

CLIMATE CHANGE RESEARCH

REPORT 7/1996

CLIMEX project:
Response of runoff chemistry
after 2 years of elevated CO_2
and temperature



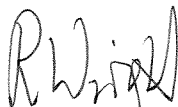
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Abstract CLIMEX is an integrated, whole-ecosystem research project studying the response of entire forested catchments to increased CO ₂ and temperature. KIM catchment receives clean rain, elevated CO ₂ and elevated air temperature. EGIL catchment receives ambient acid rain and soil warming. During the first 2 years of treatment (April 1994 - April 1996) runoff from both catchments had increased concentrations of nitrate and ammonium relative to untreated reference catchments and to pre-treatment period. Increased loss of nitrogen from the systems may be due to increased decomposition of soil organic matter induced by the higher temperatures. This increase might lead to acidification in acid-sensitive freshwaters.
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**CLIMEX project:
Response of runoff chemistry after 2 years of
elevated CO₂ and temperature**

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Preface

CLIMEX (Climate change experiment) is an interdisciplinary, international research project in which temperature and CO₂ concentrations are altered to whole forest catchment ecosystems. CLIMEX involves 7 institutions in 4 European countries. Financial support for CLIMEX has come from the Commission of European Communities (EV5V-CT91-0047 and EV5V-CT95-0185), the Dutch Global Change Programme, the Research Council of Norway, the Norwegian Ministry of Environment, the National Environment Research Council (UK), Hydrogas Norge A/S, and the Norwegian Institute for Water Research. We thank Wim Arp, Frank Bowles, Ann Kristin Buan, Rolf Høgberget, Jarle Håvardstun, Anne-Sofie Indrøy, Mette Lie, Ragnar Storhaug, Tore Sørvalg, Paul Verburg and Morten Willbergh.

CLIMEX project is a contribution to core research category 1 of the Global Change & Terrestrial Ecosystems (GCTE) core project under the International Geosphere-Biosphere Programme (IGBP).

1. Introduction

CLIMEX (Climate change experiment) is an international, co-operative research project studying the response of entire forested catchments to increased CO₂ and temperature (Jenkins *et al.* 1992, Dise and Jenkins 1995). The CLIMEX project began in December 1992 using the former RAIN project facilities catchments at Risdalsheia, near Grimstad, southernmost Norway (Wright *et al.* 1993) (Figure 1). The project involves 5 catchments (Table 1). KIM catchment is completely enclosed within a 1200-m² greenhouse in which atmospheric CO₂ is enriched to 560 ppmv during the growing season and air temperature is increased by 3-5°C above ambient; KIM catchment receives clean precipitation. EGIL catchment is covered by a 650-m² roof without walls and the soil is warmed by 3-5°C above ambient by means of electric heating cables; EGIL catchment receives ambient acid precipitation. At both KIM and EGIL catchments the uppermost 20% is not heated and serve as control site (denoted KIM-c and EGIL-c). At KIM the separation is by means of a dividing wall between KIM-t and KIM-c. Three untreated reference catchment are also monitored. The roofs were constructed and clean rain treatment started in June 1984; CLIMEX treatments began in April 1994 (Table 1).

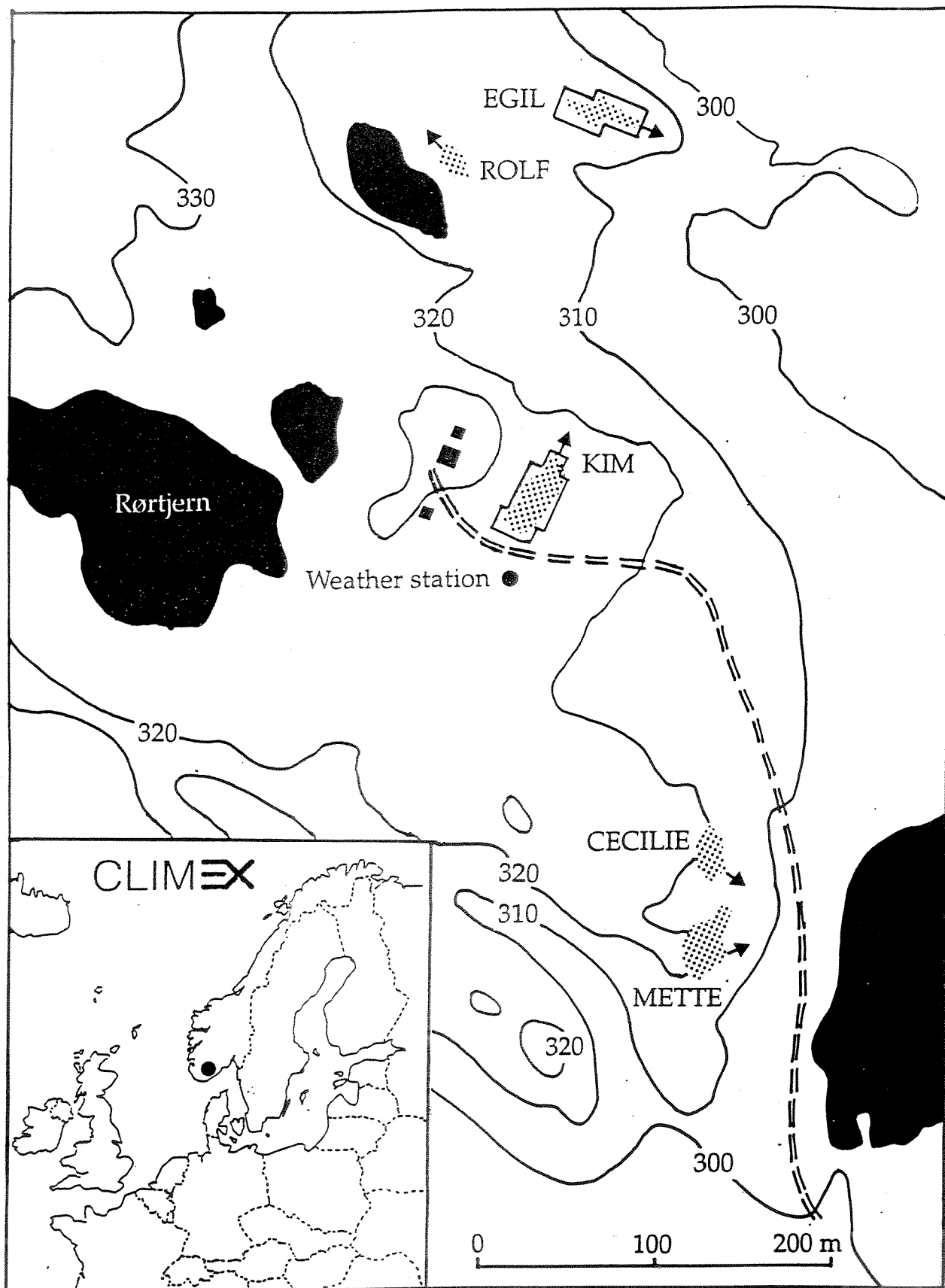


Figure 1. Location of the CLIMEX site and 5 experimental catchments at Risdalsheia near Grimstad, southernmost Norway. Contour lines are given in meters.

