN,NaHCO3, 4	Nephelometry	P, 96	Thorin	Thorin	Cd red., Griess	bulk
1993	DN,NaHCO3, 4	Nephelometry	P, 96	Thorin	Thorin	Cd red., Griess	bulk
1994	DN,NaHCO3, 4	Nephelometry	P, 96	Thorin	Thorin	Cd red., Griess	bulk
1995	DN,NaHCO3, 4	Nephelometry	P, 96	Thorin	Thorin	Cd red., Griess	bulk
1996	KOH, 24	Thorin	W40, 24	Thorin	Thorin	Cd red., Griess	bulk / wet-only
1997	KOH, 24	Thorin	W40, 24	Thorin/ IC	Thorin/IC	Cd red., Griess/IC	wet-only
1998	KOH, 24	IC	W40, 24	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



FMR. YUGO. REP. OF MACEDONIA

MK07 Lazaropole

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
MK0007	SO2air	1983	1992	NEG99	homog	-0.015	-0.099	-0.201
MK0007	SO4aq.	1978	1991	NEG99	homog	-0.04	-0.074	-0.112
MK0007	NO2	1990	1992	NOT	homog	1.111	0.062	-1.3
MK0007	NO3aq.	1978	1991	POS99	homog	0.026	0.023	0.02
MK0007	NH4aq.	1978	1991	NOT	homog	0.016	0.005	-0.005

Analysis methods are those listed for Yugolsavia

REPUBLIC OF MOLDOVA

MD12 Leovo

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
MD0012	SO2air	1988	1991	POS95	homog	0.375	0.137	0.065
MD0012	SO4air	1988	1991	NOT	homog	0.682	0.202	-0.028
MD0012	SO4aq.	1988	1991	NOT	homog	0.531	0.2	-0.199
MD0012	NO2	1988	1991	POS99	homog	1.151	0.868	0.149
MD0012	NO3air	1988	1991	NOT	homog	0.138	0.013	-0.027
MD0012	NO3aq.	1988	1991	NOT	homog	0.079	0.028	-0.02
MD0012	NH4air	1988	1991	POS90	homog	0.476	0.275	-0.03
MD0012	NH4aq.	1988	1991	NOT	homog	0.189	0.043	-0.093

Analysis methods are those given for USSR listed within Russia

THE NETHERLANDS

NL02 Witteveen
NL05 Rekken
NL06 Appelscha
NL07 Eibergen
NL08 Bilthoven
NL09Kollumerwaard
NL10 Vreedepeel

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
NL0002	SO2air	1978	1993	NEG99	homog	-0.24	-0.29	-0.348
NL0005	SO2air	1978	1983	NEG90	homog	0.138	-0.28	-0.628
NL0006	SO2air	1978	1981	POS95	homog	0.943	0.74	0.115
NL0007	SO2air	1983	1987	NOT	homog	0.186	-0.353	-0.944
NL0008	SO2air	1987	1992	NEG99	homog	-0.199	-0.345	-0.619
NL0009	SO2air	1993	1998	NEG99	homog	-0.076	-0.164	-0.262
NL0010	SO2air	1993	1998	NEG99	homog	-0.153	-0.275	-0.377
NL0002	SO4air	1978	1993	NEG99	homog	-0.018	-0.049	-0.079
NL0005	SO4air	1978	1983	NEG95	not	-0.021	-0.124	-0.32
NL0006	SO4air	1978	1981	NOT	homog	0.227	-0.14	-0.752
NL0007	SO4air	1983	1987	NOT	homog	0.102	-0.175	-0.466
NL0008	SO4air	1987	1992	POS99	homog	0.223	0.127	0.046
NL0009	SO4air	1994	1998	NEG95	homog	-0.04	-0.096	-0.152
NL0010	SO4air	1993	1998	NEG99	homog	-0.102	-0.152	-0.212
NL0002	SO4aq.	1978	1993	NOT	homog	0.017	0.003	-0.009
NL0005	SO4aq.	1978	1983	NEG90	homog	0.005	-0.095	-0.226
NL0006	SO4aq.	1978	1981	NOT	homog	0.133	0.015	-0.155
NL0007	SO4aq.	1983	1987	NOT	homog	0.039	-0.078	-0.194
NL0008	SO4aq.	1987	1991	NOT	homog	0.15	0.055	-0.012
NL0009	SO4aq.	1993	1998	POS90	homog	0.102	0.069	-0.008

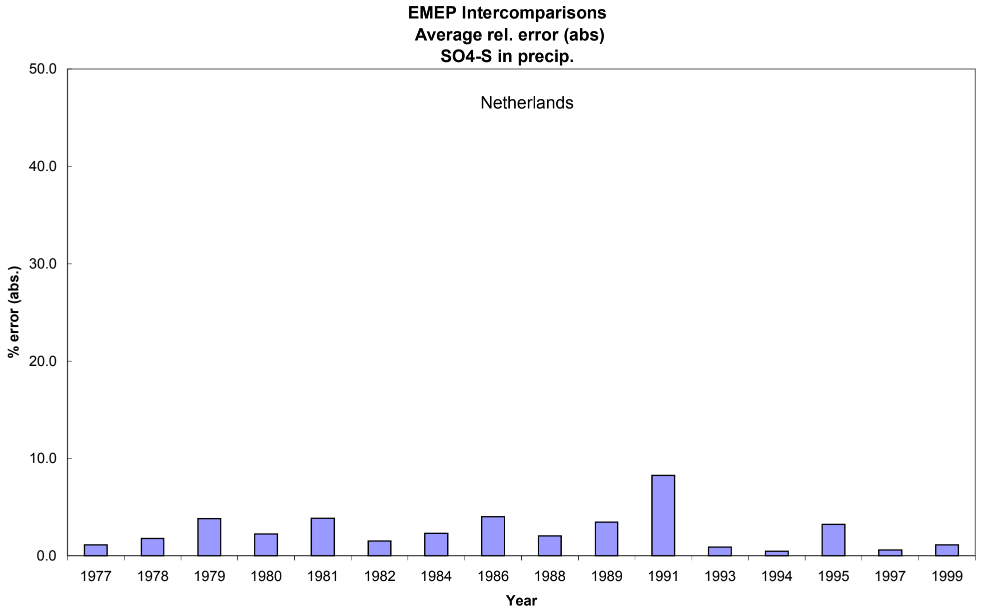
SKT trend analysis and estimates of magnitude(cont)

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
NL0002	NO2	1981	1993	NEG95	homog	-0.01	-0.09	-0.153
NL0005	NO2	1978	1983	NOT	homog	0.506	-0.017	-0.581
NL0006	NO2	1978	1981	NEG90	homog	0.069	-2.23	-3.1
NL0007	NO2	1983	1987	NOT	homog	0.596	0.27	-0.24
NL0008	NO2	1987	1992	NOT	homog	0.376	0.122	-0.193
NL0009	NO2	1993	1998	NOT	homog	0.059	-0.051	-0.155
NL0010	NO2	1993	1998	NEG90	homog	0.01	-0.133	-0.278
NL0002	NO3air	1982	1993	NEG99	homog	-0.04	-0.062	-0.078
NL0005	NO3air	1982	1983	Insuf				
NL0007	NO3air	1983	1987	NEG99	homog	-0.063	-0.125	-0.224
NL0008	NO3air	1987	1992	POS90	homog	0.1	0.053	-0.002
NL0009	NO3air	1994	1998	NOT	homog	0.03	-0.025	-0.08
NL0010	NO3air	1993	1998	NEG99	homog	-0.042	-0.084	-0.13
NL0002	NO3aq.	1978	1993	POS95	homog	0.015	0.008	0.001
NL0005	NO3aq.	1978	1983	NOT	not	0.015	-0.022	-0.055
NL0006	NO3aq.	1978	1981	NEG90	homog	0.022	-0.053	-0.132
NL0007	NO3aq.	1983	1987	NOT	homog	0.038	0.003	-0.078
NL0008	NO3aq.	1987	1991	POS90	homog	0.081	0.042	-0.001
NL0009	NO3aq.	1993	1998	NEG90	homog	0.013	-0.015	-0.097
NL0002	NH3	1993	1993	Insuf				
NL0010	NH3	1993	1998	NEG99	homog	-0.22	-0.782	-1.518
NL0002	NH4air	1992	1993	Insuf				
NL0008	NH4air	1992	1992	Insuf				
NL0009	NH4air	1994	1998	NEG90	homog	0.028	-0.08	-0.209
NL0010	NH4air	1993	1998	NEG99	homog	-0.119	-0.181	-0.281
NL0002	NH4aq.	1978	1993	POS99	homog	0.051	0.035	0.02
NL0005	NH4aq.	1978	1983	NOT	homog	0.07	0.014	-0.075
NL0006	NH4aq.	1978	1981	POS90	not	0.28	0.157	-0.029
NL0007	NH4aq.	1983	1987	NOT	homog	0.069	-0.007	-0.205
NL0008	NH4aq.	1987	1991	NOT	homog	0.118	0.023	-0.017
NL0009	NH4aq.	1993	1998	NOT	homog	0.068	0.025	-0.043

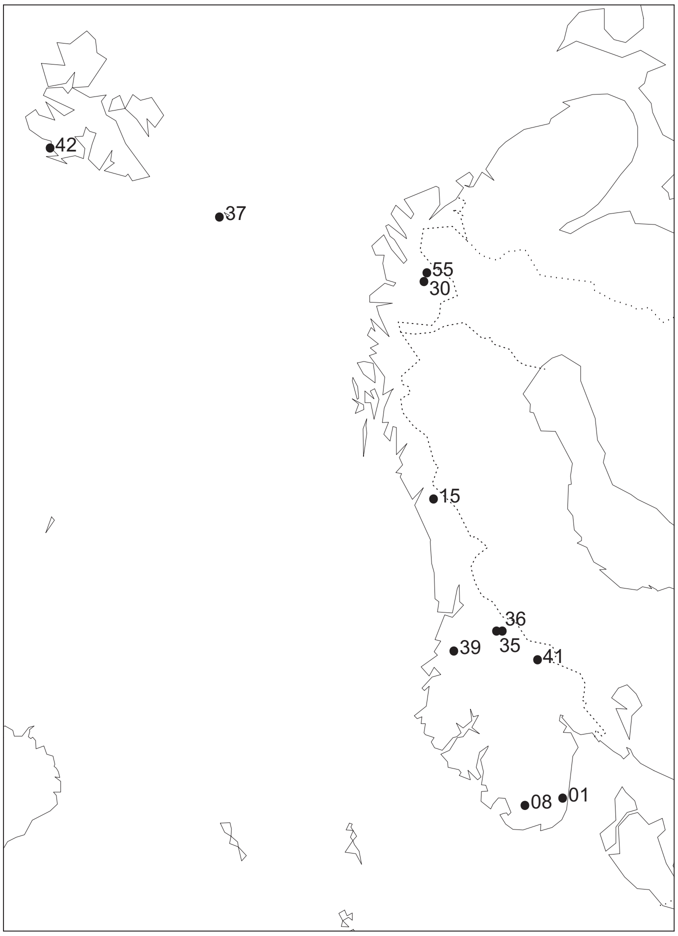
Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 4	Thorin	MA, 4000	XRF	Thorin aut.	Cd red., Griess, aut.	bulk
1980	Abs., H2O2, 4	Thorin	MA, 4000	XRF	Thorin aut.	Cd red., Griess, aut.	bulk
1981	Abs.,H2O2, 3	Thorin	MA, 4000	XRF	Thorin aut.	Cd red., Griess, aut.	bulk
1982	Abs.,H2O2, 3	Thorin	MA, 4000	XRF	Thorin aut.	Cd red., Griess, aut.	bulk
1983	Abs.,H2O2, 3	Sulfonazo III, aut.	W40, 3	XRF	Sulphonazo III, aut.	IC	bulk
1984	Abs.,H2O2, 3	Sulfonazo III, aut.	W40, 3	XRF	Sulphonazo III, aut.	IC	bulk
1985	Abs., H2O2, 3	Sulfonazo III, aut.	W40, 3	XRF	Sulphonazo III, aut.	IC	bulk
1986	Abs., H2O2, 3/ Monitor, UV-fluor	Sulfonazo III, aut.	W40, 3	XRF	Sulphonazo III, aut.	IC	bulk
1987	Abs., H2O2, 3/ Monitor, UV-fluor	UV-fluores.	W40, 3	Sulfonazo III, aut.	Sulphonazo III, aut.	IC	bulk
1988	Monitor, UV-fluor.	UV-fluores.	W42, 3	Sulfonazo III, aut.	Sulphonazo III, aut.	IC	bulk
1989	Monitor, UV-fluor.	UV-fluores.	W42, 3	Sulfonazo III, aut.	IC	IC	bulk
1990	Monitor, UV-fluor.	UV-fluores.	W42, 3	IC	IC	IC	bulk
1991	Monitor, UV-fluor.	UV-fluores.	W42, 3	IC	IC	IC	bulk
1992	Monitor, UV-fluor.	UV-fluores.	W42, 3	XRF	IC	IC	wet-only
1993	Monitor, UV-fluor.	UV-fluores.	W42, 3	IC	IC	IC	wet-only
1994	Monitor, UV-fluor.	UV-fluores.	W42, 3	IC	IC	IC	wet-only
1995	Monitor, UV-fluor.	UV-fluores.	W42, 3	IC	IC	IC	wet-only
1996	Monitor, UV-fluor.	UV-fluores.	W42, 3	IC	IC	IC	wet-only
1997	Monitor, UV-fluor.	UV-fluores.	W42, 3	IC	IC	IC	wet-only
1998	Monitor, UV-fluor.	UV-fluores.	W42, 3	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



NORWAY



NO01 Birkenes
NO08 Skreadalen
NO15 Tustervatn
NO30 Jergul
NO35 Narbuvoll
NO36 Hummelfjell
NO37 Bjørnøya
NO39 Kårvatn
NO41 Osen
NO42 Spitzbergen
NO55 Karasjok

SKT trend analysis and estimates of magnitude

Site	*Component*	*From*	*To*	*trend & significance*	*seasonal homogeneity*	*+90%*	*best est.*	*-90%*
NO0001	SO2air	1978	1998	NEG99	homog	-0.022	-0.027	-0.032
NO0008	SO2air	1978	1998	NEG99	homog	-0.021	-0.025	-0.03
NO0015	SO2air	1978	1998	NEG99	homog	-0.008	-0.01	-0.013
NO0030	SO2air	1978	1996	NEG99	homog	-0.013	-0.022	-0.03
NO0036	SO2air	1978	1987	NEG99	homog	-0.023	-0.028	-0.036
NO0037	SO2air	1978	1988	NEG99	homog	-0.006	-0.01	-0.012
NO0039	SO2air	1978	1998	NEG99	homog	-0.009	-0.01	-0.012
NO0041	SO2air	1988	1998	NEG99	homog	-0.015	-0.02	-0.026
NO0042	SO2air	1990	1998	NEG95	homog	0	-0.004	-0.007
NO0055	SO2air	1997	1998	Insuf				
NO0001	SO4air	1978	1998	NEG99	homog	-0.027	-0.032	-0.039
NO0008	SO4air	1978	1998	NEG99	homog	-0.024	-0.03	-0.035
NO0015	SO4air	1978	1998	NEG99	homog	-0.014	-0.017	-0.02
NO0030	SO4air	1978	1996	NEG99	homog	-0.013	-0.017	-0.021
NO0036	SO4air	1978	1987	NEG99	homog	-0.004	-0.013	-0.024
NO0037	SO4air	1978	1988	NOT	homog	0.004	-0.003	-0.01
NO0039	SO4air	1978	1998	NEG99	homog	-0.01	-0.012	-0.015
NO0041	SO4air	1988	1998	NEG99	homog	-0.02	-0.028	-0.035
NO0042	SO4air	1990	1998	NEG99	homog	-0.001	-0.005	-0.008

