National Institute
for Public Health
and the Environment

Report 680704009/2010

E. van der Swaluw | W.A.H. Asman | R. Hoogerbrugge

The Dutch National Precipitation Chemistry Monitoring Network over the period 1992-2004

rivm

RIVM Report 680704009/2010

The Dutch National Precipitation Chemistry Monitoring Network over the period 1992-2004

E. van der Swaluw, Centre for Environmental Monitoring
W. A. H. Asman, Global Environmental Consultancy
R. Hoogerbrugge, Centre for Environmental Monitoring

Contact:
Eric van der Swaluw
Centre for Environmental Monitoring
Eric.van.der.Swaluw@rivm.nl

This investigation has been performed by order and for the account of Directorate-General for Environmental Protection, within the framework of 680704 Reporting Air Quality

rivm

Abstract

The Dutch National Precipitation Chemistry Monitoring Network over the period 1992-2004

The deposition of acidifying and eutrophying components on soil and surface waters as rain (wet deposition) decreased in the Netherlands between 1992 and 2004. This conclusion is based on measurements taken by the RIVM within the framework of the Dutch National Precipitation Chemistry Monitoring Network. It is important to monitor these trends since the current levels of deposition from acidifying and eutrophying components are still too high in a large part of the Netherlands. The total deposition of these pollutants is still above the thresholds set in the Fourth National Environmental Policy Plan for 2010.

A fraction of airborne pollutants is washed out of the atmosphere by precipitation on soil and surface water. In the Netherlands, measurements of the chemical characteristics of precipitation have been carried out since 1978 by the Dutch National Precipitation Chemistry Monitoring Network. The stations in this network monitor and measure the wet deposition of contaminants on soil and surface water bodies and their passage into the groundwater. Wet deposition accounts for a significant part of the total deposition of contaminants.

The network consists of monitoring stations at locations distributed throughout the Netherlands. There were 15 permanent measuring stations between 1992 and 2004.

Key words: air quality, monitoring network, ammonium, monitoring

rivm

Rapport in het kort

Resultaten van het Landelijk Meetnet Regenwatersamenstelling over de periode 1992-2004

Tussen 1992 en 2004 heeft er een afname plaatsgevonden in Nederland van de hoeveelheid verontreinigende stoffen welke uit de buitenlucht via regenwater zijn neergeslagen op bodem, oppervlakte- en grondwater (natte depositie). Dit blijkt uit metingen van het RIVM van de chemische samenstelling van regenwater. Het is van belang om deze ontwikkelingen te volgen, omdat een groot deel van Nederlandse bodem en water te veel met verzurende en stikstofhoudende stoffen wordt belast. De totale depositie van bovengenoemde stoffen op bodem en water ligt namelijk nog steeds boven de doelstelling voor 2010 die hieraan gesteld is in het vierde Nationaal Milieubeleidsplan.

Als het regent komt een deel van de verontreinigende stoffen in de lucht via het regenwater in bodem en water terecht. In Nederland wordt sinds 1978 de chemische samenstelling van het regenwater gemeten middels een nationaal meetnet. Hiermee wordt onder andere de natte depositie van verontreinigende stoffen op bodem, oppervlaktewater en grondwater gemeten. Deze depositie is een significant deel van de *totale* depositie van verontreinigende stoffen op bodem en water.

Het netwerk van meetpunten is min of meer gelijkmatig over Nederland verspreid en bestond in de onderzochte periode uit 15 vaste meetlocaties.

Trefwoorden: luchtkwaliteit, meetnet, ammoniak, monitoring

rivm

Contents

rivm

Summary

Annual mean concentrations and wet deposition fluxes of major components and heavy metals over the period 1992-2004 are calculated from the measurements at the 15 monitoring stations of the Dutch National Precipitation Chemistry Monitoring Network. The values of concentrations and wet deposition fluxes of contaminants listed in this report only cover the period 2001-2004, since values from before 2001 have been listed in previous reports (see e.g. Stolk, 2001). Subsequently a trend analysis was performed of the annual mean concentrations and wet deposition fluxes of major components and heavy metals over the period 1992-2004. The trend analysis showed that there were downward trends for the annual mean concentration above the 95% significance level for ammonium, nitrate, sulfate, fluoride, nickel, zinc, cadmium and lead. A downward trend above the 95% significance level over the same time period for wet deposition flux was also found for all these contaminants except for nitrate.

The time series of the annual mean concentration in precipitation of ammonium, sulfate, nitrate, lead, cadmium, and zinc were compared with the time series of the annual mean concentration of their corresponding component in air. Except for lead, the time series of the concentrations in air for these components showed similar downward trends as the ones observed in precipitation.

Finally the spatial distribution of concentrations of precipitation from major components and heavy metals over the Netherlands is investigated for the year 2004. Maps are constructed by *ordinary interpolation methods* of the measurements. It is however emphasized that these maps are only used to *visually represent* the measurement data over the Netherlands. In this way it is easier to identify apparent large-scale gradients. The maps should definitely **not** be used to determine local values of concentrations for the different components. Because the concentrations of heavy metals are in general close to the detection limit and hence the interpolated maps were in general hampered by unclear patterns, and are therefore not included in this report.

rivm

1 Introduction

This report presents results of the analysis of the chemical composition of precipitation in the Netherlands over the period 1992-2004. The measurements are performed as part of the Dutch National Air Quality Monitoring Network, and yield among others the concentrations and wet deposition fluxes for a selected number of contaminants. These contaminants are divided into major components and heavy metals, both measured at 15 operational stations distributed over the Netherlands.

The main objectives for the Dutch National Air Quality Monitoring Network for Precipitation are:

1. to measure the acid and nitrogen deposition by precipitation over the Netherlands;
2. to perform trend analysis over long time periods (by continuously monitoring the chemical composition of precipitation) of major components and heavy metals;
3. to validate atmospheric transport models by supplying measured wet deposition fluxes of major components and heavy metals.

The Dutch National Air Quality Monitoring Network for precipitation uses wet-only samplers with an effective sampling period of four weeks. An overview is presented of the annual mean concentrations and wet deposition fluxes of major components and heavy metals at the 15 operational stations over the period 2001-2004. We do not present the concentrations for each sample (covering four weeks of measurement time) separately since these data have been collected and are on-line available for the period 1992-2004 (see http://www.lml.rivm.nl/data_val/data/lmre_1992-2005.xls).

Additionally trends are calculated of the annual mean concentrations and wet deposition fluxes across the Netherlands over the period 1992-2004 for all contaminants. The period of 1992-2004 has been chosen since during this period the configuration of the Dutch National Air Quality Monitoring Network for precipitation did not change (except for one minor replacement which is mentioned in chapter 2): in 1991 the Dutch National Air Quality Monitoring Network for precipitation was handed over from the Royal Netherlands Meteorological Institute (KNMI) to the National Institute for Public Health and the Environment (RIVM); in 2005 the configuration changed from 15 to 11 operational stations; in 2006 new wet-only samplers were set up at the remaining 11 stations. At these 11 stations measurements were started for the major components. At 4 of these 11 stations heavy metals are measured.

2 The Dutch National Precipitation Chemistry Monitoring Network

2.1 Contaminants

The following contaminants are considered in this report, which are divided into major components and heavy metals:

major components: ammonium (NH_4), nitrate (NO_3), sulfate (SO_4), phosphate (PO_4), fluoride (F), chloride (Cl), sodium (Na), potassium (K), magnesium (Mg), and calcium (Ca);
heavy metals: vanadium (V), chromium (Cr), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), and lead (Pb).

An overview of the detection limit, molar mass and uncertainty for annual averaged concentrations given in this report are given in Appendix E for all contaminants mentioned above.

2.2 Origin of compounds in precipitation in the Netherlands

Wet deposition can be split up into two main scavenging processes: in-cloud scavenging and below-cloud scavenging (see Figure 1 left panel). The process of in-cloud scavenging occurs in the interior of the cloud itself, whereas the process of below-cloud scavenging occurs below the precipitating cloud. The former process is more efficient than the latter. Furthermore for below-cloud scavenging of aerosols, the (collision) efficiency determines the strength of the scavenging rates. This collision efficiency depends on the drop size and the particle size (see Figure 1 right panel).

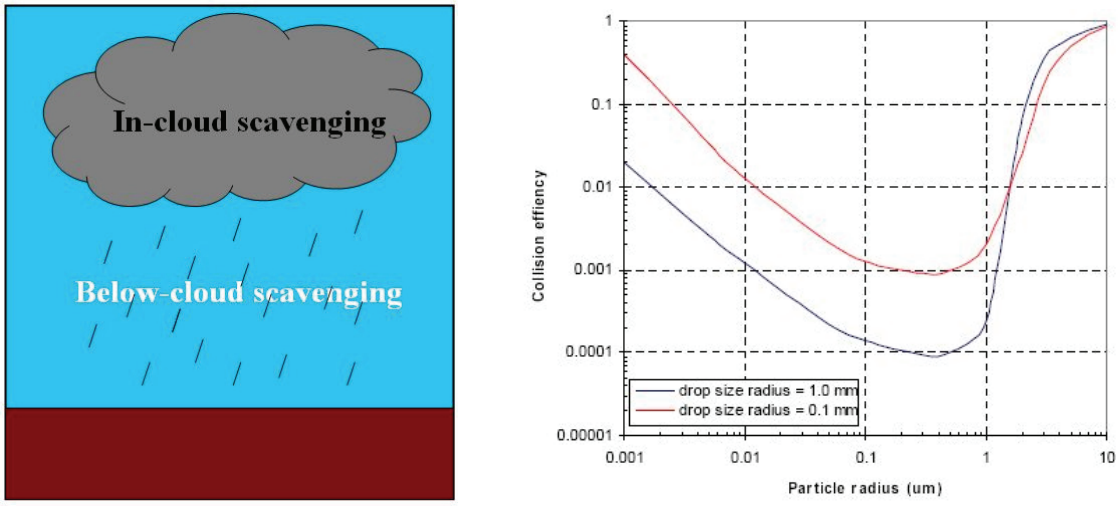

Figure 1: Wet deposition is determined by two processes: in-cloud and below-cloud scavenging (left panel). The scavenging process of below-cloud scavenging depends on the size of both the rain droplets and the aerosol size (right panel, from Van Jaarsveld (2004)).

In general wet scavenging is prescribed by a wet scavenging coefficient Λ_i, given for each contaminant *i*. The decrease in concentration ΔC_i of contaminant *i* in the atmosphere during a time interval Δt due to wet scavenging is then approximated as:

$$\Delta C_i = -\Lambda_i C_i \Delta t \, .$$

A more detailed analysis is given by Seinfeld and Pandis (1998) who show for a typical case, when Λ=3.3 $(hour)^{-1}$, that after half an hour of precipitation the initial concentration C_0 in the atmosphere has decreased to a value of C=0.19C_0 (see example 20.1 of Seinfeld and Pandis (1998) for details). This is a typical case of a gas with a high solubility in rain water like for example sulphur dioxide (SO_2).

The spatial variation in the concentration in precipitation in the Netherlands is caused by the spatial distribution of sources and their strength in the Netherlands, foreign countries and meteorological conditions such as transport patterns and rainfall. The amount of material wet deposited is also influenced by the rainfall rate in that sense that a higher amount of rainfall usually leads to a higher wet deposition. If the contribution from foreign sources to the concentrations in precipitation in the Netherlands is large, the spatial distribution will show limited differences within the country. In the case that the contribution from the Netherlands to the concentrations in precipitation in the Netherlands is largest, the spatial distribution, will somehow, reflect the spatial differences in the source strength within the Netherlands and will therefore show larger spatial differences.

Some compounds in precipitation originate from more than one airborne compound. This holds for:

- SO_4 in precipitation: this is caused by scavenging of SO_4 containing aerosol (most important) and gaseous SO_2. Almost all anthropogenic SO_4 is formed in the atmosphere by oxidation of emitted SO_2;
- NO_3 in precipitation: this is caused by scavenging of NO_3 containing aerosol and gaseous HNO_3. Almost all NO_3 containing aerosol and HNO_3 in the atmosphere originates from oxidation of emitted NO_x (nitrogen oxides: NO and NO_2);
- NH_4 in precipitation: this is caused by scavenging of NH_4 containing aerosol and gaseous NH_3. Almost all NH_4 containing aerosol is formed in the atmosphere by reaction of gaseous NH_3 with acids.

Heavy metals are usually in the atmosphere in particulate form. The removal efficiency of particles by precipitation depends to some extent on their size (distribution). An example of how the efficiency of the wet scavenging process depends on particle size is given in Figure 1 (right panel).

Table 1 gives an overview of the sources that contribute to concentrations in precipitation (Nriagu and Pacyna, 1988; Seinfeld and Pandis, 1998; Pacyna and Pacyna, 2001; Pacyna et al., 2005; Ilyin et al., 2006; Pacyna et al., 2007; Friedrich, 2007; Zevenhoven et al., 2007).

Table 1 Sources of components[a)].

Component	Origin	
NH_4	NH_3 emission from animal manure and mineral fertilizer	b)
NO_3	NO_x emission from combustion processes incl. traffic, and limited HNO_3 and NO_x emission from the chemical industry	b)
SO_4	SO_2 emission from combustion of oil (products) and coal, especially from, refineries and the power generation; traffic; the sea is a large natural source of SO_4 (sea-spray), but this contribution is subtracted in the concentrations/depositions presented in this report	b)
PO_4	Fertilizer industry, combustion of coal, soil	
F	Industry; sea spray	b)
Cl	Sea spray	
Na	Sea spray	
K	Sea spray, soil	
Mg	Sea spray, soil	
Ca	Sea spray, industry, soil	
V	Fuel combustion	
Cr	Fuel combustion, iron and steel production, cement production, soil (indirectly also form historical emissions)	b)
Fe	Iron industry, soil	
Co	Fuel combustion	
Ni	Fuel combustion, iron and steel production, cement production, non-ferrous metal production, soil (indirectly also from historical emissions)	
Cu	Traffic/transport, consumers	b)
Zn	Metal industry, soil	
As	Fuel combustion, iron, steel and metal production, traffic, cement production, incineration of waste, other industry, soil (indirectly also from historical emissions)	b)
Cd	Fuel combustion, iron and steel production, soil (is contamination in mineral fertilizer), soil (indirectly also from historical emissions)	
Pb	Iron and steel production, fuel combustion, cement production, non-ferrous production, waste disposal, before 2000 petrol (petrol does still contain some Pb as oil contains Pb), soil (indirectly also from historical emissions)	b)

a) The information is based on information for more countries than the Netherlands. The order of the sources does not necessarily reflect the importance.
b) Information partly from the Netherlands emission registration: www.emissieregistratie.nl

2.3 Configuration

The Dutch National Air Quality Monitoring Network for Precipitation over the period 1992-2004 consisted of 15 background stations which are listed in Table 2. Figure 2 shows the location of stations mentioned in Table 2 over the Netherlands. The configuration of the network did not change except for the replacement of the station Witteveen (928) by the station Valthermond (929) in 2001. Valthermond is located 19 km southwest of Witteveen. These two stations were never operational at the same time.

Table 2 The Dutch National Air Quality Monitoring Network for Precipitation over the period 2001-2004. Coordinates are given in (X,Y) ('Rijksdriehoekmeting van de Topografische Dienst' in units of kilometres) and in (Lat,Lon) (ETRS89 in units of degrees).

Station	Station Number	Coordinates			
		(X , Y)		(Lat , Lon)	
Vredepeel	131	187.3	394.7	51º32'	5º51'
Beek	134	182.4	325.1	50º55'	5º47'
Gilze-Rijen	231	123.5	397.5	51º34'	4º56'
Huijbergen	235	83.6	383.3	51º26'	4º22'
Philippine	318	40.8	368.5	51º18'	3º45'
Rotterdam	434	90.1	440.9	51º57'	4º27'
De Zilk	444	95.2	479.1	52º18'	4º31'
Wieringerwerf	538	132.3	535.2	52º48'	5º03'
De Bilt	628	140.6	456.9	52º06'	5º11'
Biddinghuizen	631	170.8	495.7	52º27'	5º37'
Eibergen	722	238.5	456.6	52º05'	6º36'
Wageningen	724	172.9	442.7	51º58'	5º39'
Speulderveld	732	177.7	476.0	52º16'	5º43'
Witteveen	928	241.4	536.9	52º49'	6º40'
Valthermond	929	259.1	544.3	52º53'	6º56'
Kollumerwaard	934	214.3	594.2	53º20'	6º17'

2.4 Sampling

Wet-only samplers are used to determine the chemical composition of precipitation. The wet-only samplers used over the period 1992-2004 were developed at the Energy research Centre of the Netherlands (Buijsman, 1989). At every operational station there are two wet-only samplers, one for major components and one for heavy metals. The opening of the funnel has a collecting area of 400 cm^2, at a height of 1.50 meter. The latter is too high to perform a proper measurement of the amount of precipitation. Therefore at each station there is an additional rain gauge (model KNMI) at a height of 0.40 meter. The data from this instrument is used to report the amount of precipitation. The funnel of the wet-only samplers used are closed with a lid when there is no precipitation, thereby insuring that there is no contribution into the collecting bottle from dry deposition. Precipitation is detected with a rain sensor, which is placed in between the wet-only samplers. Figure 3 shows the set-up of the station 131 at Vredepeel at the border of the provinces of Noord-Brabant and Limburg.

The sampling period in the Dutch National Air Quality Monitoring Network for precipitation is once every two weeks. The collecting bottles from the wet-only sampler are not cooled during the measuring period, but are protected against sun light. After collecting the samples are stored at a temperature of 4 ˚C until analyses. The content of sampling bottles for two subsequent two-weekly periods bottles is combined in the laboratory prior to chemical analysis, so that results are obtained for a period of four weeks. The two-weekly heavy metal samples are treated with acid (pH=1) prior to combining the samples for analyses. Hence, for each year there are 13 combined samples available for a chemical analysis. The sample bottle are cleaned with detergent before use and the sample bottles for heavy metals are after cleaning also treated with hydrochloric acid (pH=1). Periodically the collecting funnels are exchanged and cleaned in accordance with the sampling method. Analysis is carried out in accordance with state of the art methods (Buijsman, 1989; Van Elzakker, 2001).

Figure 2: The Dutch National Air Quality Monitoring Network for Precipitation over the period 1992-2004. The numbers are the station numbers.

Figure 3: Example of wet-only samplers with rain sensor in the middle at Vredepeel (location 131).

3 Calculation of annual mean concentrations and wet deposition fluxes

3.1 Calculation of annual mean concentrations and wet deposition fluxes

The annual mean concentration and wet deposition flux of major components and heavy metals are calculated based on 13 sample periods within each year for the period 1992-2004. The analysis of the samples results for each period *i* in a value for the concentration C_i for every component[1] and an amount of precipitation P_i (in mm). The annual mean values of the concentrations $\overline{C}$ are calculated using the following equation:

$$\overline{C} = \sum_{i=1}^{13} \widetilde{P}_i \cdot C_i \Big/ \sum_{i=1}^{13} \widetilde{P}_i ,$$

here $\widetilde{P}_i = P_i$ if C_i has been measured and $\widetilde{P}_i = 0$ if no valid measurement of the concentration C_i exists for the period *i*. The values for P_i have been directly measured and we use these for the samples 2-12 for each year. However, the value for P_i of the first (i=1) and the last sample (i=13) of a given year also has a contribution of precipitation from respectively the previous and the next year. Therefore we use linear interpolation of the amount of precipitation to obtain new values for the amount of precipitation at the start (= P_1) and at the end (= P_{13}) of each specific year. After this interpolation $\sum_{i=1}^{13} P_i$ equals the *total amount of precipitation in the considered year.*

The concentration of sulfate is influenced by sea-spray, which is a natural source. In order to get insight into the man-made contribution to sulfate and eliminate a steep gradient near the coast, the concentration of sulfate is corrected for sea-spray as in Stolk (2001):

$$[SO_4]_{corr} = [SO_4] - 0.06[Na],$$

here $[SO_4]$, [Na] and $[SO_4]_{corr}$ are the annual mean values in units of mmol/l. $[SO_4]_{corr}$ is subsequently converted back into units of mg/l. These reported sulfate concentrations are thus corrected for sea-spray.

Subsequently we calculate the coverage of the dataset available for a year and consider the data as invalid when coverage in precipitation is less than 75%. A similar criterion is used in the OSPAR assessment reports (De Leeuw et al.,. 2005; Van der Swaluw et al., 2009). The coverage *Cov,* is mathematically defined as:

$$Cov = \Big(\sum_{i=1}^{13} \widetilde{P}_i / \sum_{i=1}^{13} P_i \Big) \times 100\% .$$

[1] The units of concentration are in mg/l for major components and in µg/l for heavy metals in this report

Finally the annual wet deposition fluxes $\overline{D}$ are calculated by multiplying the annual mean concentration and the *total* precipitation over a year. This yields:

$$\overline{D} = \overline{C} \cdot \sum_{i=1}^{13} P_i \ .$$

The results of the above calculation method are presented in the tables in Appendix A and B over the period 2001-2004. We have chosen to report over this time period since this ties in with the last report on precipitation data of the Dutch National Precipitation Chemistry Monitoring Network, which covered the year 2000 (Stolk, 2001). The values in the tables are italic and underlined when the total coverage of the annual mean is less than 75%.

3.2 Trend analysis

The Excel template *MakeSense* (Salmi et al., 2002) is used to calculate trends for the concentration and wet deposition flux of major components and heavy metals over the period 1992-2004 (see chapter 4). The template uses the nonparametric Mann-Kendall test to determine whether there is a significant trend in the considered time series. *MakeSense* distinguishes between four different significance levels, i.e. 0.1%, 1%, 5% and 10%. Furthermore it calculates the magnitude of the trend in the time series by using the nonparametric Sen method. The calculated trend slope yields a linear fit described as y = a (year-1992) + b. Using this linear fit, we calculate the decrease of concentration/deposition in 2004 with respect to its value in 1992 like (12a/b) ×100%.

4 Trends over the period 1992-2004

4.1 Results

The trends for concentration in precipitation and wet deposition flux of major components and heavy metals in the Netherlands are calculated over the period 1992-2004. A time series of annual mean values for the concentration and wet deposition flux of each component in the Netherlands is calculated. This is done by averaging the annual mean concentration and wet deposition flux of each component over all available stations for each year in the period 1992-2004. The obtained values for the concentrations are shown in Table 3 for major components and in Table 4 for heavy metals. Light yellow shading indicates that there is less than 50% spatial covering, i.e. that there are less than 8 stations available for that specific year to calculate an averaged value. These mean values are considered as invalid for a proper trend analysis and hence are not taken into account for the calculation of the trends as discussed below. As can be seen from these tables, the contaminants chromium, cobalt and arsenic only have valid concentrations for the period 1999-2004, therefore a statistical analysis is performed over this period.

Table 3 Annual mean values for concentration (upper table) and wet deposition flux (lower table) of major components. Concentration is in units of mg/l; wet deposition flux is in units of mg/m^2. The yellow shading indicates that less than 50% of the stations were used to calculate averaged values for the concentration and wet deposition flux. The SO_4 concentration/deposition is corrected for sea spray.

Year	NH_4	NO_3	SO_4	PO_4	F	Cl	Na	K	Mg	Ca
1992	1.52	2.52	3.56	0.029	0.020	2.58	1.42	0.14	0.19	0.43
1993	1.31	2.24	2.91	0.019	0.016	2.74	1.50	0.18	0.20	0.34
1994	1.27	2.08	2.54	0.025	0.016	2.72	1.54	0.17	0.20	0.29
1995	1.45	2.43	2.78	0.035	0.021	4.20	2.35	0.19	0.30	0.33
1996	1.54	2.51	2.64	0.037	0.015	3.21	1.81	0.19	0.23	0.29
1997	1.60	2.29	2.59	0.050	0.018	2.01	1.13	0.14	0.15	0.31
1998	1.18	2.09	2.22	0.047	0.015	3.20	1.81	0.15	0.24	0.35
1999	1.26	2.26	2.17	0.045	0.015	3.25	1.89	0.17	0.24	0.28
2000	1.17	2.25	2.11	0.041	0.013	2.23	1.30	0.15	0.18	0.29
2001	1.09	2.07	1.78	0.038	0.013	3.06	1.74	0.14	0.23	0.23
2002	0.94	1.99	1.76	0.011	0.012	3.18	1.76	0.13	0.22	0.26
2003	1.14	2.03	1.79	0.032	0.012	3.03	1.71	0.15	0.22	0.35
2004	1.01	1.98	1.88	0.014	0.010	3.61	2.07	0.16	0.26	0.32

Year	NH_4	NO_3	SO_4	PO_4	F	Cl	Na	K	Mg	Ca
1992	1246	2071	2905	24	16	2120	1163	117	154	341
1993	1136	1932	2498	16	14	2373	1304	153	173	294
1994	1153	1884	2297	22	14	2357	1340	152	173	255
1995	1129	1890	2169	28	17	3243	1813	149	230	256
1996	913	1480	1551	21	9	1874	1059	114	134	167
1997	1083	1557	1752	32	12	1375	775	97	104	206
1998	1275	2246	2377	51	16	3437	1941	165	252	367
1999	1052	1897	1821	37	12	2814	1642	149	206	237
2000	1136	2189	2070	40	13	2198	1285	143	173	288
2001	1051	2003	1715	36	13	2959	1679	136	220	222
2002	895	1890	1683	11	12	2949	1637	122	207	244
2003	762	1353	1198	22	8	2032	1145	102	146	232
2004	847	1673	1588	11	9	3056	1750	130	218	269

Table 4 Annual mean values for concentration (upper table) and wet deposition flux (lower table) of heavy metals. Concentration is in units of µg/l; wet deposition flux is in units of µg/m². The yellow shading indicates that less than 50% of the stations were used to calculate averaged values for the concentration and wet deposition flux.