Table 1. Overview of the 5 catchments at Risdalsheia included in the CLIMEX project. The first three were run by the RAIN project for 11 years (June 1983 - May 1994). RAIN treatment began in June 1984. CLIMEX treatment began in April 1994. KIM and EGIL were divided in April 1994 to an upper control section (KIM-C, EGIL-C, no climate change) and lower treatment section (KIM-T, EGIL-T, climate change).

catchment	area m ²	enclosure	rain quality	climate treatment	monitor start
KIM	860	roof	clean	CO ₂ +air warming	June 1983
EGIL	400	roof	acid	soil warming	June 1983
ROLF	220	no roof	acid	none	June 1983
METTE	650	no roof	acid	none	June 1993
CECILIE	380	no roof	acid	none	June 1993

The flux of energy and matter across ecosystem boundaries gives an integrated measure of the whole-ecosystem response to environmental perturbation. For the CLIMEX project, changes in fluxes of water and dissolved components in runoff provide information on the catchment-scale effects of the experimentally-altered CO₂ and temperature regime as well as a direct measure of the effects on aquatic ecosystems of changes in terrestrial catchments. A central objective of CLIMEX, then, is to measure changes in chemical composition of runoff and changes in the water and chemical fluxes at the 5 catchments at Risdalsheia.

Runoff chemistry and input-output budgets were the major focus of the RAIN project, and routine measurements at 3 of these catchments (KIM, roof clean rain; EGIL roof acid rain; ROLF no roof acid rain) have been carried out since winter 1984. The runoff chemistry observed at KIM catchment relative to EGIL and ROLF catchments over the 10-year experimental period shows major changes due to the drastically reduced inputs of strong acids (Wright *et al.* 1993).

The experimental procedures of CLIMEX largely follow those of the RAIN project. New for CLIMEX is the inclusion of 2 additional untreated reference catchments, called METTE and CECILIE. Together the 3 reference catchments provide an estimate of the natural catchment-to-catchment variation with which the changes in runoff chemistry and fluxes from the 2 manipulated catchments can be compared.

Here the precipitation and runoff chemistry and the input-output budgets for the first 2 years of treatment May 1994 - May 1996 at all 5 CLIMEX catchments are presented. A complete list of publications and reports from the RAIN and CLIMEX projects is given in Appendix A.

2. Methods

2.1 Precipitation volume

At the 2 roofed catchments KIM and EGIL incoming precipitation is collected from the roofs by gutters, led to storage tanks, and pumped automatically back out under the roofs through a sprinkler system. At KIM catchment the precipitation is filtered, ion-exchanged by mixed bed

resin, and natural levels of sea salts readded (at about 1:8000 during the summer and 1:5000 during the winter). At EGIL the ambient precipitation is sprinkled untreated. At both catchments the volume of sprinkled water is metered and read at minimum weekly intervals.

For the 3 reference catchments (ROLF, METTE, CECILIE) precipitation is collected by funnel and volume measured weekly at the meteorological station located in an open area at Risdalsheia. Beginning 1992 daily measurements of precipitation volume, solar radiation, soil and air temperature (maximum, mean and minimum) are also measured at this point.

2.2 Dry deposition

Dry deposition is taken directly from estimates made for the nearby EMEP station at Birkenes (Tørseth 1996). These estimates are based on measured daily concentrations in air and assumed deposition velocities for S and N species (Table 2). Species measured and deposition velocities (cm/s) are:

SO ₂ gas	0.1 (winter) and 0.7 (summer)
SO ₄ particles	0.4
NO ₂ gas	0.3
HNO ₃ + NO ₃	2.0 for HNO ₃ and 0.4 for NO ₃ (25% is assumed HNO ₃ , 75% NO ₃)
NH ₄ + NH ₃	0.4 for NH ₄ and 0.4 for NH ₃ (92% is assumed NH ₄ , 8% NH ₃)

About 20% of dry deposition of S and 25% dry deposition of N is calculated to occur during the 6 winter months (November - April) (Tørseth 1996). Dry deposition of marine aerosol is calculated by difference from the Cl flux in runoff minus the Cl flux in bulk precipitation at each catchment for each winter and summer period.

2.3 Precipitation chemistry

Chemical composition of ambient precipitation outside the roofs is determined on bulk samples collected weekly from the funnel at the meteorological station. Samples are sent to NIVA (prior to 1993 to NILU Norwegian Institute for Air Research) for analysis of pH, electrical conductance, Ca, Mg, Na, K, NH₄, NO₃, Cl, and SO₄ by methods summarised in Table 3.

2.4 Runoff discharge

All runoff from the catchments is collected at fibreglass dams at the bottom of the catchment, led by hose to 500-l tanks which empty automatically when full. Discharge is measured by logging the number of tanks emptied. Samples for chemical analysis are collected automatically at about weekly intervals from each full tank (or a pre-set selection of tanks). These systems at Risdalsheia have been in continuous operation since March 1984 (KIM and EGIL), October 1984 (ROLF) and May 1993 (METTE and CECILIE).

Table 2. Annual mean concentrations of gaseous and particulate sulphur and nitrogen compounds in air at Birkenes and calculated dry deposition (data from Tørseth 1996).

	concentrations $\mu\text{gS}/\text{m}^3$, $\mu\text{gN}/\text{m}^3$				
	$\text{SO}_2\text{-S}$	$\text{SO}_4\text{-S}$	$\text{NO}_2\text{-N}$	$(\text{HNO}_3+\text{NO}_3)\text{-N}$	$(\text{NH}_4+\text{NH}_3)\text{-N}$
1978	1.70	1.10			
1979	1.10	1.30			
1980	1.40	1.40			
1981	0.80	1.00			
1982	1.00	1.10			
1983	0.50	0.90			
1984	0.70	1.30	1.10		
1985	0.70	0.90	0.80		
1986	0.70	0.80	1.10	0.40	0.70
1987	0.70	0.80	1.10	0.30	0.70
1988	0.60	0.80	1.30	0.30	0.60
1989	0.50	0.70	1.10	0.30	0.60
1990	0.50	0.80	1.00	0.30	0.80
1991	0.50	0.90	0.90	0.30	0.80
1992	0.40	0.65	0.69	0.24	0.53
1993	0.40	0.59	0.59	0.23	0.55
1994	0.40	0.65	0.66	0.28	0.63
1995	0.31	0.58	0.68	0.30	0.54

	dry deposition $\text{meq}/\text{m}^2/\text{yr}$			
	SO_4	NO_3	NH_4	H^+
1987	9.9	11.7	6.0	15.6
1988	9.9	12.1	6.3	15.8
1989	8.5	11.2	5.8	13.9
1990	10.4	11.9	6.2	16.2
1991	10.6	11.0	5.6	15.9
1992	8.6	8.8	4.6	12.9
1993	6.0	7.5	3.8	9.6
1994	8.0	10.0	5.1	12.8
1995	7.2	9.9	5.1	12.0

Table 3. Analytical methods used for precipitation (P) and runoff (R) samples at NIVA

Parameter	Sample type	Method	Detection limit	Standard error
pH	P, R	potentiometry	0.01	± 0.05
Na	P, R	ICP	0.02 mg/l	± 0.06
Ca	P, R	ICP	0.02 mg/l	± 0.01
Mg	P, R	ICP	0.003 mg/l	± 0.04
K	P, R	atomic adsorption spectrophotometry	0.02 mg/l	± 0.01
NH ₄ -N	P, R	automated colorimetry	5 µgN/l	± 5
NO ₃ -N	P, R	automated colorimetry	1 µgN/l	± 2
Cl	P, R	ion chromatography (IC)	0.2 mg/l	± 0.08
SO ₄	P, R	ion chromatography	0.2 mg/l	± 0.12
react-Al	R	automated colorimetry	10 µg/l	± 3
org-Al	R	cation exchange, automated colorimetry	10 µg/l	± 3
TOC	R	oxidation, spectrophotometry	0.2 mgC/l	± 0.01
Tot-N	R	oxidation, automated colorimetry	5 µgN/l	± 5
Tot-P	R	oxidation, automated colorimetry	1 µgP/l	± 0.2
SiO ₂	R	automated colorimetry	0.1 mg/l	± 0.16
F	R	potentiometry, ion-specific electrode	0.1 mg/l	± 0.08

2.5 Runoff chemistry

Runoff samples are analysed at NIVA for pH, electrical conductance, Ca, Mg, Na, K, NH₄, NO₃, Cl, SO₄, aluminium species (reactive-Al and organic-Al), total organic carbon, total nitrogen, total phosphorus, silica and fluoride by methods given in Table 1. Inorganic monomeric Al species are defined as the difference reactive-Al (RAL) minus organic-Al (ILAl). Organic anions (A⁻) are calculated by difference from the ionic balance. Acid neutralising capacity (ANC) is defined as the equivalent sum of base cations (SBC = Ca, Mg, Na, K, NH₄) minus the equivalent sum of strong acid anions (SSA = NO₃, Cl, SO₄). Non-marine fraction (denoted by asterisk) is calculated in the usual manner by subtracting the marine fraction (assumed to be all of the Cl⁻ and for the other ions their ratios to Cl⁻ in seawater).