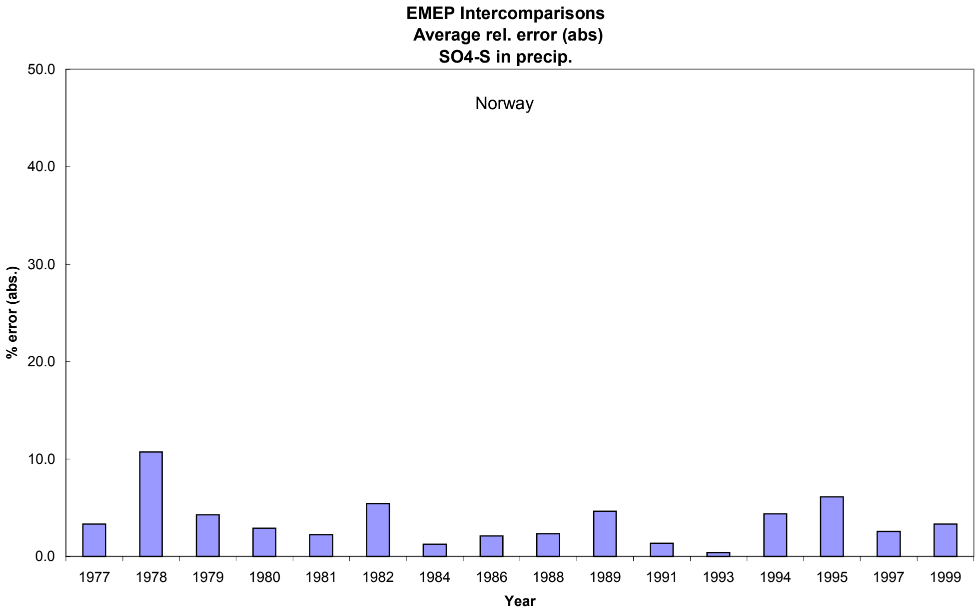
SKT trend analysis and estimates of magnitude(est)

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
NO0042	SO4air	1990	1998	NEG99	homog	-0.001	-0.005	-0.008
NO0055	SO4air	1997	1998	Insuf				
NO0001	SO4aq.	1978	1998	NEG99	homog	-0.028	-0.032	-0.04
NO0008	SO4aq.	1978	1998	NEG99	homog	-0.008	-0.012	-0.016
NO0015	SO4aq.	1978	1998	NEG99	homog	-0.007	-0.008	-0.01
NO0030	SO4aq.	1978	1996	NEG99	homog	-0.007	-0.01	-0.013
NO0035	SO4aq.	1978	1987	NOT	homog	0.006	-0.004	-0.014
NO0037	SO4aq.	1978	1985	NOT	homog	0.031	0	-0.046
NO0039	SO4aq.	1978	1998	NEG99	homog	-0.006	-0.008	-0.009
NO0041	SO4aq.	1988	1998	NEG99	homog	-0.009	-0.019	-0.03
NO0055	SO4aq.	1997	1998	Insuf				
NO0001	NO2	1982	1998	NEG99	homog	-0.02	-0.027	-0.034
NO0008	NO2	1984	1998	NEG99	homog	-0.01	-0.017	-0.021
NO0015	NO2	1988	1998	NEG99	homog	-0.02	-0.023	-0.027
NO0030	NO2	1984	1996	NEG99	homog	-0.017	-0.021	-0.025
NO0039	NO2	1987	1998	NEG99	homog	-0.006	-0.012	-0.018
NO0041	NO2	1988	1998	NEG99	homog	-0.015	-0.023	-0.033
NO0042	NO2	1991	1994	POS95	homog	0.01	0.006	0
NO0055	NO2	1997	1998	Insuf				
NO0001	NO3HNO3	1985	1998	NEG95	homog	0	-0.005	-0.01
NO0008	NO3HNO3	1988	1998	NOT	homog	0	-0.003	-0.007
NO0015	NO3HNO3	1988	1998	POS90	homog	0.003	0.001	0
NO0030	NO3HNO3	1985	1996	NOT	homog	0.002	0	0
NO0039	NO3HNO3	1987	1998	NOT	homog	0.001	0	0
NO0041	NO3HNO3	1988	1998	NOT	homog	0	0	-0.003
NO0042	NO3HNO3	1990	1998	POS99	homog	0.003	0.002	0
NO0055	NO3HNO3	1997	1998	Insuf				
NO0001	NO3aq.	1978	1998	NOT	homog	0.001	-0.002	-0.007
NO0008	NO3aq.	1978	1998	POS90	homog	0.004	0.002	0
NO0015	NO3aq.	1978	1998	NOT	homog	0.001	0	0
NO0030	NO3aq.	1978	1996	NOT	homog	0.002	0	-0.001
NO0035	NO3aq.	1978	1987	NOT	homog	0.006	0	-0.007
NO0037	NO3aq.	1978	1985	NOT	homog	0.01	0.002	-0.005
NO0039	NO3aq.	1978	1998	NEG95	homog	0	-0.001	-0.001
NO0041	NO3aq.	1988	1998	NEG90	homog	0	-0.005	-0.01
NO0055	NO3aq.	1997	1998	Insuf				
NO0001	NH3+4	1985	1998	NEG99	homog	-0.006	-0.013	-0.02
NO0008	NH3+4	1988	1998	NOT	not	0.023	0.004	-0.022
NO0015	NH3+4	1988	1998	POS99	homog	0.051	0.037	0.027
NO0030	NH3+4	1985	1996	NEG99	homog	-0.001	-0.006	-0.01
NO0039	NH3+4	1987	1998	NOT	not	0.003	-0.002	-0.007
NO0041	NH3+4	1988	1998	NOT	homog	0.005	-0.002	-0.007
NO0042	NH3+4	1990	1998	POS99	homog	0.005	0.003	0.002
NO0055	NH3+4	1997	1998	Insuf				
NO0001	NH4aq.	1978	1998	NEG99	homog	-0.003	-0.008	-0.013
NO0008	NH4aq.	1978	1998	NOT	homog	0.002	0	-0.003
NO0015	NH4aq.	1978	1998	POS99	homog	0.004	0.003	0.002
NO0030	NH4aq.	1978	1996	NEG99	homog	0	-0.001	-0.002
NO0035	NH4aq.	1978	1987	NOT	homog	0.01	0.003	-0.003
NO0037	NH4aq.	1978	1985	NEG99	homog	-0.011	-0.033	-0.059
NO0039	NH4aq.	1978	1998	NOT	homog	0.001	0	0
NO0041	NH4aq.	1988	1998	NOT	homog	0.01	0.006	-0.002
NO0055	NH4aq.	1997	1998	Insuf				

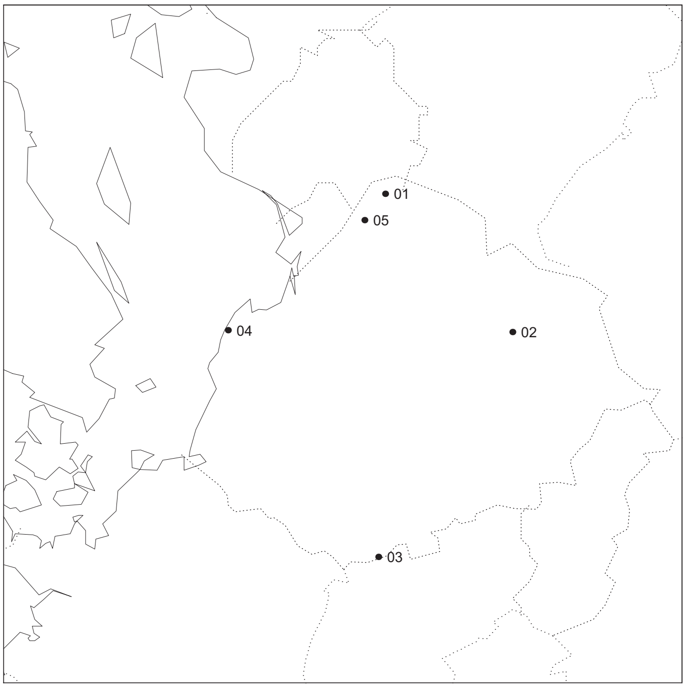
Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	KOH, 18	Thorin	W40, 18	IC	IC	IC	bulk
1980	KOH, 18	Thorin	W40, 18	IC	IC	IC	bulk
1981	KOH, 18	Thorin	W40, 18	IC	IC	IC	bulk
1982	KOH, 18	Thorin	W40, 18	IC	IC	IC	bulk
1983	KOH, 18	Thorin	W40, 18	IC	IC	IC	bulk
1984	KOH, 18	Thorin	W40, 18	IC	IC	IC	bulk
1985	KOH, 20	Thorin	W40, 18	IC	IC	IC	bulk
1986	KOH, 20	IC	W40, 25	IC	IC	IC	bulk
1987	KOH, 20	IC	W40, 25	IC	IC	IC	bulk
1988	KOH, 20	IC	W40, 25	IC	IC	IC	bulk
1989	KOH, 20	IC	W40/T,GZ, 2 u, 25	IC	IC	IC	bulk
1990	KOH, 20	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk
1991	KOH, 20	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk
1992	KOH, 25	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk
1993	KOH, 25	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk
1994	KOH, 25	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk
1995	KOH, 25	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk
1996	KOH, 25	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk
1997	KOH, 25	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk
1998	KOH, 25	IC	T,GZ, 2 u, 25	IC	IC	IC	bulk

Performance in laboratory intercalibrations for sulphate in solution



POLAND



PL01 Suwlaki
PL02 Jarczew
PL03 Sniezka
PL04 Leba
PL05 Diabla Gora

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
PL0001	SO2air	1978	1993	NEG99	homog	-0.059	-0.098	-0.129
PL0002	SO2air	1985	1998	NEG99	homog	-0.158	-0.215	-0.278
PL0003	SO2air	1991	1998	NEG99	homog	-0.133	-0.213	-0.27
PL0004	SO2air	1993	1998	NEG99	homog	-0.225	-0.293	-0.342
PL0005	SO2air	1993	1998	NEG99	homog	-0.088	-0.149	-0.234
PL0001	SO4air	1978	1993	NOT	homog	0.01	-0.015	-0.04
PL0002	SO4air	1985	1998	NEG99	homog	-0.176	-0.204	-0.25
PL0003	SO4air	1991	1998	NEG99	homog	-0.09	-0.134	-0.181
PL0004	SO4air	1993	1998	NEG99	homog	-0.062	-0.16	-0.222
PL0005	SO4air	1993	1998	NOT	homog	0.062	0.004	-0.042
PL0001	SO4aq.	1978	1993	NEG99	homog	-0.043	-0.059	-0.07
PL0002	SO4aq.	1985	1998	NEG99	homog	-0.114	-0.134	-0.154
PL0003	SO4aq.	1991	1998	NEG99	homog	-0.045	-0.099	-0.144
PL0004	SO4aq.	1993	1998	NEG95	homog	-0.004	-0.055	-0.107
PL0005	SO4aq.	1993	1998	NEG99	homog	-0.026	-0.064	-0.092
PL0001	NO2	1984	1993	NEG99	homog	-0.055	-0.123	-0.2
PL0002	NO2	1985	1998	NEG99	homog	-0.1	-0.133	-0.167
PL0003	NO2	1991	1998	NEG99	homog	-0.03	-0.07	-0.102
PL0004	NO2	1993	1998	NOT	homog	0.033	0	-0.05
PL0005	NO2	1993	1998	NEG99	homog	-0.049	-0.088	-0.132
PL0002	NO3air	1994	1998	NOT	homog	0.03	0.002	-0.041
PL0003	NO3air	1994	1998	POS95	homog	0.02	0.015	0.004
PL0004	NO3air	1994	1998	NOT	homog	0.033	0.006	-0.02
PL0005	NO3air	1993	1994	Insuf				

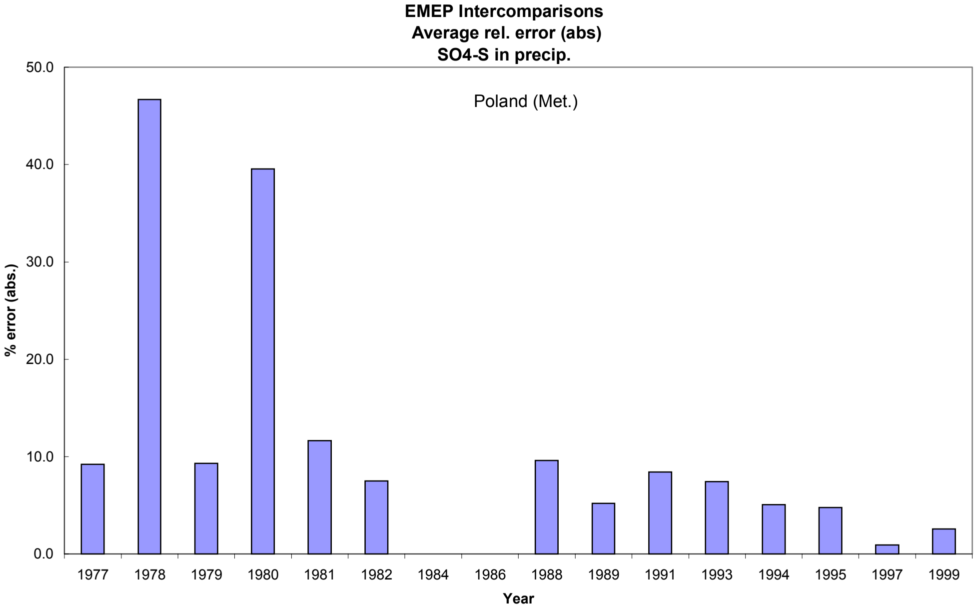
SKT trend analysis and estimates of magnitude(cont)

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
PL0001	NO3HNO3	1991	1993	NEG99	homog	-0.082	-0.145	-0.207
PL0002	NO3HNO3	1991	1998	NOT	homog	0.019	0	-0.024
PL0003	NO3HNO3	1991	1998	NEG95	homog	-0.004	-0.02	-0.043
PL0004	NO3HNO3	1994	1998	NOT	homog	0.004	-0.015	-0.03
PL0005	NO3HNO3	1994	1998	POS95	homog	0.047	0.024	0.003
PL0001	NO3aq.	1978	1993	NEG95	homog	0	-0.005	-0.011
PL0002	NO3aq.	1985	1998	NEG99	homog	-0.016	-0.023	-0.032
PL0003	NO3aq.	1991	1998	NOT	homog	0.021	-0.007	-0.035
PL0004	NO3aq.	1993	1998	NOT	homog	0.017	-0.011	-0.03
PL0005	NO3aq.	1993	1998	POS99	homog	12.004	8.82	0.314
PL0001	NH4air	1979	1993	NEG99	homog	-0.055	-0.078	-0.101
PL0002	NH4air	1985	1998	NEG99	homog	-0.157	-0.188	-0.221
PL0003	NH4air	1991	1998	NEG99	homog	-0.03	-0.06	-0.08
PL0004	NH4air	1993	1998	NEG99	homog	-0.02	-0.061	-0.135
PL0005	NH4air	1993	1994	Insuf				
PL0001	NH3+4	1991	1993	NOT	homog	0.382	-0.058	-1.915
PL0002	NH3+4	1991	1998	NOT	not	0.057	-0.025	-0.129
PL0003	NH3+4	1991	1998	NEG99	homog	-0.202	-0.293	-0.43
PL0004	NH3+4	1994	1998	NOT	homog	0.031	-0.057	-0.17
PL0005	NH3+4	1994	1998	NEG99	homog	-0.06	-0.12	-0.204
PL0001	NH4aq.	1978	1993	NEG99	homog	-0.028	-0.039	-0.049
PL0002	NH4aq.	1985	1998	NEG99	homog	-0.051	-0.068	-0.083
PL0003	NH4aq.	1991	1998	NEG99	homog	-0.027	-0.074	-0.107
PL0004	NH4aq.	1993	1998	NOT	homog	0.04	0.004	-0.02
PL0005	NH4aq.	1993	1998	POS99	homog	12.008	8.849	0.461