Year	V	Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
1992	1.55	0.32	50.12	0.02	0.63	1.87	16.72	0.23	0.16	3.83
1993	2.26	0.14	52.37		1.73	1.87	14.71	0.06	0.18	3.81
1994			43.43			1.57	14.19		0.16	3.33
1995	1.85	0.22	40.51		0.77	1.85	12.91	0.06	0.15	3.85
1996	1.56	0.22	43.12		0.95	1.91	13.26	0.30	0.20	3.41
1997	2.05	0.15	57.92		0.89	1.88	12.85	0.13	0.15	3.30
1998			43.40			1.44	11.96		0.18	2.80
1999	0.96	0.10	29.78	0.05	0.44	2.05	9.99	0.15	0.09	2.87
2000	0.99	0.13	48.98	0.06	0.39	2.07	9.30	0.15	0.09	3.18
2001	0.90	0.19	28.56	0.05	0.44	2.13	9.24	0.12	0.08	2.73
2002	0.80	0.17	29.79	0.04	0.34	1.75	7.92	0.13	0.06	2.33
2003	0.87	0.19	44.51	0.06	0.37	1.85	7.87	0.15	0.07	2.63
2004	0.92	0.18	27.03	0.04	0.36	1.69	7.78	0.13	0.05	2.49

Year	V	Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
1992	1326	297	40946	17	544	1584	13972	217	136	3235
1993	1963	117	45116		1503	1626	12967	52	154	3298
1994			38760			1415	12948		148	3057
1995	1324	157	30878		556	1404	9654	41	113	2912
1996	809	121	24724		518	1101	7693	164	114	1976
1997	1292	95	37939		560	1235	8478	84	101	2202
1998			45809			1563	12565		190	3012
1999	843	87	25182	39	385	1739	8401	131	80	2444
2000	963	122	46502	55	374	1981	8885	143	85	3074
2001	914	184	28749	52	444	2100	9227	117	80	2722
2002	781	169	28664	42	331	1696	7653	123	60	2244
2003	586	127	30005	39	250	1244	5300	103	46	1787
2004	795	155	23480	36	312	1441	6582	109	45	2122

Figure 4 shows an example of the trend analysis performed for the concentration of NH_4. The slope is downwards and this downward trend is statistically significant. Appendix C and D show graphs like these for the concentration and deposition of all major components and heavy metals. Tables 5 and 6 contain the results of all calculations performed on the time series for respectively major components and heavy metals. The first rows show the slope of the trend, the second show at which level the trends are statistically significant. The changes in the values in 2004 with respect to 1992 are shown in the third row for those contaminants which have a significant trend curve. The sign – indicates that no trend curves above the 90% level were found in the analysis.

Since long-term trends are used the influence of year-to-year variations in meteorology do not alter the trends to a large extent. Therefore, meteorological corrections were not applied to the trends.

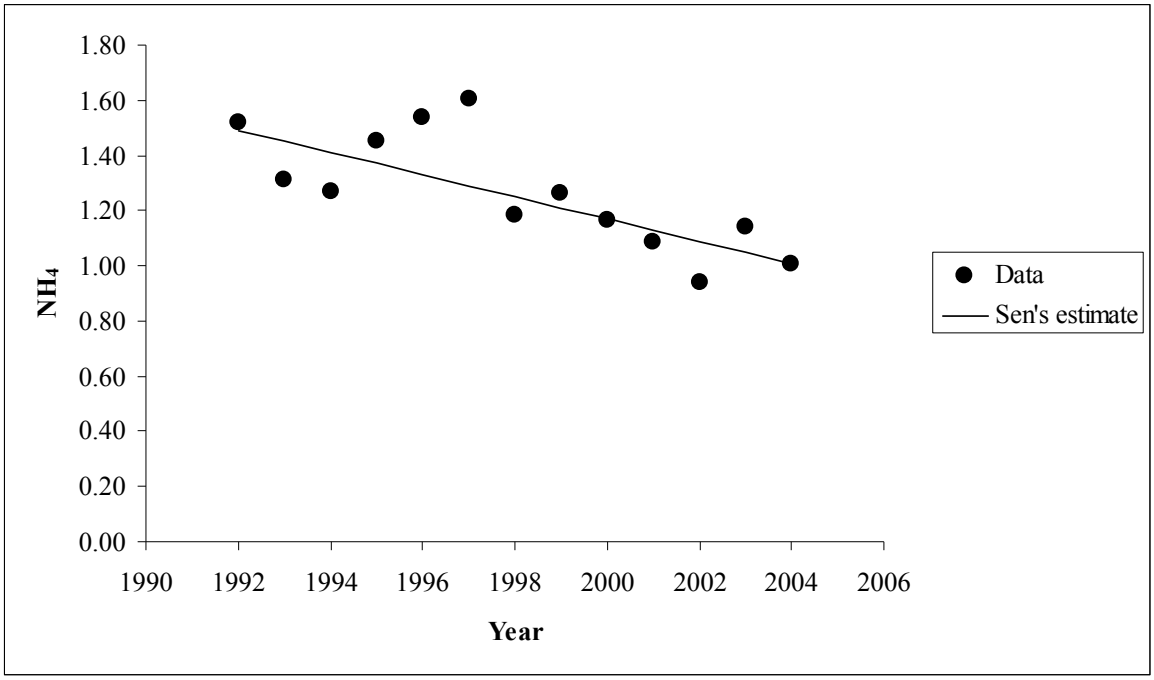

Figure 4: Time series of ammonium concentrations (in mg/l) in precipitation.

Table 5 Results of trend analysis of major components for concentration (1st three rows) and wet deposition flux (2nd three rows). The slope for concentration is in units of mg/l/yr and the slope for wet deposition flux is in units of mg/m²/yr. The change (given in %) is for the values in 2004 with respect to 1992. The sign – indicates that no trend curves above the 90% level were found in the analysis. The SO_4 concentration/deposition is corrected for sea spray.

	NH_4	NO_3	SO_4	PO_4	F	Cl	Na	K	Mg	Ca
Concentration										
Slope	-0.033	-0.037	-0.122	-	-0.001	-	-	-	-	-
Significance	1%	5%	0.1%	-	0.1%	-	-	-	-	-
Change	-27%	-18%	-47%	-	-60%	-	-	-	-	-
Deposition										
Slope	-23	-	-101	-	-0.54	-	-	-	-	-
Significance	5%	-	1%	-	5%	-	-	-	-	-
Change	-23%	-	-47%	-	-41%	-	-	-	-	-

Table 6 Result trend analysis of heavy metals for concentration (1st three rows) and wet deposition flux (2nd three rows). The slope for concentration is in units of µg/l/yr and the slope for wet deposition flux is in units of µg/m²/yr. The change (given in %) is for the values in 2004 with respect to 1992. The sign – indicates that no trend curves above the 90% level were found in the analysis.

	V	Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Concentration										
Slope	-	-	-1.73	-	-0.02	-	-0.72	-	-0.01	-0.12
Significance	-	-	10%	-	5%	-	0.1%	-	1%	0.1%
Change	-	-	-41%	-	-43%	-	-55%	-	-69%	-37%
Deposition										
Slope	-46	-	-	-	-21	-	-582	-	-8	-94
Significance	10%	-	-	-	5%	-	1%	-	0.1%	5%
Change	-41%	-	-	-	-47%	-	-52%	-	-69%	-35%

4.2 A comparison with trends measured elsewhere

Long-term trends in the concentrations/depositions depend on changes in the emission to the air of the involved components both in the Netherlands and foreign countries, and are not influenced by the inter-annual meteorological fluctuations to a large extent. The changes depend on new laws or international agreements and the availability of new techniques. Moreover they can be influenced by starting up or stopping industrial activities in general. For these reasons trends for the same component do not need to be the same in different countries (see e.g. Fagerli and Aas, 2008). In this section only information on trends is used if this was available for around the period 1992-2004 for which trends for the Netherlands network are published in this report. It should also be noted here, that in some countries a decrease in wet deposition of some components is measured, for which there is no significant decrease in the Netherlands. Finally the reader is referred to a recent report of the OSPAR commission (Van der Swaluw et al., 2009), where trends and the values of concentrations of nitrogen and heavy metals in precipitation are presented from monitoring stations at the coastal regions of the North-East Atlantic Ocean.

It was intended to incorporate information on trends from the UK as well (Fowler et al., 2006). Unfortunately there are lacking data for quite a few years in the UK, which makes conclusions about trends uncertain. For that reason this information was left out.

NH_4

In Birkenes, southern Norway is the NH_4 concentration slightly lower in 2003 than in 1992. Whether this trend is significant is not known (Aas et al., 2004). In Denmark a decrease of about 20% in NH_4 wet deposition was observed for all stations over the period 1989-1999, although this only significant (> 99%) for one station (Sutton et al., 2003). The trend in Denmark is of the same order as in The Netherlands (decrease of 27%) and is likely to be mainly the result of national policies as a substantial fraction of NH_4 in wet deposition in Denmark and the Netherlands originates from national sources.

NO_3

In Birkenes, southern Norway is the NO_3 concentration slightly lower in 2003 than in 1992. Whether this trend is significant is not known (Aas et al., 2004). Fagerli and Aas (2008) report a decrease in the

modelled and measured wet deposition of NO_3 for the period 1980-2003 for many EMEP stations in Europe. In the Netherlands a decrease of 18% was observed from 1992 to 2004.

SO_4
In Birkenes, southern Norway is the SO_4 concentration, corrected for sea spray decreased by about 55% over the period 1992-2003. Whether this trend is significant is not known (Aas et al., 2004). In Denmark also a decrease in wet deposition of SO_4 has occurred, which was over the period 1989-2001 larger in the south close to the German border (80%) than in other places (40%) (Ellermann et al., 2003). Whether this trend is significant is not known. The decrease in the SO_4 concentration or wet deposition is caused by a decrease in the SO_2 emission in Europe due international agreements. In the Netherlands a decrease of 47% was observed, which is of the same order as in Denmark.

F
For F no trend data are available for other countries.

Ni
In Norway the Ni concentration in precipitation was measured at Lista at the southern coast. The concentration decreased by 60% between 1993 and 2005, which was a statistically significant change (Berg et al., 2008). This change was somewhat larger than in the Netherlands (decrease by 43% in the period 1992-2004)

Zn
In Norway the Zn concentration at the station Lista on the southern coast decreased by 30% between 1991 and 2005, which was a statistically significant change (Berg et al., 2008). In Denmark is the wet deposition of Zn decreased by about 10% from 1990 to 2000 according to Hovmand et al. (2008), whereas Ellermann et al. (2007) give more detailed results for wet deposition, showing a decrease by about 30% over the period 1992-2004. Whether this decrease is significant is not known. The decrease in the Netherlands was somewhat larger: 55% the period 1992-2004.

Cd
In Norway the concentration of Cd in precipitation at the station Birkenes on the southern coast has decreased by 49% over the period 1991-2005 which was statistically significant (Berg et al., 2008). In Denmark is the wet deposition of Cd decreased with about 55% from 1990 to 2000 (Hovmand et al., 2008), whereas Ellermann et al. (2007) give more detailed results showing a decrease by about 50% over the period 1992-2004. Whether this decrease is significant is not known. The decrease in the Netherlands from 1992-2004 was somewhat larger: 71%.

Pb
In Norway the concentration of Pb in precipitation at the station Birkenes on the southern coast has decreased from about 4 to 1 µg/l over the period 1993-2005 (Berg et al., 2008), which is a decrease of 75%. At the station Lista on the southern coast in Norway the decrease was not significant. In Denmark the wet deposition of Pb decreased with about 80% from 1990 to 2002 (Ellermann et al., 2007). Whether this decrease is significant is not known. The decrease in the Netherlands from 1992-2004 was 36%, which is less than was observed at some other places. This decrease is due to the removal of Pb from petrol and measures taken by industries to reduce the emission.

5 A comparison of the trend in air concentration and concentration in precipitation

The time series of concentration in *precipitation* in the Netherlands as calculated in chapter 4 are compared with time series of concentration in *air* for a few major components and heavy metals. The annual mean concentrations for these considered components have been taken from the annual review of the Dutch National Air Quality Monitoring Network (Beijk et al., 2008). All time series are presented in Table 7. The slope of each time series was calculated with *MakeSense,* which yields the trend over the period 1992-2004. From this linear fit the decrease in 2004 in percentage is calculated with respect to 1992 (as explained in section 3.2). Note that trends for the concentration of sulfate, nitrate and ammonium from respectively the aerosol measurements and the precipitation measurements are not expected to directly correlate since sulfur dioxide in air contributes as well to sulfate in precipitation; nitric acid contributes as well to nitrate in precipitation; and ammonia contributes as well to ammonium in precipitation (see section 2.2).

5.1 Major components

Figure 5 shows the comparison for ammonium. The trends are both downward above the 99% significance level. The concentration in air went down by 46%, whereas the concentration in precipitation went down by 27%.

Figure 6 shows the comparison for sulfate. The trends in air and precipitation are both downward, respectively above the 99% and 99.9% significance level. The concentration in air went down by 53%, whereas the concentration in precipitation went down by 47%.

Figure 7 shows the comparison for nitrate. The trends are both downward above the 99% significance level. The concentration in air went down by 32%, whereas the concentration in precipitation went down by 18%.

Finally, we compare the major components discussed above with their corresponding gas component:

Figure 8 shows the comparison between ammonium in precipitation and ammonia in the air. The trends in air and precipitation are both downward above the 99% significance level. The concentration in air went down by 36%, whereas the concentration in precipitation went down by 27%.

Figure 9 shows the comparison between sulfate in precipitation and sulphur dioxide in air. The trends in air and precipitation are both downward above the 99.9% significance level. The concentration in air went down by 85%, whereas the concentration in precipitation went down by 47%.

Figure 10 shows the comparison between nitrate in precipitation and NO_x in air. The trends are both downward above the 99% significance level. The concentration in air went down by 31%, whereas the concentration in precipitation went down by 18%.

5.2 Heavy metals

Figure 11 shows the comparison for lead. The trends are both downward above the 99% significance level. The concentration in air went down by 81%, whereas the concentration in precipitation went down by 36%.

Figure 12 shows the comparison for cadmium. The trends in air and precipitation are both downward, respectively above the 99.9% and 99% significance level. The concentration in air went down by 68%, whereas the concentration in precipitation went down by 69%.

Figure 13 shows the comparison for zinc. The trends are both downward above the 99.9% significance level. The concentration in air went down by 53%, whereas the concentration in precipitation went down by 55%

Table 7 Annual mean values for concentrations of major components and heavy metals in air (average for all stations in the Netherlands). Concentrations are in units of ng/m^3.

Year	NH_4	NO_3	SO_4	NH_3	NO_x	SO_2	Pb	Cd	Zn
1992	2.96	4.78	4.80	-	40.26	8.66	31.87	5.29	45.35
1993	3.09	4.99	5.06	10.90	39.09	8.12	28.96	4.41	52.76
1994	2.54	4.61	4.20	9.84	38.30	6.50	27.99	5.35	50.26
1995	2.36	4.25	3.71	9.40	36.07	5.45	21.62	3.82	42.63
1996	2.51	4.34	3.99	9.26	40.02	6.82	18.21	3.67	43.39
1997	2.13	4.06	3.22	10.16	37.61	4.62	15.02	3.25	34.20
1998	1.95	3.83	2.80	7.37	30.74	3.81	14.55	2.93	35.15
1999	1.65	3.49	2.37	8.50	27.78	3.20	11.93	2.58	30.04
2000	1.67	3.40	2.39	7.38	27.55	3.06	10.24	2.29	25.52
2001	1.86	3.80	2.62	8.90	30.75	2.54	11.04	2.48	29.84
2002	1.86	3.62	2.77	6.57	29.15	2.47	10.69	2.60	31.55
2003	1.99	4.25	2.97	8.25	32.32	2.48	11.02	2.56	29.84
2004	1.64	3.29	2.59	6.65	29.96	2.22	8.57	2.06	24.17

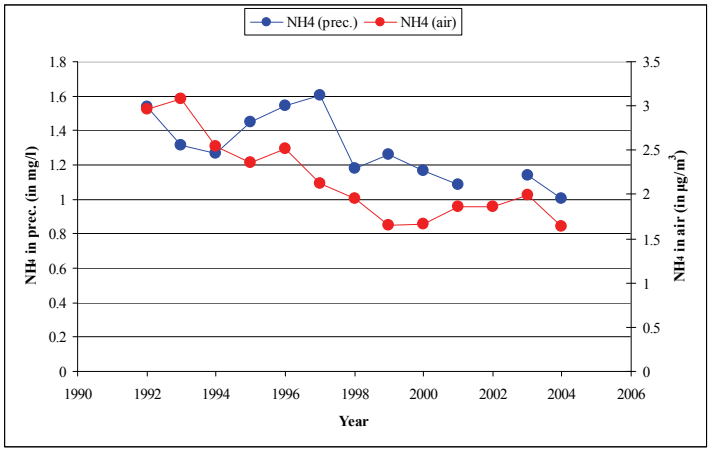

Figure 5: The concentration of ammonium in precipitation and in air over the period 1992-2004.

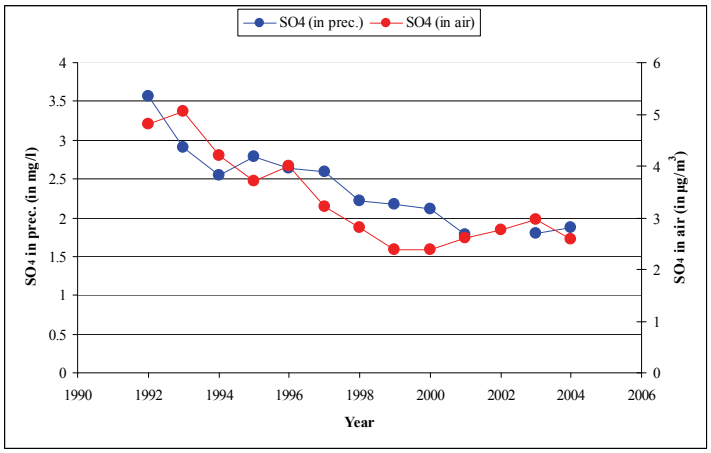

Figure 6: The concentration of sulfate in precipitation and in air over the period 1992-2004.

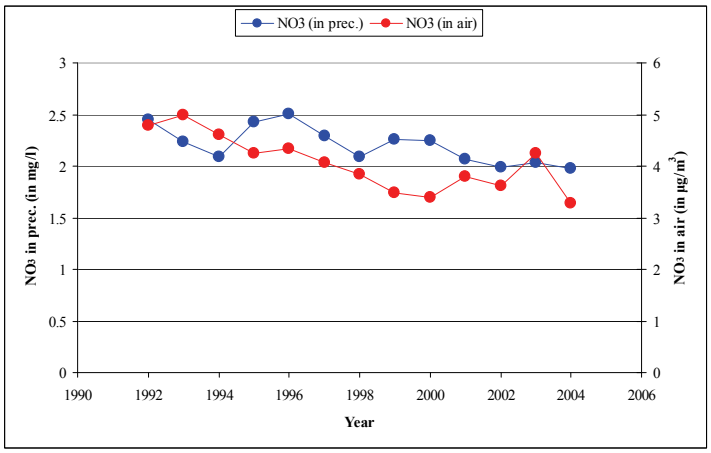

Figure 7: The concentration of nitrate in precipitation and in air over the period 1992-2004.

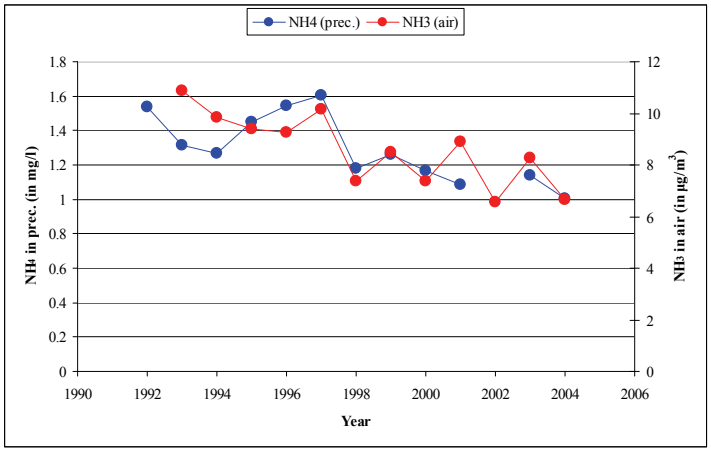

Figure 8: The concentration of ammonium in precipitation and ammonia in air over the period 1992-2004.

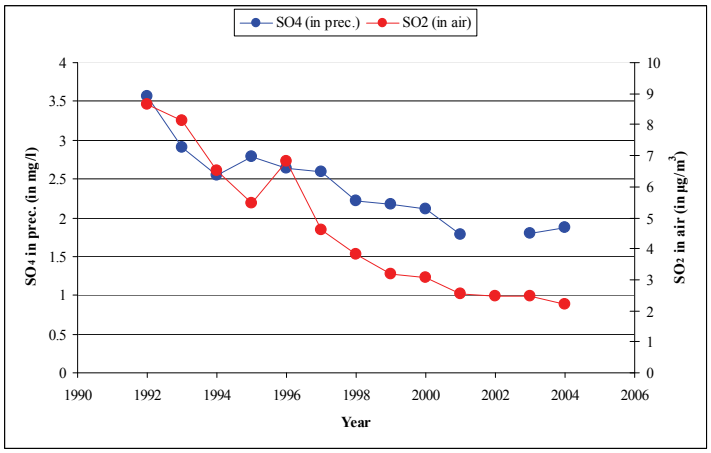

Figure 9: The concentration of sulfate in precipitation and sulphur dioxide in air over the period 1992-2004.

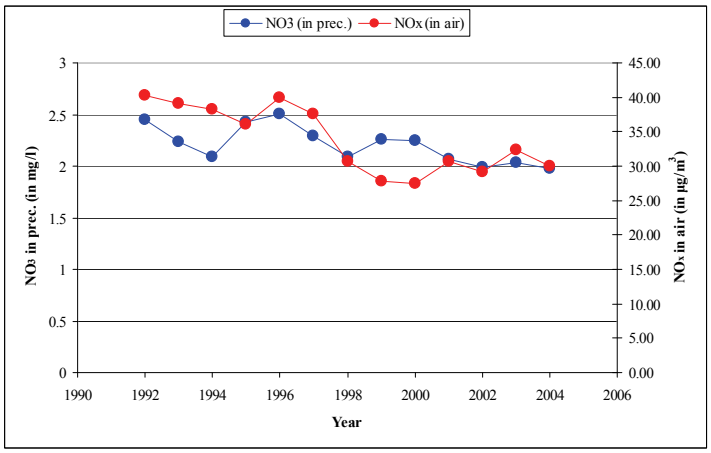

Figure 10: The concentration of nitrate in precipitation and NO_x in air over the period 1992-2004.

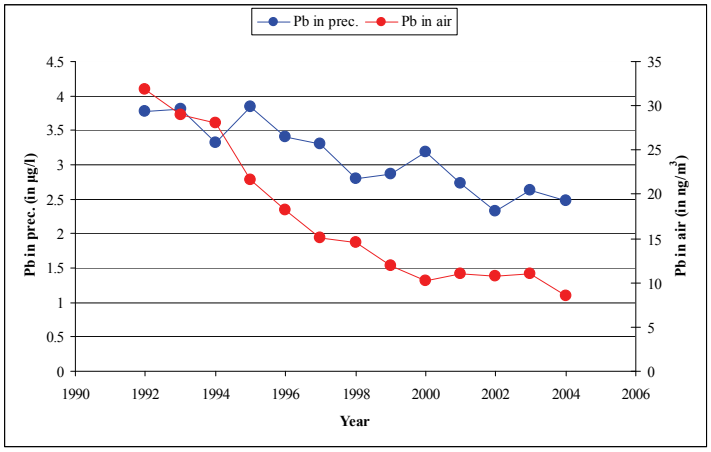

Figure 11: The concentration of lead in precipitation and in air over the period 1992-2004.

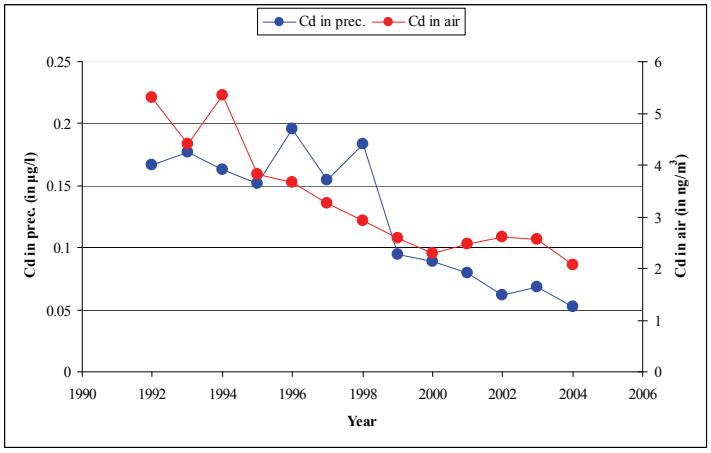

Figure 12: The concentration of cadmium in precipitation and in air over the period 1992-2004.

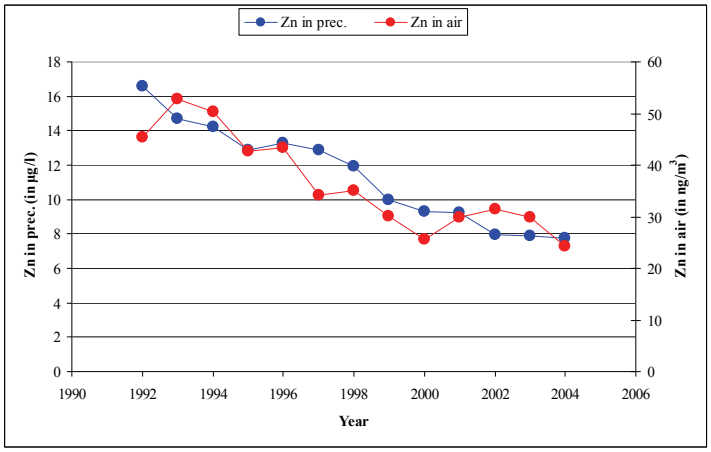

Figure 13: The concentration of zinc in precipitation and in air over the period 1992-2004.

6 The spatial distribution of concentrations in precipitation in the Netherlands in 2004

Maps were constructed of the spatial distribution over the Netherlands in 2004 of the concentration in precipitation for major components and heavy metals. The maps of the concentration of a component are calculated via the interpolation of the measured values at all stations onto a uniform grid covering the Netherlands. The calculations are performed using the software package INTERPOL, which calculates the value of the concentration of a component v_{int} for each grid point as the weighted mean of the measured values of the surrounding stations v_i. This reads:

$$v_{\text{int}} = \sum_{i=1}^{n} w_i \cdot v_i \ .$$

The weighting factor w_i is a function of the distance between a grid cell to each individual station d_i :

$$w_i = \frac{\exp(-d_i / d_s)}{\sum_{j=1}^{n} \exp(-d_j / d_s)}$$

The quantity d_s is the radius of interpolation, a length scale which indicates on which distance measurement values are still correlated with each other. The radius of interpolation is normally obtained from the semivariogram, a mathematical function to indicate spatial correlation in the observed values measured at sample locations. However in this study its value is set equal to 35 km. This distance has been obtained by calculating for each station the distance *d* to its most nearby station. Next the mean value of *d* for all stations are taken, which yield a value of approximately 50 km. The obtained distribution do not differ significantly when we reduce the value to 35 km**,** but the advantage of the latter interpolation value is that the differences between maxima and minima are more close to the observed values.

The maps obtained with the above described method are *ordinary interpolation maps*. It should hence be *stressed* that they are only used to *visually represent* the measurement data over the Netherlands. In this way it is easier to identify apparent large-scale gradients. The maps should definitely **not** be used to determine local values of concentrations for the different components. Because the concentrations of heavy metals are in general close to the detection limit and hence the interpolated maps were in general hampered by unclear patterns, and are therefore not included in this report.