2.6 Randomised Intervention Analysis

We use the statistical technique of Randomised Intervention Analysis (RIA), Carpenter *et al.* (1989) to test for significance of changes in concentrations of chemical components in runoff due to the CLIMEX treatments. RIA compares paired, chronologically-ordered samples for pre- and post-treatment periods from manipulated (KIM, EGIL) and reference (ROLF, METTE, CECILIE) catchments. The catchments were paired by treatment/reference, treatment/treatment, and reference/reference. For each of 1000 random assignments the

change in the mean inter-catchment differences of various parameters was computed. Three years of pre-treatment data (June 1991 - May 1994) were compared to 2 years of treatment data (June 1994 - May 1996).

2.7 Flux calculations

Fluxes are calculated for each winter and summer period (Table 4). Start of winter is set at the date at which the sprinkling systems are switched off due to frost (usually sometime in November). Start of summer is set at the date at which snowmelt is completed and the extra watering has been added (usually sometime in May). Precipitation inputs are calculated from the chemical concentrations measured in weekly precipitation samples multiplied by the weekly precipitation volume for the reference catchments or the weekly metered amount of water sprinkled beneath the roofs for the manipulated catchments. For KIM catchment the chemical composition of input water is calculated from the amounts of seasalts added assuming that the ion-exchanged water contains no chemicals.

Runoff fluxes are calculated from the chemical composition measured in the weekly samples and the volume of water discharged during the week. An interpolation routine is used by which daily chemical composition is calculated assuming linear change between weekly samples. Discharge during the week is assumed to be evenly distributed among the days.

Table 3. Start and end dates for summer and winter periods used for flux calculations.

Period	Start	End
winter 1984	25 Mar 1984	12 Jun 1984
summer 1984	13 Jun 1984	13 Dec 1984
winter 1985	14 Dec 1984	01 May 1985
summer 1985	02 May 1985	14 Nov 1985
winter 1986	15 Nov 1985	10 May 1986
summer 1986	11 May 1986	18 Dec 1986
winter 1987	19 Dec 1986	12 May 1987
summer 1987	13 May 1987	23 Nov 1987
winter 1988	26 Nov 1987	11 May 1988
summer 1988	12 May 1988	25 Nov 1988
winter 1989	26 Nov 1988	11 May 1989
summer 1989	12 May 1989	24 Nov 1989
winter 1990	25 Nov 1989	31 May 1990
summer 1990	01 Jun 1990	29 Nov 1990
winter 1991	30 Nov 1990	13 Jun 1991
summer 1991	14 Jun 1991	05 Dec 1991
winter 1992	06 Dec 1991	17 May 1992
summer 1992	18 May 1992	11 Dec 1992
winter 1993	12 Dec 1992	14 May 1993
summer 1993	15 May 1993	02 Dec 1993
winter 1994	03 Dec 1993	26 May 1994
summer 1994	27 May 1994	31 Oct 1994
winter 1995	01 Nov 1994	06 Jun 1995
summer 1995	07 Jun 1995	28 Nov 1995
winter 1996	29 Nov 1995	02 Jun 1996

3. Results

3.1 Sulphate, strong base cations and acid neutralising capacity

Sulphate concentrations in runoff have decreased markedly since the onset of the clean rain treatment at KIM catchment in June 1984 (Figures 2 and 3). Concentrations levelled off to a new steady-state by about 1991. A new decline in sulphate concentrations has occurred during the 2 years of CLIMEX treatment following the enclosing of the catchment in April 1994, presumably due to the reduced dry-deposition within the greenhouse.

Input-output budgets indicate that KIM catchment is still “bleeding” old sulphate. Estimated deposition of sulphate is lower than flux of sulphate in runoff (Figure 3). This conclusion is uncertain, however, due to uncertainty in the estimate of dry deposition. Dry deposition is set to zero after mid-1994, and thus is clearly underestimated by an unknown amount. At KIM catchment wet deposition of sulphate is quite low being comprised only of seasalts.

Sulphate concentrations have also declined somewhat in runoff from EGIL catchment and the 3 reference catchments, all of which receive ambient acid wet and dry deposition (Figures 2 and 3). This decline parallels a general decline in sulphate deposition in southern Norway (and northern Europe) due to decreased emission of sulphur compounds to the atmosphere. The input-output budgets for EGIL and ROLF catchments indicate a steady-state with no long-term net storage or releases of sulphur in the catchment (Figure 4).

Base cation concentrations in runoff from the catchments at Risdalsheia have also decreased over the 12-year period, both at the clean rain KIM catchment and at the acid rain catchments (Figure 2). The decline in base cations is probably mainly due to the decreased concentrations of the strong acid anion sulphate. F-factor ($\Delta\text{SBC}/\Delta\text{SO}_4$) at Risdalsheia is about 0.1.

Most of the decrease of strong acid anion concentrations at KIM and the other catchments has been compensated by an increase in acid neutralising capacity (ANC) (Figure 2). ANC is defined in the usual way as the difference in equivalent sum of strong base cations (SBC: $\text{Ca}+\text{Mg}+\text{Na}+\text{K}+\text{NH}_4$) less the equivalent sum of strong acid anions (SSA: $\text{NO}_3+\text{Cl}+\text{SO}_4$).