Sampling and analytical methods

	SO2		SO4 in air		SO4 prec	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs.,H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1980	Abs.,H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1981	Abs.,H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1982	Abs.,H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1983	Abs.,H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1984	Abs.,H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1985	Abs.,H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1986	KOH, 4	Thorin	W40, 3	Thorin	Thorin	NH2NH2 red., Griess	bulk
1987	KOH, 4	Thorin	W40, 4	Thorin	Thorin	NH2NH2 red., Griess	bulk
1988	KOH, 4	Thorin	W40, 4	Thorin	Thorin	NH2NH2 red., Griess	bulk
1989	KOH, 4	Thorin	W40, 4	Thorin	Thorin	NH2NH2 red., Griess	bulk
1990	KOH, 4	Thorin	W40, 4	Thorin	Thorin	NH2NH2 red., Griess	bulk
1991	KOH, 4	Thorin	W40, 4	Thorin	Thorin	NH2NH2 red., Griess	bulk
1992	KOH,5	Thorin/IC	W40, 3	Thorin/IC	Thorin/IC	NH2NH2 red., Griess/IC	bulk
1993	KOH,5	Thorin/IC	W40, 3	Thorin/IC	Thorin/IC	NH2NH2 red., Griess/IC	bulk
1994	KOH,5	Thorin/IC	W40, 3	Thorin/IC	Thorin/IC	NH2NH2 red., Griess/IC	bulk
1995	KOH,5	Thorin/IC	W40, 3	Thorin/IC	Thorin/IC	NH2NH2 red., Griess/IC	bulk
1996	KOH,5	Thorin/IC	W40, 3	Thorin/IC	IC	IC	bulk
1997	KOH,5	Thorin/IC	W40, 3	Thorin/IC	IC	IC	bulk
1998	KOH,5	Thorin/IC	W40, 3	Thorin/Plasma em. spectr.	IC	IC	bulk

Performance in laboratory intercalibrations for sulphate in solution



PORTUGAL

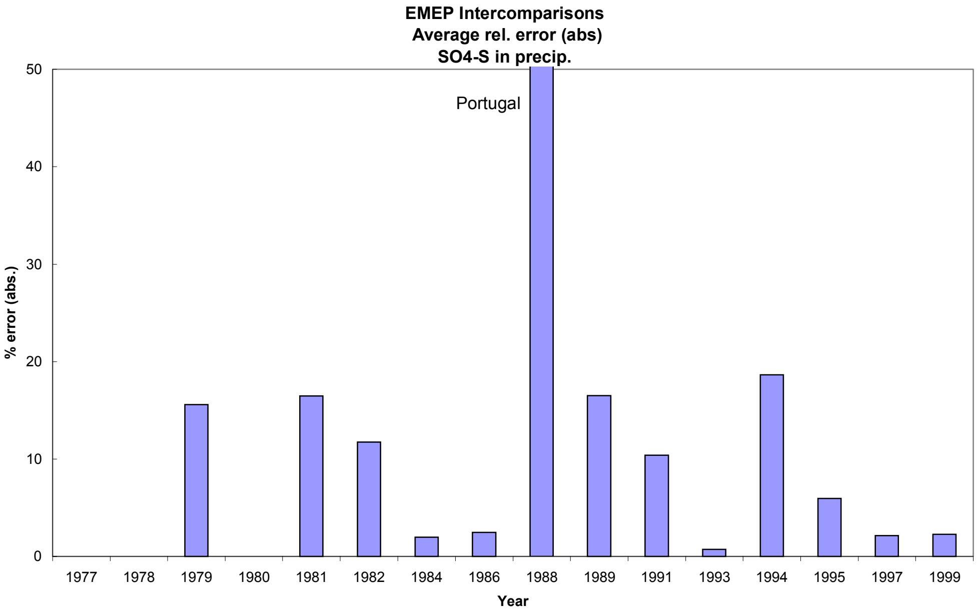
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
PT0001	SO2air	1979	1996	POS90	homog	0.07	0.03	-0.008
PT0002	SO2air	1979	1987	POS99	homog	0.147	0.095	0.031
PT0003	SO2air	1987	1990	Insuf				
PT0004	SO2air	1988	1996	NEG99	not	-0.254	-0.389	-0.587
PT0005	SO2air	1990	1993	NOT	homog	1.544	0.49	-1.178
PT0001	SO4air	1979	1996	NEG99	homog	-0.014	-0.03	-0.05
PT0002	SO4air	1979	1987	NOT	not	0.031	-0.034	-0.09
PT0003	SO4air	1987	1990	Insuf				
PT0004	SO4air	1988	1996	NEG99	homog	-0.107	-0.153	-0.228
PT0005	SO4air	1990	1993	NOT	homog	1.022	0.512	-0.27
PT0001	SO4aq.	1989	1998	NEG95	homog	-0.003	-0.026	-0.055
PT0003	SO4aq.	1989	1998	NOT	homog	0.02	0.01	-0.003
PT0004	SO4aq.	1989	1998	NOT	homog	0.051	0.019	-0.019
PT0001	NO3aq.	1979	1998	POS99	homog	0.011	0.009	0.007
PT0002	NO3aq.	1979	1986	NOT	homog	0.018	0.005	-0.024
PT0003	NO3aq.	1987	1998	POS99	homog	0.024	0.017	0.011
PT0004	NO3aq.	1989	1998	POS95	homog	0.04	0.017	0.003
PT0001	NH4aq.	1979	1998	POS95	homog	0.015	0.008	0.001
PT0002	NH4aq.	1979	1986	NOT	homog	0.007	-0.012	-0.034
PT0003	NH4aq.	1987	1998	POS99	homog	0.03	0.017	0.01
PT0004	NH4aq.	1989	1998	NOT	homog	0.04	0.01	-0.003

Sampling and analytical methods

	SO2		SO4 in air		SO4prec	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1980	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1981	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1982	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1983	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1984	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1985	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1986	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1987	Abs., H2O2, 3	Thorin	W40, 4	Thorin	Thorin	Cd red., Griess	wet-only
1988	Abs., H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	wet-only
1989	Abs., H2O2, 3	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	wet-only
1990	Abs., H2O2, 3/Monitor, UV-fluor	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	wet-only
1991	Abs., H2O2, 3/Monitor, UV-fluor	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1992	Abs., H2O2, 3/Monitor, UV-fluor	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1993	Abs., H2O2, 3/Monitor, UV-fluor	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1994	Abs., H2O2, 3/Monitor, UV-fluor	Thorin	W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1995	Abs., H2O2, 3/Monitor, UV-fluor	IC	W40, 3	IC	IC	IC	bulk
1996	Abs., H2O2, 3/Monitor, UV-fluor	IC	W40, 3	IC	IC	IC	bulk
1997	Abs., H2O2, 3/Monitor, UV-fluor	IC	W40, 3	IC	IC	IC	bulk
1998	Abs., H2O2, 3/Monitor, UV-fluor	IC	W40, 3	IC	IC	IC	bulk

Performance in laboratory intercalibrations for sulphate in solution



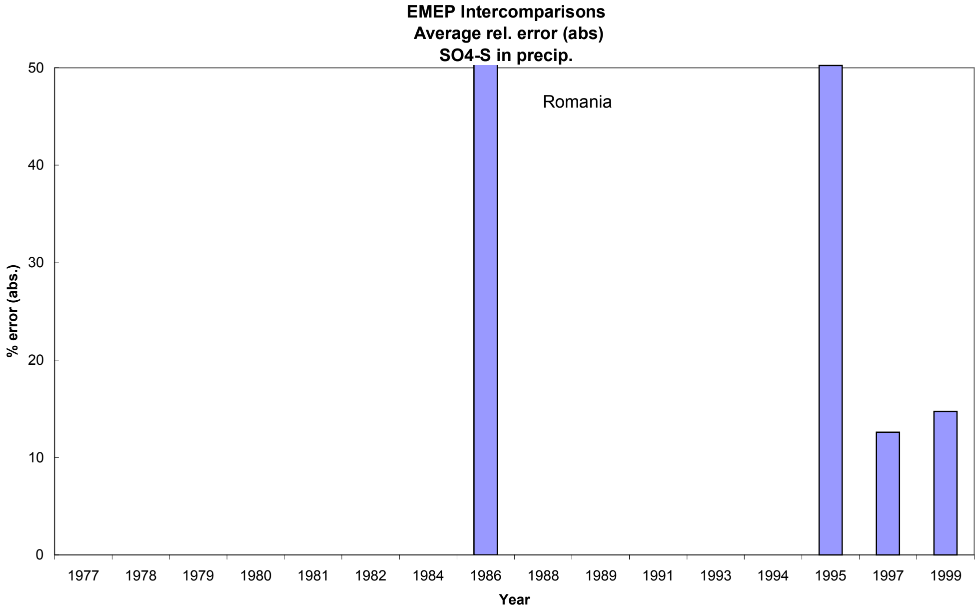
ROMANIA

RO01 Rarau
RO02 Stina de Vale
RO03 Semenic
RO04 Paring
RO05 Fundata
RO06 Turia

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
RO0001	SO2air	1983	1984	Insuf				
RO0002	SO2air	1982	1985	NOT	homog	13.005	0.515	-11.54
RO0003	SO2air	1982	1982	Insuf				
RO0004	SO2air	1983	1986	Insuf				
RO0005	SO2air	1983	1985	Insuf				
RO0006	SO2air	1984	1985	Insuf				
RO0001	SO4aq.	1980	1987	NOT	homog	0.117	-0.178	-0.337
RO0002	SO4aq.	1980	1987	NOT	homog	0.079	-0.007	-0.176
RO0003	SO4aq.	1980	1986	NOT	homog	0.707	0.265	-0.114
RO0004	SO4aq.	1980	1987	NOT	homog	0.147	-0.076	-0.201
RO0005	SO4aq.	1980	1987	NEG95	homog	-0.056	-0.27	-0.48
RO0006	SO4aq.	1980	1987	NEG95	homog	0.016	-0.13	-0.378
RO0001	NO3aq.	1980	1987	NOT	homog	0.019	-0.018	-0.056
RO0002	NO3aq.	1980	1987	NOT	homog	0.06	0.01	-0.01
RO0003	NO3aq.	1980	1986	NOT	homog	0.086	0.015	-0.031
RO0004	NO3aq.	1980	1987	NOT	homog	0.05	0.003	-0.046
RO0005	NO3aq.	1980	1987	NOT	homog	0.035	0.01	-0.027
RO0006	NO3aq.	1980	1987	NOT	homog	0.05	0	-0.054
RO0001	NH4aq.	1980	1987	NOT	homog	0.113	0.056	-0.015
RO0002	NH4aq.	1980	1987	NOT	homog	0.058	-0.08	-0.306
RO0003	NH4aq.	1980	1986	NOT	homog	0.196	-0.075	-0.243
RO0004	NH4aq.	1980	1987	NOT	homog	0.09	0.01	-0.065
RO0005	NH4aq.	1980	1987	NOT	homog	0.183	0.082	-0.068
RO0006	NH4aq.	1980	1987	NEG90	homog	0.02	-0.1	-0.242

Performance in laboratory intercalibrations for sulphate in solution



RUSSIA

RU01 Janiskoski
RU08 Lesogorsky
RU13 Pinega
RU14 Pushinskie Gory
RU16 Shepeljovo

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
RU0001	SO2air	1985	1998	NOT	homog	0.049	0.014	-0.009
RU0013	SO2air	1991	1998	NEG95	homog	0	-0.012	-0.025
RU0014	SO2air	1990	1995	NEG90	homog	0.01	-0.084	-0.157
RU0016	SO2air	1994	1998	NOT	homog	0.04	-0.01	-0.096
RU0001	SO4air	1979	1998	NEG99	homog	-0.032	-0.043	-0.05
RU0008	SO4air	1979	1985	NEG90	homog	0.032	-0.295	-0.513
RU0013	SO4air	1991	1998	POS95	homog	0.02	0.01	0
RU0014	SO4air	1990	1995	NEG99	homog	-0.05	-0.087	-0.14
RU0016	SO4air	1994	1998	NOT	homog	0.035	-0.011	-0.054
RU0001	SO4aq.	1981	1998	NEG99	homog	-0.004	-0.01	-0.017
RU0008	SO4aq.	1981	1988	NOT	homog	0.155	0.048	-0.028
RU0013	SO4aq.	1990	1998	NOT	homog	0.007	-0.011	-0.032
RU0014	SO4aq.	1990	1995	NOT	homog	0.046	0.02	-0.038
RU0016	SO4aq.	1994	1998	NEG99	homog	-0.016	-0.076	-0.144
RU0001	NO2	1986	1997	NEG99	homog	-0.012	-0.02	-0.036
RU0013	NO2	1991	1997	NEG99	homog	-0.052	-0.073	-0.094
RU0014	NO2	1990	1995	NEG99	homog	-0.261	-0.341	-0.796
RU0016	NO2	1994	1997	NOT	homog	0.125	0.015	-0.118
RU0001	NO3air	1986	1998	POS99	homog	0.003	0.002	0.001
RU0014	NO3air	1990	1995	NEG99	homog	-0.01	-0.02	-0.03
RU0016	NO3air	1994	1998	NOT	homog	0.02	0.01	-0.01
RU0001	NO3aq.	1986	1998	POS99	homog	0.005	0.002	0
RU0008	NO3aq.	1986	1988	Insuf				
RU0013	NO3aq.	1990	1998	NOT	homog	0.007	0	-0.005
RU0014	NO3aq.	1990	1995	POS99	homog	0.087	0.05	0.02
RU0016	NO3aq.	1994	1998	NEG95	homog	0	-0.026	-0.05
RU0001	NH4air	1982	1998	POS90	homog	0.006	0.003	0
RU0008	NH4air	1982	1985	POS99	homog	0.503	0.315	0.171
RU0013	NH4air	1991	1998	POS99	homog	0.04	0.027	0.017
RU0014	NH4air	1990	1995	NOT	homog	0.01	-0.02	-0.1
RU0016	NH4air	1994	1998	NOT	homog	0.033	0	-0.04
RU0001	NH3+4	1991	1998	NOT	homog	0.01	0	-0.01
RU0001	NH4aq.	1981	1998	NOT	not	0	0	-0.002
RU0013	NH4aq.	1990	1998	NOT	homog	0.027	0.003	-0.008
RU0014	NH4aq.	1990	1995	NOT	homog	0.024	-0.01	-0.043
RU0016	NH4aq.	1994	1998	NEG95	homog	0.002	-0.04	-0.074