6.1 The spatial distribution of concentrations in 2004

6.1.1 Major components

SO_4 corrected for sea spray reflects to a large part anthropogenic sources and shows much higher concentrations in the south of the country than in the north (about a factor of two difference). Due to the spatial distribution of SO_2 sources in Europe and the fact that it takes time to convert SO_2 to SO_4, the concentration of SO_4 in precipitation is dominated by foreign sources (Van Jaarsveld, 1995). Model

calculations with the Operational Priority Substance (OPS) model (De Ruiter et al., 2006) contain the period 1992-2002 which show that only 15% of the wet deposition of SO_4 in this period in the Netherlands was caused by sources in the Netherlands. The gradient is determined by the position of important source areas and the dominating south-westerly wind associated with precipitation periods.

NO_3 shows also a gradient with somewhat higher concentrations in the south than in the north. Due to the spatial distribution of NO_x sources in Europe and the fact that it takes time to bring to convert NO_x that is not removed well by precipitation to HNO_3 and NO_3 containing aerosol that is removed at a substantial rate, the concentration of NO_3 in precipitation is likely to be dominated by foreign sources (Van Jaarsveld, 1995). Recent model calculations with the OPS model mentioned above show that 21% of the wet deposition of NO_3 over the period 1992-2002 in the Netherlands was caused by sources in the Netherlands (De Ruiter et al., 2006).

NH_4 shows a gradient from lower concentrations near the coast to higher values inland. This reflects the fact that a much larger fraction is likely to come from sources in The Netherlands. Recent model calculations with the OPS model mentioned above show that 60-70% of the wet deposition of NH_4 over the period 1992-2002 in the Netherlands was caused by sources in the Netherlands De Ruiter et al., 2006).

F shows a gradient from higher concentrations in the south and inland to lower concentrations in the north and the coast (at least a factor of two). It looks if there is some contribution from foreign continental sources. It is difficult to give more information as there is no information on the spatial distribution of the source strength within Europe.

PO_4 does not show a very clear gradient. This could be caused by a large contribution from local sources (soil containing PO_4), but this is not completely certain.

Cl, Na, Ca and Mg show high concentrations near the coast that decrease rather fast with distance to the coast. This is in agreement with e.g. the Cl measurements of Leeflang (1938), who also found a steep gradient from the coast to inland. The reason for this pattern is that the majority of these components in the Netherlands originate from sea spray.

K does not show a very clear pattern. It could be that it depends on local sources (soil containing K) and near the coast on input from sea spray, but this is not completely certain.

6.1.2 Heavy metals

V shows high concentrations in the western part of the country (2 stations). It could be that this has something to do with the oil and petrochemical industry in this part of the country, but there is not enough information to confirm that.

Cr shows high concentrations in the western part of the country (3 stations), but otherwise there is not a very clear pattern.

Fe does not show a very clear pattern over the country.

Co shows a little bit higher concentrations in the south-western part of the country, but the differences are not large. This could have something to do with the greater population density in that part of the country, which leads to higher fuel consumption per km^2.

Ni shows somewhat higher concentrations in the western part of the country with one station with a relatively high concentration and others with higher concentrations. This pattern could have something to do with the higher fuel consumption per km^2 in the more densely populated western part of the country.

Cu shows a gradient with higher concentrations in the southern part of the country and lower in the northern part. This could possibly indicate some influence from foreign sources.

Zn shows a clear gradient with higher concentrations in the southern part of the country and lower in the northern part. This could possibly indicate an influence from foreign sources.

As shows a gradient with higher concentrations in the southern part of the country (except near the coast) than in the northern part. The As emission density is larger in the part of Belgium adjacent to the Netherlands (Friedrich, 2007) and it is likely that there is some influence from Belgian sources. In Germany close to the eastern border of the Netherlands there is also a higher As emission density. Due to the prevailing south-westerly wind direction associated with precipitation periods it is likely, however, that this area has not so much influence on the concentrations in precipitation in the Netherlands.

Zn and Cd show a clear gradient with higher concentrations in the southern part of the country. The Zn and Cd emission density is larger in the part of Belgium adjacent to the Netherlands (Friedrich, 2007). In Germany close to the eastern border of the Netherlands there is also a higher Zn and Cd emission density. Due to the prevailing south-westerly wind direction associated with precipitation periods it is likely, however, that this area has not so much influence on the concentrations in precipitation in the Netherlands. Results of the EMEP model for heavy metals show that only 12% of the wet deposition of Cd is directly caused by sources in the Netherlands, 20% is directly caused by foreign sources, whereas 57% is caused by resuspension of already deposited material and the rest comes from outside Europe (Ilia Ilyin, EMEP-East, Moscow, personal communication, 2009).

Pb concentrations in precipitation seem to be somewhat lower in the north, but somewhere high and low concentrations are found rather close to each other, which makes the picture less clear. Results of the EMEP-model for heavy metals show that only 7% of the wet deposition of Pb is directly caused by sources in the Netherlands, 16% is directly caused by foreign sources, whereas 68% is caused by resuspension of already deposited material and the rest comes from outside Europe (Ilia Ilyin, EMEP-East, Moscow, personal communication, 2009).

It was tried to see whether there would be any correlation between the concentrations of different heavy metals in precipitation. A strong correlation was found between V and Ni (R^2=0.92) in the spatial distribution. This strong correlation indicates that both components are probably originating from the same source. This source is most likely linked with fuel consumption.

6.2 A comparison with nearby foreign stations

In this subsection the results of the Netherlands precipitation chemistry network as calculated in the previous subsection are compared with nearby stations from the networks of the neighbouring countries to see whether there are discrepancies near the border that might indicate errors in the Netherlands precipitation chemistry network. This is done for the year 2004.

Belgium: Flanders
In Flanders (Belgium) there is a precipitation chemistry network with wet-only collectors (VMM, 2005). The distance from between the stations Beek and Maasmechelen is about 10 km, the distance between Huijbergen and Kapellen is about 15 km, the distance between Philipine and Gent is about 30 km.

Table 8 gives the results of the comparison for the major components. The underlined value indicates that it is based on measurements that are only available for less than 75% of the time. The largest difference can be expected for NH_4 as it is influenced much more by local sources than SO_4 and NO_3. In general the wet deposition of these components is very similar at nearby stations in both countries. The wet deposition of SO_4 and NO_3 at Philipine, however, is about 30% higher than at Gent. The Belgian station Wingene, which is situated about 25 km west of Gent has wet depositions that are very similar to those of Gent (results not presented here). This could indicate a systematic difference between the depositions of SO_4 and NO_3 at Philipine and the Belgian measuring locations, or that there is an influence of nearby sources. This should be investigated further. At the moment measurements of wet-only samplers from the Netherlands and Flanders are being compared at the operational station at Philipine. This could offer a solution to the discrepancy mentioned above.

Table 8 Amount of precipitation and wet deposition of major components at stations in Flanders (wet deposition only) and the Netherlands (wet deposition only) close to the border for the year 2004.

Station[2]	Precipitation **(mm)**	SO_4 **corr.**[3] **(mg/m^2)**	NO_3 **(mg/m^2)**	NH_4 **(mg/m^2)**
1a. Beek (NL)	**758**	**1390**	**1649**	**847**
1b. Maasmechelen (B)	**736**	**1214**	**1507**	**596**
2a. Huijbergen (NL)	**816**	**2005**	**1950**	**953**
2b. Kapellen (B)	**795**	**1925**	**1761**	**797**
3a. Philipine (NL)	**771**	**1630**	**1653**	**783**
3b. Gent (B)	**700**	**1186**	**1277**	**703**

In the year 2004 there were no other precipitation networks with wet-only collectors near the Netherlands. There were, however, precipitation networks that used bulk-collectors, i.e. collectors without a lid that are always open. These collectors also sample some dry deposition. For that reason it can be expected that the deposition measured with such devices is higher than measured with wet-only collectors.

The results of the precipitation network in the Netherlands for the year 2004 were compared with the results of a precipitation network for heavy metals in Flanders that uses bulk collectors (Natacha Claeys, VMM, Belgium, personal communication, 2009). The comparison was done for the same stations for which the major components were reported above. It was found that the wet depositions at the stations in Flanders were always higher for all the components that could be compared (As, Cd, Cu, Pb, Zn, Ce, Ni, Fe), which seems to be in line with the fact that the deposition in open collectors is higher.

[2] The station 1a should be compared with the station 1b et cetera.

[3] Sea-spray corrected

Niedersachsen

The results of the precipitation network in the Netherlands for the year 2004 were also compared with the results of two networks in Niedersachsen in Germany (Richard Lochte, Staatliches Gewerbeaufsichtsamt Hildesheim, Zentrale Unterstützungsstelle Luftreinhaltung und Gefahrstoffe Hildesheim, Germany, personal communication 2009, who also provided information from the network of the Niedersächsischer Landesbetrieb für Wasserwirtschaft Küsten- und Naturschutz, Hannover-Hildesheim, Germany). The German stations use bulk collectors, that are always open and for that reason it can be expected that they have higher depositions. The results of the stations Kollumerwaard and Valthermond in the Netherlands were compared with the results of the stations Emden/Twixlum and Lingen in Niedersachsen. The results of the station Eibergen in the Netherlands and the station Bad Bentheim in Niedersachsen were also compared. This was done for the following components NH_4, NO_3, SO_4, PO_4, Cl, Na, V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb. Not all components were measured at all stations. For some components for some stations at both sides of the border the depositions were about the same. This holds for NO_3, NH_4, Cr (with the exception of Lingen), As, Cd. For all other components usually higher values are observed in Niedersachsen, which is likely to the fact that bulk collectors are used, which also partly collect the dry deposition. This dry deposition can also be of more local character (resuspension of already deposited dust or due to local industries).

Nordrhein-Westfalen

The results of the precipitation network in the Netherlands for the year 2004 were also compared with the results of two networks in Nordrhein-Westfalen in Germany (Peter Altenbeck and Mathias Burggraf, Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen, Germany, personal communication 2009). The results of the station Vredepeel (Netherlands) were compared with the results of the stations Kleve and Duisburg-Ruhrort in Nordrhein-Westfalen. The result of the station Beek in the Netherlands and the station Rott in Nordrhein-Westfalen were also compared. This was done for the following components NH_4, NO_3, SO_4 (corrected for sea spray), PO_4, Cl, Na, K, Mg, Ca, Zn. The deposition of PO_4 and Zn was not measured at all stations. With one exception the wet deposition was always higher at the stations at the stations Nordrhein-Westfalen than in the Netherlands. The exception was the deposition of NH_4, which was lower at Duisburg-Ruhrort than in Vredepeel. This could be caused by the rather high NH_3 emission density near Vredepeel, compared to the very low emission density in the urban environment of Duisburg-Ruhrort. So also here the results are in line with what can be expected.

7 Conclusion

In this report annual mean concentrations and wet deposition fluxes of major components and heavy metals over the period 1992-2004 were calculated from the measurements at the 15 stations of the Dutch National Precipitation Chemistry Monitoring Network, a period during which the configuration of the monitoring network remained roughly the same. The values of concentrations and wet deposition fluxes of contaminants listed in this report only cover the period 2001-2004, since values from before 2001 have been listed in previous reports (see e.g. Stolk, 2001).

Subsequently a trend analysis was performed of the annual mean concentrations and wet deposition fluxes of major components and heavy metals over the period 1992-2004. The trend analysis showed that there were downward trends for the annual mean concentration above the 95% significance level for ammonium, nitrate, sulfate, fluoride, nickel, zinc, cadmium and lead. A downward trend above the 95% significance level over the same time period for wet deposition flux was also found for all these contaminants except for nitrate.

The observed downward trends in the annual mean concentrations for ammonium, sulfate and nitrate were compared with the time series available of the air concentrations of their corresponding gas and aerosol component. These results were as follows[4]:

Ammonium: the downward trend of ammonium in precipitation (27%) was closest to the downward trend of ammonia in the air (36%). The aerosol component of ammonium showed a stronger downward trend (46%). Hence ammonia in the air is in general contributing more to ammonium in precipitation than the ammonium aerosol in the air.

Sulfate: the downward trend of sulfate (47%) was closest to the downward trend of the sulfate aerosol in the air (53%). The gas component sulfur dioxide showed a much stronger downward trend (85%). Hence the sulfate aerosol contributes mostly to the sulfate concentrations in precipitation as expected (see main text in section 2.2).

Nitrate: the concentrations of the nitrate aerosol and NO_x both showed a stronger decrease (~30%) compared to the concentration of nitrate in precipitation (17%).

The observed downward trends in the annual mean concentrations for lead, cadmium and zinc were compared with the time series available of the air concentrations of their corresponding aerosol component. These results were as follows[4]:

Lead: the downward trend of lead in precipitation (36%) is much smaller than the downward trend of the lead aerosol in the air (81%). The reason for this is not well understood and will be investigated in more detail in another report.

Cadmium: the downward trend of cadmium in precipitation (69%) is similar to the downward trend of the cadmium aerosol in the air (68%) as expected.

[4] Values in between brackets indicate the decrease of concentration in 2004 with respect to 1992 using the Sen's method fit to the measurements (see section 3.2)

Zinc: the downward trend of zinc in precipitation (55%) is similar to the downward trend of the zinc aerosol in the air (53%) as expected.

Finally the spatial distribution of concentrations of precipitation from major components and heavy metals over the Netherlands was investigated. A summary is given for those contaminants which have both a downward trend and an identifiable large-scale gradient:

Ammonium: a gradient with high values inland and low values near the coast which indicates that a large fraction is coming from sources in the Netherlands. Recent modelling with the OPS model indeed show that 60-70% of the wet deposition of ammonium over the period 1992-2002 is caused by sources in the Netherlands.

Sulfate: a gradient from high values at the borders of the Netherlands in the Southwest to low values in the Northern part of the Netherlands, which indicates a significant contribution of sources from abroad. Recent modelling with the OPS model indeed show that only 15% of the wet deposition of sulfate over the period 1992-2002 is caused by sources in the Netherlands.

Nitrate: a gradient from high values at the borders of the Netherlands in the Southern part to low values in the Northern part of the Netherlands, which indicates a significant contribution of sources from abroad. Recent modelling with the OPS model indeed show that only 21% of the wet deposition of nitrate over the period 1992-2002 is caused by sources in the Netherlands.

Lead: no clear large-scale gradients were found in the Netherlands for lead. Recent modelling with the EMEP model shows that only 7% of the wet deposition of lead is directly caused by sources in the Netherlands and 68% is caused by resuspension of previous deposited material.

Cadmium: a clear gradient with higher concentrations in the Southern part of the Netherlands near the borders, which indicates a significant contribution of sources from abroad. Recent modelling with the EMEP model shows that only 12% of the wet deposition of cadmium is directly caused by sources in the Netherlands and 57% is caused by resuspension of previous deposited material.

rivm

References

Aas, W., Solberg, S., Berg, T., Manø, S.M., Yttri, K.E. (2004). Overvåking av langtransportert forurenset luft og nedbør: atmosfærisk tilførsel, 2003 (Monitoring of polluted air and precipitation from far away: atmospheric deposition, 2003, in Norwegian). Norsk Institutt for Luftforskning, Kjeller, Norway, pp. 166.

Asman, W.A.H., Ridder, T.B., Reijnders, H.F.R., Slanina J. (1982). Influence and prevention of bird droppings in precipitation chemistry experiments. Water, Air and Soil Pollut. 17, 415-420.

Asman, W.A.H., Van Jaarsveld, J.A. (1990). A variable-resolution statistical transport model applied for ammonia and ammonium. Bilthoven: Rijksinstituut voor Volksgezondheid en Milieu (RIVM). Rapport nr. 228471007.

Beijk, R., Mooibroek, D., Hoogerbrugge, R. (2009). Jaaroverzicht Luchtkwaliteit 2009. Bilthoven: Rijksinstituut voor Volksgezondheid en Milieu (RIVM). Rapport nr. 680704008.

Berg, T., Aas, W., Pacyna, J., Uggerud, H.T., Vadset, M. (2008). Atmospheric trace metal concentrations at Norwegian background sites during 25 years and its relation to European emissions. Atmospheric Environment 42, 7494-7501.

Blank, F.T. (2001). Meetonzekerheid Landelijk Meetnet Luchtkwaliteit (LML) KEMA 50050870-KPS/TCM 01-3063.

Buijsman, E. (1989). Kwaliteitsaspecten van het Landelijk Meetnet Regenwatersamenstelling. I. Hoofdcomponenten. Bilthoven: Rijksinstituut voor Volksgezondheid en Milieu (RIVM). Rapport nr. 228703006.

De Leeuw, F., Barrett, K., Claeys, N., Coleman, P., Grimvall, A., Koopmans, M. (2005). Assessment of trends in atmospheric concentration and deposition of hazardous pollutants to the OSPAR maritime area. Evaluation of the CAMP network. OSPAR commission 2005

De Ruiter, J.F., Van Pul, W.A.J., Van Jaarsveld, H.A., Buijsman, E. (2006). Deposition in the Netherlands between 1981 and 2002. Bilthoven: Rijksinstituut voor Volksgezondheid en Milieu (RIVM). Rapport nr. 500037005.

Ellermann, T., Andersen, H.V., Bossi, R., Christensen, J., Frohn, L.N., Geels, C., Kemp, K., Løfstrøm, P., Mogensen, B.B., Monies, C. (2007). Atmosfærisk deposition 2006. Report 645, National Environmental Research Institute, Roskilde, Denmark.

Ellermann, T., Hertel, O., Kemp, K., Monies, C. (2003). Atmosfærisk deposition. Report 418. National Environmental Research Institute, Roskilde, Denmark.

Fagerli, H., Aas, W. (2008). Trends of nitrogen in air and precipitation: Model results and observations at EMEP sites in Europe, 1980-2003. Environ. Pollut. 154, 448-461.

Fowler, D., McDonald, A.G., Crossley, A., Nemitz, E., Leaver, D., Cape, J.N., Smith, R.I., Anderson, D., Rowland, P., Ainsworth, G., Lawlor, A.H., Guyatt, H., Harmens, H. (2006). UK heavy metal monitoring network. Report for project C02164. Centre for Ecology and Hydrology, Edinburgh Research Station, Bush Estate, Penicuik, U.K.

Friedrich, R. (coordinator) (2007). ESPREME, Estimation of willingness-to-pay to reduce risks of exposure to heavy metals and cost-benefits analysis for reducing heavy metals occurrence in Europe, publishable final activity report, University of Stuttgart, Germany.

Hovmand, M.F., Kemp, K., Kystol, J., Johnsen, I., Riis-Nielsen, T., Pacyna, J.M. (2008). Atmospheric heavy metal deposition accumulated in rural forest soils of southern Scandinavia. Environ. Pollut. 155, 537-541.

Ilyin, I., Travnikov, O., Aas, W. (2006). Heavy metals: transboundary pollution of the environment. EMEP Status Report 2/2006.

Leeflang, K.W.H. (1938). De chemische samenstelling van den neerslag in Nederland. Chem. Weekbl. 35, 658-664.

Nriagu, J.O., Pacyna, J.M. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134-139.

Pacyna, J.M., Pacyna, E.G., Aas, W. (2009). Changes of emissions and atmospheric deposition of mercury, lead and cadmium. Atmospheric Environment 43, 117-127.

Pacyna, J.M., Pacyna, E.G. (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ. Rev. 9. 269-298.

Pacyna, J.M. ,Pacyna, E.G., Panasiuk, D.,Fudała,J., Strzelecka-Jastrząb, E., Hławiczka, S. (2005) Heavy metal emissions in Europe: First results from the ESPREME project. Paper presented at TFEIP & ESPREME workshop heavy metals and POPs, Rovaniemi, Finland, 18-19 October, 2005.
http://espreme.ier.uni-stuttgart.de/homepage_old/workshop/papers/Pacyna%20-%20keynote.pdf

Pacyna,E.G., Pacyna, J., Fudała,J., Strzelecka-Jastrząb, E., Hławiczka, S., Panasiuk, D., Nitter, S., Pregger, T., Pfeiffer, H., Friedrich, R. (2007). Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. Atmospheric Environment 41, 8557-8566.

Ridder, T.B., Baard, J.H., Buishand, T.A. (1984). De invloed van monsternamemethoden en analysetechnieken op gemeten chemische concentraties in regenwater (The influence of sampling methods and anlysis techniques on the chemical composition of rainwater, in Dutch). Technical Report TR55. KNMI, De Bilt, The Netherlands.

Salmi, T., Määttä, A., Anttila, P., Ruoho-Airola, T., Amnell, T. (2002). Detecting trends of annual values of atmospheric pollutants by the Mann-Kendall test and Sen's slope estimates-the excel template application MAKESENS. Helsinki, Meteorologiska Institutet, Report code FMI-AQ-31

Seinfeld, J.H., Pandis, S.N. (1998). Atmospheric chemistry and physics. John Wiley, New York, USA, pp. 1326.

Stolk, A.P. (2001). Landelijk Meetnet Regenwatersamenstelling Meetresultaten 2000, Bilthoven: Rijksinstituut voor Volksgezondheid en Milieu (RIVM). Rapport nr. 723101057.

Sutton, M.A., Asman, W.A.H., Ellermann, T., Van Jaarsveld, J.A., Acker, K., Aneja, V., Duyzer, J., Horvath, L., Paramonov, S. Mitosinkova, M., Tang, Y.S., Achermann, B., Gauger, T., Bartniki, J., Neftel, A., Erisman, J.W. (2003). Establishing the link between ammonia emission control and measurements of reduced nitrogen concentrations and deposition. Environ. Monit. Assessment 82, 149-185.

Van der Swaluw, E., van Pul, A., Grimvall, A., Barrett, K., Moxon, R. (2009). Trends in atmospheric concentrations and deposition of nitrogen and selected hazardous substannces to the OSPAR maritime area. OSPAR commission 2009

Van Elzakker, B.G.(2001). Monitoring activities in the Dutch National Air Quality Monitoring Network in 2001 and 2001. Bilthoven: Rijksinstituut voor Volksgezondheid en Milieu (RIVM). Rapport nr. 723101055.

Van Jaarsveld, J.A. (1995). Modelling the long-term atmospheric behaviour of pollutants on various spatial scales. Ph.D. Thesis, University of Utrecht, The Netherlands, pp. 235.

Van Jaarsveld, J.A. (2004). The Operational Priority Substances model. Description and validation of OPS-Pro 4.1 Bilthoven: Rijksinstituut voor Volksgezondheid en Milieu (RIVM). Rapport nr. 500045001

VVM (2005). “Zure regen” in Vlaanderen, depositiemeetnet verzuring 2004. Vlaamse Milieumaatschappij, Erembodegem, Belgium.

Zevenhoven, R., Mukherjee, A.B., Bhattacharya, P. (2007). Chapter 20. Arsenic flows in the environment of the European Union: a synoptic review. In: Bhattacharya, P., Mukherjee, A.B., Bundschuh, J., Zevenhoven, R., Loeppert, R.H. (Eds.) Trace metals and other contaminants in the Environment. 9, 527-547.