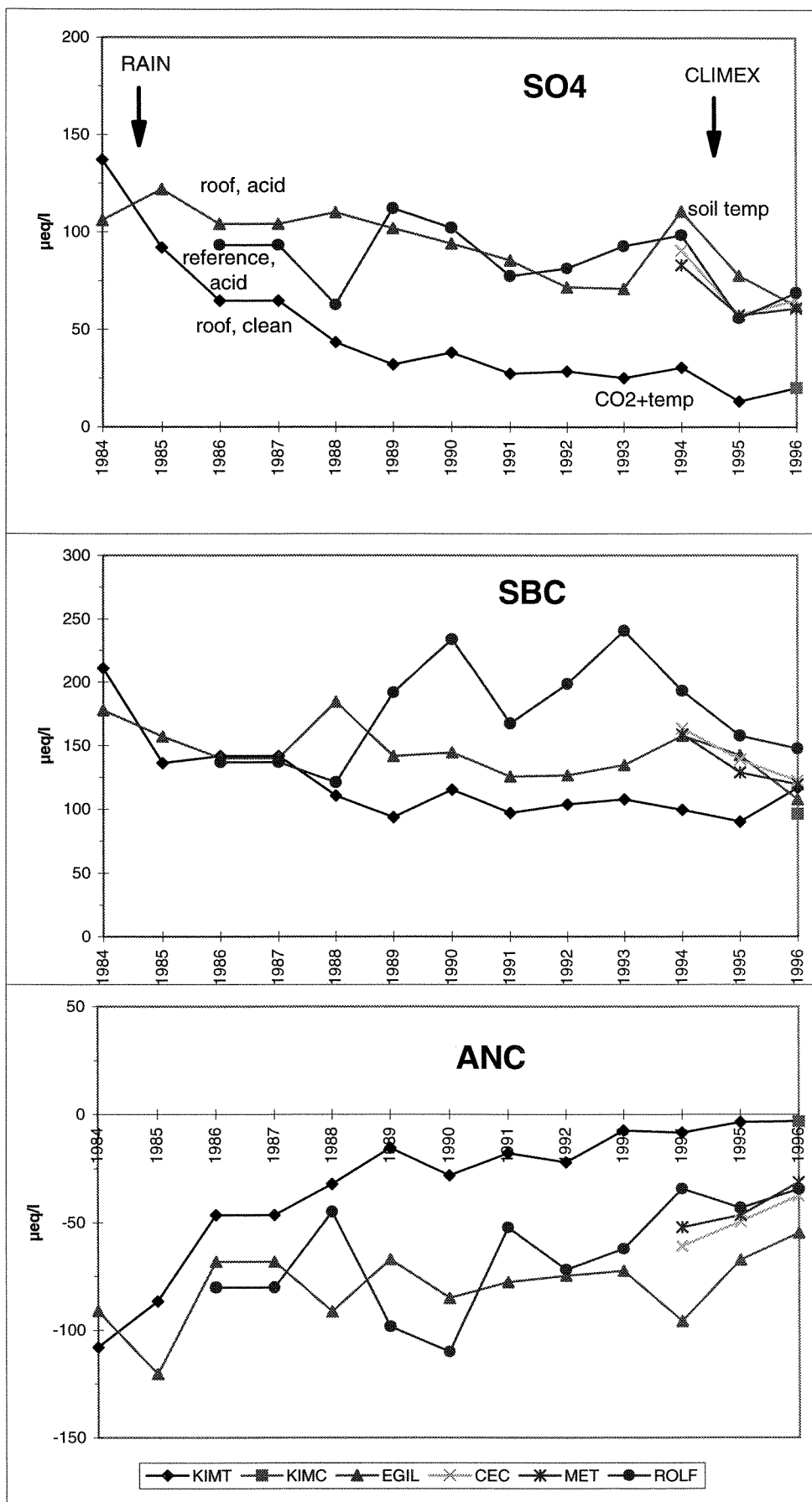


Figure 2. Mean annual volume-weighted concentrations of sulphate, sum of base cations (SBC), and acid neutralising capacity (ANC) in runoff from catchments at Risdalsheia.

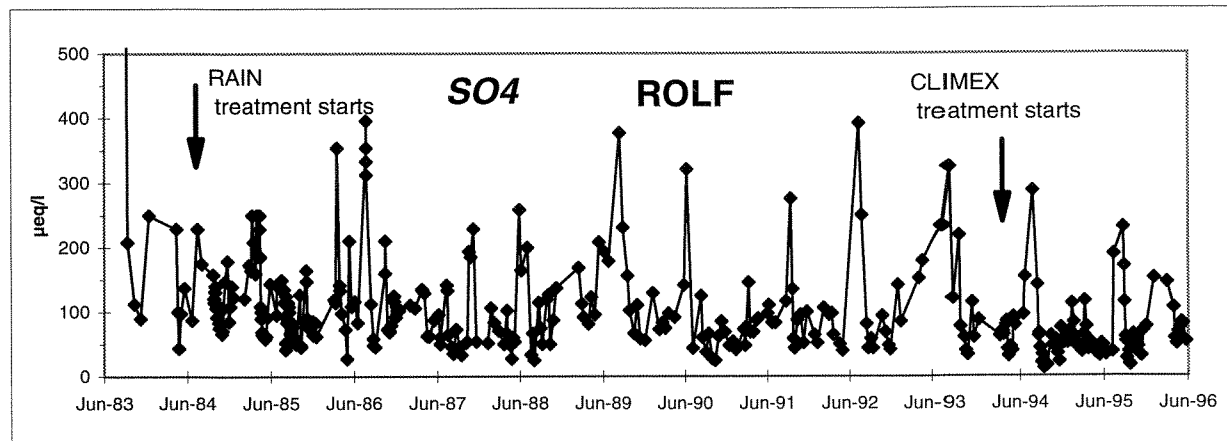
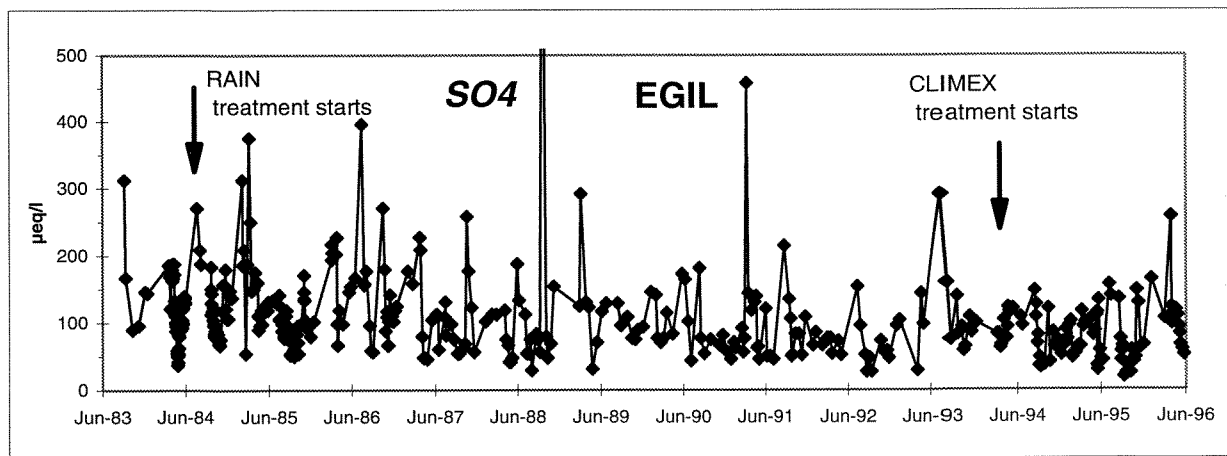
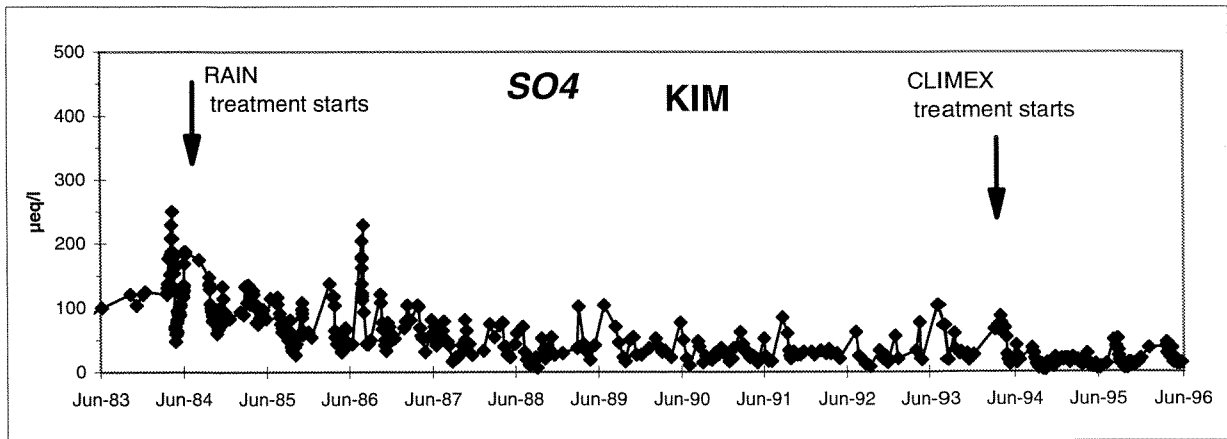


Figure 3. Concentrations of sulphate in individual samples of runoff at KIM catchment (roof, clean rain; CO₂ and temperature), EGIL catchment (roof, acid rain; soil warming), and ROLF catchment (untreated reference) for the 13-year period June 1983 - June 1996.