Sampling and analytical methods

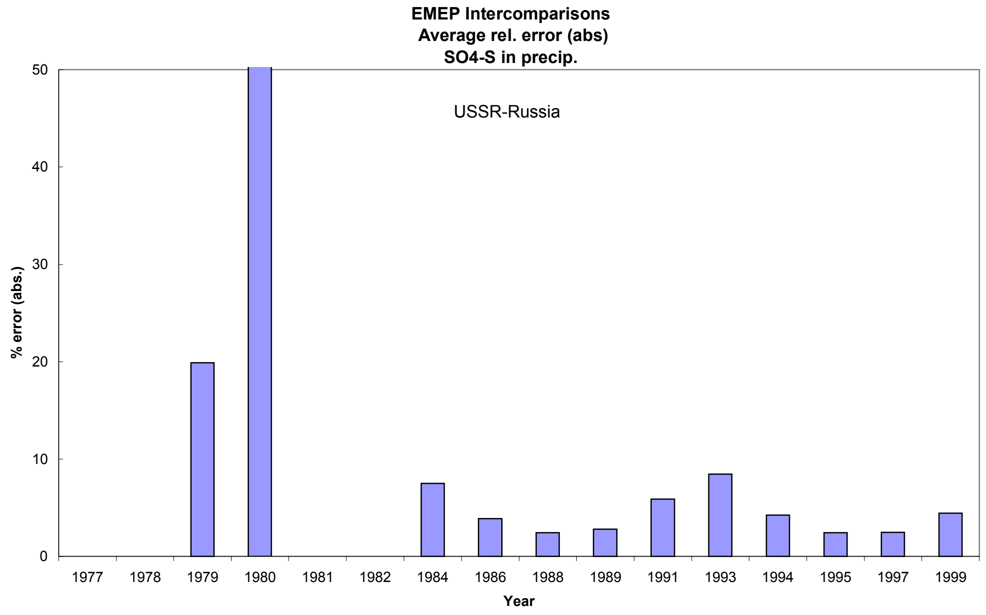
USSR:

	SO2		SO4 in air		SO4 prec	NO3 in precip.	Precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sampl
1978							
1979			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1980			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1981			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1982			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1983			W40, 3	Thorin	Thorin	Cd red., Griess	bulk
1984			W40, 3 / 17	Thorin	Thorin	Cd red., Griess	bulk
1985			W40, 17	Thorin	Thorin	Cd red., Griess	bulk
1986			W40, 17	Thorin	Thorin	Cd red., Griess	bulk
1987			W40, 17	Thorin	Thorin	Cd red., Griess	bulk
1988	Abs. tubes, TCM, 3	IC	W40, 15	Thorin	Thorin(IC)	Cd/NH2NH2., Griess	bulk
1989	Abs. tubes, TCM, 3	Pararosanilin	W40, 15	Thorin	Thorin(IC)	Cd/NH2NH2., Griess	bulk
1990	NaOH, 15	Pararosanilin	W40, 15	Thorin	Thorin(IC)	Cd red., Griess	bulk
1991		Pararosanilin			Thorin(IC)		

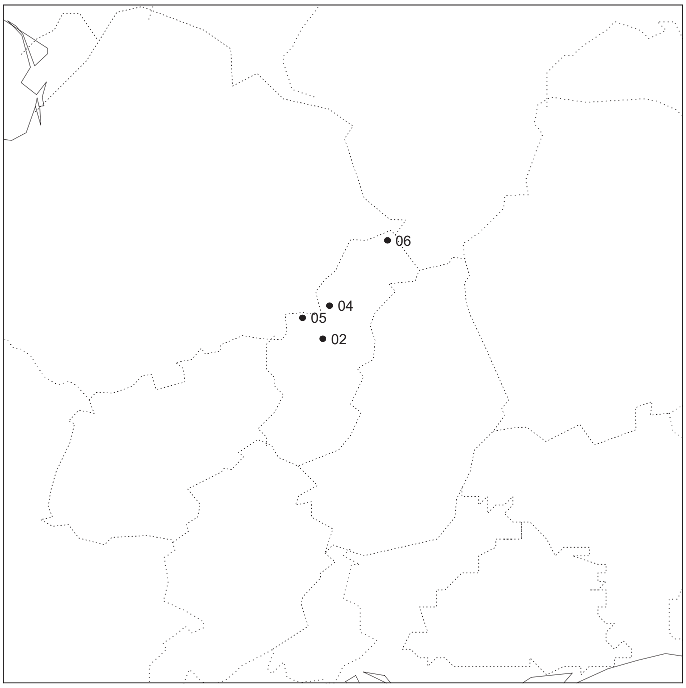
RUSSIA:

	SO2		SO4 in air		SO4 prec	NO3 in precip.	Precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sampl
`1990						Cd red., Griess/IC	
1991	NaOH, 15		W40, 15	Thorin		Cd red., Griess/IC	
1992	NaOH, 15	IC/UV-fluores.	W40, 15	IC	IC	IC	bulk
1993	NaOH, 15	IC/UV-fluores.	W40, 15	IC	IC	IC	bulk
1994	NaOH, 15	IC/UV-fluores.	W40, 15	IC	IC	IC	bulk
1995	NaOH, 15	IC/UV-fluores.	W40, 15	IC	IC	IC	bulk
1996	NaOH, 15	IC/UV-fluores.	W40, 15	IC	IC	IC	bulk
1997	NaOH, 15	IC/UV-fluores.	W40, 15	IC	IC	IC	bulk
1998	NaOH, 15	IC/UV-fluores.	W40, 15	IC	IC	IC	bulk

Performance in laboratory intercalibrations for sulphate in solution



SLOVAKIA



SK02 Chopok
SK04 Stara Lesna
SK05 Liesek
SK06 Starina

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
SK0002	SO2air	1978	1998	NEG99	homog	-0.053	-0.069	-0.082
SK0004	SO2air	1993	1998	NEG95	homog	-0.001	-0.083	-0.18
SK0005	SO2air	1993	1998	NEG95	homog	-0.003	-0.09	-0.235
SK0006	SO2air	1994	1998	NOT	homog	0.057	-0.079	-0.151
SK0002	SO4air	1978	1998	NEG99	homog	-0.01	-0.016	-0.022
SK0004	SO4air	1993	1998	NEG99	homog	-0.07	-0.107	-0.135
SK0005	SO4air	1993	1998	NEG99	not	-0.1	-0.15	-0.18
SK0006	SO4air	1994	1998	NEG99	homog	-0.117	-0.159	-0.226
SK0002	SO4aq.	1992	1998	NEG99	homog	-0.047	-0.082	-0.125
SK0004	SO4aq.	1993	1998	NEG99	homog	-0.05	-0.101	-0.152
SK0005	SO4aq.	1993	1998	NEG99	homog	-0.06	-0.097	-0.149
SK0006	SO4aq.	1994	1998	NEG99	homog	-0.105	-0.16	-0.281
SK0002	NO2	1985	1998	NOT	homog	0.017	0.001	-0.011
SK0004	NO2	1993	1998	NOT	homog	0.042	0.001	-0.043
SK0005	NO2	1993	1998	NEG99	homog	-0.05	-0.1	-0.15
SK0006	NO2	1994	1998	NEG95	homog	-0.02	-0.052	-0.091
SK0002	NO3air	1992	1998	NEG99	homog	-0.016	-0.027	-0.037
SK0004	NO3air	1993	1998	NEG99	homog	-0.015	-0.03	-0.04
SK0005	NO3air	1993	1998	NEG99	homog	-0.02	-0.03	-0.05
SK0006	NO3air	1994	1998	NEG99	homog	-0.035	-0.04	-0.055
SK0002	NO3HNO3	1995	1995	Insuf				
SK0004	NO3HNO3	1995	1995	Insuf				
SK0005	NO3HNO3	1995	1995	Insuf				
SK0006	NO3HNO3	1995	1995	Insuf				
SK0002	HNO3	1992	1998	NOT	homog	0.007	0.002	-0.002
SK0004	HNO3	1993	1998	POS99	homog	0.015	0.011	0.008
SK0005	HNO3	1993	1998	POS99	not	0.01	0.008	0.005
SK0006	HNO3	1994	1998	POS99	homog	0.04	0.03	0.02

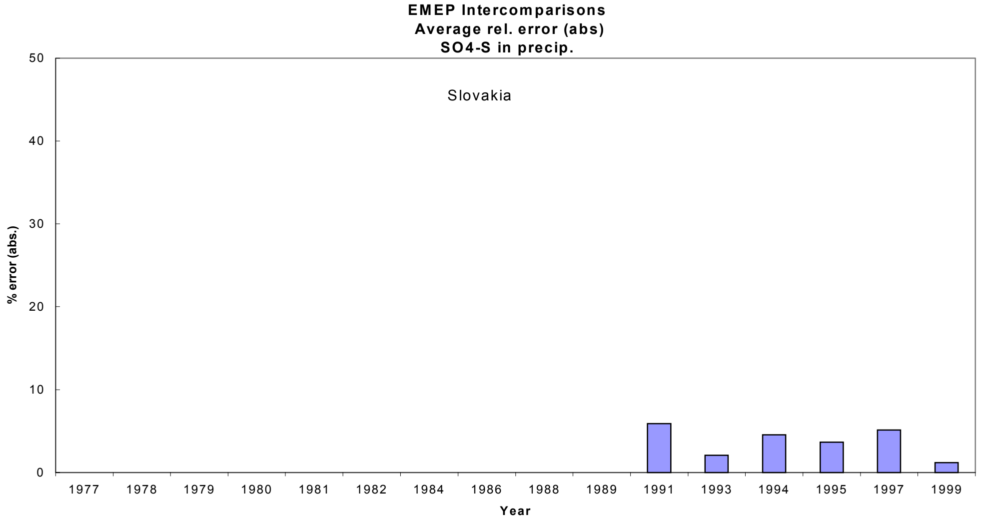
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend significance	& seasonal homogeneity	+90%	best est.	-90%
SK0002	NO3aq.	1985	1998	NEG99	homog	-0.005	-0.012	-0.02
SK0004	NO3aq.	1993	1998	NEG95	homog	-0.01	-0.03	-0.074
SK0005	NO3aq.	1993	1998	NEG99	homog	-0.006	-0.027	-0.048
SK0006	NO3aq.	1994	1998	NEG90	homog	0	-0.042	-0.086
SK0002	NH4aq.	1994	1998	NOT	homog	0.019	-0.036	-0.115
SK0004	NH4aq.	1994	1998	NEG99	homog	-0.058	-0.1	-0.139
SK0005	NH4aq.	1994	1998	NEG99	homog	-0.052	-0.09	-0.114
SK0006	NH4aq.	1994	1998	NEG99	homog	-0.06	-0.125	-0.25

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip.	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	KOH, 24	Thorin	W40, 25	Thorin	Thorin		bulk
1980	KOH, 24	Thorin	W40, 25	Thorin	Thorin		bulk
1981	KOH, 24	Thorin	W40, 25	Thorin	Thorin		bulk
1982	KOH, 24	Thorin	W40, 25	Thorin	Thorin		bulk
1983	KOH, 8	Thorin	W40, 10	Thorin	Thorin		bulk
1984	KOH, 8	Thorin	W40, 10	Thorin	Thorin		bulk
1985	KOH, 8	Thorin	W40, 10	Thorin			bulk
1986	KOH, 8	Thorin	W40, 10	Thorin		UV spect.	bulk
1987	KOH, 8	Thorin	W40, 10	Thorin		UV spect.	bulk
1988	KOH, 8	Thorin	W40, 8	XRF		UV spect./IC	bulk
1989	KOH, 8	Thorin	W40, 8	IC		IC	bulk
1990	KOH, 8	Thorin	W40, 8	IC		IC	bulk
1991	KOH, 8	Thorin	W40, 8	IC		IC	bulk
1992	KOH, 8	Thorin	W40, 8	IC	IC	IC	bulk
1993	KOH, 8	Thorin	W40, 8	IC	IC	IC	bulk
1994	KOH, 8	IC	W40, 8	IC	IC	IC	wet-only
1995	KOH, 8	IC	W40, 8	IC	IC	IC	wet-only
1996	KOH, 8	IC	W40, 8	IC	IC	IC	wet-only
1997	KOH, 8	IC	W40, 8	IC	IC	IC	wet-only
1998	KOH, 8	IC	W40, 8	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



SLOVENIA

SI01 Masun
SI08 Iskrba

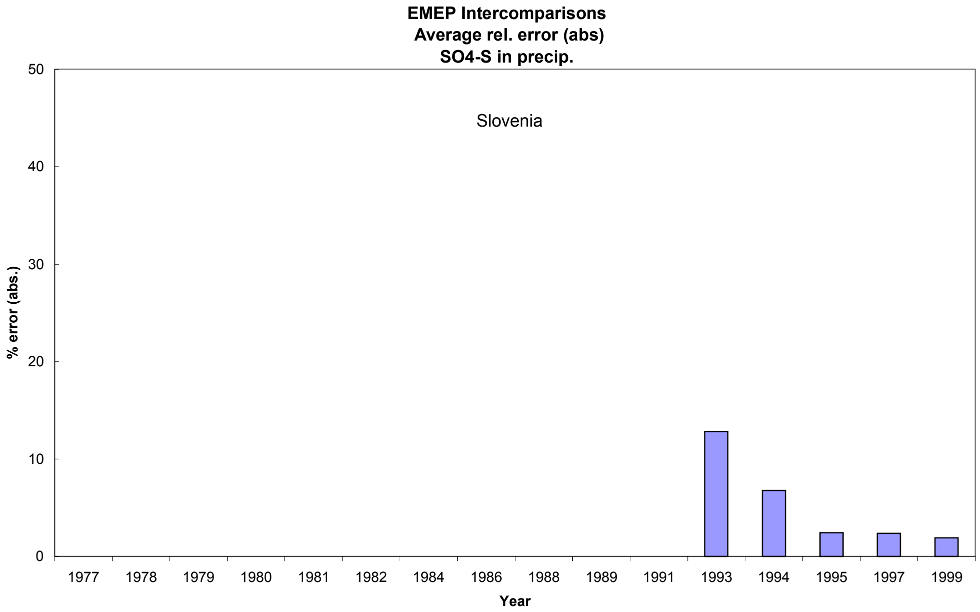
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
SI0001	SO2air	1984	1988	NEG99	homog	-0.298	-0.587	-1.173
SI0008	SO2air	1996	1998	NOT	homog	0.194	0.12	-0.093
SI0008	SO4air	1996	1998	NOT	homog	0.087	-0.075	-0.359
SI0001	SO4aq.	1980	1991	NOT	homog	0.035	-0.01	-0.038
SI0008	NO3HNO3	1996	1998	NOT	homog	0.03	-0.005	-0.03
SI0001	NO3aq.	1980	1991	POS99	homog	0.022	0.017	0.01
SI0008	NH3+4	1996	1998	NOT	homog	0.046	-0.005	-0.264
SI0001	NH4aq.	1980	1991	NOT	homog	0.008	-0.002	-0.013

Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	Precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979							
1980							
1981							
1982							
1983							
1984							
1985							
1986							
1987							
1988							
1989							
1990							
1991	Abs., TCM, 2						bulk
1992							
1993							
1994							
1995							
1996	KOH, 22	IC	TN, 1 u, 22	IC			
1997	KOH, 22	IC	T,GZ, 2 u, 22	IC			
1998	KOH, 22	IC	T,GZ, 2 u, 22	IC			

Performance in laboratory intercalibrations for sulphate in solution



SPAIN

ES01 Toledo
ES02 La Cartuja
ES03 Roquetas
ES04 Logrono
ES05 Noia
ES06 Mahon
ES07 Viznar