Acknowledgement

We are grateful to Philip van Avermaet and Natacha Claeys (VVM, Belgium), Peter Altenbeck and Mathias Burggraf (Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen, Recklinghausen, Germany), Richard Lochte (Staatliches Gewerbeaufsichtsamt Hildesheim, Zentrale Unterstützungsstelle Luftreinhaltung und Gefahrstoffe Hildesheim, Germany) for providing us with data from the precipitation chemistry networks in their region. We are also grateful to Alexey Gusev and Ilia Ilyin (EMEP-East, Moscow, Russia) for providing detailed calculations of the contribution of countries to the wet deposition of Cd and Pb in the Netherlands. Finally, thanks to Addo van Pul for a careful reading of the manuscript and the many suggestions he gave to improve this report.

rivm

Appendix A1 Annual mean concentrations of the major components over the period 1992-2004

Table A1: Concentrations are in units of mg/l and precipitation is in units of mm. Values underlined are below the 75% coverage as discussed in chapter 3

Stn	Year	Prec	NH_4	NO_3	SO_4	PO_4	F	Cl	Na	K	Mg	Ca
134	2001	864	1.12	2.04	1.96	0.053	0.024	0.93	0.56	0.10	0.09	0.28
134	2002	976	1.06	2.14	1.83	0.014	0.021	0.77	0.47	0.08	0.07	0.22
134	2003	594	1.25	2.21	1.95	0.051	0.019	1.12	0.69	0.14	0.10	0.41
134	2004	758	1.12	2.18	1.83	0.017	0.014	1.18	0.79	0.15	0.10	0.26
631	2001	1017	0.96	1.87	1.50	0.005	0.008	2.59	1.48	0.11	0.19	0.23
631	2002	892	0.96	1.87	1.52	0.024	0.008	3.28	1.80	0.14	0.23	0.33
631	2003	581	1.28	2.15	1.67	0.041	0.009	2.66	1.50	0.16	0.20	0.42
631	2004	929	*1.19*	*1.89*	*1.67*	*0.062*	*0.007*	*2.64*	*1.55*	*0.14*	*0.20*	*0.31*
318	2001	1031	1.09	1.72	1.80	0.114	0.017	4.25	2.34	0.22	0.31	0.31
318	2002	1087	*0.95*	*1.68*	*1.80*	*0.032*	*0.018*	*2.70*	*1.53*	*0.17*	*0.19*	*0.34*
318	2003	741	1.15	1.68	1.76	0.069	0.020	3.44	1.99	0.22	0.24	0.32
318	2004	771	*1.02*	2.14	2.11	*0.004*	0.015	2.99	1.70	*0.17*	0.22	0.41
628	2001	1023	1.17	2.40	1.99	0.005	0.012	2.64	1.50	0.11	0.19	0.20
628	2002	1004	0.92	1.90	1.67	0.005	0.011	1.94	1.11	0.09	0.14	0.19
628	2003	616	1.12	2.01	1.87	0.006	0.010	3.41	1.88	0.14	0.24	0.31
628	2004	870	0.86	1.85	1.67	0.017	0.008	3.97	2.31	0.17	0.27	0.24
444	2001	950	0.69	2.21	1.66	0.003	0.010	6.29	3.51	0.20	0.46	0.28
444	2002	887	0.65	2.05	1.84	0.018	0.010	5.22	2.87	0.17	0.36	0.26
444	2003	733	0.80	1.91	1.79	0.049	0.008	5.30	2.94	0.18	0.37	0.30
444	2004	753	0.62	1.85	1.75	0.019	0.008	8.87	4.85	0.27	0.60	0.40
722	2001	826	*1.58*	*2.45*	*1.92*	*0.054*	*0.012*	*1.17*	*0.69*	*0.14*	*0.10*	*0.21*
722	2002	965	*1.18*	*1.75*	*1.30*	*0.018*	*0.009*	*0.79*	*0.49*	*0.12*	*0.07*	*0.20*
722	2003	735	1.26	1.92	1.46	0.021	0.008	1.60	0.94	0.12	0.12	0.22
722	2004	817	*1.45*	*2.28*	*1.75*	*0.024*	*0.009*	*1.55*	*0.93*	*0.20*	*0.12*	*0.18*
231	2001	943	1.24	1.85	2.07	0.074	0.013	2.16	1.26	0.13	0.16	0.15
231	2002	1017	*1.14*	*1.86*	*1.99*	*0.037*	*0.013*	*1.47*	*0.91*	*0.15*	*0.11*	*0.17*
231	2003	695	1.12	1.89	2.02	0.010	0.013	2.43	1.37	0.13	0.17	0.27
231	2004	854	*1.30*	2.20	2.28	*0.039*	0.011	2.52	1.51	*0.22*	0.19	0.35
235	2001	966	*0.95*	*1.87*	*2.05*	*0.035*	*0.016*	*3.01*	*1.68*	*0.13*	*0.22*	*0.21*
235	2002	1064	0.87	1.92	2.19	0.008	0.014	1.97	1.11	0.11	0.14	0.21
235	2003	707	1.03	1.97	2.24	0.012	0.016	2.17	1.28	0.13	0.16	0.31
235	2004	816	1.17	2.39	2.46	0.002	0.016	2.71	1.53	0.17	0.19	0.30

Table A1 continued

Stn	Year	Prec	NH_4	NO_3	SO_4	PO_4	F	Cl	Na	K	Mg	Ca
934	2001	1029	*1.10*	*2.25*	*1.54*	*0.026*	*0.007*	*5.61*	*3.28*	*0.22*	*0.44*	*0.66*
934	2002	1108	*1.21*	*2.28*	*1.54*	*0.049*	*0.008*	*2.04*	*1.17*	*0.16*	*0.18*	*0.66*
934	2003	715	1.07	2.04	1.40	0.146	0.006	4.92	2.73	0.20	0.37	0.91
934	2004	862	0.80	1.64	1.23	0.010	0.002	4.61	2.53	0.16	0.33	0.53
434	2001	1276	*1.04*	*2.54*	*2.66*	*0.024*	*0.015*	*2.88*	*1.67*	*0.18*	*0.22*	*0.34*
434	2002	1145	*0.74*	*1.54*	*2.08*	*0.041*	*0.015*	*5.21*	*2.88*	*0.19*	*0.35*	*0.34*
434	2003	627	0.95	2.01	2.30	0.018	0.017	4.32	2.45	0.16	0.30	0.38
434	2004	966	*0.84*	1.99	2.28	*0.025*	0.014	5.91	3.33	*0.24*	0.42	0.39
732	2001	1079	1.31	2.41	1.83	0.006	0.010	2.12	1.23	0.10	0.16	0.17
732	2002	963	*1.20*	*2.06*	*1.66*	*0.003*	*0.008*	*1.99*	*1.15*	*0.12*	*0.15*	*0.16*
732	2003	654	1.36	2.47	1.81	0.016	0.009	2.60	1.45	0.14	0.18	0.28
732	2004	1045	1.01	1.90	1.59	0.004	0.006	2.74	1.61	0.10	0.19	0.19
929	2001	869	1.02	2.01	1.49	0.007	0.011	2.80	1.58	0.13	0.20	0.18
929	2002	870	*1.10*	*2.25*	*1.58*	*0.006*	*0.010*	*2.74*	*1.43*	*0.13*	*0.18*	*0.20*
929	2003	678	1.01	2.02	1.37	0.024	0.006	2.19	1.20	0.13	0.14	0.20
929	2004	851	*1.05*	*1.99*	*1.46*	*0.050*	*0.007*	*2.35*	*1.40*	*0.22*	*0.17*	*0.22*
131	2001	879	*1.86*	*2.50*	*2.32*	*0.010*	*0.013*	*1.09*	*0.69*	*0.13*	*0.09*	*0.21*
131	2002	978	*1.54*	*1.93*	*2.22*	*0.010*	*0.012*	*1.26*	*0.75*	*0.10*	*0.10*	*0.21*
131	2003	724	1.44	1.95	1.71	0.011	0.008	1.45	0.83	0.10	0.11	0.24
131	2004	864	1.22	1.62	1.61	0.002	0.007	1.91	1.16	0.11	0.14	0.19
724	2001	947	1.36	2.27	1.93	0.023	0.017	1.63	0.96	0.11	0.12	0.21
724	2002	926	1.31	2.10	1.76	0.006	0.014	1.39	0.78	0.08	0.10	0.20
724	2003	616	1.36	2.27	1.97	0.007	0.017	2.60	1.47	0.19	0.19	0.35
724	2004	758	1.26	2.05	1.86	0.043	0.013	2.25	1.39	0.14	0.17	0.27
538	2001	923	0.90	1.95	1.54	0.090	0.008	5.17	2.93	0.21	0.38	0.29
538	2002	909	0.81	1.94	1.52	0.005	0.007	7.70	4.21	0.24	0.52	0.40
538	2003	631	0.90	1.94	1.60	0.005	0.008	5.21	2.86	0.16	0.35	0.32
538	2004	917	*0.68*	*1.76*	*1.52*	*0.022*	*0.007*	*6.76*	*3.72*	*0.21*	*0.45*	*0.30*

Appendix A2 Annual wet deposition fluxes of the major components over the period 1992-2004

Table A2: Wet deposition fluxes are in units of mg/m² and precipitation is in units of mm. Values underlined are below the 75% coverage as discussed in chapter 3

Stn	Year	Prec	NH_4	NO_3	SO_4	PO_4	F	Cl	Na	K	Mg	Ca
134	2001	864	971	1760	1690	46	21	800	484	83	74	238
134	2002	976	1037	2091	1783	14	20	752	457	80	65	213
134	2003	594	743	1317	1158	30	11	664	411	85	60	242
134	2004	758	847	1649	1390	13	11	896	602	111	76	197
631	2001	1017	973	1905	1525	5	8	2637	1506	111	196	239
631	2002	892	852	1669	1359	22	7	2926	1603	121	206	297
631	2003	581	743	1251	971	24	5	1544	871	90	118	242
631	2004	929	*1104*	*1755*	*1555*	*57*	*7*	*2450*	*1436*	*134*	*185*	*283*
318	2001	1031	1125	1769	1856	117	18	4379	2418	223	324	319
318	2002	1087	*1031*	*1826*	*1954*	*35*	*20*	*2930*	*1663*	*184*	*201*	*365*
318	2003	741	853	1244	1302	51	15	2548	1472	160	178	233
318	2004	771	*783*	1653	1630	*3*	12	2307	1308	*131*	171	317
628	2001	1023	1195	2456	2036	5	12	2703	1533	117	198	210
628	2002	1004	919	1904	1674	5	11	1951	1119	90	141	194
628	2003	616	687	1240	1153	4	6	2101	1160	86	147	188
628	2004	870	751	1609	1457	15	7	3459	2013	149	238	212
444	2001	950	657	2105	1578	3	9	5979	3340	186	435	266
444	2002	887	577	1822	1629	16	8	4632	2548	153	319	231
444	2003	733	586	1400	1316	36	6	3884	2155	134	273	223
444	2004	753	467	1396	1315	14	6	6674	3653	202	454	299
722	2001	826	*1308*	*2021*	*1583*	*45*	*10*	*969*	*568*	*113*	*83*	*172*
722	2002	965	*1141*	*1693*	*1256*	*17*	*8*	*765*	*474*	*111*	*64*	*190*
722	2003	735	926	1413	1071	16	6	1177	692	88	86	158
722	2004	817	*1183*	*1859*	*1431*	*19*	*8*	*1265*	*756*	*163*	*95*	*146*
231	2001	943	1172	1748	1949	70	13	2041	1188	123	150	139
231	2002	1017	*1163*	*1893*	*2022*	*38*	*13*	*1498*	*926*	*153*	*114*	*170*
231	2003	695	780	1311	1407	7	9	1690	954	88	119	184
231	2004	854	*1109*	1879	1943	*33*	10	2154	1293	*185*	165	298
235	2001	966	*916*	*1808*	*1980*	*34*	*16*	*2907*	*1627*	*129*	*211*	*199*
235	2002	1064	927	2039	2328	8	15	2094	1177	115	151	221
235	2003	707	728	1390	1581	9	11	1538	903	89	113	217
235	2004	816	953	1950	2005	2	13	2213	1246	138	158	245

Table A2 continued

Stn	Year	Prec	NH_4	NO_3	SO_4	PO_4	F	Cl	Na	K	Mg	Ca
934	2001	1029	*1134*	*2319*	*1581*	*26*	*7*	*5766*	*3370*	*222*	*450*	*681*
934	2002	1108	*1344*	*2524*	*1702*	*55*	*9*	*2264*	*1297*	*180*	*195*	*728*
934	2003	715	768	1460	1001	104	4	3515	1952	140	266	653
934	2004	862	693	1412	1058	8	2	3980	2185	136	284	455
434	2001	1276	*1328*	*3237*	*3392*	*31*	*19*	*3668*	*2124*	*225*	*277*	*431*
434	2002	1145	*851*	*1761*	*2379*	*47*	*17*	*5968*	*3296*	*218*	*401*	*384*
434	2003	627	594	1258	1441	11	10	2706	1537	102	191	238
434	2004	966	*809*	1917	2198	*24*	13	5710	3217	*235*	402	373
732	2001	1079	1414	2602	1975	7	11	2293	1332	105	172	188
732	2002	963	*1152*	*1980*	*1595*	*2*	*8*	*1914*	*1104*	*115*	*141*	*152*
732	2003	654	890	1612	1182	10	6	1698	947	89	120	181
732	2004	1045	1052	1980	1664	4	6	2866	1683	109	200	202
929	2001	869	884	1746	1293	6	10	2437	1377	110	177	156
929	2002	870	*959*	*1959*	*1377*	*5*	*8*	*2388*	*1248*	*112*	*159*	*176*
929	2003	678	684	1366	926	17	4	1482	811	89	98	135
929	2004	851	*898*	*1694*	*1242*	*42*	*6*	*2005*	*1196*	*185*	*145*	*184*
131	2001	879	*1633*	*2200*	*2040*	*9*	*12*	*960*	*606*	*118*	*76*	*183*
131	2002	978	*1502*	*1889*	*2173*	*10*	*12*	*1235*	*733*	*99*	*101*	*202*
131	2003	724	1047	1409	1240	8	6	1049	600	72	80	173
131	2004	864	1050	1402	1394	2	6	1651	1002	93	118	161
724	2001	947	1290	2144	1831	22	16	1547	911	107	117	201
724	2002	926	1216	1946	1625	5	13	1291	723	78	95	184
724	2003	616	837	1398	1212	5	10	1605	909	116	114	213
724	2004	758	959	1552	1412	32	9	1709	1052	103	130	202
538	2001	923	827	1796	1419	83	7	4775	2707	198	354	268
538	2002	909	737	1761	1383	5	6	6993	3828	219	474	365
538	2003	631	567	1224	1012	3	5	3288	1801	104	222	205
538	2004	917	*628*	*1611*	*1391*	*20*	*6*	*6197*	*3413*	*188*	*416*	*277*

rivm

Appendix B1 Annual mean concentrations of the heavy metals over the period 1992-2004

Table B1: Concentrations are in units of µg/l and precipitation is in units of mm. Values underlined are below the 75% coverage as discussed in chapter 3

Stn	Year	nsl	V	Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
134	2001	864	*0.82*	*0.30*	*24.76*	*0.05*	*0.36*	*2.08*	*14.00*	*0.11*	*0.10*	*3.11*
134	2002	976	0.80	0.25	29.77	0.05	0.31	2.19	13.14	0.14	0.08	2.82
134	2003	594	*0.89*	*0.22*	*51.46*	*0.07*	*0.38*	*3.13*	*15.55*	*0.17*	*0.09*	*2.95*
134	2004	758	0.76	0.13	*18.45*	0.04	0.33	1.71	12.60	0.12	0.06	2.74
631	2001	1017	0.76	0.18	44.99	0.05	0.37	1.75	9.62	0.13	0.10	2.69
631	2002	892	0.74	0.18	79.52	0.05	0.33	1.35	7.38	0.18	0.07	1.85
631	2003	581	0.77	0.18	76.77	0.07	0.37	2.18	9.11	0.20	0.08	1.82
631	2004	929	0.85	0.17	43.96	0.04	0.31	1.32	6.04	0.13	0.04	1.31
318	2001	1031	*1.07*	*0.20*	*55.38*	*0.06*	*0.45*	*2.16*	*10.51*	*0.19*	*0.10*	*3.87*
318	2002	1087	*0.72*	*0.12*	*21.50*	*0.03*	*0.32*	*1.82*	*8.00*	*0.13*	*0.10*	*3.11*
318	2003	741	0.83	0.13	28.70	0.06	0.35	1.65	7.25	0.14	0.09	2.63
318	2004	771	0.92	0.15	21.05	0.04	0.37	1.68	9.89	0.13	0.07	2.26
628	2001	1023	0.98	0.18	24.32	0.06	0.42	2.30	9.43	0.15	0.07	3.46
628	2002	1004	0.72	0.18	21.56	0.05	0.30	1.61	7.67	0.12	0.06	2.36
628	2003	616	0.87	0.22	31.08	0.04	0.39	2.20	8.13	0.13	0.07	2.93
628	2004	870	0.90	0.26	37.40	0.05	0.36	1.59	7.07	0.11	0.05	2.28
444	2001	950	0.87	0.23	20.90	0.04	0.37	2.00	7.14	0.10	0.06	3.19
444	2002	887	0.84	0.15	15.77	0.03	0.33	1.52	6.15	0.11	0.05	2.96
444	2003	733	0.86	0.22	41.35	0.07	0.37	1.87	7.01	0.13	0.06	2.51
444	2004	753	0.95	0.16	16.85	0.04	0.36	1.71	5.41	0.09	0.03	2.43
722	2001	826	*0.58*	*0.25*	*18.31*	*0.04*	*0.31*	*1.45*	*7.53*	*0.12*	*0.05*	*2.96*
722	2002	965	*0.55*	*0.16*	*23.14*	*0.04*	*0.23*	*1.78*	*7.51*	*0.12*	*0.05*	*2.62*
722	2003	735	0.65	0.19	27.25	0.05	0.26	1.79	7.80	0.14	0.06	4.15
722	2004	817	0.62	0.20	22.32	0.04	0.27	1.40	6.86	0.12	0.04	3.39
231	2001	943	0.98	0.22	19.01	0.05	0.40	2.40	11.66	0.12	0.11	2.65
231	2002	1017	*0.96*	*0.22*	*21.97*	*0.05*	*0.40*	*1.99*	*10.73*	*0.16*	*0.09*	*2.71*
231	2003	695	0.87	0.14	28.81	0.06	0.35	2.10	9.56	0.14	0.08	2.53
231	2004	854	1.11	0.14	31.95	0.05	0.42	2.10	10.34	0.18	0.07	2.95
235	2001	966	1.29	0.13	26.28	0.04	0.53	2.04	9.69	0.14	0.08	4.21
235	2002	1064	*1.18*	*0.19*	*26.32*	*0.05*	*0.44*	*1.67*	*8.57*	*0.16*	*0.09*	*4.32*
235	2003	707	1.29	0.16	36.00	0.06	0.48	1.72	8.27	0.19	0.07	3.94
235	2004	816	1.41	0.23	22.17	0.05	0.47	2.01	8.85	0.18	0.08	4.49

Table B1 continued

Stn	Year	nsl	V	Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
934	2001	1029	*0.67*	*0.26*	*88.33*	*0.07*	*0.30*	*2.44*	*7.88*	*0.23*	*0.07*	*1.54*
934	2002	1108	*0.67*	*0.27*	*63.14*	*0.05*	*0.26*	*1.43*	*6.02*	*0.21*	*0.06*	*1.28*
934	2003	715	0.91	0.35	145.80	0.10	0.36	1.33	7.02	0.29	0.05	1.60
934	2004	862	*0.69*	*0.20*	*48.96*	*0.05*	*0.29*	*0.96*	*4.98*	*0.14*	*0.05*	*1.21*
434	2001	1276	1.55	0.19	47.66	0.11	0.81	2.20	13.08	0.14	0.12	2.90
434	2002	1145	1.47	0.22	42.36	0.06	0.69	2.06	7.67	0.12	0.06	2.18
434	2003	627	1.54	0.23	51.85	0.08	0.69	2.52	10.29	0.16	0.09	2.77
434	2004	966	1.64	0.22	33.34	0.05	0.68	2.11	7.86	0.12	0.05	2.20
732	2001	1079	0.70	0.21	17.10	0.03	0.32	1.74	6.99	0.09	0.05	2.70
732	2002	963	0.64	0.13	15.66	0.03	0.26	1.71	6.13	0.12	0.05	3.35
732	2003	654	0.81	0.19	36.25	0.06	0.37	1.89	7.80	0.17	0.07	4.74
732	2004	1045	0.80	0.13	16.43	0.03	0.34	1.26	5.81	0.11	0.04	3.55
929	2001	869	0.62	0.13	22.64	0.03	0.30	2.25	7.65	0.10	0.06	2.08
929	2002	870	0.57	0.09	21.45	0.03	0.23	1.48	6.16	0.11	0.06	1.86
929	2003	678	0.66	0.13	29.60	0.04	0.33	1.44	6.04	0.09	0.04	2.28
929	2004	851	0.71	0.24	31.64	0.03	0.26	1.34	6.12	0.10	0.04	1.98
131	2001	879	0.69	0.20	31.53	0.05	0.32	2.52	11.41	0.11	0.09	1.97
131	2002	978	0.72	0.19	22.48	0.05	0.30	2.08	9.52	0.14	0.08	1.78
131	2003	724	0.66	0.16	28.25	0.04	0.25	2.01	8.79	0.11	0.08	1.68
131	2004	864	0.74	0.18	32.66	0.05	0.30	2.36	10.00	0.17	0.07	2.13
724	2001	947	0.81	0.19	27.98	0.05	0.62	2.06	8.48	0.11	0.06	2.35
724	2002	926	0.68	0.17	19.52	0.03	0.28	1.75	7.51	0.12	0.06	1.84
724	2003	616	0.79	0.19	29.50	0.05	0.31	1.77	7.34	0.15	0.06	1.73
724	2004	758	0.74	0.16	21.26	0.04	0.28	1.82	7.13	0.12	0.05	1.76
538	2001	923	0.70	0.17	31.72	0.04	0.36	2.19	6.49	0.11	0.07	1.83
538	2002	909	*0.60*	*0.18*	*29.87*	*0.03*	*0.27*	*1.55*	*5.36*	*0.12*	*0.05*	*1.44*
538	2003	631	0.65	0.14	31.97	0.03	0.34	1.47	5.73	0.11	0.05	1.52
538	2004	917	0.79	0.15	20.42	0.03	0.31	1.29	4.98	0.10	0.04	1.34

Appendix B2 Annual mean wet deposition fluxes of the heavy metals over the period 1992-2004

Table B2: Wet deposition fluxes are in units of µg/m² and precipitation is in mm. Values underlined are below the 75% coverage as discussed in chapter 3

Stn	Year	nsl	V	Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
134	2001	864	*706*	*261*	*21403*	*43*	*309*	*1794*	*12099*	*97*	*84*	*2686*
134	2002	976	785	247	29071	49	300	2135	12830	138	77	2752
134	2003	594	*529*	*131*	*30595*	*42*	*229*	*1862*	*9246*	*98*	*56*	*1756*
134	2004	758	573	96	*13973*	31	251	1295	9548	93	49	2073
631	2001	1017	776	185	45767	50	372	1783	9790	136	104	2741
631	2002	892	659	158	70954	47	297	1203	6588	158	61	1652
631	2003	581	446	105	44588	39	213	1265	5292	118	49	1055
631	2004	929	787	160	40831	39	292	1229	5611	117	39	1212
318	2001	1031	*1107*	*208*	*57114*	*57*	*463*	*2228*	*10838*	*199*	*108*	*3996*
318	2002	1087	*784*	*129*	*23372*	*36*	*349*	*1983*	*8699*	*144*	*104*	*3382*
318	2003	741	618	97	21253	43	259	1220	5373	103	69	1950
318	2004	771	709	118	16241	28	284	1294	7626	101	51	1742
628	2001	1023	1000	183	24887	57	427	2351	9648	155	75	3544
628	2002	1004	719	179	21644	52	302	1618	7702	119	55	2371
628	2003	616	537	136	19147	26	241	1356	5007	79	46	1804
628	2004	870	782	226	32551	45	313	1381	6155	99	42	1986
444	2001	950	823	220	19858	34	356	1900	6785	91	56	3028
444	2002	887	747	133	13993	26	294	1349	5452	97	47	2625
444	2003	733	634	160	30319	52	272	1368	5141	95	42	1841
444	2004	753	718	123	12679	32	274	1290	4074	70	22	1825
722	2001	826	*478*	*205*	*15126*	*30*	*252*	*1196*	*6222*	*96*	*45*	*2443*
722	2002	965	*528*	*157*	*22330*	*35*	*220*	*1717*	*7249*	*116*	*53*	*2531*
722	2003	735	474	139	20023	34	192	1317	5729	101	41	3051
722	2004	817	504	160	18242	37	221	1148	5606	101	34	2772
231	2001	943	920	206	17927	49	376	2267	10995	113	105	2495
231	2002	1017	*980*	*226*	*22351*	*46*	*402*	*2024*	*10909*	*168*	*94*	*2753*
231	2003	695	607	97	20019	40	246	1457	6645	97	59	1761
231	2004	854	947	117	27272	46	356	1795	8829	151	59	2516
235	2001	966	1252	129	25401	43	516	1975	9364	132	78	4065
235	2002	1064	*1257*	*206*	*28001*	*48*	*469*	*1780*	*9118*	*172*	*96*	*4601*
235	2003	707	915	113	25463	39	337	1216	5851	133	48	2784
235	2004	816	1154	191	18082	37	380	1636	7218	148	68	3661

Table B2 continued

Stn	Year	nsl	V	Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
934	2001	1029	*685*	*264*	*90855*	*69*	*311*	*2512*	*8106*	*232*	*67*	*1585*
934	2002	1108	*739*	*301*	*69941*	*54*	*293*	*1588*	*6671*	*237*	*66*	*1421*
934	2003	715	651	252	104200	71	257	952	5014	207	38	1146
934	2004	862	*597*	*176*	*42227*	*44*	*248*	*828*	*4298*	*123*	*42*	*1040*
434	2001	1276	1980	238	60801	143	1032	2804	16686	179	157	3701
434	2002	1145	1680	250	48497	74	785	2364	8780	142	70	2500
434	2003	627	967	146	32501	53	431	1583	6453	101	58	1736
434	2004	966	1582	210	32193	52	653	2040	7589	119	50	2125
732	2001	1079	753	221	18463	37	348	1883	7543	95	55	2915
732	2002	963	618	125	15082	29	249	1649	5902	114	49	3229
732	2003	654	527	126	23694	38	244	1236	5099	114	45	3100
732	2004	1045	836	139	17159	36	358	1321	6072	113	42	3710
929	2001	869	536	115	19671	30	264	1953	6645	91	51	1811
929	2002	870	496	80	18669	23	199	1287	5357	95	50	1618
929	2003	678	448	86	20055	27	224	974	4095	58	28	1542
929	2004	851	608	205	26936	25	223	1142	5214	86	36	1682
131	2001	879	609	179	27701	44	281	2211	10023	100	83	1729
131	2002	978	704	186	21994	48	297	2035	9316	135	78	1741
131	2003	724	480	117	20462	29	182	1458	6364	82	56	1220
131	2004	864	643	159	28214	40	261	2038	8635	146	64	1840
724	2001	947	763	183	26483	49	587	1948	8025	101	54	2224
724	2002	926	625	158	18069	31	260	1621	6948	111	52	1706
724	2003	616	489	118	18179	32	191	1093	4523	91	35	1066
724	2004	758	562	121	16121	33	215	1383	5404	91	35	1332
538	2001	923	649	160	29286	36	330	2024	5997	100	63	1689
538	2002	909	*542*	*161*	*27139*	*28*	*248*	*1406*	*4867*	*109*	*43*	*1304*
538	2003	631	411	89	20167	22	215	929	3615	69	32	961
538	2004	917	723	139	18724	25	284	1186	4565	91	38	1232

rivm

Appendix C Graphs of trends in major components

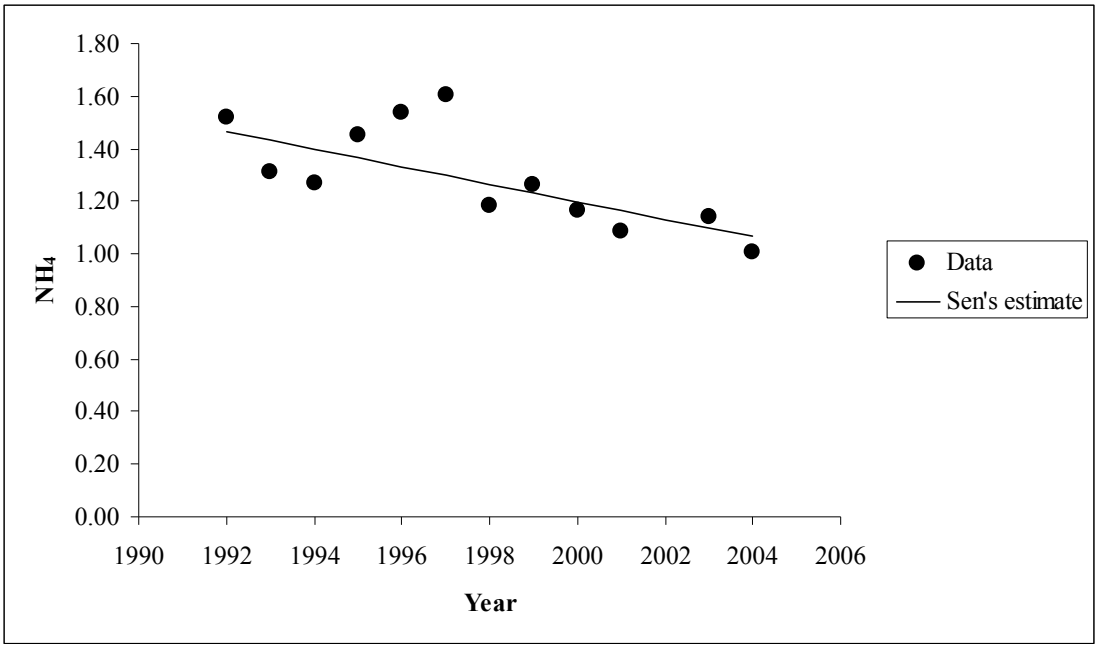

Figure C1: Time series of ammonium concentrations (in mg/l) in precipitation.