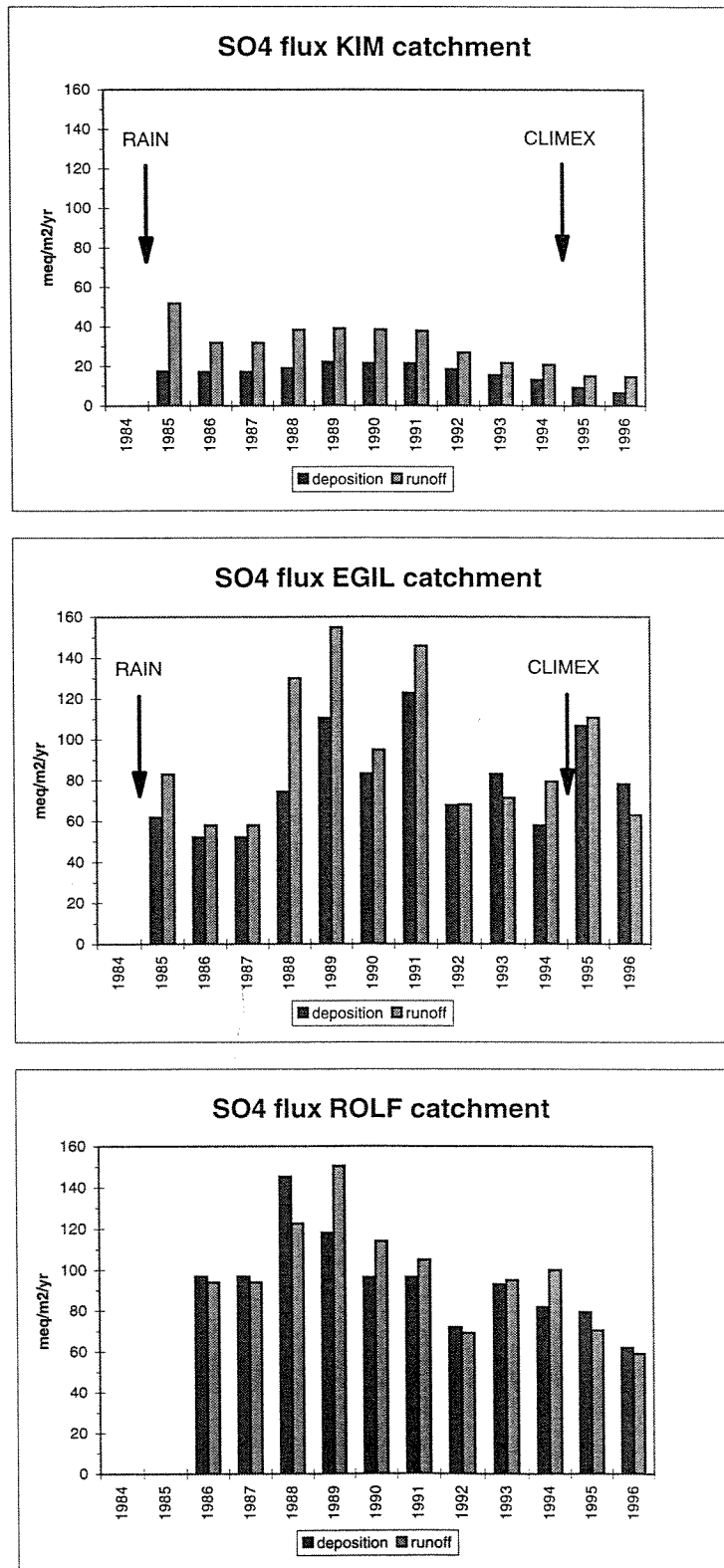


Figure 4. Annual (June to June) flux of sulphate in dry+wet deposition and runoff at KIM catchment (clean rain, CO₂+air temperature), EGIL catchment (acid rain, soil warming) and ROLF catchment (acid rain, reference).

3.2 Nitrate and ammonium

Concentrations of both nitrate and ammonium decreased sharply immediately after the onset of the clean rain treatment at KIM catchment in June 1984 (Figure 5). Annual volume-weighted concentrations were below 10 and 5 $\mu\text{eq/l}$, respectively, for the 4 years prior to the start of the CLIMEX treatments in April 1994, but increased especially during the second CLIMEX treatment year 1995-96. At KIM-C concentrations remained low.

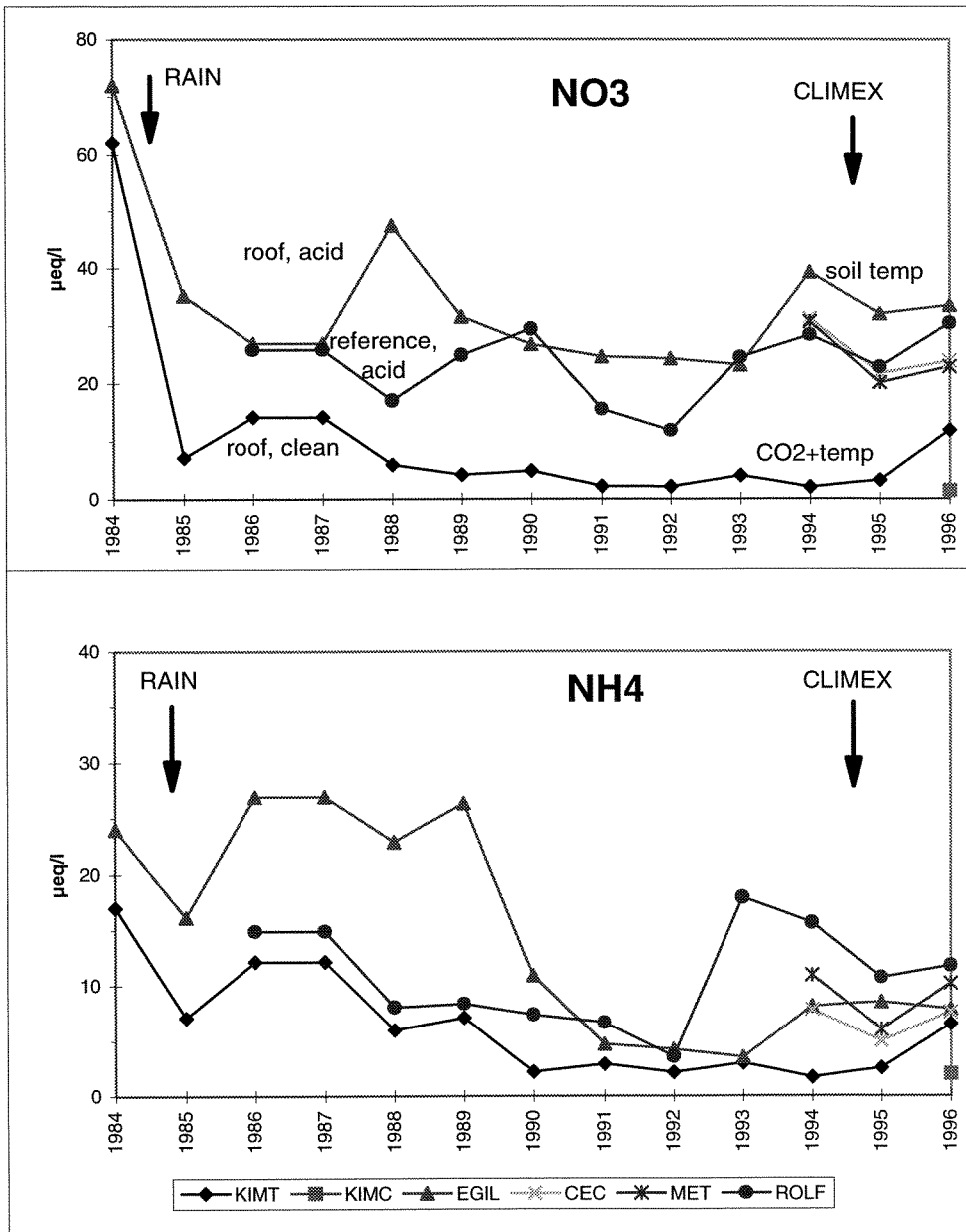


Figure 5. Mean annual volume-weighted concentrations of nitrate and ammonium in runoff from catchments at Risdalsheia.