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
ES0001	SO2air	1984	1998	NEG99	homog	-0.051	-0.084	-0.123
ES0002	SO2air	1987	1995	NEG99	homog	-0.168	-0.275	-0.394
ES0003	SO2air	1987	1998	NEG99	homog	-0.082	-0.149	-0.213
ES0004	SO2air	1988	1998	NEG99	homog	-0.336	-0.46	-0.574
ES0005	SO2air	1993	1998	NEG99	homog	-0.183	-0.305	-0.428
ES0006	SO2air	1994	1998	NEG99	homog	-0.301	-0.413	-0.54
ES0007	SO2air	1995	1998	NEG95	homog	-0.004	-0.162	-0.561
ES0001	SO4air	1985	1998	POS99	homog	0.027	0.02	0.01
ES0002	SO4air	1987	1995	NOT	homog	0.018	-0.021	-0.058
ES0003	SO4air	1987	1998	NEG95	homog	-0.002	-0.029	-0.049
ES0004	SO4air	1988	1998	NEG99	homog	-0.019	-0.043	-0.064
ES0005	SO4air	1993	1998	NOT	homog	0.036	-0.02	-0.07
ES0006	SO4air	1994	1998	NOT	homog	0.009	-0.072	-0.16
ES0007	SO4air	1995	1998	POS95	homog	0.129	0.052	0.007
ES0001	SO4aq.	1984	1998	POS95	homog	0.02	0.012	0.003
ES0002	SO4aq.	1987	1995	POS99	not	0.143	0.075	0.032
ES0003	SO4aq.	1987	1998	NOT	homog	0.023	-0.002	-0.028
ES0004	SO4aq.	1988	1998	NEG99	homog	-0.037	-0.064	-0.1
ES0005	SO4aq.	1993	1998	NOT	homog	0.064	0.015	-0.035
ES0006	SO4aq.	1994	1998	NOT	homog	2.088	0.262	-1.659
ES0007	SO4aq.	1995	1998	POS95	homog	0.194	0.09	0.022
ES0001	NO2	1986	1998	NOT	homog	0.079	0.002	-0.096
ES0002	NO2	1987	1995	POS99	homog	0.608	0.339	0.132
ES0003	NO2	1987	1998	NOT	homog	0.158	0.03	-0.1
ES0004	NO2	1988	1998	NEG90	homog	0.002	-0.093	-0.255
ES0005	NO2	1993	1998	NEG95	homog	-0.081	-0.537	-0.8
ES0006	NO2	1994	1998	NOT	homog	0.28	-0.098	-0.42
ES0007	NO2	1995	1998	POS95	homog	1.304	0.6	0.078

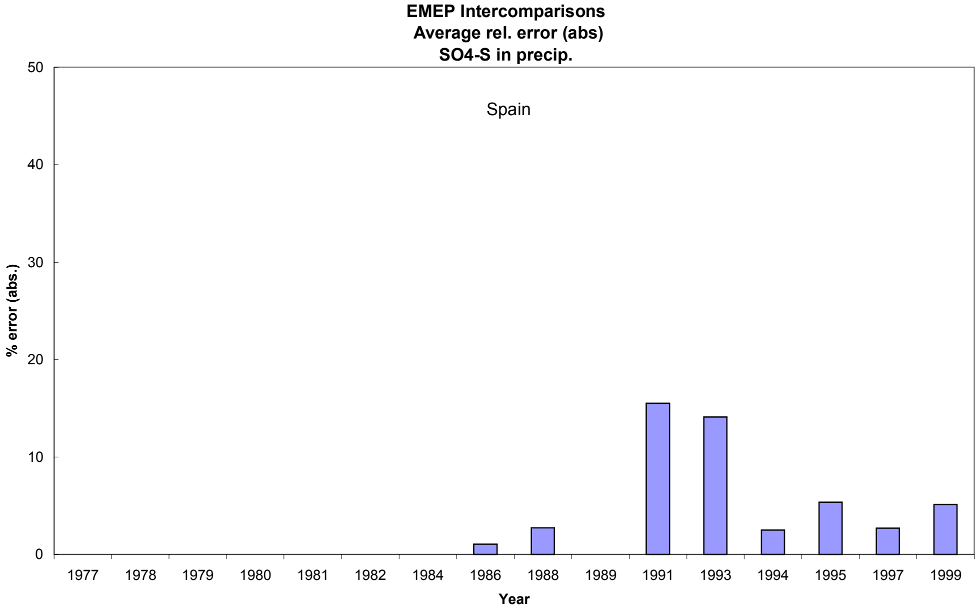
SKT trend analysis and estimates of magnitude (cont)

Site	*Component*	*From*	*To*	*trend & significance*	*seasonal homogeneity*	*+90%*	*best est.*	*-90%*
ES0001	NO3HNO3	1988	1998	POS90	homog	0.013	0.005	0
ES0002	NO3HNO3	1989	1995	NEG99	homog	-0.033	-0.052	-0.074
ES0003	NO3HNO3	1989	1998	NEG99	homog	-0.04	-0.059	-0.075
ES0004	NO3HNO3	1988	1998	NEG99	homog	-0.05	-0.058	-0.067
ES0005	NO3HNO3	1993	1998	NOT	homog	0.02	0.001	-0.018
ES0006	NO3HNO3	1994	1998	NEG99	homog	-0.061	-0.116	-0.162
ES0007	NO3HNO3	1995	1998	POS99	homog	0.17	0.125	0.081
ES0001	NO3aq.	1984	1998	NOT	homog	0.008	0.003	-0.001
ES0002	NO3aq.	1987	1995	POS99	homog	0.085	0.043	0.022
ES0003	NO3aq.	1987	1998	POS99	homog	0.05	0.03	0.016
ES0004	NO3aq.	1988	1998	NOT	homog	0.008	-0.002	-0.01
ES0005	NO3aq.	1993	1998	POS95	homog	0.044	0.027	0.002
ES0006	NO3aq.	1994	1998	NOT	homog	1.67	0.342	-0.177
ES0007	NO3aq.	1995	1998	POS90	homog	0.147	0.035	-0.023
ES0001	NH4air	1985	1998	POS99	homog	0.025	0.02	0.014
ES0002	NH4air	1987	1995	POS99	homog	0.076	0.06	0.05
ES0003	NH4air	1987	1998	POS99	homog	0.037	0.026	0.012
ES0004	NH4air	1988	1998	POS90	homog	0.032	0.016	-0.003
ES0005	NH4air	1993	1998	NOT	homog	0.027	0.007	-0.031
ES0006	NH4air	1994	1998	NOT	homog	0.01	-0.01	-0.045
ES0007	NH4air	1995	1998	NOT	homog	0.11	0.027	-0.06
ES0001	NH3+4	1988	1998	NEG99	homog	-0.086	-0.11	-0.128
ES0002	NH3+4	1989	1995	NEG99	homog	-0.21	-0.322	-0.477
ES0003	NH3+4	1989	1998	NEG99	homog	-0.449	-0.593	-0.726
ES0004	NH3+4	1988	1998	NEG99	homog	-0.07	-0.125	-0.19
ES0005	NH3+4	1993	1998	NEG95	homog	-0.033	-0.07	-0.117
ES0006	NH3+4	1994	1998	NEG90	homog	0.065	-0.222	-0.402
ES0007	NH3+4	1995	1998	NOT	homog	0.35	0.128	-0.049
ES0001	NH4aq.	1984	1998	NOT	homog	0.007	0.002	-0.002
ES0002	NH4aq.	1987	1995	NOT	homog	0.03	0.01	-0.025
ES0003	NH4aq.	1987	1998	NEG95	homog	0	-0.015	-0.03
ES0004	NH4aq.	1988	1998	NOT	homog	0.033	0.009	-0.021
ES0005	NH4aq.	1993	1998	POS95	homog	0.024	0.015	0
ES0006	NH4aq.	1994	1998	POS95	homog	0.41	0.16	0.046
ES0007	NH4aq.	1995	1998	NOT	homog	0.06	-0.01	-0.03

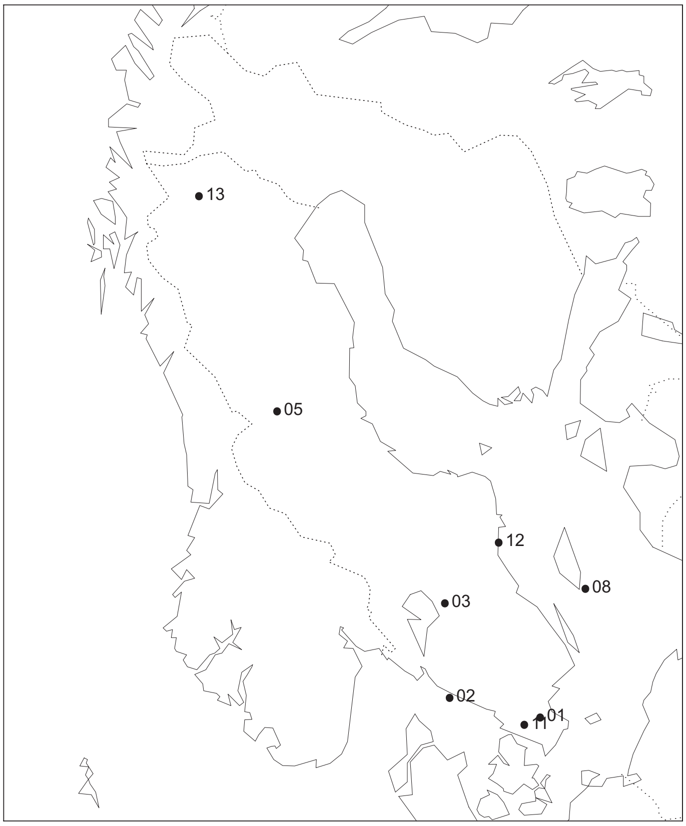
Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979				Thorin			
1980				Thorin			
1981							wet-only
1982							
1983							
1984		Thorin		Thorin	Thorin	UV spect.	wet-only
1985	Abs., H2O2, 3	Thorin	WGF/A, 770	Thorin	Thorin	UV spect.	wet-only
1986	Abs., H2O2, 3	Thorin	WGF/A, 770	Thorin	IC	IC	wet-only
1987	Abs., H2O2, 3	Thorin	WGF/A, 770	Thorin	IC	IC	wet-only
1988	Abs., H2O2, 3	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1989	Abs., H2O2, 3	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1990	Abs., H2O2, 3	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1991	Abs., H2O2, 3	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1992	Abs., H2O2, 2	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1993	Abs., H2O2, 2	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1994	Abs., H2O2, 2	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1995	Abs., H2O2, 2	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1996	Abs., H2O2, 2	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1997	Abs., H2O2, 2	Thorin	WGF/A, 770	IC	IC	IC	wet-only
1998	Abs., H2O2, 2	Thorin	WGF/A, 770	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



SWEDEN



SE01 Ekeröd
SE02 Rörvik
SE03 Velen
SE05 Bredkalen
SE08 Hoburg
SE11 Vavihill
SE12 Aspvreten
SE13 Esrange

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
SE0001	SO2air	1979	1984	NEG95	homog	-0.025	-0.137	-0.315
SE0002	SO2air	1978	1998	NEG99	homog	-0.136	-0.149	-0.164
SE0003	SO2air	1979	1990	NEG99	homog	-0.03	-0.062	-0.101
SE0005	SO2air	1979	1998	NEG99	homog	-0.06	-0.066	-0.074
SE0008	SO2air	1978	1998	NEG99	homog	-0.082	-0.095	-0.107
SE0011	SO2air	1984	1998	NEG99	homog	-0.243	-0.271	-0.305
SE0012	SO2air	1984	1998	NEG99	homog	-0.06	-0.072	-0.091
SE0013	SO2air	1990	1997	NEG99	homog	-0.048	-0.06	-0.075
SE0001	SO4air	1979	1984	NEG99	homog	-0.061	-0.144	-0.266
SE0002	SO4air	1978	1998	NEG99	homog	-0.067	-0.08	-0.094
SE0003	SO4air	1979	1990	NEG99	homog	-0.02	-0.04	-0.057
SE0005	SO4air	1979	1998	NEG99	homog	-0.017	-0.02	-0.024
SE0008	SO4air	1978	1998	NEG99	homog	-0.053	-0.062	-0.071
SE0011	SO4air	1984	1998	NEG99	homog	-0.053	-0.065	-0.076
SE0012	SO4air	1984	1998	NEG99	homog	-0.031	-0.04	-0.052
SE0013	SO4air	1990	1997	NEG99	homog	-0.01	-0.018	-0.025
SE0001	SO4aq.	1979	1984	NOT	homog	0.099	-0.033	-0.097
SE0002	SO4aq.	1978	1998	NEG99	homog	-0.03	-0.038	-0.047
SE0003	SO4aq.	1979	1990	NOT	homog	0.026	0.003	-0.022
SE0005	SO4aq.	1979	1998	NEG99	homog	-0.017	-0.022	-0.026
SE0008	SO4aq.	1978	1991	NOT	homog	0.025	0.003	-0.024
SE0011	SO4aq.	1984	1998	NEG99	homog	-0.043	-0.054	-0.064
SE0012	SO4aq.	1984	1998	NEG99	homog	-0.05	-0.062	-0.081
SE0013	SO4aq.	1990	1991	Insuf	not	0	0	0

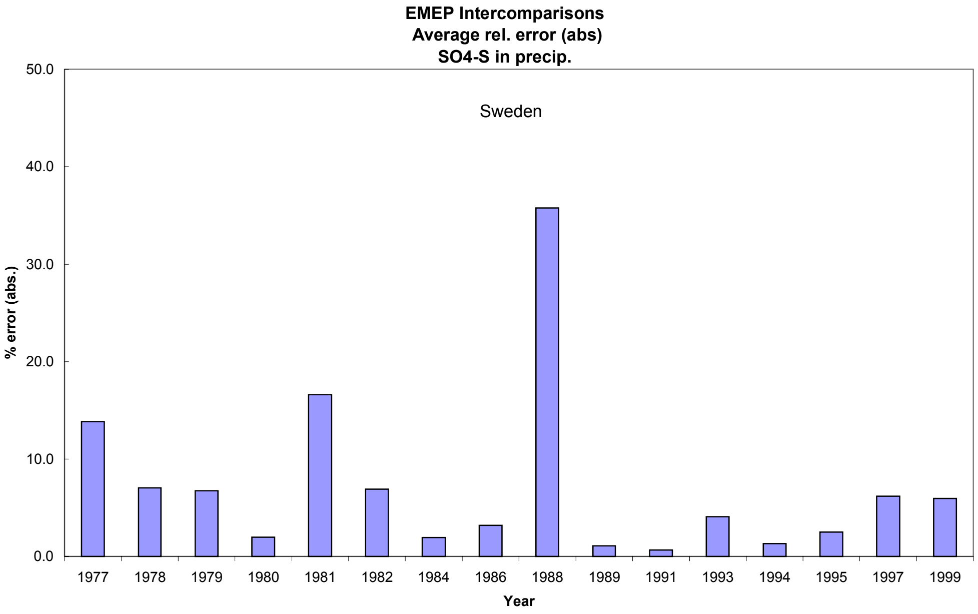
SKT trend analysis and estimates of magnitude(cont)