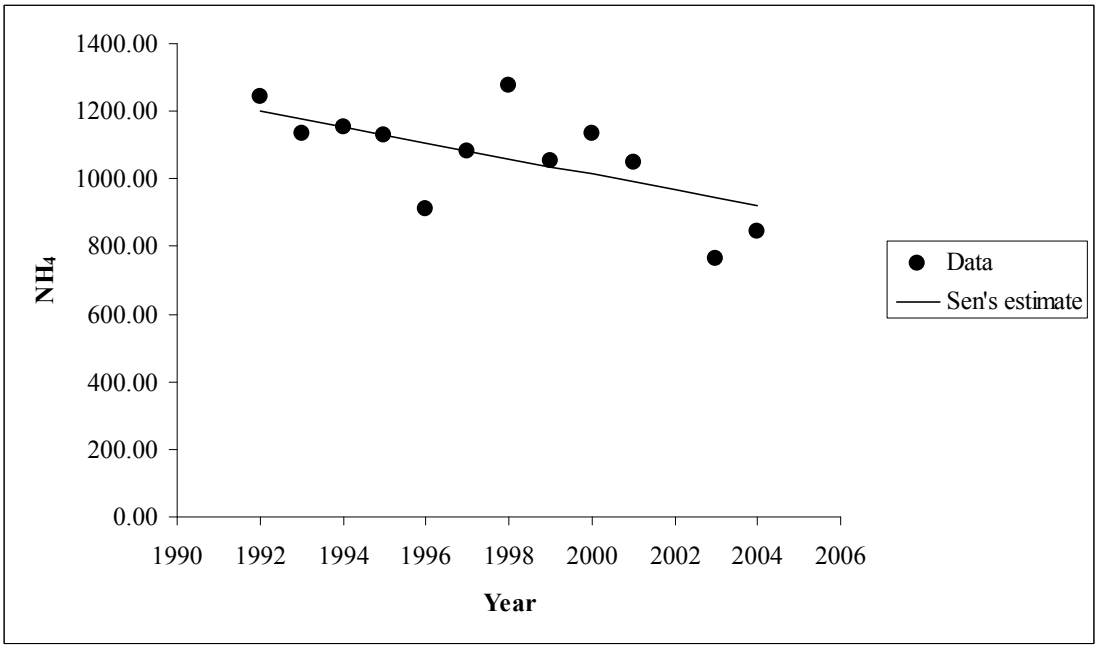

Figure C2: Time series of ammonium wet deposition flux (in mg/m^2)

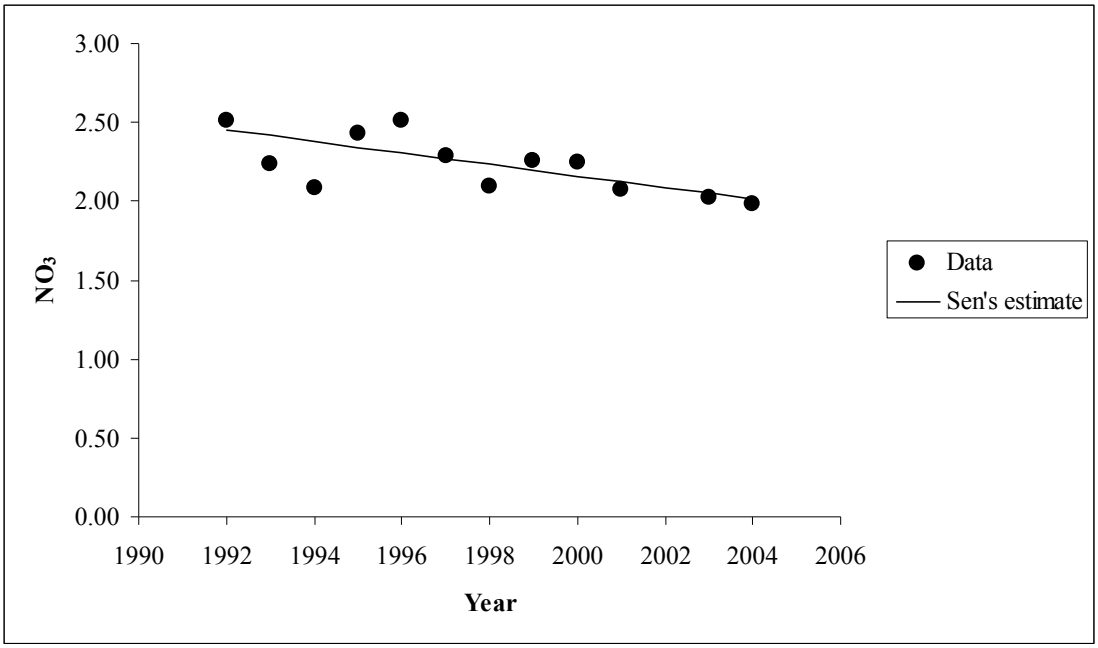

Figure C3: Time series of nitrate concentrations (in mg/l) in precipitation.

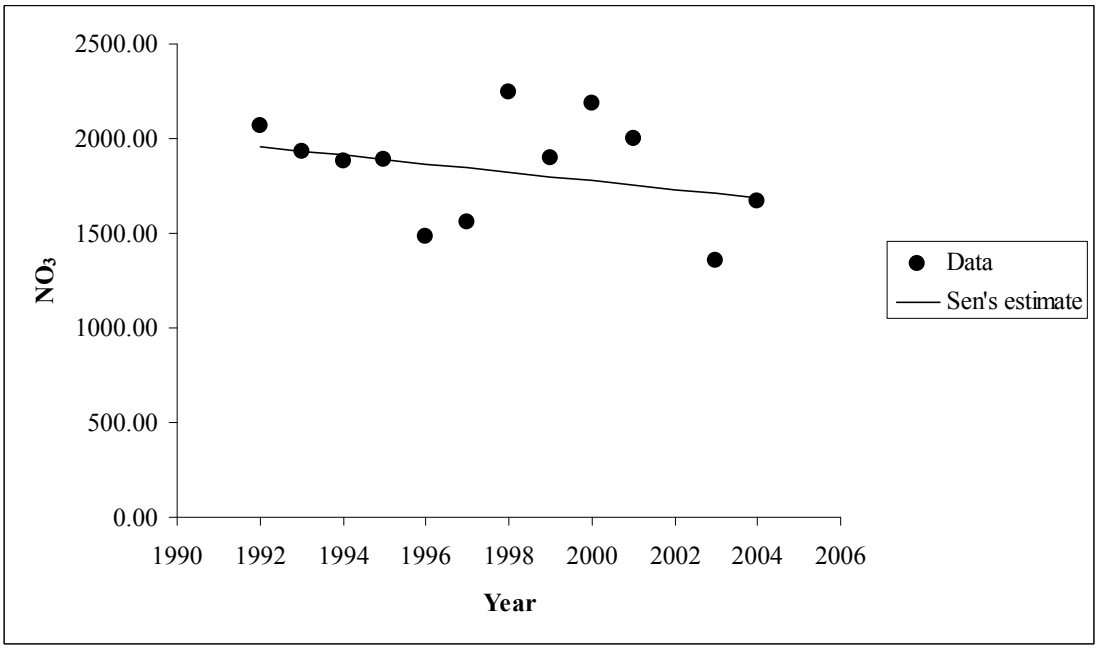

Figure C4: Time series of nitrate wet deposition flux (in mg/m^2).

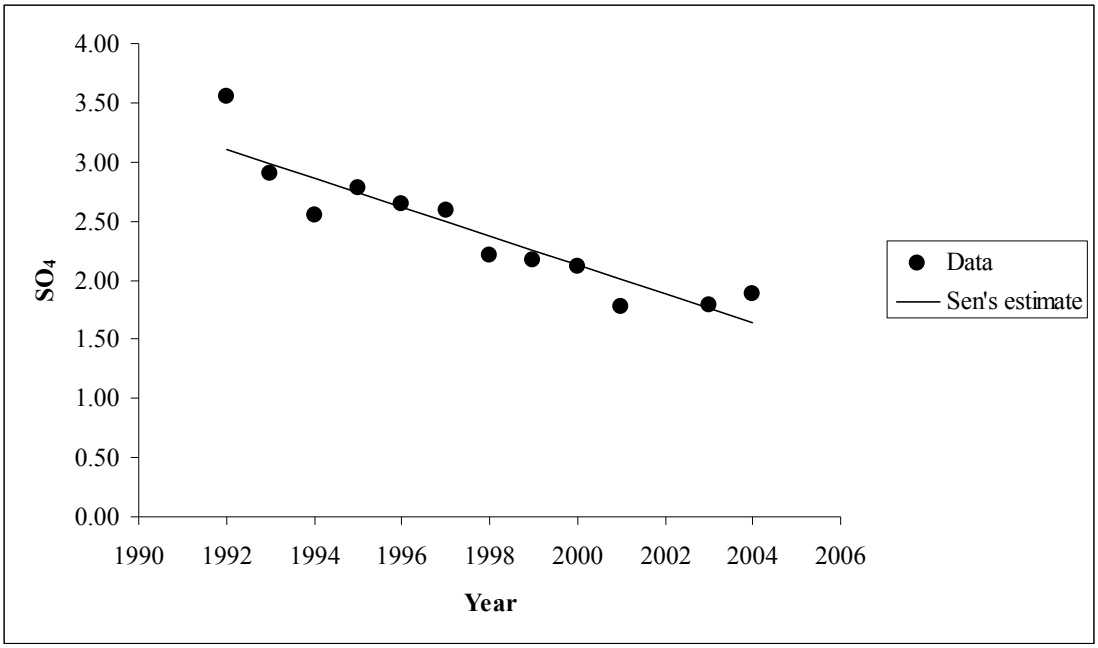

Figure C5: Time series of sulfate concentrations (in mg/l) in precipitation.

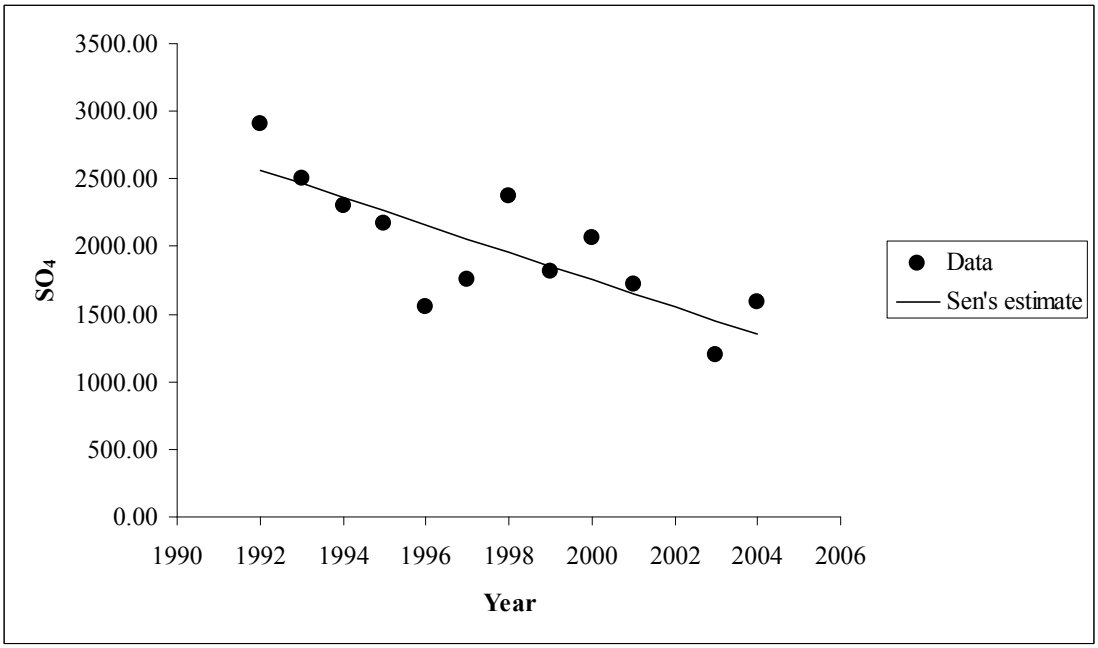

Figure C6: Time series of sulfate wet deposition flux (in mg/m²).

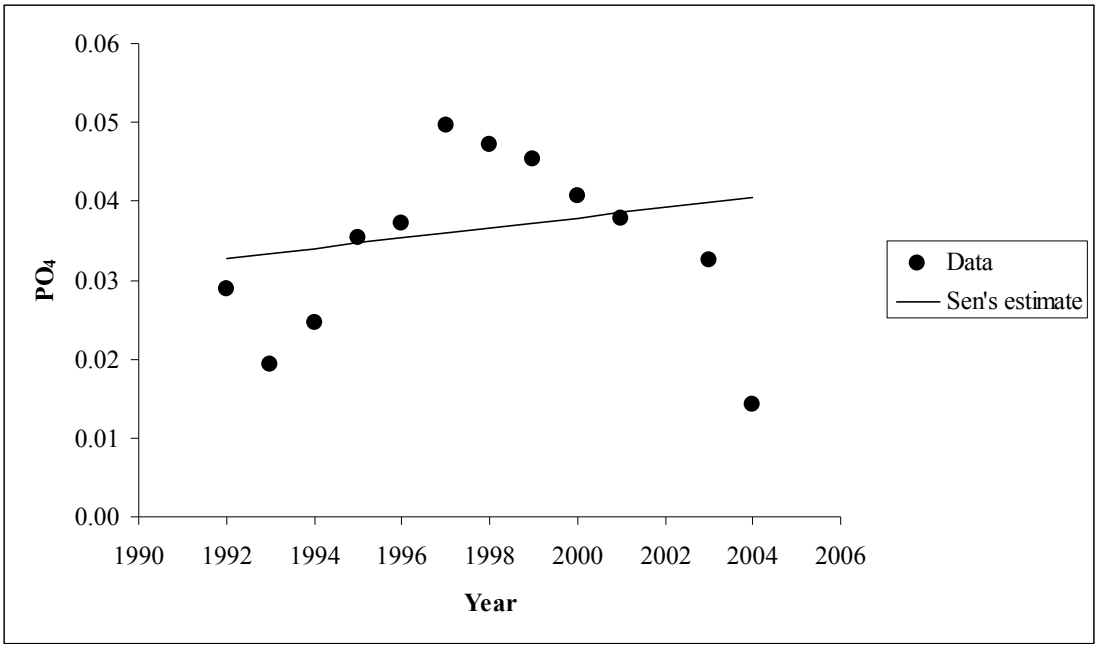

Figure C7: Time series of phosphate concentrations (in mg/l) in precipitation. Note that the observed concentrations of PO_4 are close to the detection limit (see Appendix E).

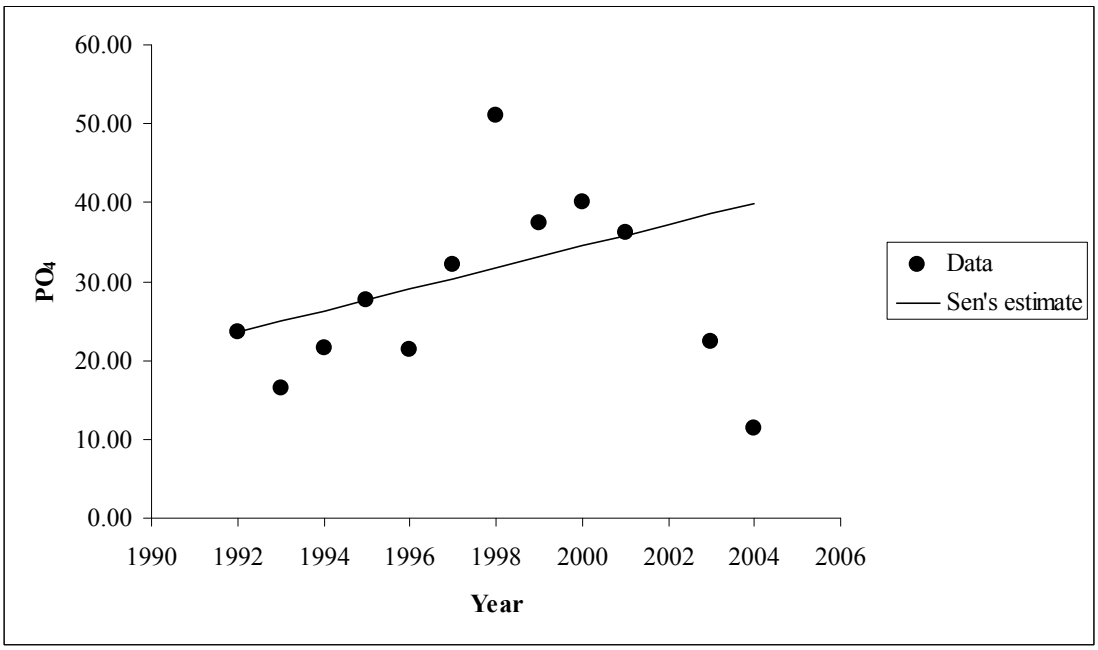

Figure C8: Time series of phosphate wet deposition flux (in mg/m²).

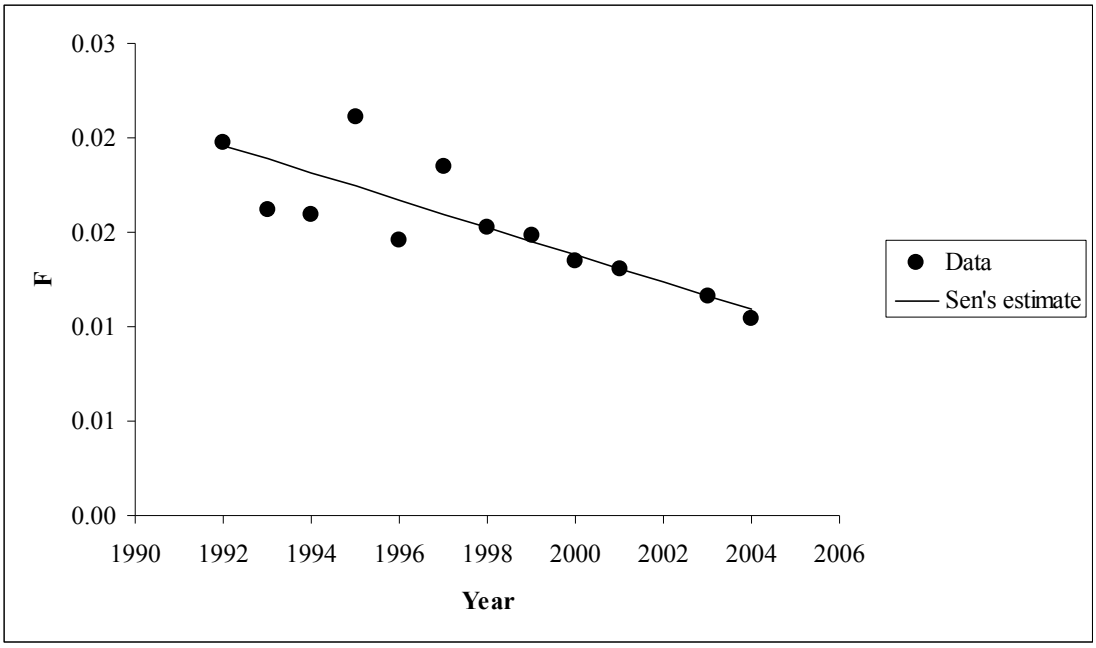

Figure C9: Time series of fluoride concentrations (in mg/l) in precipitation.

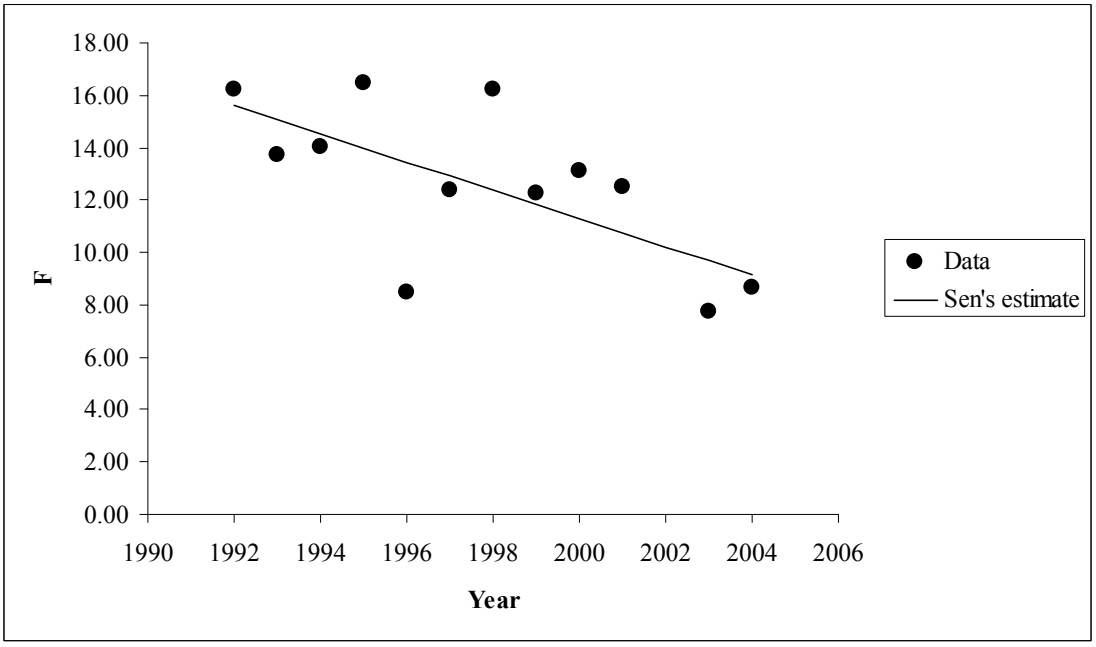

Figure C10: Time series of fluoride wet deposition flux (in mg/m^2).

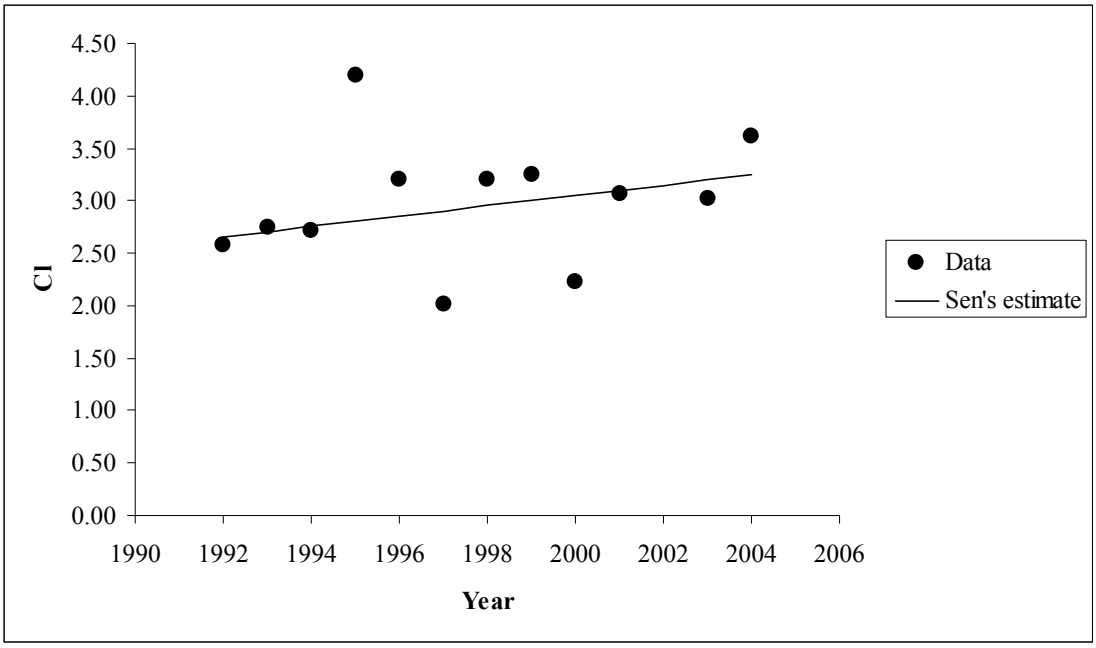

Figure C11: Time series of chloride concentrations (in mg/l) in precipitation.

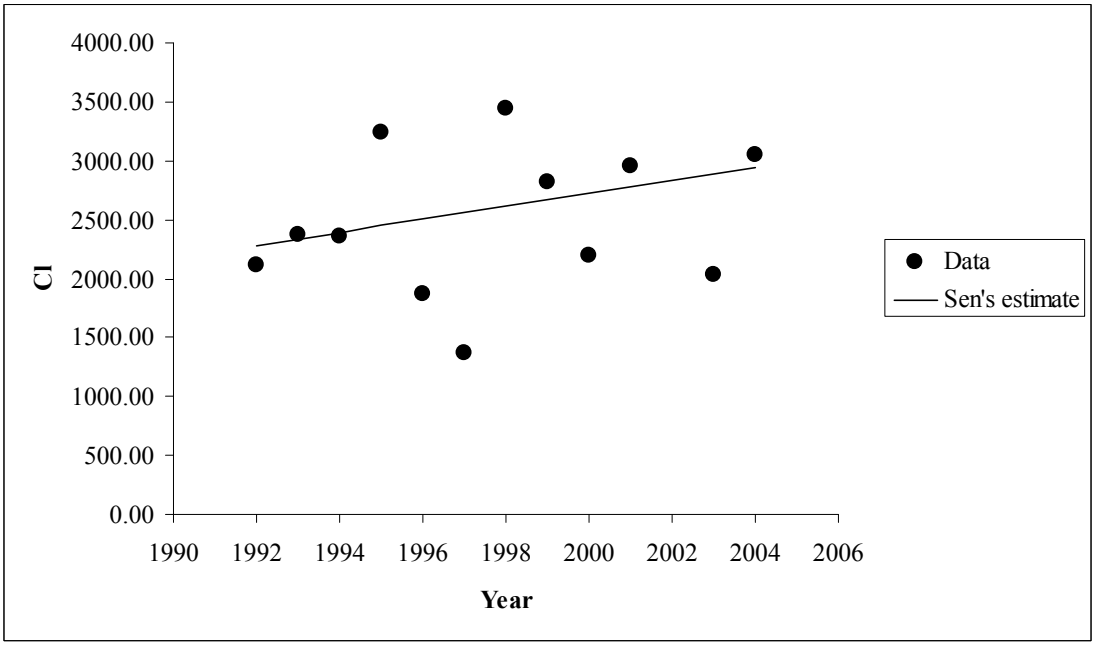

Figure C12: Time series of chloride wet deposition flux (in mg/m^2).