At EGIL catchment and ROLF catchment there have been no significant long-term trends for nitrate and ammonium during the period prior to start of CLIMEX (Figure 5). Levels of nitrate and ammonium were similar among the 3 reference catchments (CECILIE, METTE and ROLF) for the CLIMEX pre-treatment year 1993-94 and the 2 treatment years 1994-95 and 1995-96 (Figures 6 and 7).

For EGIL catchment there has been a significant increase in both nitrate and ammonium concentrations relative to the reference ROLF catchment since the onset of the CLIMEX treatment (Figures 8 and 9). The increase is statistically significant at the 95% level by the randomised intervention analysis (RIA) test. The increase was evident already after the first year of treatment (Lükewille and Wright, in press).

Input-output budgets for inorganic nitrogen ($\text{NO}_3 + \text{NH}_4$) show that under ambient acid rain conditions with N inputs (wet+dry) of about $100 \text{ meq/m}^2/\text{yr}$ (14 kgN/ha/yr) the catchments retain about 60%; runoff flux is about $40 \text{ meq/m}^2/\text{yr}$ (Figure 10). At KIM catchment the roof and clean rain treatment substantially reduced the input of inorganic N to about $15 \text{ meq/m}^2/\text{yr}$ (mostly as dry deposition), and the catchment retained about 60% with runoff flux of only about $5 \text{ meq/m}^2/\text{yr}$. With the enclosure of the catchment in April 1994 at start of CLIMEX treatment, inputs decreased further in that much of the dry deposition was excluded, yet runoff flux during the first 2 years of treatment has increased, also relative to the samples from KIM-C. In the absence of an appropriate statistical test, it is difficult to assess the significance of this apparent increase.

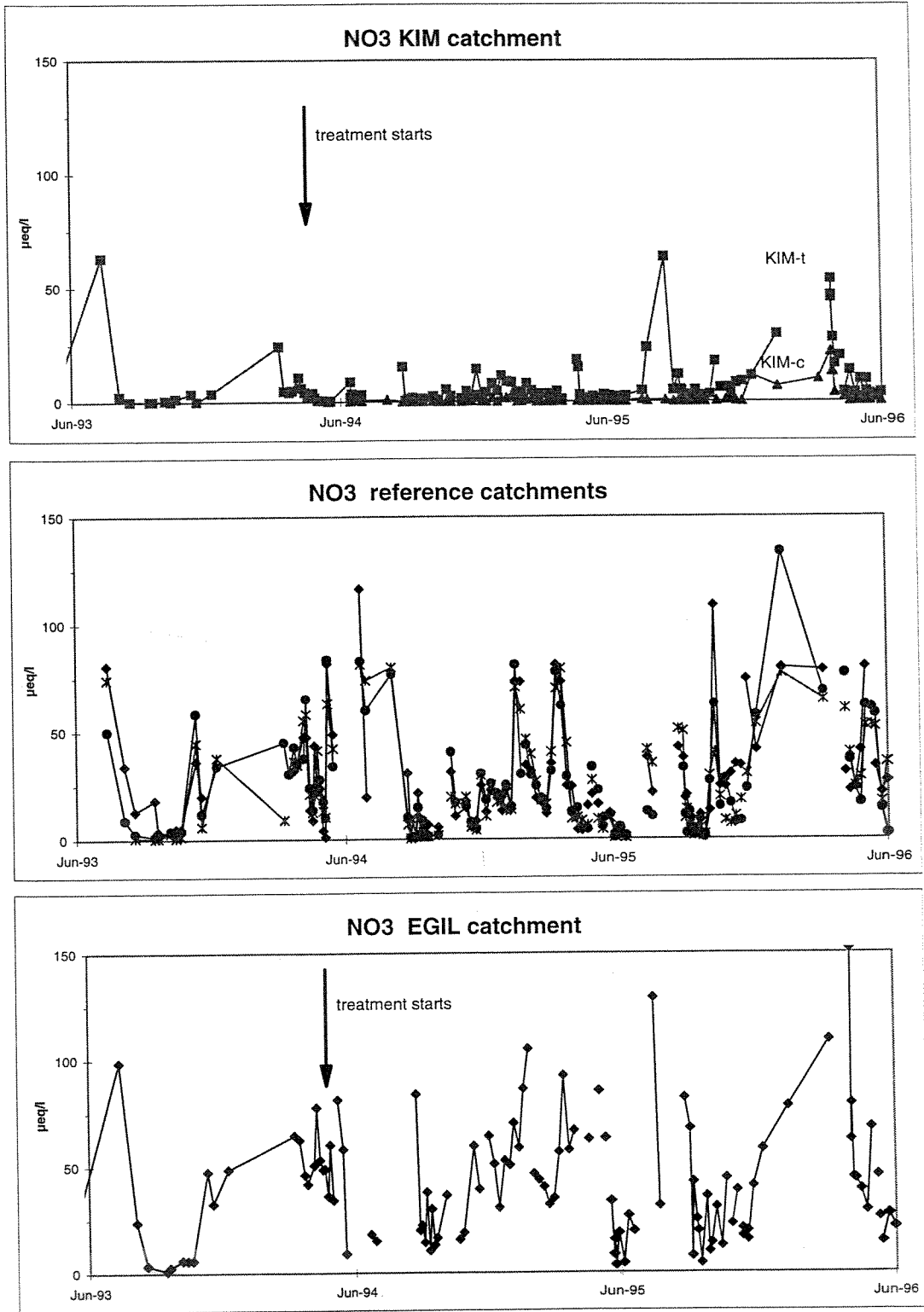


Figure 6. Concentrations of nitrate in individual samples of runoff at KIM-T catchment (roof, clean rain; CO₂ and temperature), KIM-C catchment (roof, clean rain; control), EGIL catchment (roof, acid rain; soil warming), and CECILIE, METTE and ROLF catchments (untreated references) for the 3-year period June 1993 - June 1996 (CLIMEX pre-treatment year and treatment years 1 and 2).