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
SE0001	NO2	1982	1984	NOT	homog	0.502	0.1	-0.058
SE0002	NO2	1982	1998	POS99	homog	0.028	0.02	0.011
SE0003	NO2	1982	1990	POS99	homog	0.032	0.02	0.011
SE0005	NO2	1982	1998	NEG99	homog	-0.01	-0.013	-0.017
SE0008	NO2	1982	1998	POS99	homog	0.034	0.029	0.022
SE0011	NO2	1984	1998	POS99	homog	0.03	0.02	0.007
SE0012	NO2	1985	1998	NEG99	homog	-0.016	-0.022	-0.029
SE0013	NO2	1990	1997	NEG99	homog	-0.01	-0.013	-0.02
SE0012	NO3air	1986	1986	Insuf				
SE0002	NO3HNO3	1985	1998	NEG99	homog	-0.01	-0.018	-0.025
SE0003	NO3HNO3	1986	1990	NEG95	homog	-0.004	-0.022	-0.055
SE0005	NO3HNO3	1986	1998	NEG95	homog	0	0	-0.001
SE0008	NO3HNO3	1994	1994	Insuf				
SE0011	NO3HNO3	1986	1998	NEG99	homog	-0.027	-0.032	-0.04
SE0012	NO3HNO3	1985	1998	NEG99	homog	-0.012	-0.015	-0.02
SE0013	NO3HNO3	1990	1990	Insuf				
SE0001	NO3aq.	1979	1984	NOT	homog	0.032	0.003	-0.02
SE0002	NO3aq.	1978	1998	NEG99	homog	-0.003	-0.008	-0.013
SE0003	NO3aq.	1979	1990	POS99	homog	0.029	0.018	0.01
SE0005	NO3aq.	1979	1998	NEG95	homog	0	-0.002	-0.004
SE0008	NO3aq.	1978	1991	POS95	homog	0.03	0.017	0.005
SE0011	NO3aq.	1984	1998	NEG90	homog	0.001	-0.006	-0.014
SE0012	NO3aq.	1984	1998	NEG99	homog	-0.014	-0.022	-0.03
SE0013	NO3aq.	1990	1991	Insuf				
SE0012	NH4air	1984	1986	NEG99	homog	-0.045	-0.15	-0.24
SE0002	NH3+4	1985	1998	NEG99	homog	-0.03	-0.04	-0.053
SE0003	NH3+4	1986	1990	NEG95	homog	-0.048	-0.099	-0.144
SE0005	NH3+4	1986	1998	NEG99	homog	-0.014	-0.018	-0.022
SE0008	NH3+4	1994	1994	Insuf				
SE0011	NH3+4	1986	1998	NEG99	homog	-0.07	-0.083	-0.098
SE0012	NH3+4	1985	1998	NEG99	homog	-0.03	-0.037	-0.046
SE0013	NH3+4	1990	1990	Insuf				
SE0001	NH4aq.	1979	1984	NOT	homog	0.054	-0.009	-0.057
SE0002	NH4aq.	1978	1998	NEG99	homog	-0.008	-0.013	-0.02
SE0003	NH4aq.	1979	1990	POS95	not	0.025	0.015	0.001
SE0005	NH4aq.	1979	1998	NEG99	homog	-0.005	-0.007	-0.009
SE0008	NH4aq.	1979	1991	POS99	not	0.082	0.041	0.014
SE0011	NH4aq.	1984	1998	NEG95	homog	-0.002	-0.012	-0.022
SE0012	NH4aq.	1984	1998	NEG99	homog	-0.02	-0.03	-0.038
SE0013	NH4aq.	1990	1991	Insuf				

Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 3	IC	W40, 2	XRF	IC	IC	bulk
1980	Abs., H2O2, 3	IC	W40, 2	XRF	IC	IC	bulk
1981	Abs., H2O2, 3	IC	W40, 2	XRF	IC	IC	bulk
1982	Abs., H2O2, 3	IC	W40, 2	XRF	IC	IC	bulk
1983	Abs., H2O2, 3	IC	W40, 2	XRF	IC	IC	wet-only
1984	Abs., H2O2, 3	IC	W40, 2	XRF	IC	IC	wet-only
1985	Abs., H2O2, 2	IC	W40, 2	XRF	IC	IC	wet-only
1986	Abs., H2O2, 2	IC	W40, 2	XRF	IC	IC	wet-only
1987	Abs., H2O2, 2	IC	W40, 2	XRF	IC	IC	wet-only
1988	Abs., H2O2, 2/KOH, 24	IC	W40, 2/24	IC	IC	IC	wet-only
1989	Abs., H2O2, 2/KOH, 24	IC	W40, 2/24	IC	IC	IC	wet-only
1990	Abs., H2O2, 2/KOH, 24	IC	W40, 2/24	IC	IC	IC	wet-only
1991	Abs., H2O2, 2	IC	W40, 2	IC	IC	IC	wet-only
1992	Abs., H2O2, 2	IC	T,GZ, 2 u, 2	IC	IC	IC	wet-only
1993	KOH, 20	IC	T,GZ, 2 u, 2	IC	IC	IC	wet-only
1994	KOH, 20	IC	T,GZ, 2 u, 20	IC	IC	IC	wet-only
1995	KOH, 20	IC	T,GZ, 2 u, 20	IC	IC	IC	wet-only
1996	KOH, 20	IC	T,GZ, 2 u, 20	IC	IC	IC	wet-only
1997	KOH, 20	IC	T,GZ, 2 u, 20	IC	IC	IC	wet-only
1998	KOH, 20	IC	T,GZ, 2 u, 20	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



SWITZERLAND

CH01 Jungfraujoch
CH02 Payerne
CH03 Taenikon
CH04 Chaumont
CH05 Rigi

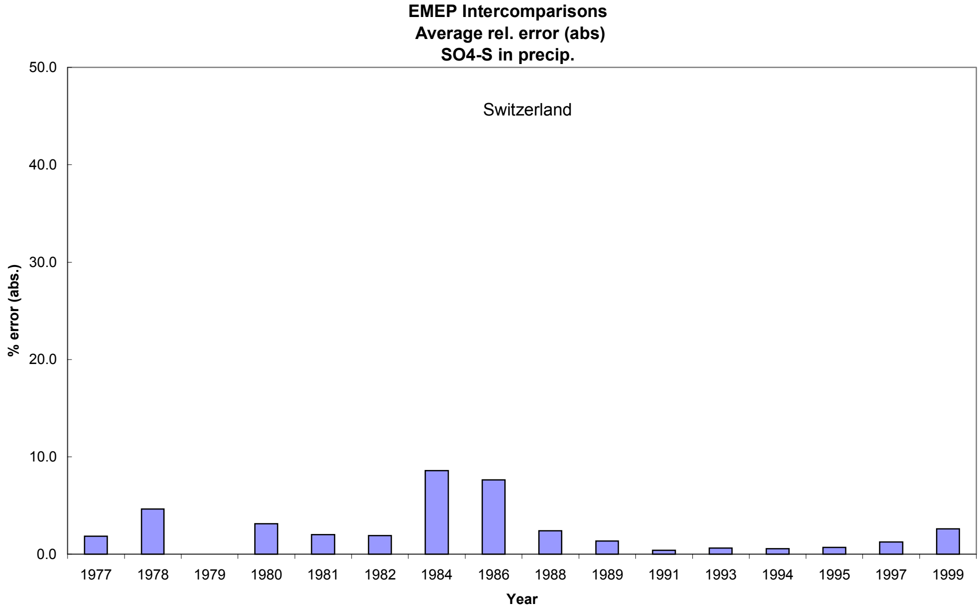
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend significance &	seasonal homogeneity	+90%	best est.	-90%
CH0001	SO2air	1980	1998	NEG99	homog	-0.022	-0.026	-0.03
CH0002	SO2air	1979	1998	NEG99	homog	-0.099	-0.117	-0.138
CH0003	SO2air	1992	1998	NEG99	homog	-0.055	-0.082	-0.117
CH0004	SO2air	1992	1998	NEG99	homog	-0.08	-0.117	-0.156
CH0005	SO2air	1992	1998	NEG99	homog	-0.065	-0.09	-0.116
CH0001	SO4air	1980	1998	NEG99	homog	-0.017	-0.02	-0.025
CH0002	SO4air	1979	1998	NEG99	homog	-0.087	-0.103	-0.12
CH0003	SO4air	1992	1996	NEG99	homog	-0.063	-0.171	-0.247
CH0004	SO4air	1992	1996	NEG95	homog	-0.008	-0.074	-0.195
CH0005	SO4air	1992	1998	NEG99	homog	-0.067	-0.104	-0.147
CH0001	SO4aq.	1981	1992	NOT	homog	0.001	-0.005	-0.011
CH0002	SO4aq.	1984	1998	NEG99	homog	-0.029	-0.035	-0.044
CH0003	SO4aq.	1997	1998	Insuf				
CH0004	SO4aq.	1997	1998	Insuf				
CH0005	SO4aq.	1997	1998	Insuf				
CH0001	NO2	1993	1998	NOT	homog	0.006	-0.002	-0.007
CH0002	NO2	1985	1998	NEG99	homog	-0.047	-0.074	-0.117
CH0003	NO2	1992	1998	NOT	homog	0.098	0.032	-0.028
CH0004	NO2	1992	1998	NOT	homog	0.111	0.047	-0.014
CH0005	NO2	1992	1998	NOT	homog	0.1	0.027	-0.024
CH0002	NO3HNO3	1993	1998	NOT	homog	0.026	-0.013	-0.054
CH0001	NO3aq.	1981	1992	NOT	homog	0.003	0	-0.003
CH0002	NO3aq.	1984	1998	NEG99	homog	-0.003	-0.007	-0.011
CH0003	NO3aq.	1997	1998	Insuf				
CH0004	NO3aq.	1997	1998	Insuf				
CH0005	NO3aq.	1997	1998	Insuf				
CH0002	NH3+4	1993	1998	NOT	homog	0.149	0.025	-0.122
CH0001	NH4aq.	1981	1992	NOT	homog	0.001	-0.002	-0.006
CH0002	NH4aq.	1984	1998	NEG95	homog	-0.001	-0.008	-0.016
CH0003	NH4aq.	1997	1998	Insuf				
CH0004	NH4aq.	1997	1998	Insuf				
CH0005	NH4aq.	1997	1998	Insuf				

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip.	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 3	Thorin		XRF	Thorin aut.	Cd red., Griess	wet-only
1980	Abs., H2O2, 3	Thorin		XRF	Thorin aut.	Cd red., Griess	wet-only
1981	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin aut.	Cd red., Griess	wet-only
1982	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin aut.	Cd red., Griess	wet-only
1983	Abs., H2O2, 3	Thorin	W40, 3	XRF	Thorin aut.	Cd red., Griess	bulk/wet-only
1984	Abs., H2O2, 3	Thorin	W40, 3	XRF	IC	IC	bulk/wet-only
1985	Abs., H2O2, 4	Thorin	W40, 4	XRF	IC	IC	bulk/wet-only
1986	Abs., H2O2, 4	Thorin	W40, 4	XRF	IC	IC	bulk/wet-only
1987	Abs., H2O2, 4	Thorin	W40/ S, 4	XRF	IC	IC	bulk/wet-only
1988	Abs., H2O2, 4/ Monitor, UV-fluor.	Thorin/UV-fluores.	S, 4	XRF	IC	IC	bulk/wet-only
1989	Abs., H2O2, 4/ Monitor, UV-fluor.	Thorin/IC	S, 4	XRF	IC	IC	bulk/wet-only
1990	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	bulk/wet-only
1991	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	bulk/wet-only
1992	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	bulk/wet-only
1993	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	bulk/wet-only
1994	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	bulk/wet-only
1995	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	bulk/wet-only
1996	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	wet-only
1997	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	wet-only
1998	Abs., H2O2, 4/ Monitor, UV-fluor.	IC/UV-fluores.	S, 4	XRF	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



TURKEY

TR01 Cubuk II

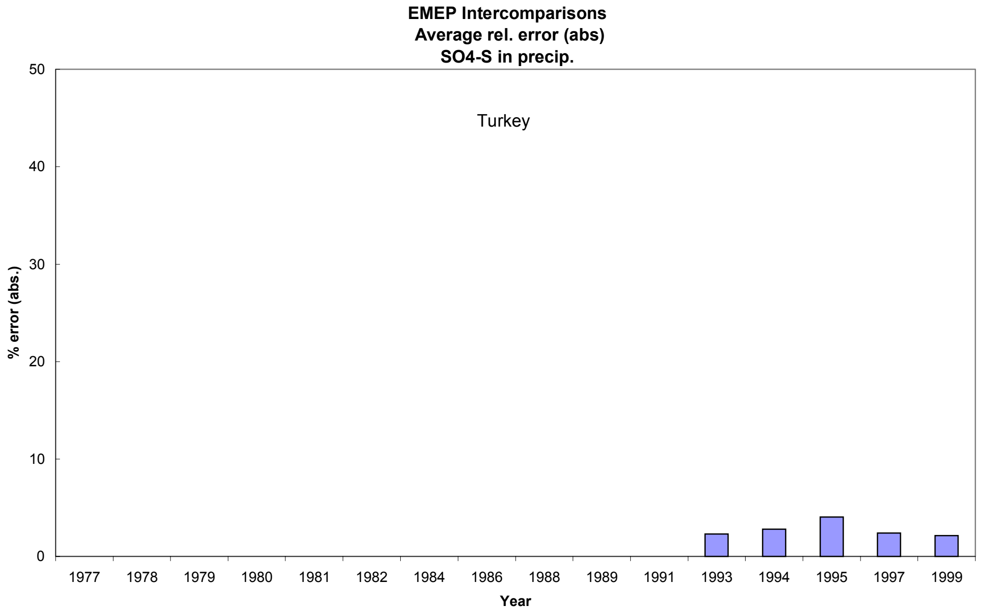
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
TR0001	SO2air	1993	1998	NOT	homog	0.07	0.01	-0.05
TR0001	SO4air	1993	1998	NEG99	homog	-0.09	-0.135	-0.17
TR0001	SO4aq.	1993	1998	NOT	homog	0.058	-0.04	-0.112
TR0001	NO2	1993	1998	NOT	homog	0.028	-0.002	-0.046
TR0001	NO3air	1993	1998	NEG99	homog	-0.014	-0.02	-0.02
TR0001	NO3HNO3	1993	1998	NEG95	homog	-0.004	-0.013	-0.035
TR0001	HNO3	1993	1998	NOT	homog	0.007	0	-0.005
TR0001	NO3aq.	1993	1998	NOT	homog	0.028	-0.015	-0.076
TR0001	NH3	1993	1998	NOT	homog	0.01	-0.003	-0.03
TR0001	NH4air	1993	1998	NEG99	homog	-0.053	-0.062	-0.088
TR0001	NH3+4	1993	1998	NEG99	homog	-0.034	-0.054	-0.094
TR0001	NH4aq.	1993	1998	NEG99	homog	-0.097	-0.229	-0.429

Sampling and analytical methods

	SO2		SO4 in air		SO4 in precip	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979							
1980							
1981							
1982							
1983							
1984							
1985							
1986							
1987							
1988							
1989							
1990							
1991							
1992							
1993	Abs., TCM, 1					IC	wet-only
1994	Abs., TCM, 1				IC	IC	wet-only
1995	Abs., TCM, 1		W40, 35		IC	IC	wet-only
1996	Abs., TCM, 1		W40, 35		IC	IC	wet-only
1997	Abs., TCM, 1		W40, 35		IC	IC	wet-only
1998	Abs., TCM, 1		W40, 35		IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