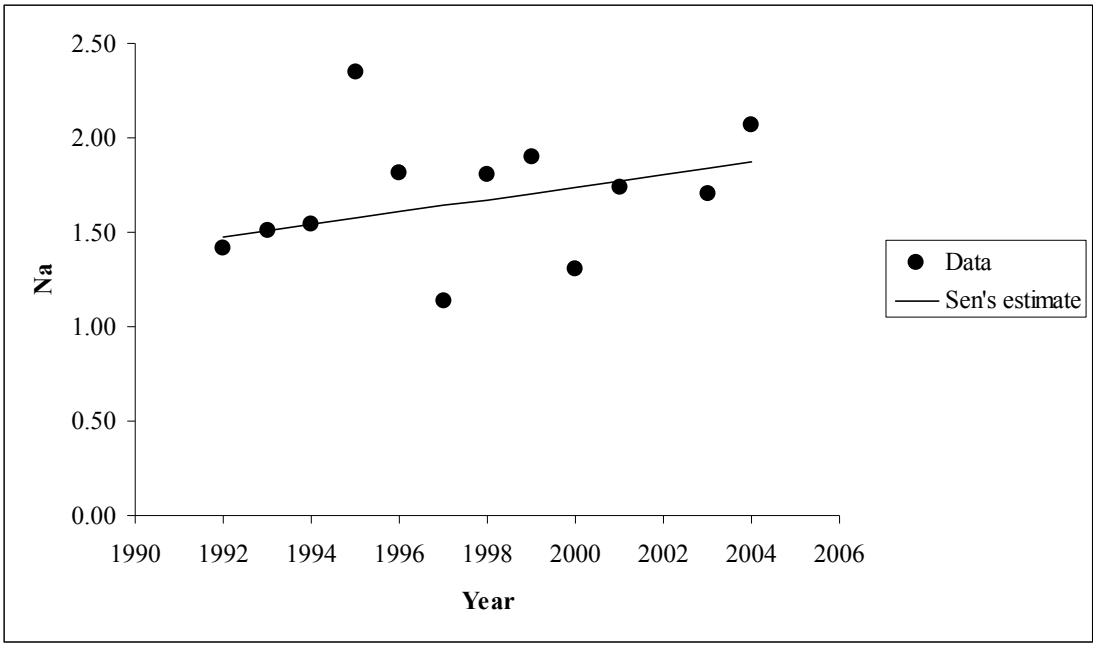

Figure C13: Time series of sodium concentrations (in mg/l) in precipitation.

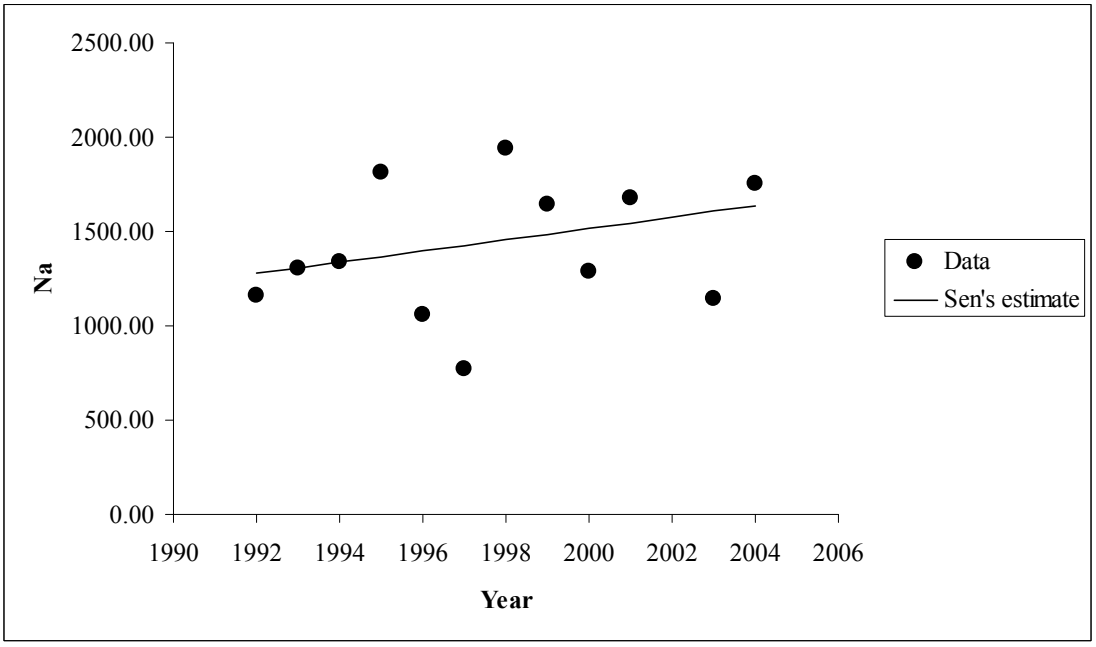

Figure C14: Time series of sodium wet deposition flux (in mg/m^2).

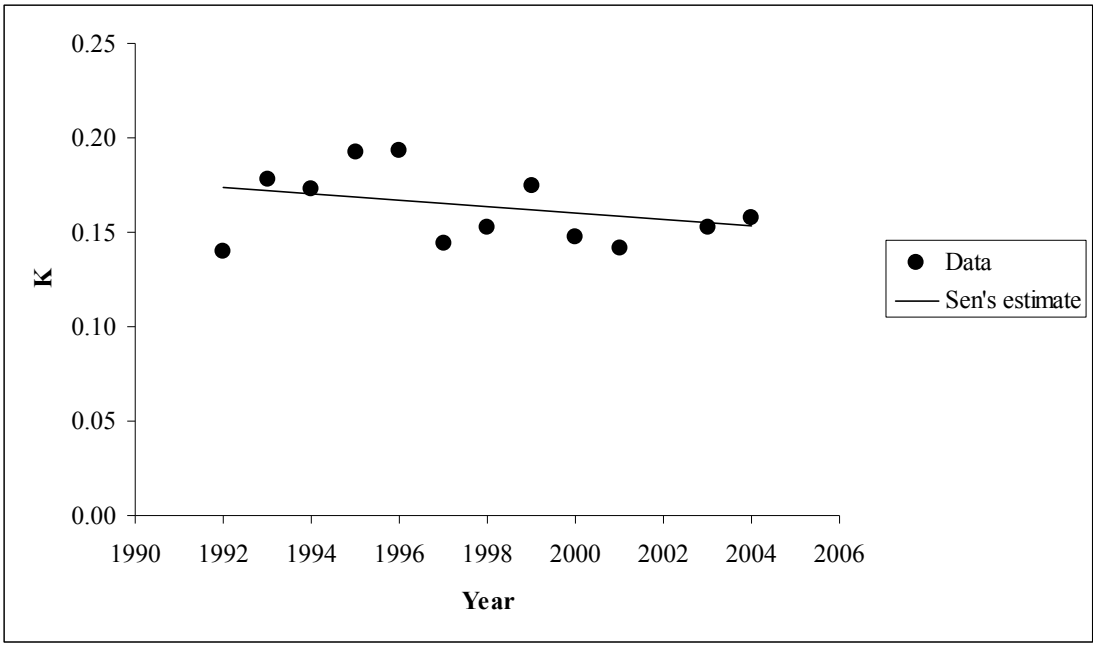

Figure C15: Time series of potassium concentrations (in mg/l) in precipitation.

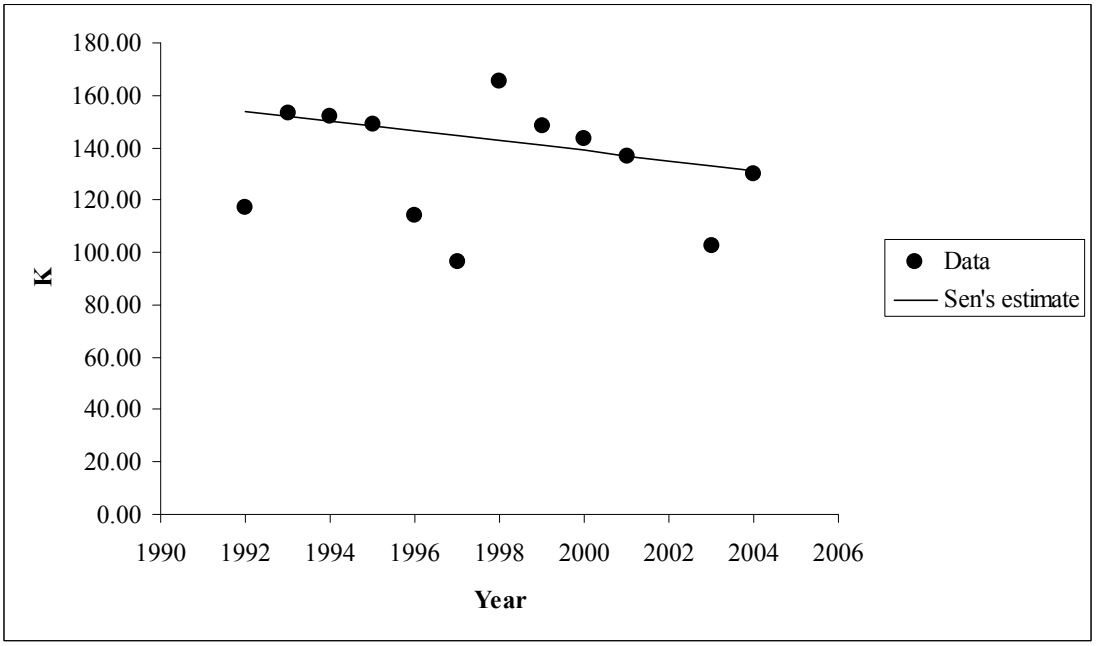

Figure C16: Time series of potassium wet deposition flux (in mg/m^2).

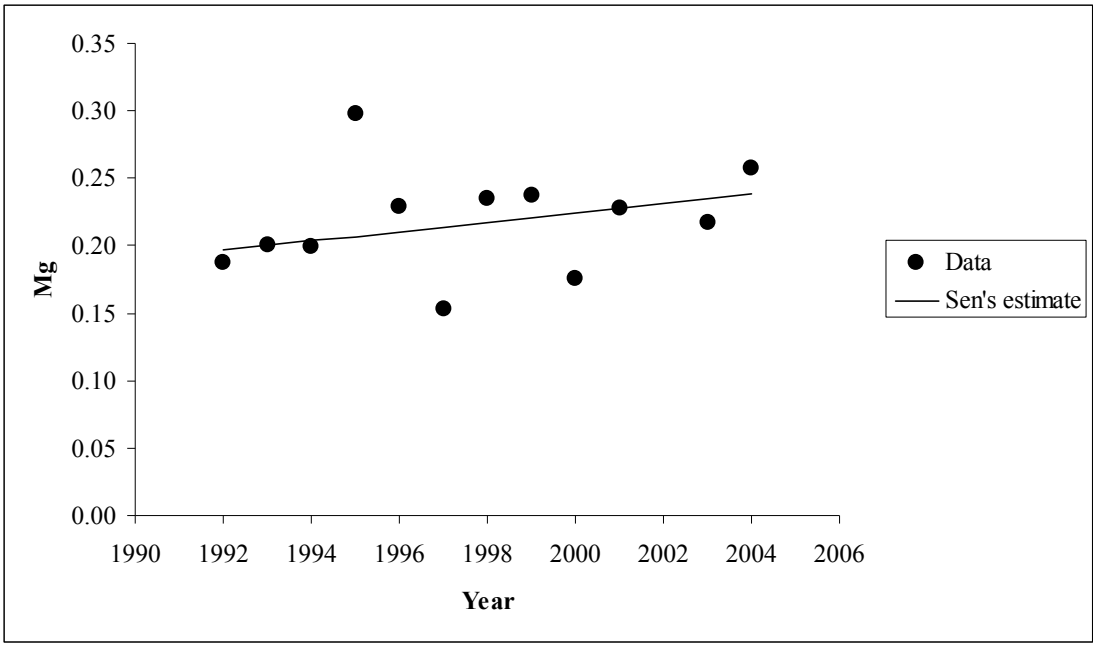

Figure C17: Time series of magnesium concentrations (in mg/l) in precipitation.

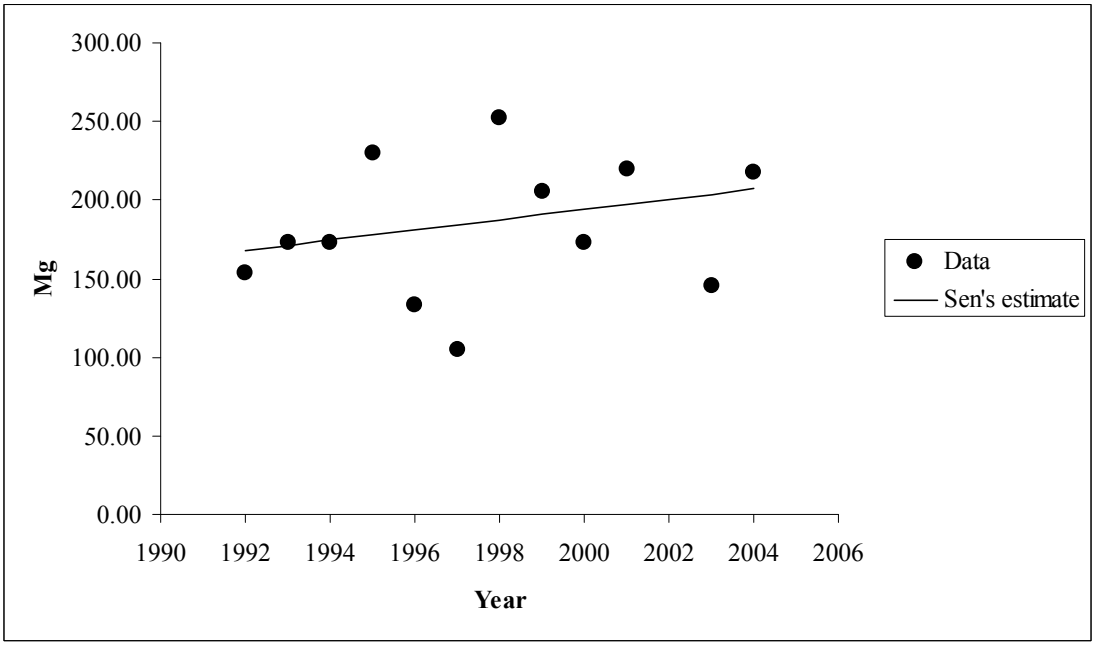

Figure C18: Time series of magnesium wet deposition flux (in mg/m^2).

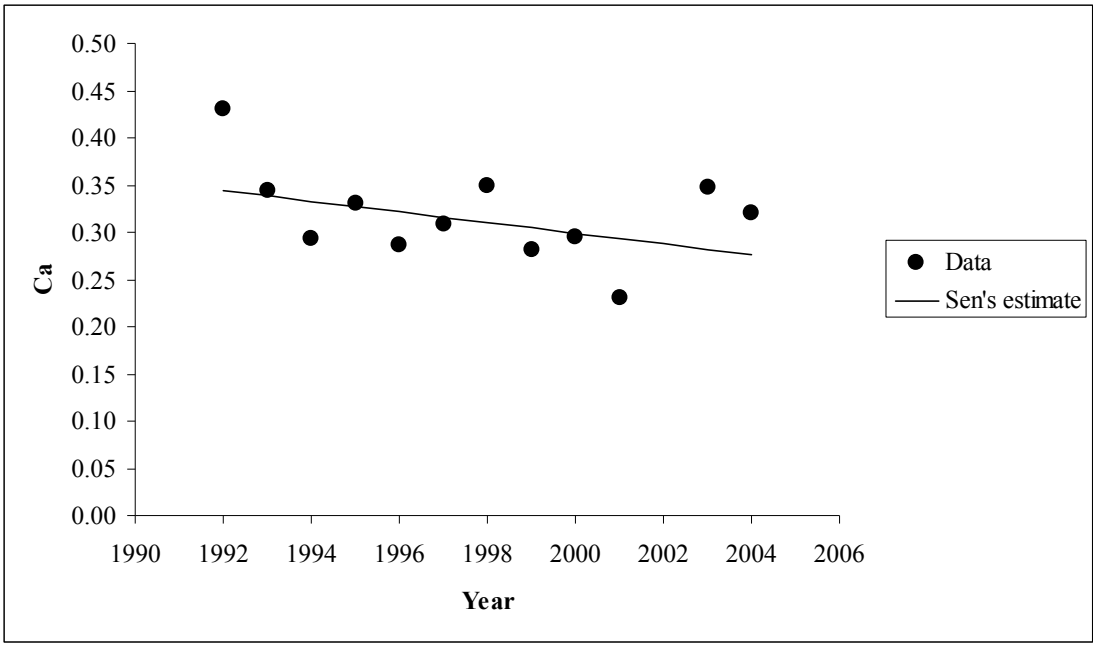

Figure C19: Time series of calcium concentrations (in mg/l) in precipitation.

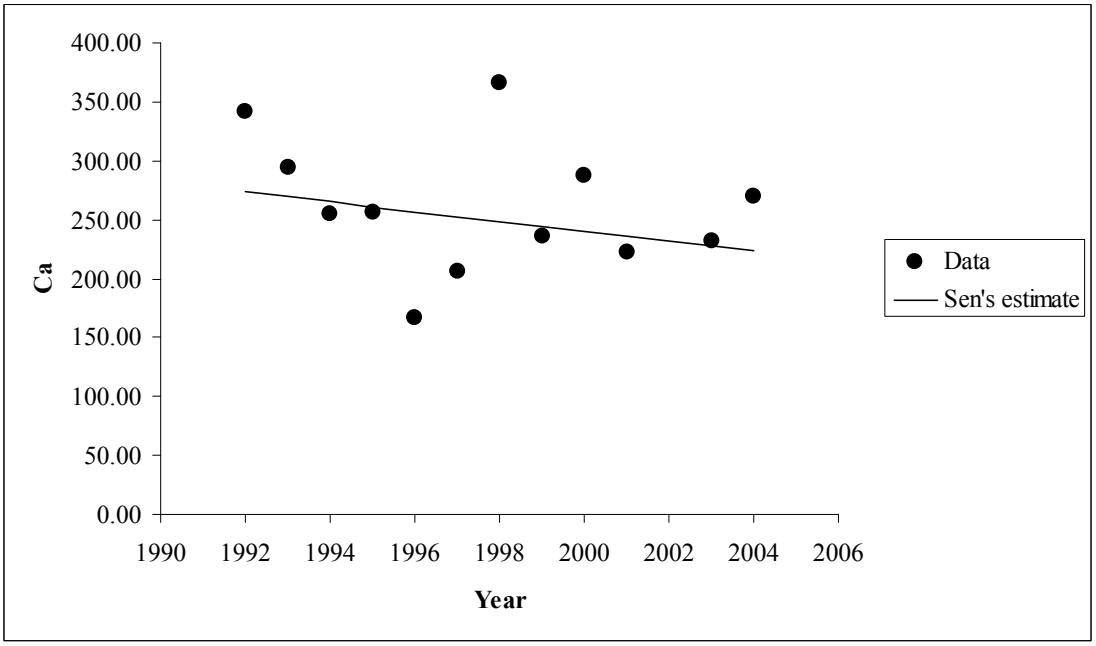

Figure C20: Time series of calcium wet deposition flux (in mg/m^2).

Appendix D Graphs of trends in heavy metals

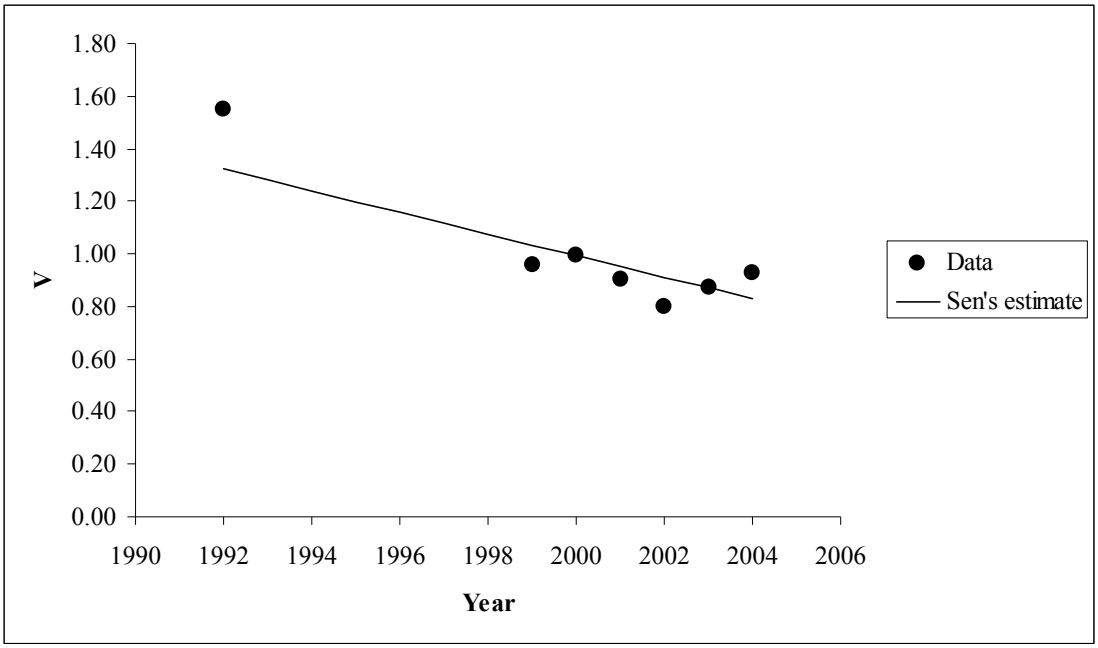

Figure D1: Time series of vanadium concentrations (in µg/l) in precipitation[5]

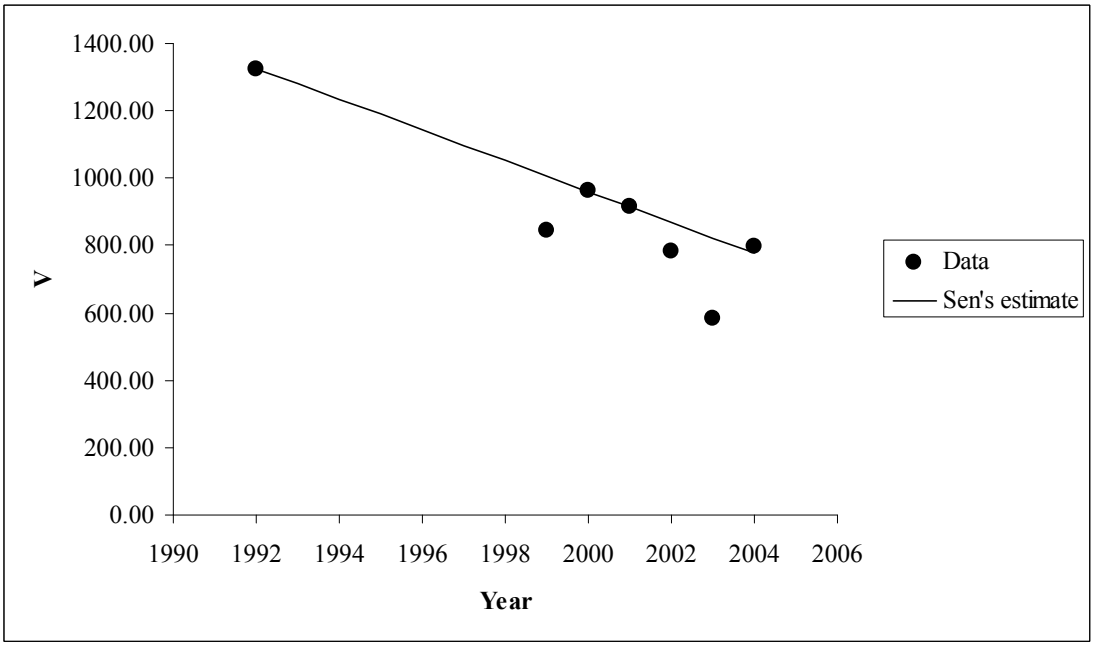

Figure D2: Time series of vanadium wet deposition flux (in µg/m^2)[5]

[5] Sen's estimate gives the best fit to the available data, however notice the missing data from 1993-1998 which prevents obtaining a proper regression analysis

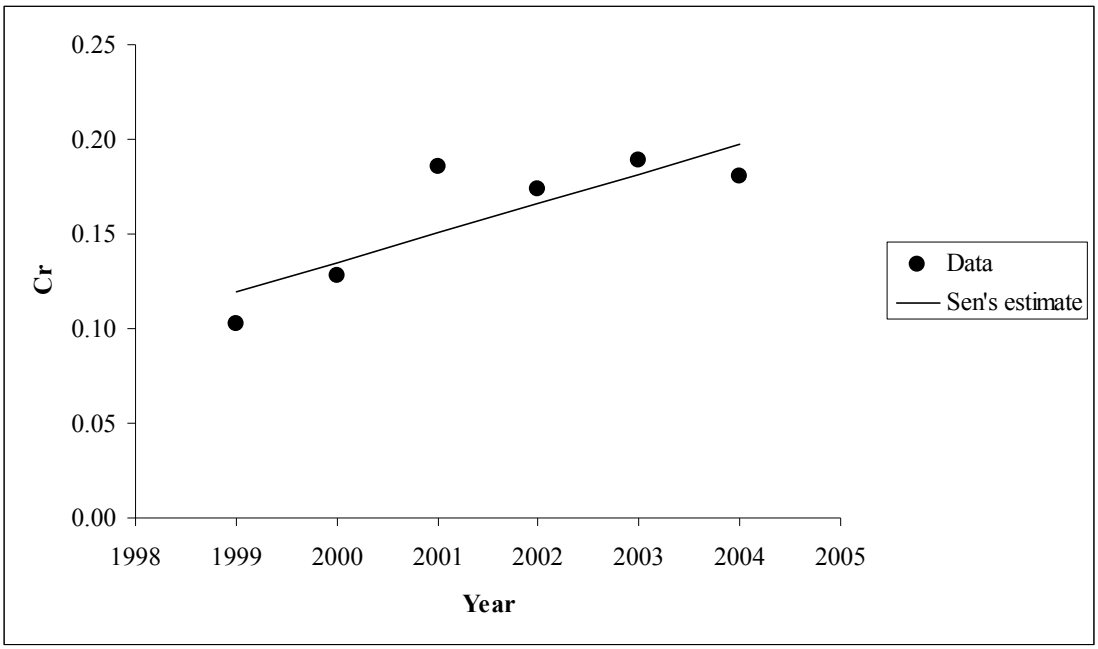

Figure D3: Time series of chromium concentrations (in µg/l) in precipitation.