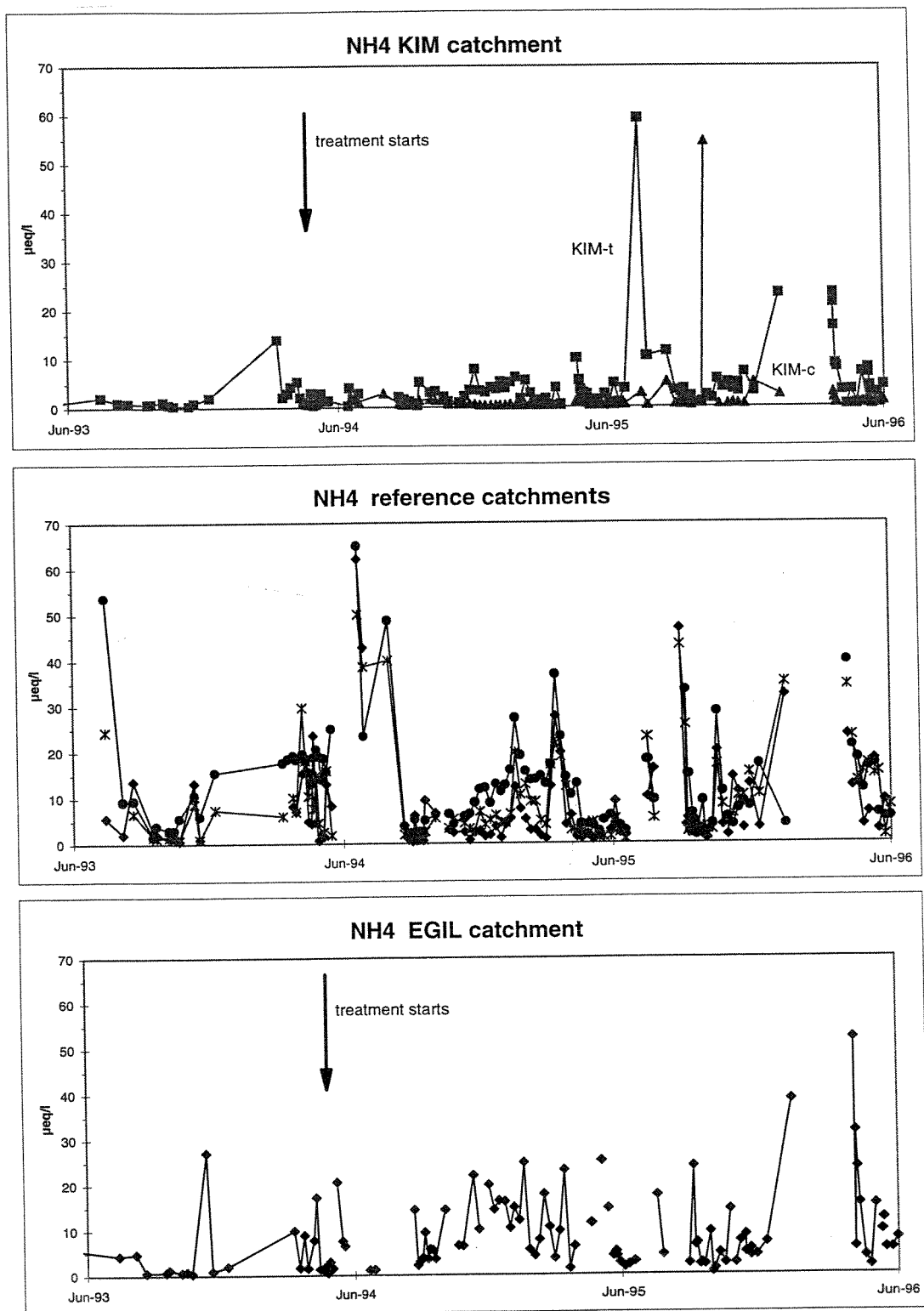


Figure 7. Concentrations of ammonium in individual samples of runoff at KIM-T catchment (roof, clean rain; CO₂ and temperature), KIM-C catchment (roof, clean rain; control), EGIL catchment (roof, acid rain; soil warming), and CECILIE, METTE and ROLF catchments (untreated references) for the 3-year period June 1993 - June 1996 (CLIMEX pre-treatment year and treatment years 1 and 2).

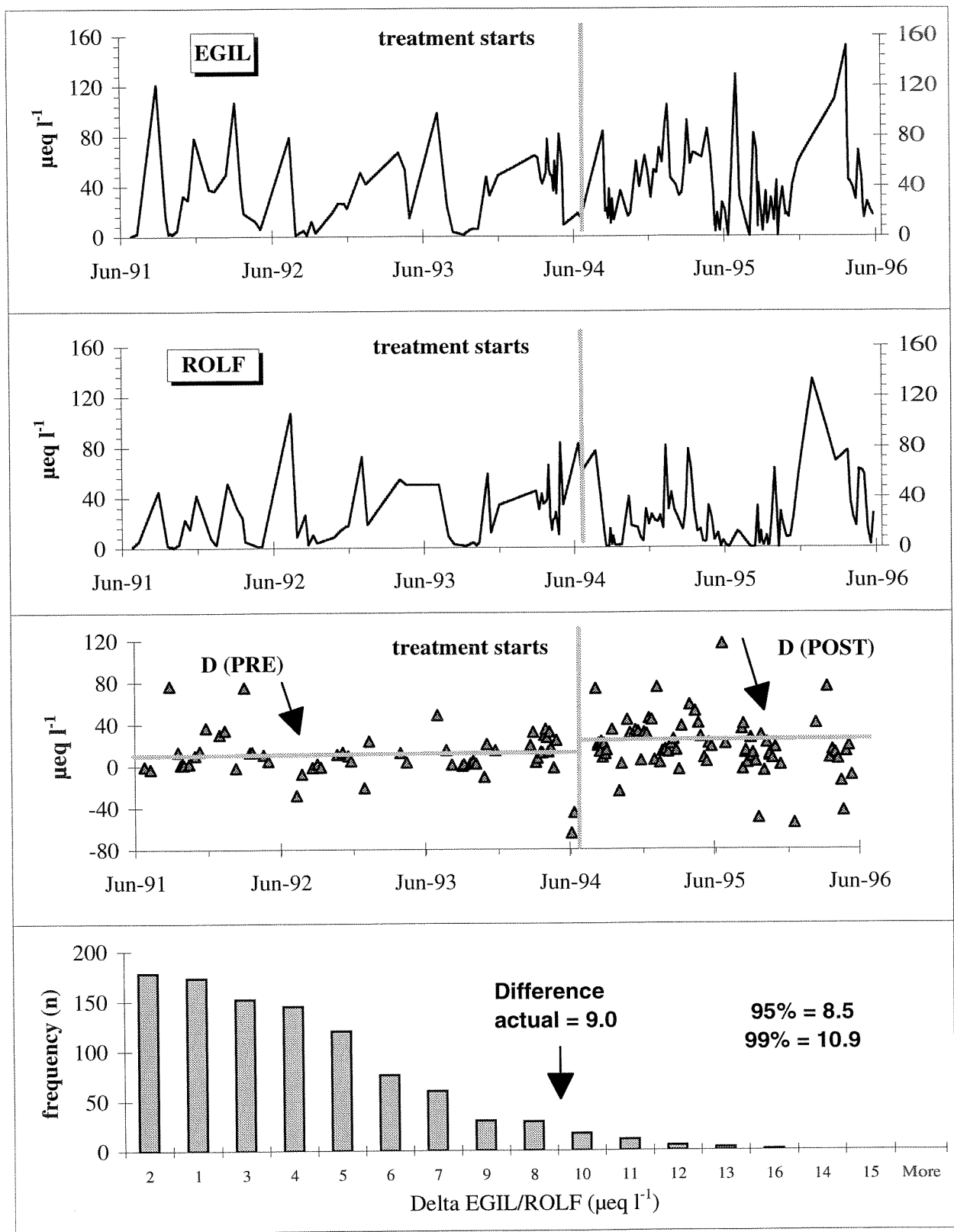


Figure 8. Randomised intervention analysis of nitrate concentrations in paired samples of runoff from EGIL (soil warming) and ROLF (reference) catchments for the pre-treatment period June 1991- June 1994 and the first 2 years of treatment June 1994 - June 1996.