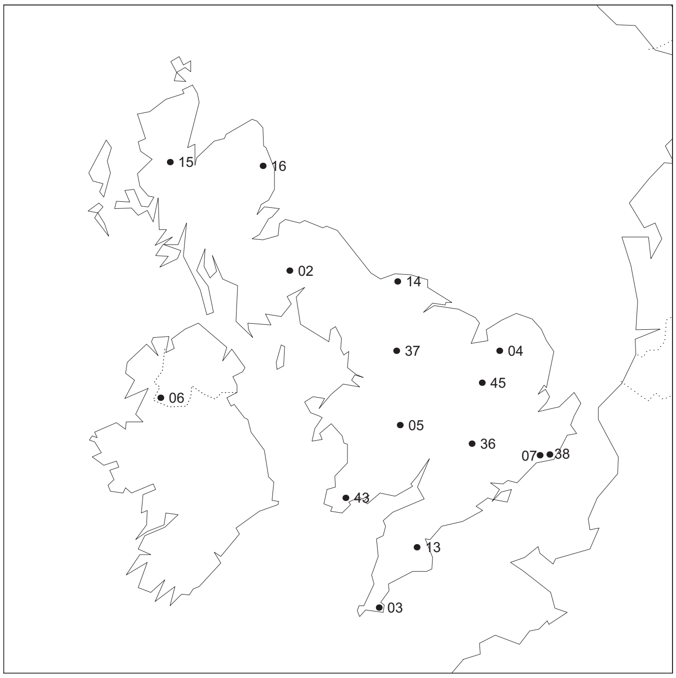
UKRAINE

UA05 Svityar
UA06 Rava-Russkaya
UA07 Beregovo

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
UA0005	SO2air	1986	1991	POS95	homog	0.265	0.189	0.075
UA0006	SO2air	1985	1991	NOT	homog	0.32	-0.009	-0.277
UA0007	SO2air	1985	1989	POS99	homog	1.261	0.68	0.168
UA0005	SO4air	1979	1991	NEG99	homog	-0.04	-0.102	-0.183
UA0006	SO4air	1979	1991	NEG99	homog	-0.066	-0.134	-0.197
UA0007	SO4air	1979	1989	NEG99	homog	-0.157	-0.381	-0.481
UA0005	SO4aq.	1981	1991	POS99	homog	0.1	0.063	0.023
UA0006	SO4aq.	1981	1991	POS95	homog	0.102	0.049	0.004
UA0007	SO4aq.	1981	1989	POS99	homog	0.246	0.15	0.088
UA0005	NO2	1986	1991	POS90	homog	0.466	0.125	-0.015
UA0006	NO2	1986	1991	POS99	homog	3.148	2.337	1.581
UA0007	NO2	1986	1989	POS99	homog	1.865	1.067	0.602
UA0005	NO3air	1986	1991	NEG99	homog	-0.04	-0.08	-0.126
UA0006	NO3air	1986	1991	POS99	homog	0.146	0.077	0.039
UA0007	NO3air	1986	1989	POS95	homog	0.296	0.17	0.011
UA0005	NO3aq.	1986	1991	POS90	homog	0.08	0.049	-0.005
UA0006	NO3aq.	1986	1991	NOT	homog	0.05	-0.012	-0.061
UA0007	NO3aq.	1986	1989	NOT	homog	0.204	0.008	-0.084
UA0005	NH4air	1982	1991	NOT	homog	0.094	0.031	-0.051
UA0006	NH4air	1982	1991	POS99	homog	0.2	0.127	0.078
UA0007	NH4air	1982	1989	POS95	homog	0.197	0.116	0.03
UA0005	NH4aq.	1981	1991	NOT	homog	0.004	-0.014	-0.04
UA0006	NH4aq.	1981	1991	NOT	not	0.031	-0.01	-0.064
UA0007	NH4aq.	1981	1989	NOT	homog	0.112	0.013	-0.064

UNITED KINGDOM



GB02 Eskdalemuir
GB03 Goonhilly
GB04 Stoke ferry
GB05 Ludlow
GB06 Lough Navar
GB07 Barcombe Mills
GB13 Yarner Wood
GB14 High Muffles
GB15 Starth Vaich Dam
GB16 Glen Dye
GB36 Harwell
GB37 Ladybower
GB38 Lullington Heath
GB43 Narberth
GB45 Wicken Fen

SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
GB0002	SO2air	1978	1998	NEG99	homog	-0.125	-0.141	-0.16
GB0003	SO2air	1979	1988	NEG99	homog	-0.177	-0.26	-0.334
GB0004	SO2air	1981	1998	NEG99	homog	-0.273	-0.297	-0.327
GB0006	SO2air	1985	1998	NEG99	homog	-0.02	-0.03	-0.045
GB0007	SO2air	1985	1998	NEG99	homog	-0.171	-0.212	-0.257
GB0013	SO2air	1987	1998	NEG99	homog	-0.076	-0.115	-0.159
GB0014	SO2air	1987	1998	NEG99	homog	-0.255	-0.311	-0.387
GB0015	SO2air	1987	1998	NOT	homog	0.016	0	-0.015
GB0016	SO2air	1987	1998	NEG99	homog	-0.053	-0.073	-0.105
GR0001	SO2air	1978	1997	NOT	homog	0.063	0.005	-0.033
GB0002	SO4air	1978	1998	NEG99	homog	-0.009	-0.015	-0.02
GB0003	SO4air	1979	1988	POS95	homog	0.058	0.032	0
GB0004	SO4air	1981	1998	NEG99	homog	-0.024	-0.035	-0.052
GB0005	SO4air	1981	1987	NEG95	homog	-0.019	-0.085	-0.176
GB0006	SO4air	1984	1998	NEG95	homog	0	-0.01	-0.024
GB0007	SO4air	1985	1998	NEG99	homog	-0.028	-0.045	-0.064
GB0013	SO4air	1987	1998	NEG99	homog	-0.032	-0.06	-0.078
GB0014	SO4air	1987	1998	NEG99	homog	-0.063	-0.081	-0.1
GB0015	SO4air	1987	1998	NEG99	homog	-0.01	-0.022	-0.036
GB0016	SO4air	1987	1998	NEG99	homog	-0.025	-0.039	-0.056

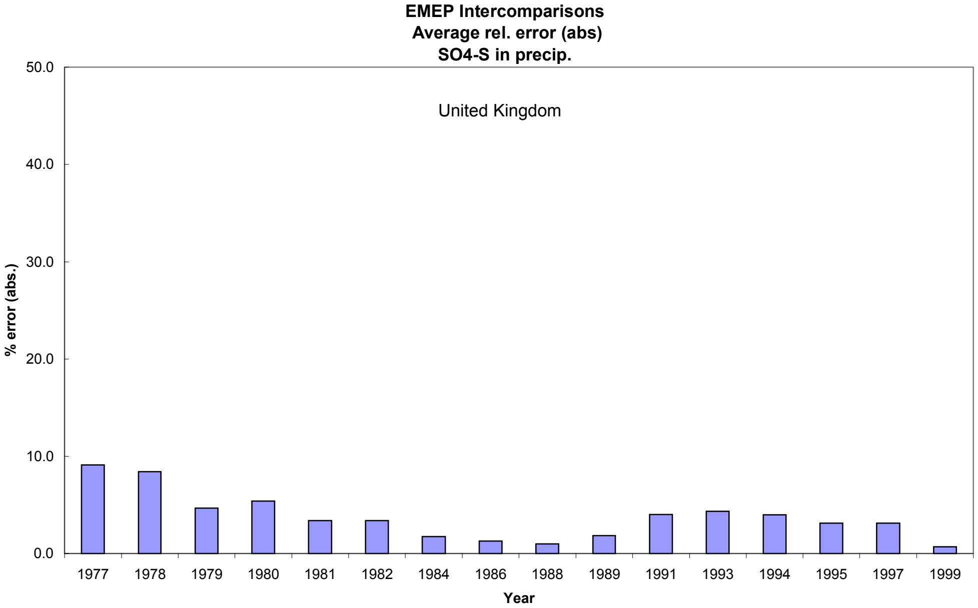
SKT trend analysis and estimates of magnitude (cont)

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
GB0002	SO4aq.	1978	1998	NEG99	homog	-0.015	-0.019	-0.023
GB0003	SO4aq.	1979	1988	NOT	homog	0.008	-0.013	-0.042
GB0004	SO4aq.	1980	1989	NOT	not	0.025	-0.011	-0.062
GB0005	SO4aq.	1984	1988	NEG99	homog	-0.059	-0.12	-0.216
GB0006	SO4aq.	1984	1998	NEG99	homog	-0.006	-0.011	-0.016
GB0007	SO4aq.	1987	1989	NEG95	homog	0.172	-0.29	-0.682
GB0013	SO4aq.	1987	1998	NOT	homog	0.003	-0.006	-0.014
GB0014	SO4aq.	1987	1998	NEG99	homog	-0.012	-0.026	-0.04
GB0015	SO4aq.	1987	1998	NOT	homog	0.002	-0.003	-0.009
GB0016	SO4aq.	1987	1989	NOT	homog	0.191	-0.025	-0.118
GB0015	NO2	1995	1997	POS90	homog	0.185	0.07	-0.038
GB0036	NO2	1995	1998	NOT	homog	0.342	-0.535	-1.081
GB0037	NO2	1995	1998	NEG99	homog	-0.258	-0.414	-0.57
GB0038	NO2	1995	1998	NEG90	homog	0.02	-0.188	-0.537
GB0043	NO2	1997	1998	Insuf				
GB0045	NO2	1997	1998	Insuf				
GB0002	NO3HNO3	1989	1998	NEG95	homog	-0.002	-0.01	-0.018
GB0014	NO3HNO3	1989	1998	NOT	homog	0.009	-0.006	-0.024
GB0002	NO3aq.	1979	1998	NOT	homog	0.002	0	-0.002
GB0003	NO3aq.	1979	1988	NEG90	homog	0.001	-0.007	-0.02
GB0004	NO3aq.	1980	1989	NOT	not	0.022	0.007	-0.015
GB0005	NO3aq.	1984	1988	NEG99	homog	-0.016	-0.05	-0.111
GB0006	NO3aq.	1984	1998	NOT	homog	0.002	0	-0.003
GB0007	NO3aq.	1987	1989	NEG95	homog	0.024	-0.135	-0.41
GB0013	NO3aq.	1987	1998	NOT	homog	0.009	0.001	-0.004
GB0014	NO3aq.	1987	1998	NEG90	homog	0	-0.007	-0.015
GB0015	NO3aq.	1987	1998	NOT	homog	0.005	0.001	-0.001
GB0016	NO3aq.	1987	1989	NOT	homog	0.323	0.04	-0.142
GB0005	NH4air	1982	1987	NEG99	homog	-0.093	-0.19	-0.479
GB0006	NH4air	1984	1985	Insuf				
GB0002	NH3+4	1989	1998	NEG90	homog	0.006	-0.014	-0.041
GB0014	NH3+4	1989	1998	NOT	homog	0.043	-0.021	-0.058
GB0002	NH4aq.	1980	1998	NEG95	homog	0	-0.003	-0.006
GB0003	NH4aq.	1980	1988	NEG95	homog	0	-0.01	-0.029
GB0004	NH4aq.	1980	1989	NOT	not	0.042	0.013	-0.017
GB0005	NH4aq.	1984	1988	NEG99	homog	-0.333	-0.425	-0.554
GB0006	NH4aq.	1984	1998	NEG99	homog	-0.01	-0.017	-0.024
GB0007	NH4aq.	1987	1989	NOT	homog	0.144	-0.13	-0.504
GB0013	NH4aq.	1987	1998	NOT	homog	0.007	-0.004	-0.012
GB0014	NH4aq.	1987	1998	NOT	homog	0.007	-0.003	-0.02
GB0015	NH4aq.	1987	1998	NEG90	homog	0	-0.001	-0.003
GB0016	NH4aq.	1987	1989	NOT	homog	0.304	-0.04	-0.331

Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in prec	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	bulk
1980	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	bulk
1981	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	bulk
1982	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	bulk
1983	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	bulk
1984	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	bulk
1985	Abs., H2O2, 4	IC	W40, 3	XRF	IC	IC	bulk
1986	Abs., H2O2, 4	IC	W40, 3	XRF	IC	IC	bulk/wet-only
1987	Abs., H2O2, 4	IC	W40, 3	XRF	IC	IC	bulk/wet-only
1988	Abs., H2O2, 4	IC	W40, 3	XRF	IC	IC	bulk/wet-only
1989	Abs., H2O2, 4	IC	W40, 3	XRF	IC	IC	bulk/wet-only
1990	Abs., H2O2, 4	IC	W40, 3	XRF	IC	IC	bulk/wet-only
1991	Abs., H2O2, 4	IC	W40, 3	XRF	IC	IC	bulk/wet-only
1992	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	wet-only
1993	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	wet-only
1994	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	wet-only
1995	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	wet-only
1996	Abs., H2O2, 3	IC	W40, 3	XRF	IC	IC	wet-only
1997	Abs., H2O2, 3	IC	W40, 3	IC	IC	IC	wet-only
1998	Abs., H2O2, 3	IC	W41, 1	IC	IC	IC	wet-only

Performance in laboratory intercalibrations for sulphate in solution



YUGOSLAVIA

YU05 Kamenicki Vis
YU08 Zabljak

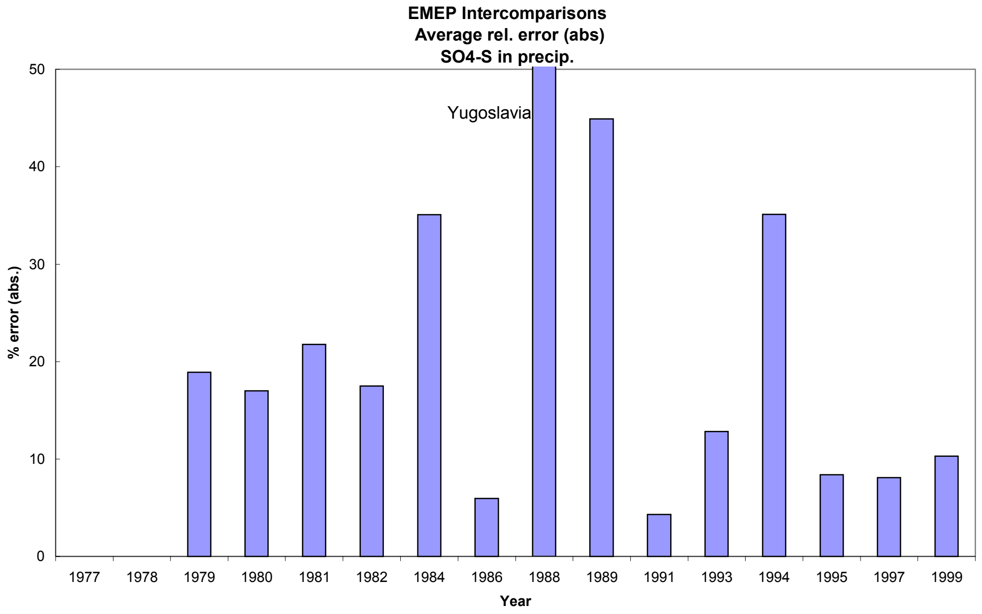
SKT trend analysis and estimates of magnitude

Site	Component	From	To	trend & significance	seasonal homogeneity	+90%	best est.	-90%
YU0005	SO2air	1984	1998	NEG99	homog	-0.346	-0.487	-0.607
YU0008	SO2air	1993	1998	NOT	homog	0.27	0.098	-0.021
YU0005	SO4aq.	1984	1998	NEG99	homog	-0.058	-0.1	-0.144
YU0008	SO4aq.	1993	1998	NOT	homog	0.02	-0.05	-0.12
YU0005	NO2	1990	1998	NOT	homog	0.045	-0.046	-0.122
YU0008	NO2	1993	1998	POS95	homog	0.267	0.139	0.026
YU0005	NO3aq.	1984	1998	POS99	not	0.018	0.013	0.007
YU0008	NO3aq.	1993	1998	POS95	homog	0.047	0.026	0.005
YU0005	NH4aq.	1984	1998	NOT	homog	0.02	0.005	-0.012

Sampling and analytical methods

	SO2		SO4 in air		SO4 in prec	NO3 in precip.	precip
	Sample	Analysis	Sample	Analysis	Analysis	Analysis	sample
1978							
1979					Thorin	Cd red., Griess	wet-only
1980					Thorin	Cd red., Griess	wet-only
1981					Thorin	Cd red., Griess	wet-only
1982					Thorin	Cd red., Griess	wet-only
1983					Thorin	Cd red., Griess	wet-only
1984					Thorin	Cd red., Griess	wet-only
1985	Abs., TCM, 2				Thorin	Cd red., Griess	wet-only
1986	Abs., TCM, 2				Thorin	Cd red., Griess	wet-only
1987	Abs., TCM, 2				Thorin	Cd red., Griess	wet-only
1988	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk/wet-only
1989	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk/wet-only
1990	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk/wet-only
1991	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk/wet-only
1992	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk
1993	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk
1994	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk
1995	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk
1996	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk
1997	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk
1998	Abs., TCM, 2	Pararosanilin			Thorin	Cd red., Griess	bulk

Performance in laboratory intercalibrations for sulphate in solution



Appendix B

Summary of statistical techniques in trend analysis

Statistical analysis has been undertaken in the following ways in this report:

a) test for existence of trends at each site,
b) test for existence of trends across regions,
c) evaluation of slope of trends both at sites and for regions,
d) cartographic display of changing deposition.