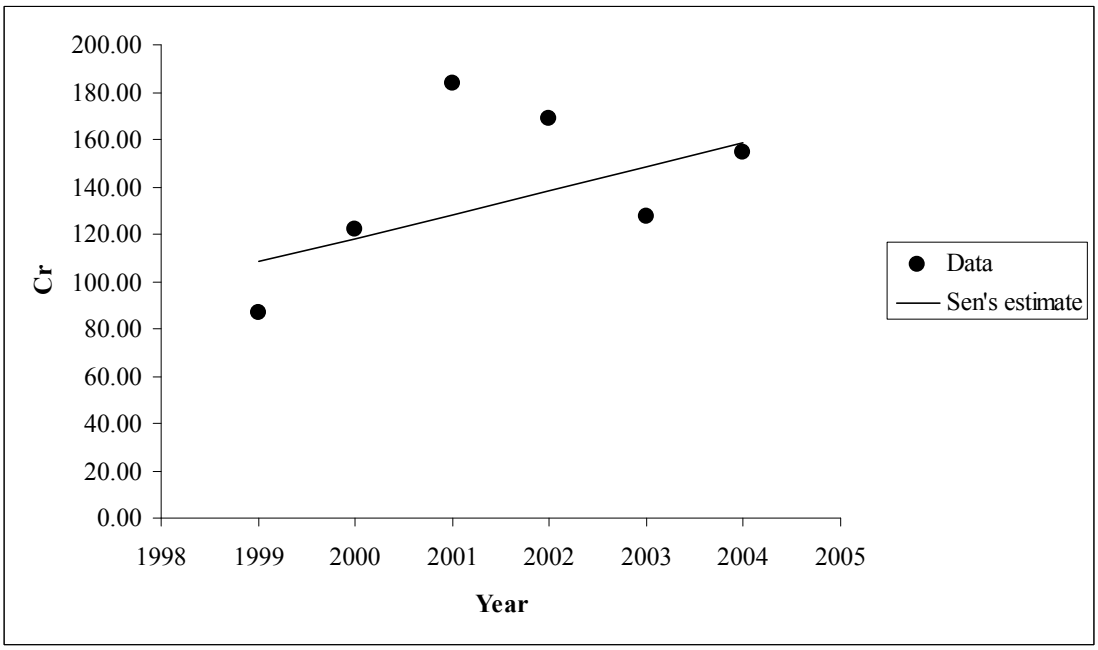

Figure D4: Time series of chromium wet deposition flux (in µg/m²).

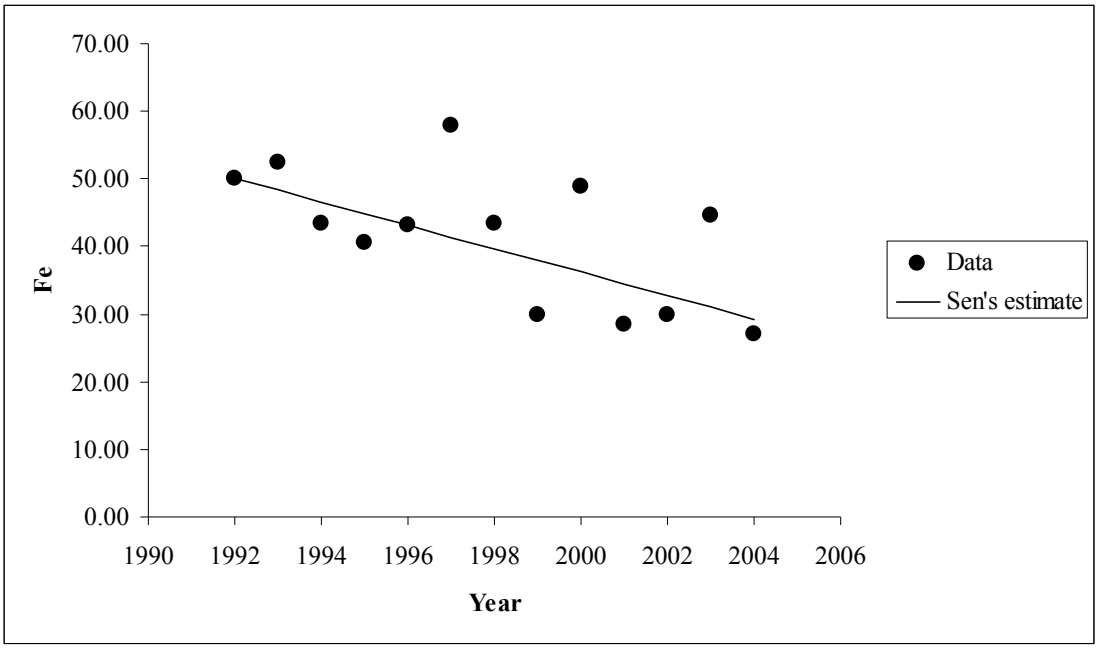

Figure D5: Time series of iron concentrations (in µg/l) in precipitation.

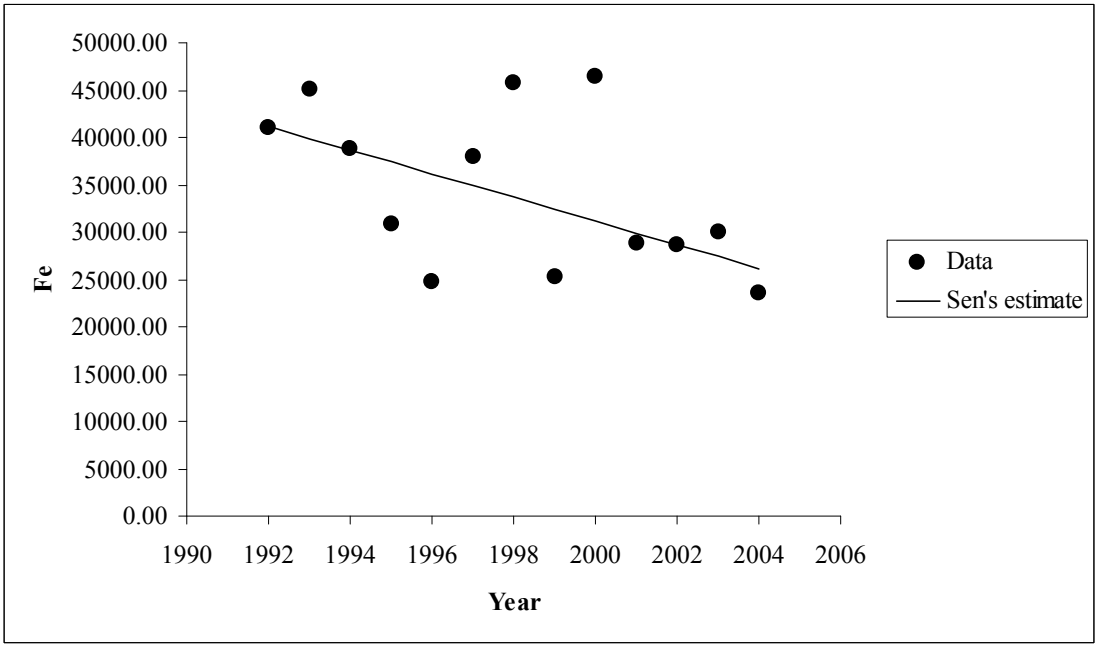

Figure D6: Time series of iron wet deposition flux (in µg/m²).

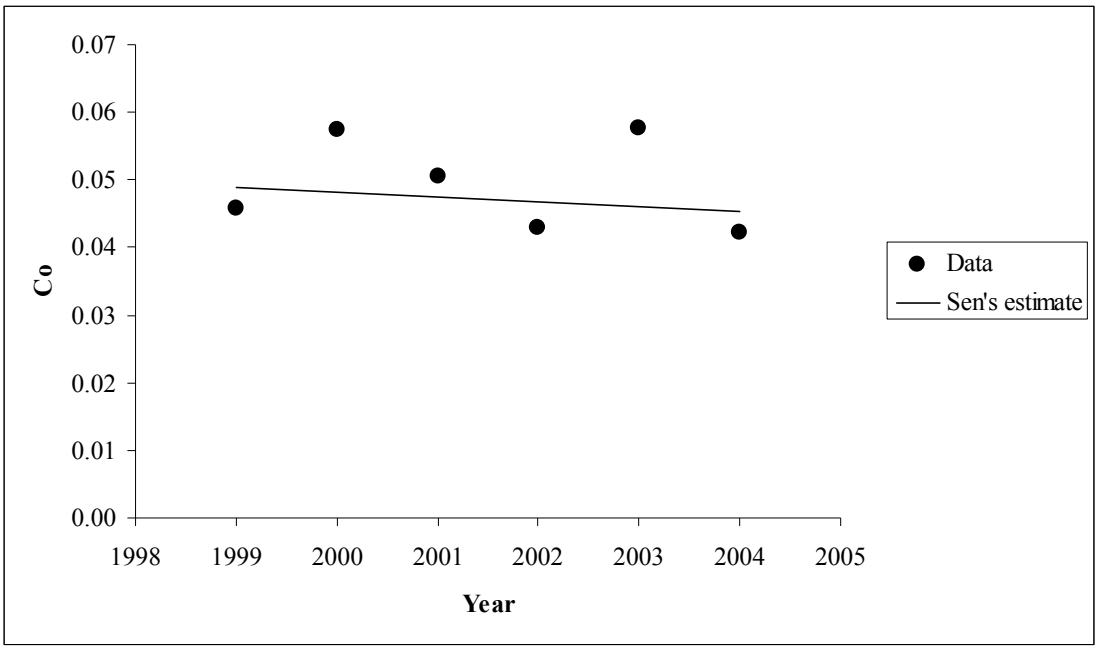

Figure D7: Time series of cobalt concentrations (in µg/l) in precipitation.

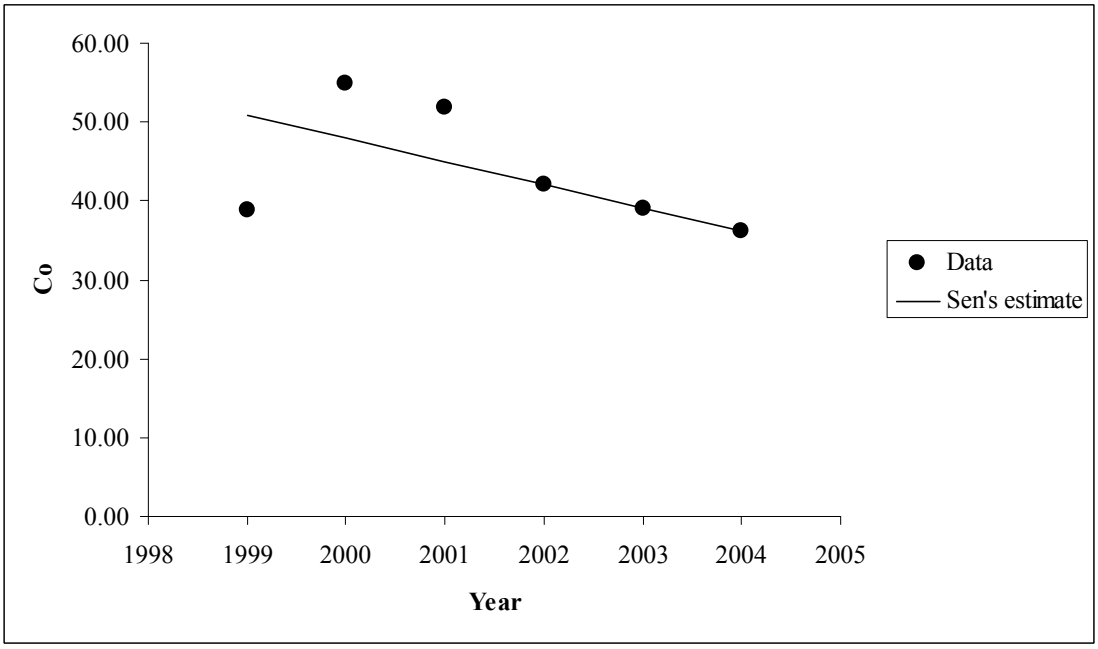

Figure C8: Time series of cobalt wet deposition flux (in µg/m²).

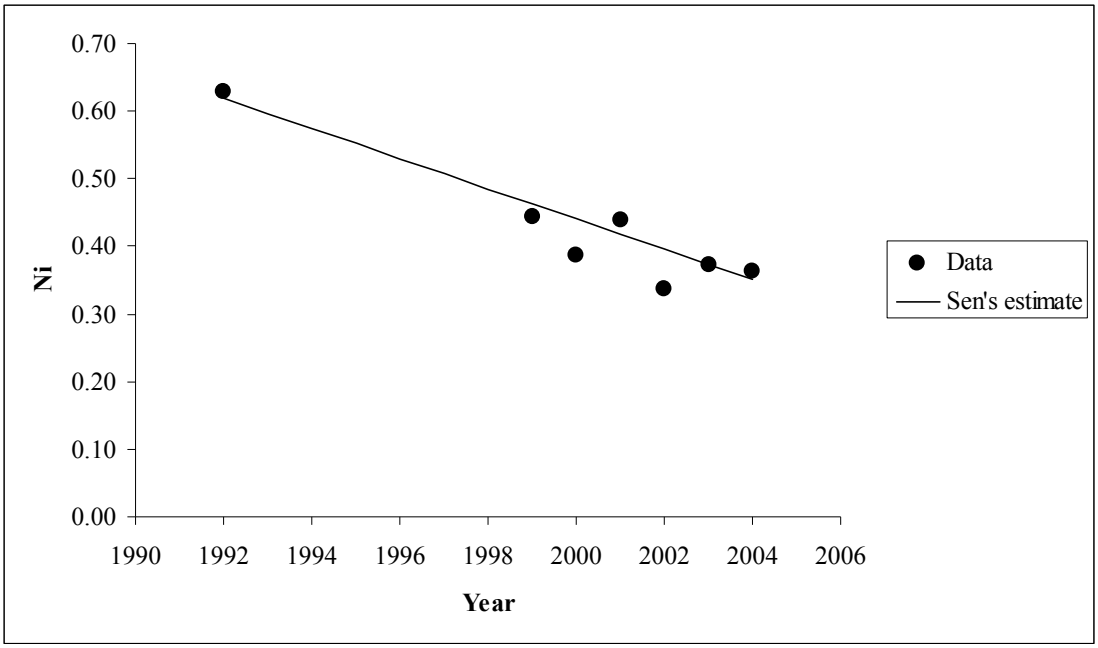

Figure D9: Time series of nickel concentrations (in µg/l) in precipitation[6]

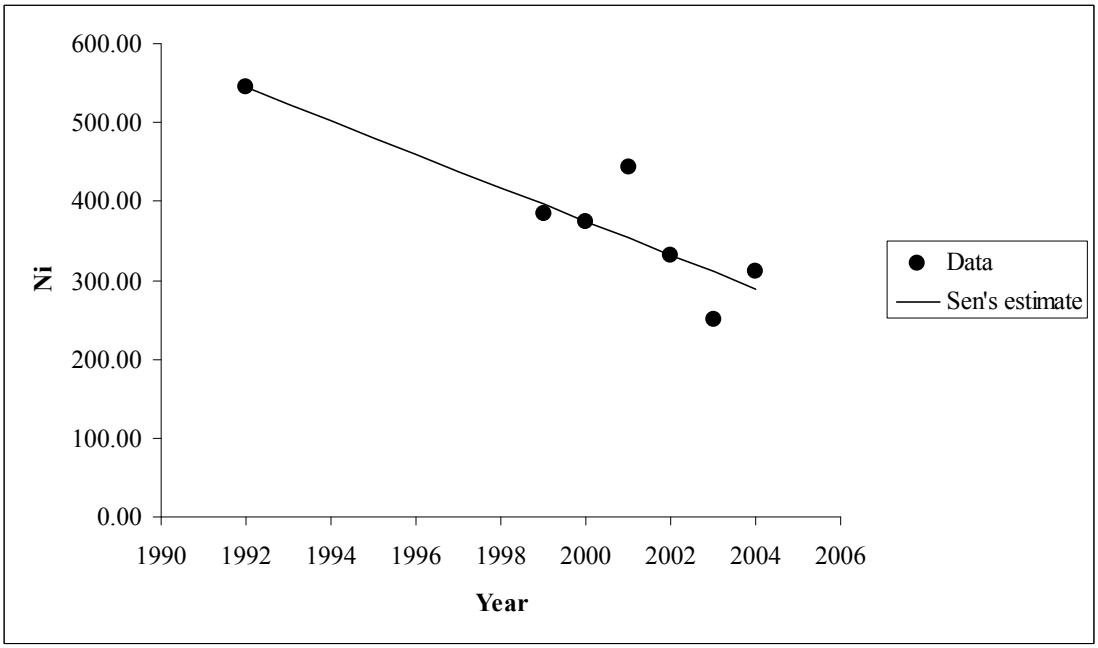

Figure D10: Time series of nickel wet deposition flux (in µg/m²)[6]

[6] Sen's estimate gives the best fit to the available data, however notice the missing data from 1993-1998 which prevents obtaining a proper regression analysis

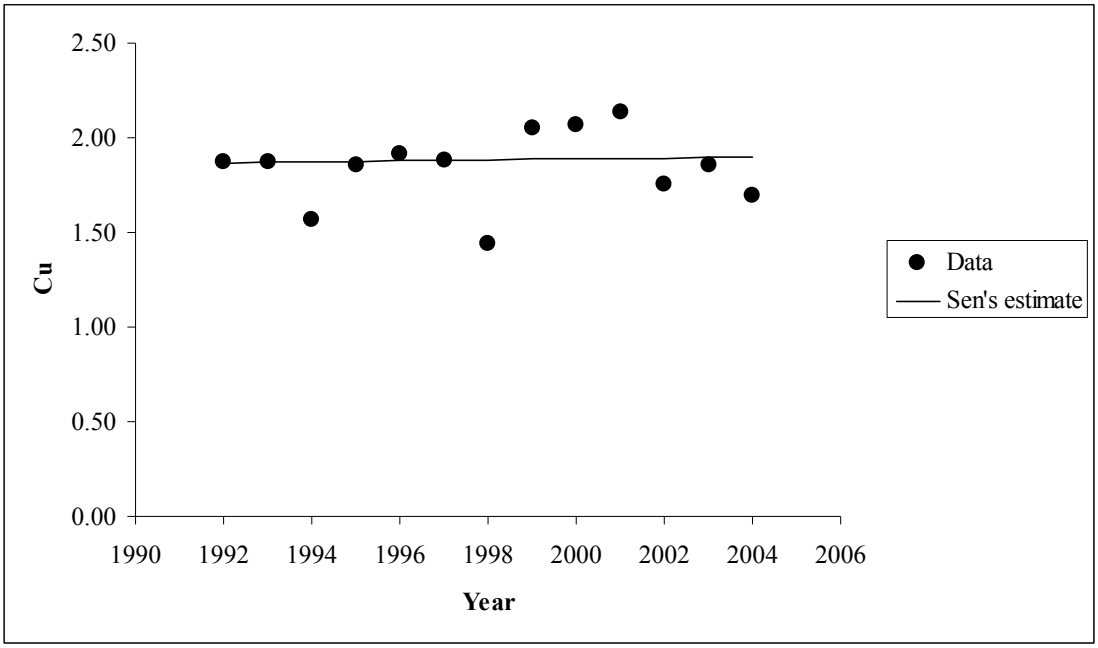

Figure D11: Time series of copper concentrations (in µg/l) in precipitation.

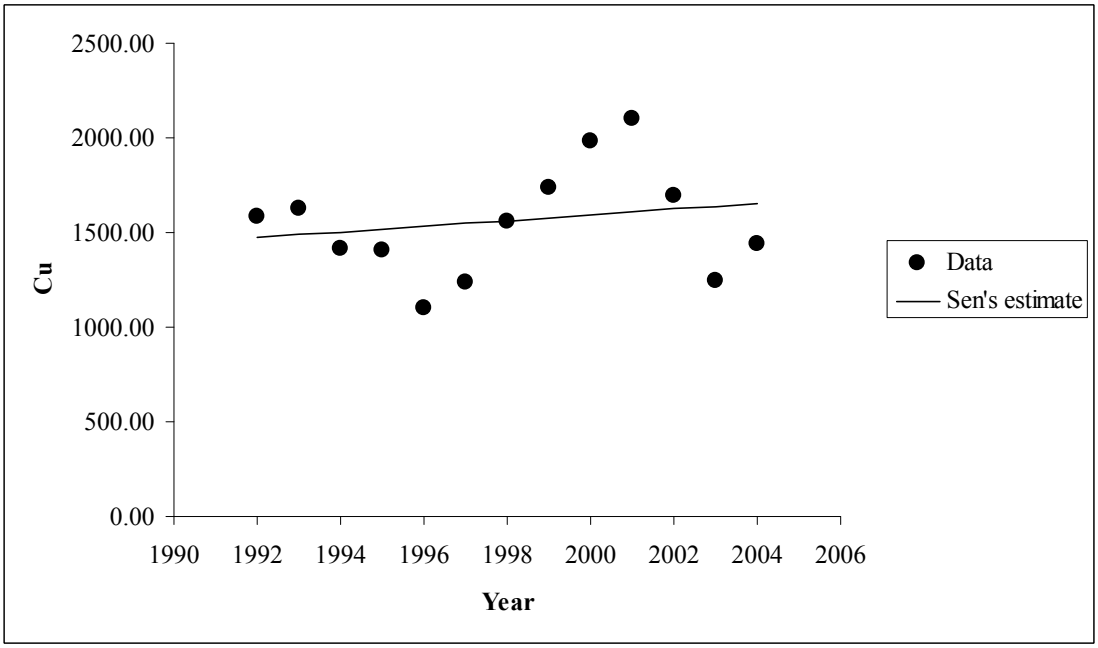

Figure D12: Time series of copper wet deposition flux (in µg/m²).

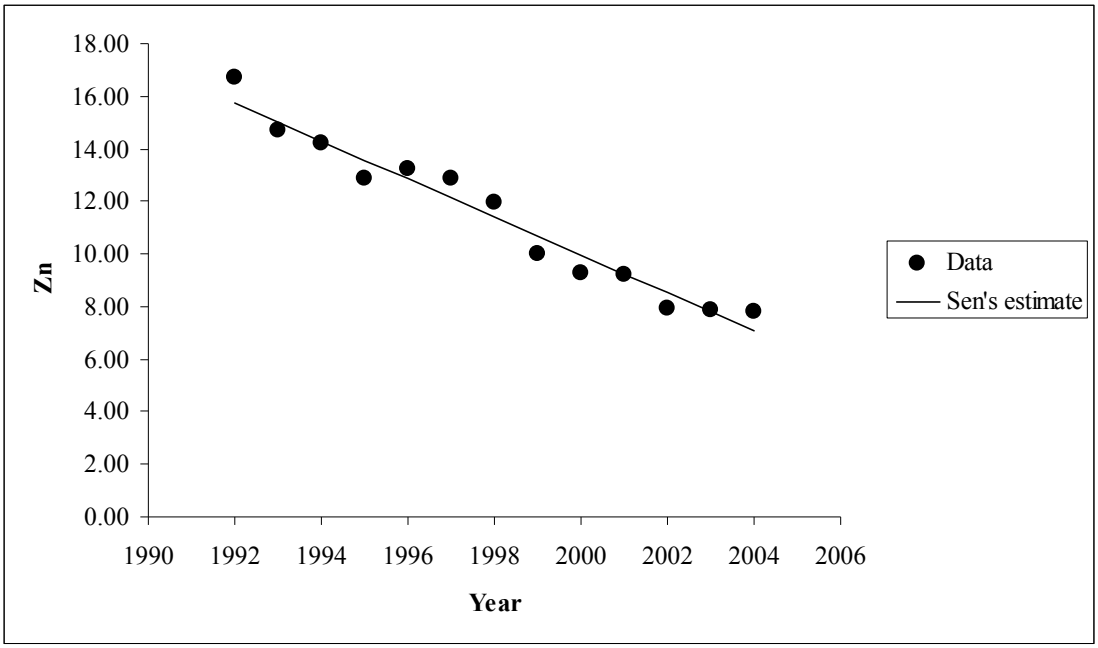

Figure D13: Time series of zinc concentrations (in µg/l) in precipitation.

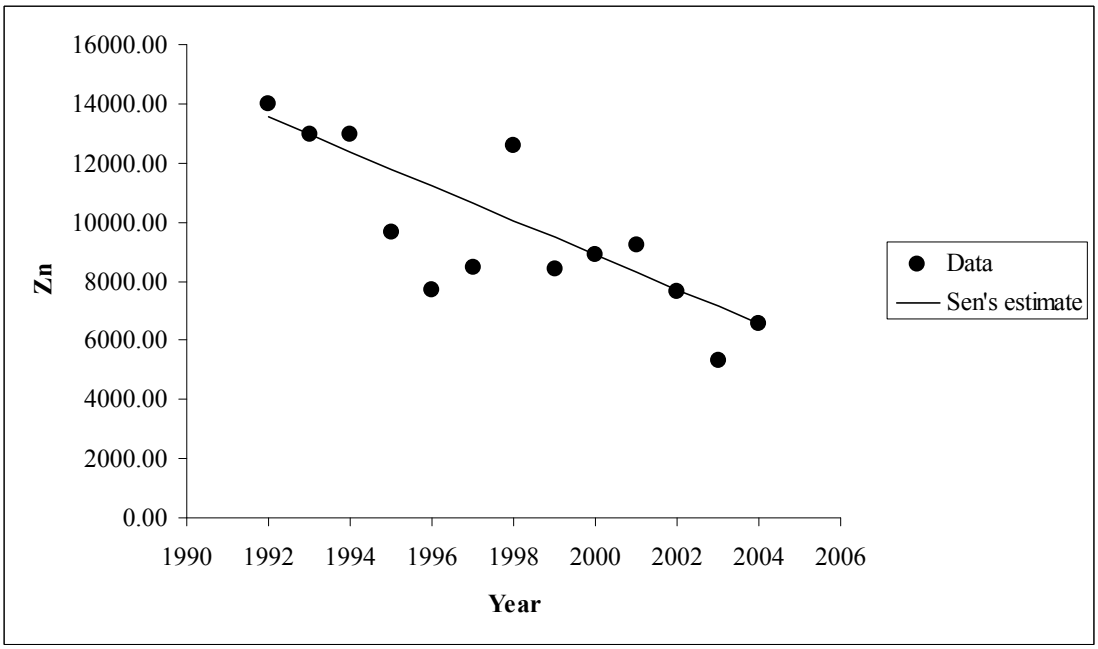

Figure D14: Time series of zinc wet deposition flux (in µg/m²).