In this Appendix we provide a brief overview of the methods employed for each of these. Please refer to original references or standard texts for detailing of procedures.

a) test for existence of trend

Environmental data often exhibits such characteristics as missing values, detection limit values, seasonality, non-normality, and so forth. When faced with these characteristics the Seasonal Kendall Test (SKT) has become something of a normal choice for test tool. Where data is seasonal the variation added to data makes it more difficult to detect long term trends. Rather than transforming data to remove trends the SKT is a test which is unaffected. A generalisation of the Mann-Kendall Test which examines the relative magnitudes of data points, this approach takes data aggregated in 'seasonal' units (consistent time blocks) across several years and compares the rank for each seasonal value with the ranked values of subsequent data for the same season. A Mann-Kendall Z statistic and its variance is produced for each season. If the trends for each season are found to be homogenous, the Z statistics are combined to produce an overall trend result. The Z values are compared to standard normal tables at given critical level to establish significance, and the sign of the Z value indicates the direction of trend (positive upwards, negative downwards). The only limitation is that the trend must proceed in one direction, i.e. be monotonic. It need not be linear. The method may be found in standard statistical texts. We have used Gilbert (1987).

As originally developed by Hirsch, Slack and Smith (1982) the test was used for 12 "seasons" in a year, i.e. monthly data. It is in this format that we have used EMEP data for analysis. Hirsch *et al.* (1982) suggest the method is preferred to standard or seasonal regression tests if data is skewed, cyclical or serially correlated. Notably, linear regressions can indicate a significant slope with seasonal data when the true slope is zero. Furthermore, the ability to deal with such irregularities as missing data and manipulated values, e.g. detection limit values, is very important. Many parametric tests rely on regular data, introducing data manipulation to overcome difficulties. The potential may then exist for creating artefact conclusions through consequent influence on summary data. The SKT is a nonparametric test which, as explained, is able to accommodate missing and managed data on account of its use of relative magnitudes rather than absolute values.

b) test for existence of trends across regions

With data collected over regions there is interest in making region-wide statements about trends. The technique is to combine results from the SKT analysis of individual sites with the intention to determine whether the distribution of individual tests deviates from the distribution expected by chance. The

Z statistics are combined and tested against a chi-square distribution to establish trend significance, or otherwise, at given critical level. We have used a 90% significance criterion throughout. Where a trend is found to be significantly different from zero (i.e. no trend) at the 90% significance level, an estimate of the trend (from section c below - the SKT does not estimate the magnitude of the trend, only its significance level) is given in bold type. Where trends were found not statistically significant from zero only the direction (+-) is given, and no value is quoted. Originally described by Van Belle and Hughes (1984), the technique has been previously been used for determining regional trends during work in support of the Convention for Long Range Transport of Air Pollution. The ICP on Assessment and Monitoring of Acidification of Rivers and Lakes employed the approach within its nine-year review (Lükewille *et al.*, 1997). Once again, details may be found in standard texts and we have employed Gilbert, 1987.

Sites should exhibit similar trends for this to be a meaningful procedure, i.e. sites must be homogenous in the same way that seasons need to be homogenous in the SKT. Hard and fast rules for this do not exist. Initially, visual inspection of time series will offer an indication as to the reasonableness of combining trends across geographic areas. The common approach to objective testing, adopted here, is to attribute the variance in Z-statistics between factors influencing, and test this against a chi-square distribution. If any factor is found to be significantly different, the reasonableness of continuing to combine sites should be considered. In the analysis conducted here, variance has been tested for the effect of station homogeneity, seasonal homogeneity and for homogeneity in station-season interaction, following Gilbert (1987). These have each been tested at the 90% confidence level and the results of this test are presented within the statistical summary tables in chapter 3. Using symbolic notation, each region is assigned a selection of characters along with a number indicating the number of stations combined. As an example, in the case of full homogeneity, in sites, seasons, and site-season interaction, for 4 sites the following symbol would be used:

(+=4)*

The notation is as follows:

+	indicates homogeneity between sites
*	indicates homogeneity between seasons
=	indicates homogeneity in site-season interaction
4	indicates four sites were used.

An absence of any symbol indicates an absence of homogeneity for that factor at the 90% level. However, firm accepted standards for adopting or rejecting results, do not exist. Therefore, the complete homogeneity test information is supplied in this report to allow judgement to be made as to the value of the result when taken alongside other factors, such as consistency between regions, expectations, etc.

c) evaluation of slope of trends

The SKT and the Mann-Kendall test from which it was derived do not estimate the magnitude of trends, i.e. the slope of the line which may describe a trend. A common technique for this is Sen's slope estimator, here used in its seasonal form (seasonal Kendall slope estimator). The slope is estimated between each data point (season) and every subsequent data point, slope estimates are then ranked and the median value becomes the seasonal Kendall slope estimator. Confidence intervals about this slope may also be calculated based on the variance in the Z-statistics, giving maximum and minimum slopes for given confidence criteria. The slope can be calculated whether or not a trend is deemed significantly different from zero. It is an approach which is not grossly affected by data errors or outliers, and can be calculated when data is missing. It is closely related to the Mann-Kendall test and SKT above. In this report the slope estimate itself is given ("best estimate") along with the confidence intervals at 90%. The estimate itself is expressed as a percentage of initial concentration over the whole period of concern (where the trend was deemed significant using SKT), and the confidence limits as original units per annum. For example, a downward trend whose slope has 90% confidence intervals of 0.062 to 0.105 mg SO_2-S m^{-3} yr^{-1}, and for which the best estimate between those limits produced a 35% decrease in air concentrations between the first and last year of interest would be expressed as:

-35
-0.062 -0.105

Calculation of the percentage change involved estimating total change, and the initial concentrations across the stations combined. The Sen's slope estimator is a linear estimator of slope at each station, and so total change per station is given as time multiplied by slope, i.e.

$$\Delta C = s_s \cdot \Delta t \tag{c1}$$

where s_s = Sen's station slope estimator, C = concentration, and t = time. The initial concentration can then be estimated using ΔC and the arithmetic mean of all values $\overline{C}$:

$$C_0 = \overline{C} - 0.5\Delta C \tag{c2}$$

In a similar way, the estimate of the concentration at any point in the period of interest can be estimated from these equations using the slope estimator multiplied by time period. Thus, should it be necessary, the station slope estimators for sites in a region which have not monitored the same time periods can be used to provide estimates of the air concentration at each station at a common point in time. This approach can be used to determine the appropriate value of the mean concentration over a region during the time period of interest. Thus, for the 21 year period 1978-1998 should station k monitor during years 1978-1992, and station l monitor 1984-1998, a concentration for each representing the mid point, 1988, can be estimated. The arithmetic mean of estimated mid-point air concentrations across all stations in a region is taken as the mean for the region during the period of interest ($\overline{C}$), and the initial concentration is then estimated from (c2) in which k_s the Kendall slope estimator for regional trends replaces s_s

the Sen's slope estimator for stations. From this the relative change, expressed as a percentage of initial concentration, is given by:

$$R = \frac{100\Delta C}{C_0} \tag{c3}$$

d) Mapped changes in sulphur deposition.

The concept behind producing krigged maps has been given in the body of the text, in section 4.2. The technique can be used to estimate unknown data from neighbouring values, and is here used to estimate European deposition fields on the basis of point measurements. Such maps have been produced for estimated average annual total sulphur deposition for the three year periods 1980-82, 1985-87, 1990-92, and 1995-97. Wet deposition is directly monitored as total precipitation amount and concentration of sulphate in precipitation. All stations reporting precipitation amount are also reporting sulphate concentrations, and so to produce akrigged map from these values when employing purely the EMEP monitoring network is a reasonable estimate of wet deposition. Dry deposition has been estimated by multiplying observed SO_2 and airborne SO_4 concentrations by a deposition velocity, this calculated using the method traditionally employed by the EMEP acid deposition lagrangian model (e.g. Barrett *et al.,* 1995). The three krigged maps, of wet deposition, and of dry sulphur dioxide and of sulphate aerosol deposition were then summed for each of the three-year periods. The resulting maps are presented in Figures 4.1-4.4. All stations measuring any of the three components across the three year periods were used to produce the krigged maps, and these are listed in Table B.1.

Table B.1: Stations used to produce krigged maps of total sulphur deposition.

1980-1982		**1985-1987**		**1990-1992**		**1995-1997**	
AT0002R	GB0002R	AT0002R	HU0002R	AT0002R	GB0002R	AT0002R	HR0002R
BE0001R	GB0003R	AT0003R	IE0001R	AT0003R	GB0004R	AT0004R	HR0004R
CH0001R	GB0004R	AT0004R	IT0001R	AT0004R	GB0006R	AT0005R	HU0002R
CH0002R	GB0005R	BE0001R	IT0002R	BA0006R	GB0007R	CH0002R	IE0001R
CS0001R	HU0002R	CH0001R	IT0003R	BE0001R	GB0013R	CH0003R	IE0002R
CS0002R	IE0001R	CH0002R	IT0004R	BY0004R	GB0014R	CH0004R	IE0003R
DD0001R	NL0002R	CS0001R	IT0005R	CH0001R	GB0015R	CH0005R	IE0004R
DD0002R	NL0005R	CS0002R	NL0002R	CH0002R	GB0016R	CS0001R	IT0001R
DE0001R	NL0006R	DD0001R	NL0007R	CH0003R	GR0001R	CS0003R	IT0004R
DE0002R	NO0001R	DD0002R	NL0008R	CH0004R	HR0002R	DE0001R	LT0015R
DE0003R	NO0008R	DE0001R	NO0001R	CH0005R	HR0004R	DE0002R	LV0010R
DE0004R	NO0015R	DE0002R	NO0008R	CS0001R	HU0002R	DE0003R	LV0016R
DE0005R	NO0030R	DE0003R	NO0015R	CS0002R	IE0001R	DE0004R	NL0009R
DE0011R	NO0035R	DE0004R	NO0030R	CS0003R	IE0002R	DE0005R	NL0010R
DE0012R	NO0036R	DE0005R	NO0035R	CS0004R	IT0004R	DE0007R	NO0001R
DE0013R	NO0037R	DE0011R	NO0036R	CS0005R	IT0005R	DE0008R	NO0008R
DE0014R	NO0039R	DE0012R	NO0037R	DD0001R	LT0015R	DE0009R	NO0015R
DE0015R	PL0001R	DE0013R	NO0039R	DE0001R	LV0010R	DK0003R	NO0030R
DE0016R	PT0001R	DE0014R	PL0001R	DE0002R	MD0012R	DK0005R	NO0039R
DE0017R	PT0002R	DE0015R	PL0002R	DE0003R	NL0002R	DK0008R	NO0041R
DE0018R	SE0001R	DE0016R	PT0001R	DE0004R	NL0008R	EE0009R	NO0042R
DE0019R	SE0002R	DE0017R	PT0002R	DE0005R	NO0001R	EE0011R	NO0055R
DE0020R	SE0003R	DE0018R	PT0003R	DE0007R	NO0008R	ES0001R	PL0002R
DK0003R	SE0005R	DE0019R	SE0002R	DE0008R	NO0015R	ES0002R	PL0003R
DK0005R	SE0008R	DE0020R	SE0003R	DE0012R	NO0030R	ES0003R	PL0004R
DK0007R	SU0001R	DK0003R	SE0005R	DE0013R	NO0039R	ES0004R	PL0005R
FI0004R	SU0002R	DK0005R	SE0008R	DE0014R	NO0041R	ES0005R	PT0001R
FI0007R	YU0001R	DK0007R	SE0011R	DE0015R	PL0001R	ES0006R	PT0003R
FI0009R	YU0002R	ES0001R	SE0012R	DE0016R	PL0002R	ES0007R	PT0004R
FR0001R	YU0004R	ES0002R	SU0001R	DE0017R	PL0003R	FI0004R	RU0001R
FR0003R	YU0006R	ES0003R	SU0002R	DE0018R	PT0001R	FI0009R	RU0013R
FR0005R	YU0007R	FI0004R	SU0003R	DE0019R	PT0003R	FI0017R	RU0014R
FR0006R		FI0007R	SU0004R	DE0020R	PT0004R	FI0022R	RU0016R
FR0007R		FI0009R	SU0005R	DK0003R	PT0005R	FI0037R	SE0002R
		FR0001R	SU0006R	DK0005R	RU0001R	FR0003R	SE0005R
		FR0003R	SU0007R	DK0007R	RU0013R	FR0005R	SE0008R
		FR0005R	SU0008R	DK0008R	RU0014R	FR0008R	SE0011R
		GB0002R	SU0009R	EE0002R	SE0002R	FR0009R	SE0012R
		GB0003R	SU0010R	EE0009R	SE0003R	FR0010R	SE0013R
		GB0004R	YU0001R	ES0001R	SE0005R	FR0011R	SI0008R
		GB0005R	YU0002R	ES0002R	SE0008R	FR0012R	SK0002R
		GB0006R	YU0004R	ES0003R	SE0011R	GB0002R	SK0004R
		GB0007R	YU0005R	ES0004R	SE0012R	GB0004R	SK0005R
		GB0013R	YU0006R	FI0004R	SE0013R	GB0006R	SK0006R
		GB0014R	YU0007R	FI0009R	SI0001R	GB0007R	TR0001R
		GB0015R		FI0017R	SU0003R	GB0013R	YU0005R
		GB0016R		FI0022R	SU0011R	GB0014R	YU0008R
				FR0003R	UA0005R	GB0015R	
				FR0005R	UA0006R	GB0016R	
				FR0008R	YU0005R		
				FR0009R	YU0007R		
				FR0010R			
				FR0011R			
				FR0012R			