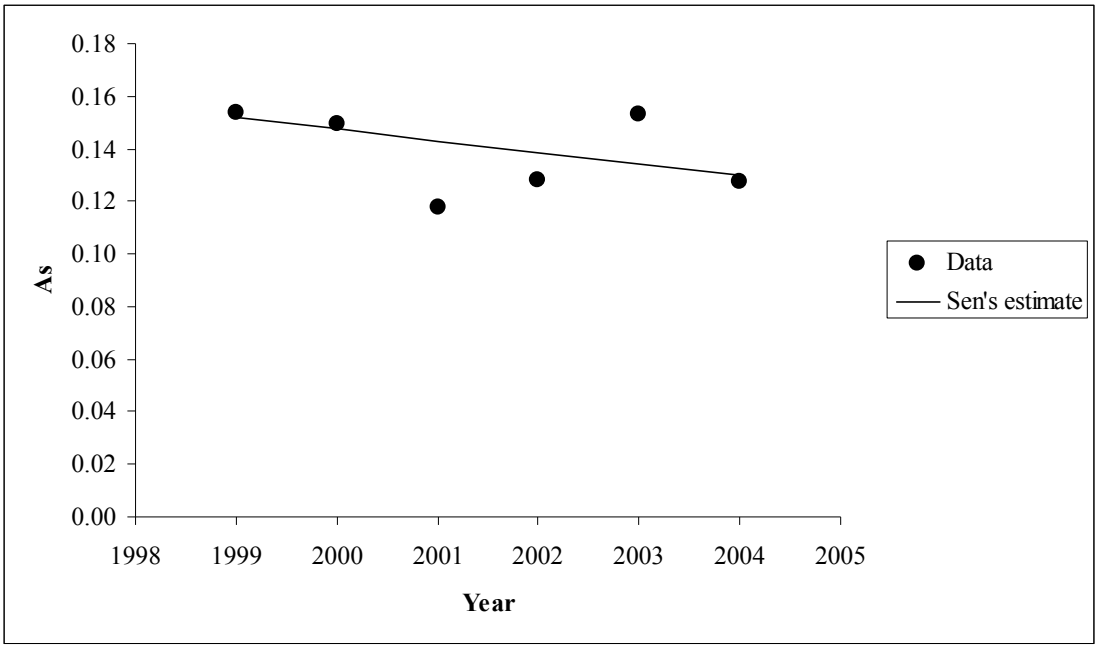

Figure D15: Time series of arsenic concentrations (in µg/l) in precipitation.

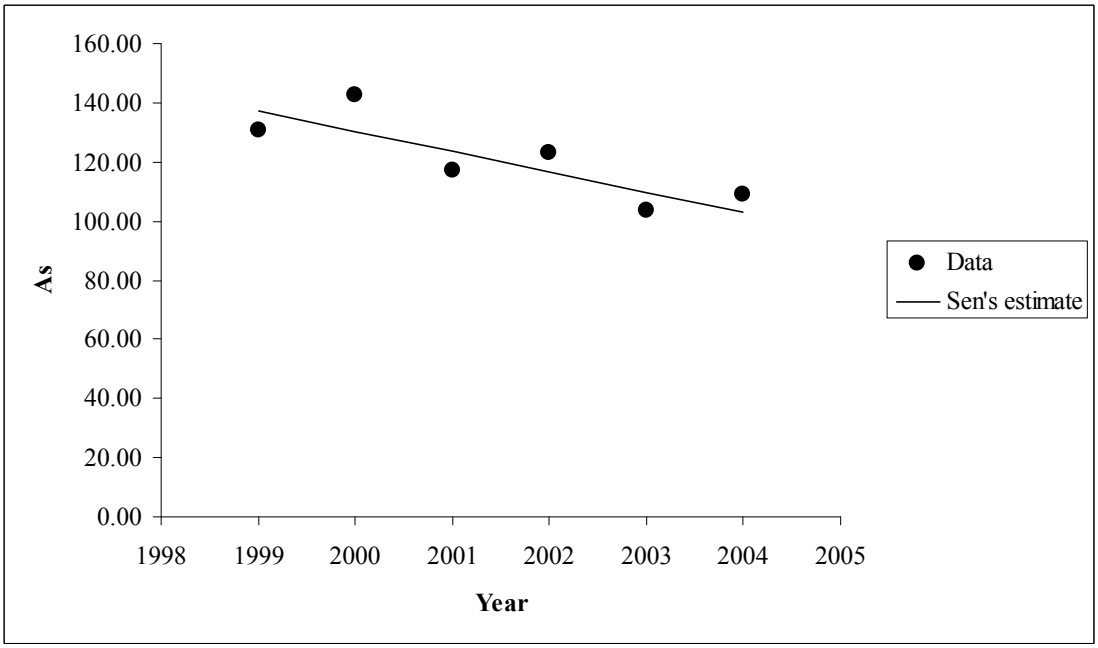

Figure D16: Time series of arsenic wet deposition flux (in µg/m^2).

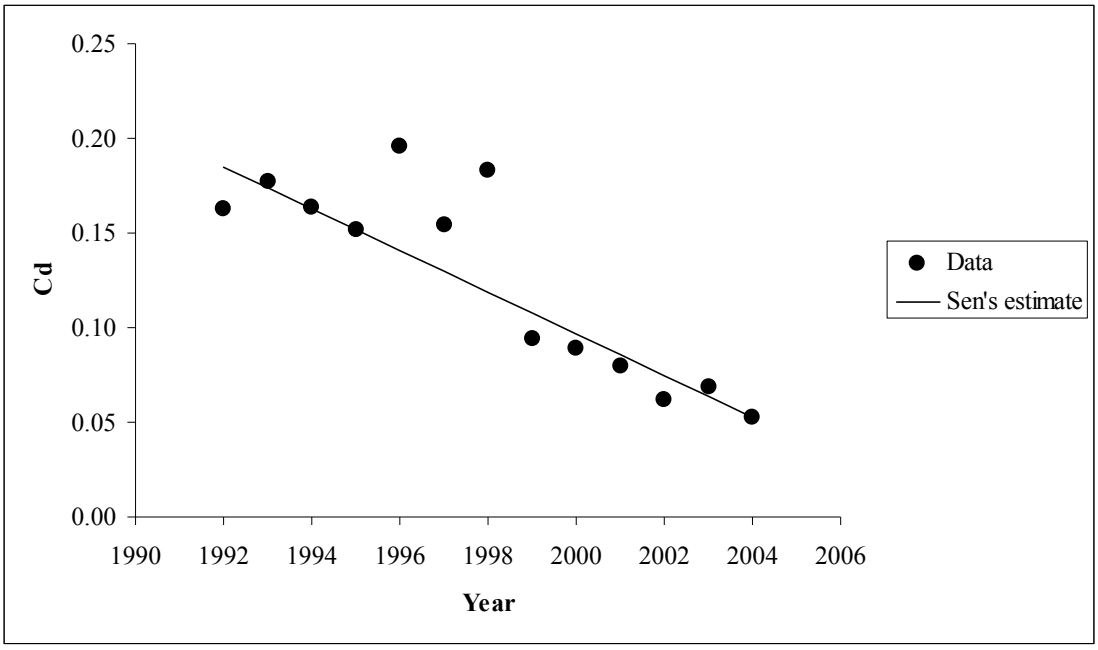

Figure D17: Time series of cadmium concentrations (in µg/l) in precipitation.

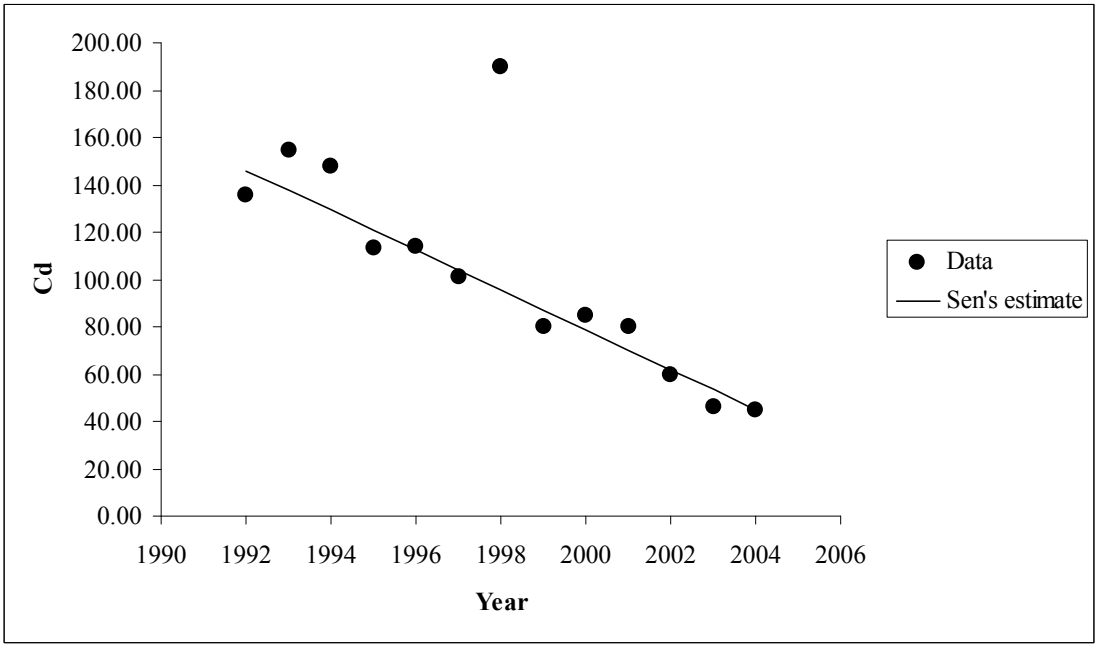

Figure D18: Time series of cadmium wet deposition flux (in µg/m²).

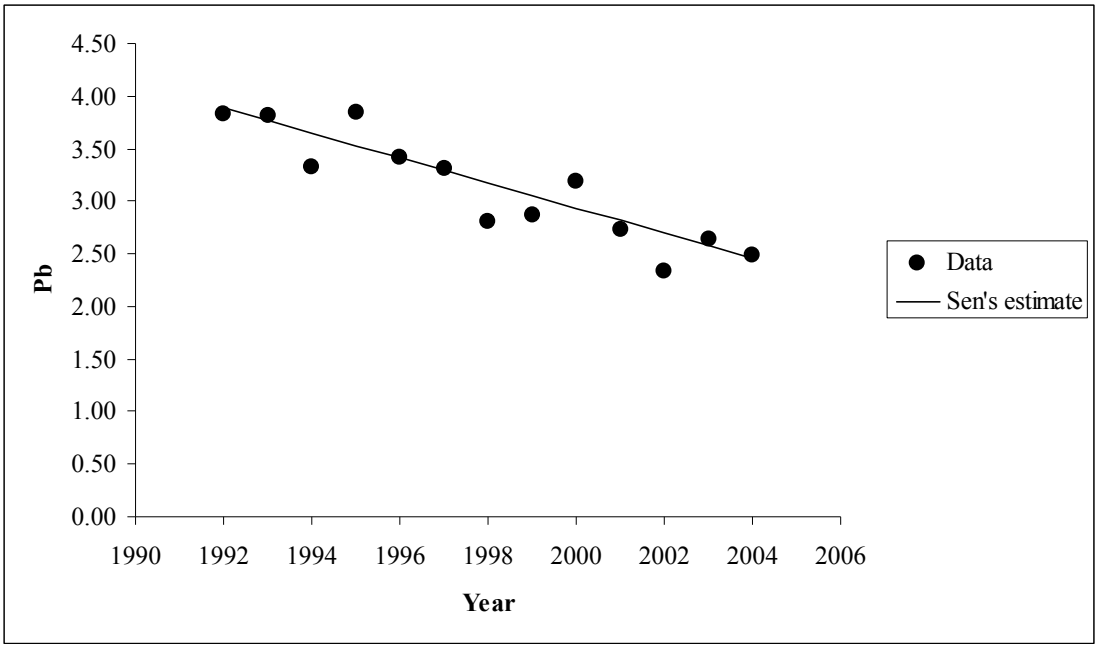

Figure D19: Time series of lead concentrations (in µg/l) in precipitation.

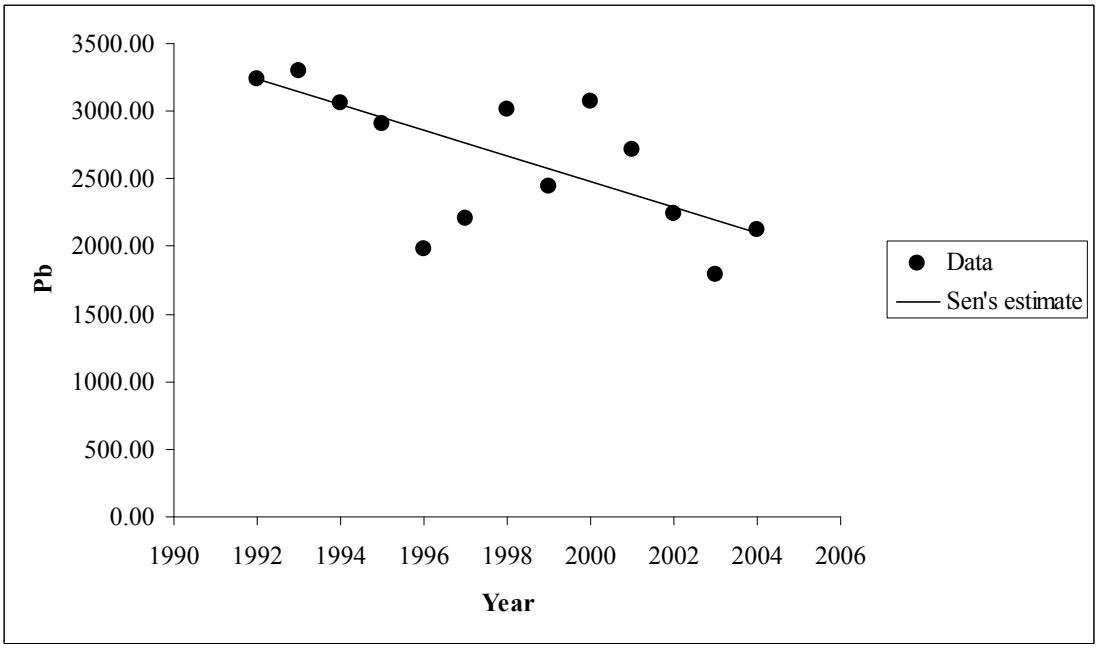

Figure 20: Time series of lead wet deposition flux (in µg/m²).

Appendix E Detection limit, molar mass and uncertainty of contaminants in measurements

Table E1 Information of measured contaminants on detection limit, molar mass and uncertainty for annual averaged concentration

Component	Abbreviation	Detection limit[7]	Molar mass	Uncertainty[8]
Ammonium	NH_4	0.04 mg/l	18.0	5.8%
Nitrate	NO_3	0.25 mg/l	62.0	5.9%
Sulfate	SO_4	0.2 mg/l	96.1	5.9%
Phosphate	PO_4	0.04 mg/l	95.0	60.0%
Fluoride	F	0.008 mg/l	19.0	15.2%
Chloride	Cl	0.18 mg/l	35.5	5.9%
Sodium	Na	0.046 mg/l	23.0	6.3%
Potassium	K	0.04 mg/l	39.1	7.9%
Magnesium	Mg	0.024 mg/l	24.3	6.6%
Calcium	Ca	0.06 mg/l	40.1	7.0%
Vanadium	V	0.2 µg/l	50.9	n/a
Chromium	Cr	0.5 µg/l	52.0	n/a
Iron	Fe	22.36 µg/l	55.9	11.2%
Cobalt	Co	0.12 µg/l	58.9	n/a
Nickel	Ni	0.4 µg/l	58.7	n/a
Copper	Cu	0.4 µg/l	63.5	8.4%
Zinc	Zi	4.0 µg/l	65.4	8.4%
Arsenic	As	0.15 µg/l	74.9	n/a
Cadmium	Cd	0.03 µg/l	112.4	6.9%
Lead	Pb	0.4 µg/l	207.2	7.3%

[7] Values of detection levels in 2004, for levels in 2000 see Stolk (2001)

[8] From Blank (2001)

Appendix F Spatial distribution of major components

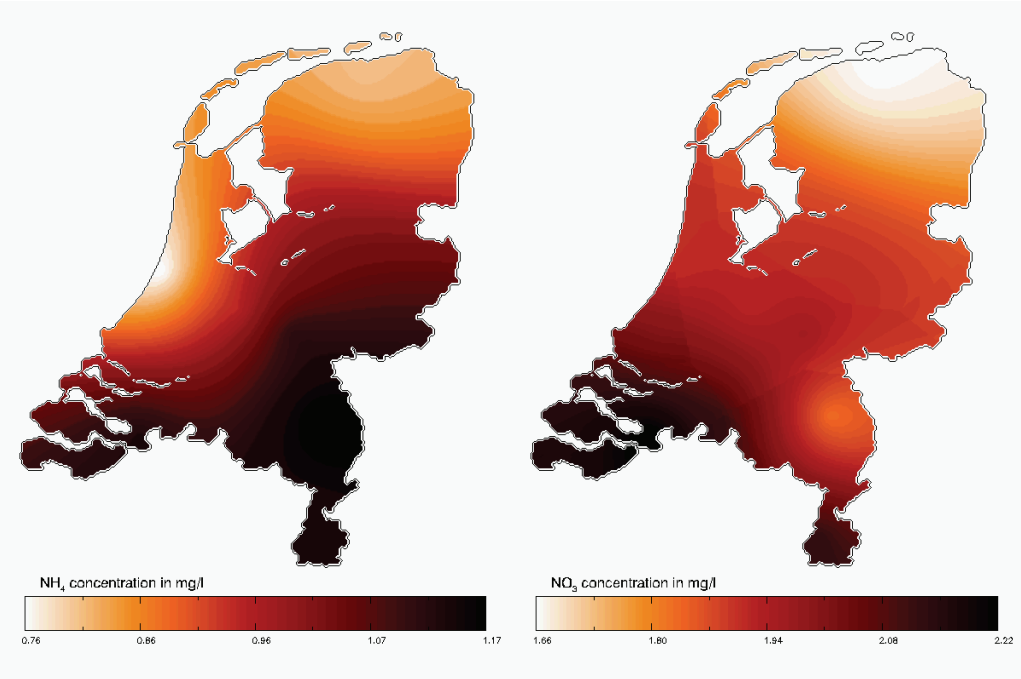

Figure F1: **Concentrations of ammonium (left panel) and nitrate (right panel) in precipitation over the Netherlands.**

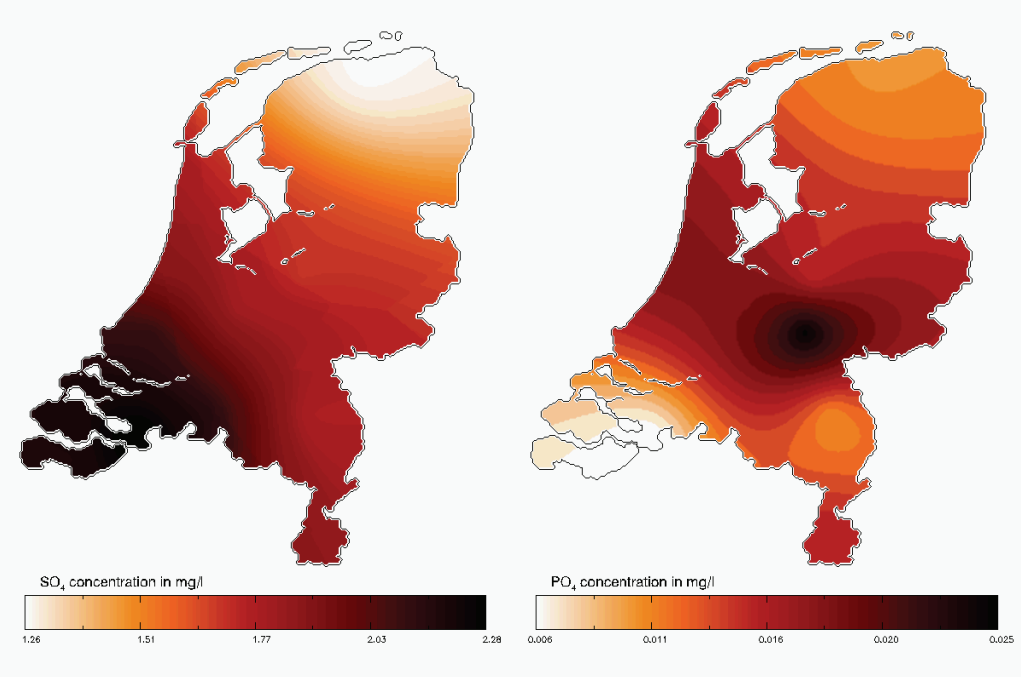

Figure F2: Concentrations of sulfate (left panel) and phosphate (right panel) in precipitation over the Netherlands.

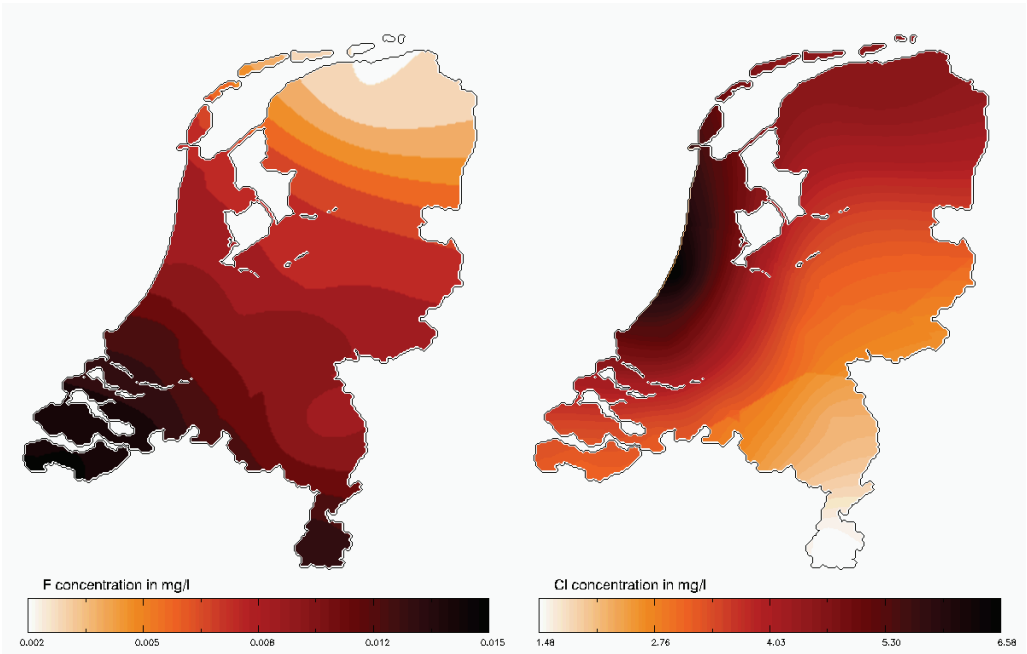

Figure F3: Concentrations of fluoride (left panel) and chloride (right panel) in precipitation over the Netherlands.

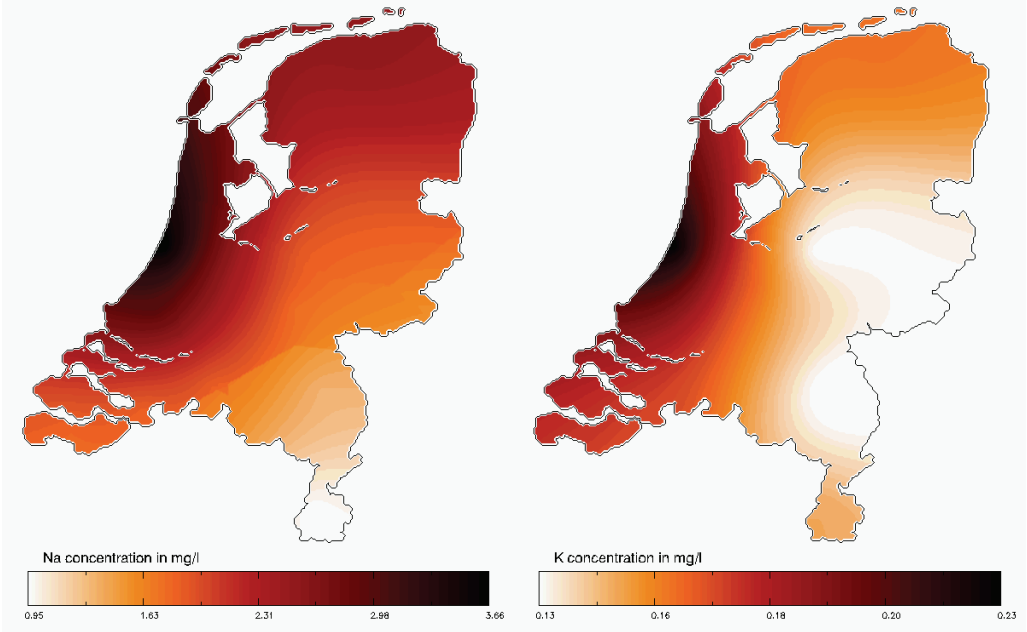

Figure F4: Concentrations of sodium (left panel) and potassium (right panel) in precipitation over the Netherlands.

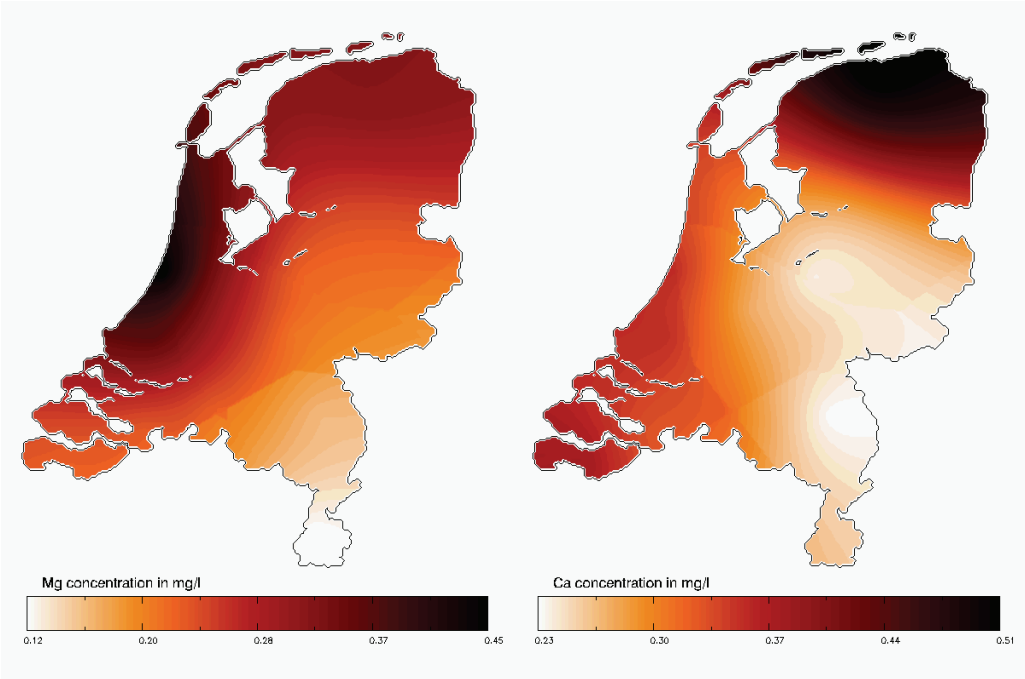

Figure F5: Concentrations of magnesium (left panel) and calcium (right panel) in precipitation over the Netherlands.

RIVM

National Institute
for Public Health
and the Environment

P.O. Box 1
3720 BA Bilthoven
The Netherlands
www.rivm.nl