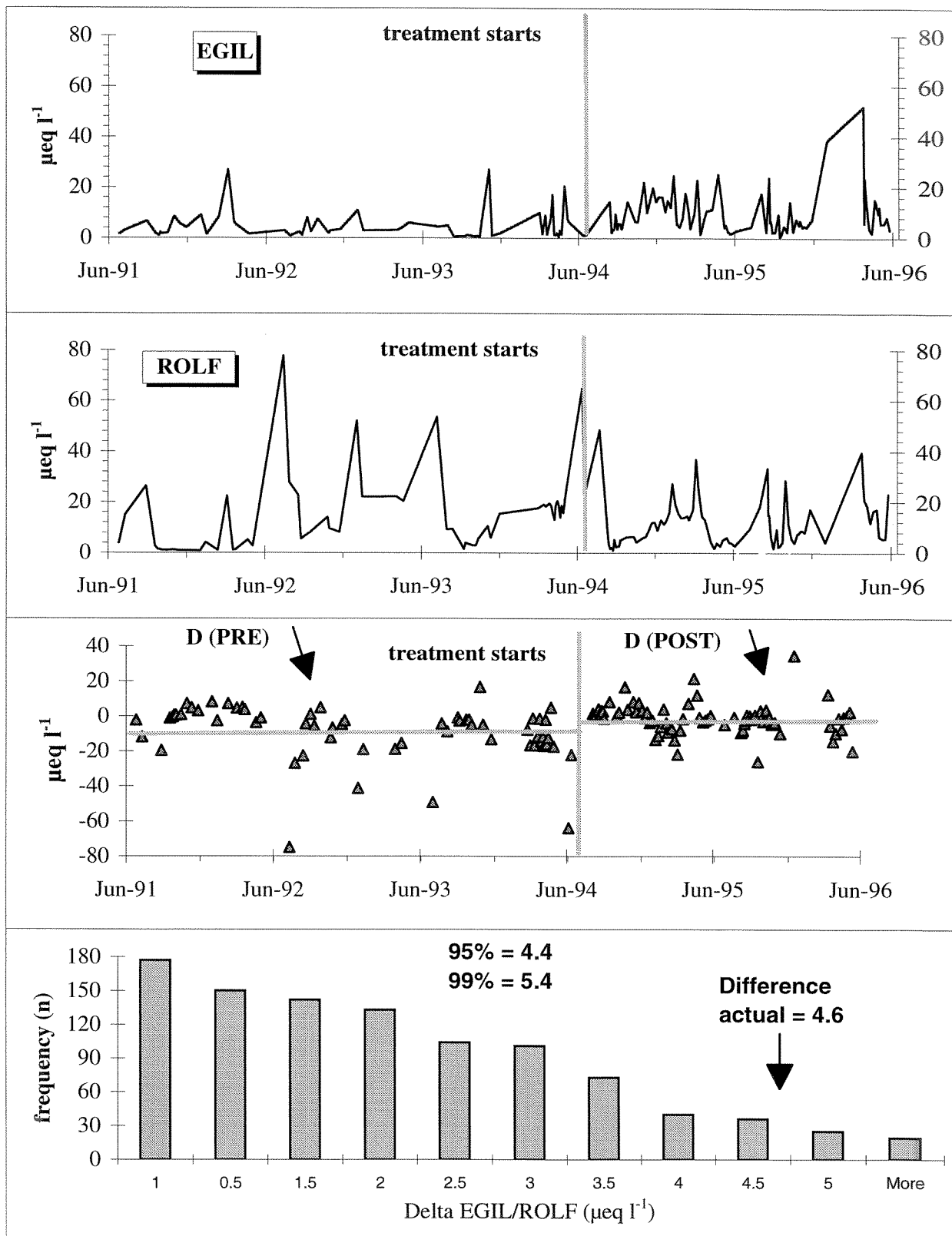


Figure 9. Randomised intervention analysis of ammonium concentrations in paired samples of runoff from EGIL (soil warming) and ROLF (reference) catchments for the pre-treatment period June 1991- June 1994 and the first 2 years of treatment June 1994 - June 1996.

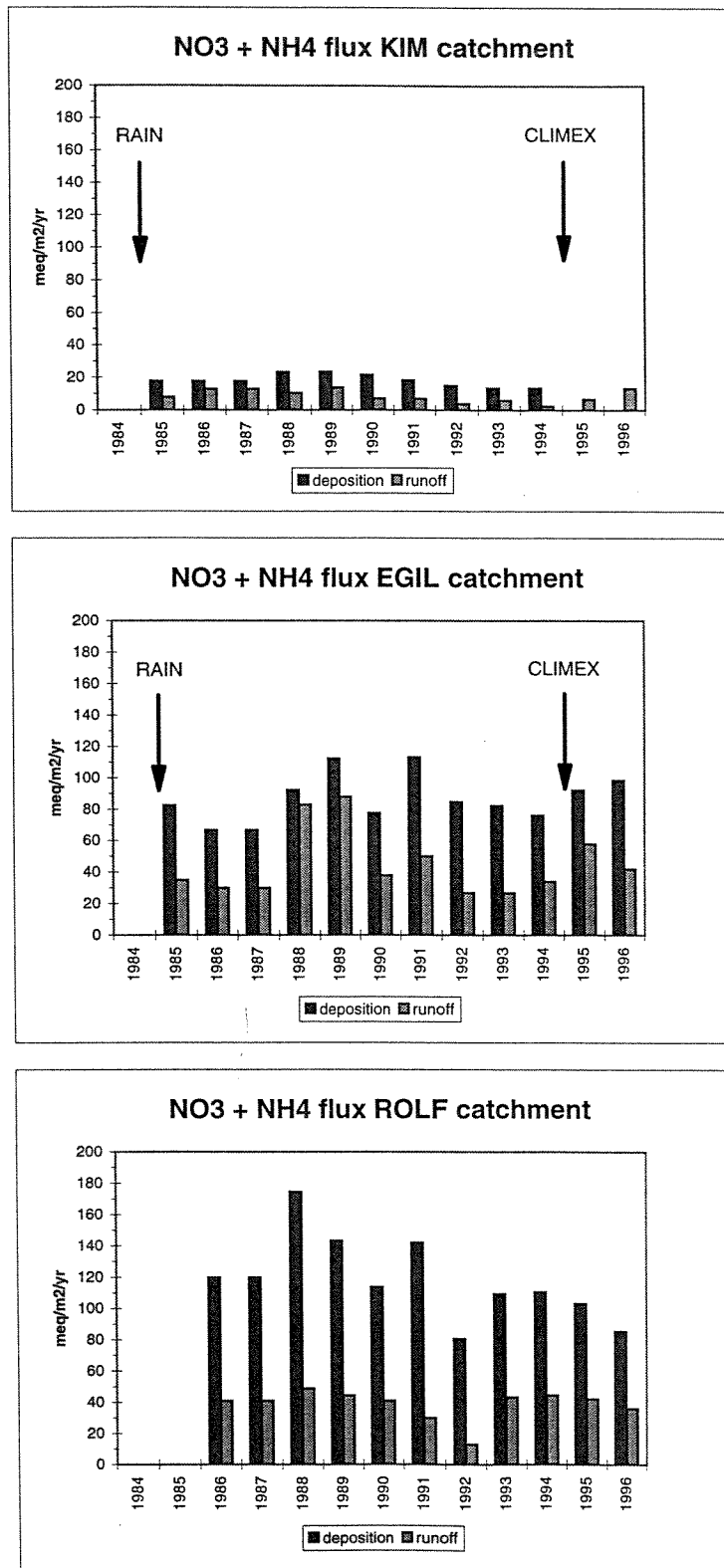


Figure 10. Annual (June to June) flux of inorganic nitrogen (NO₃ + NH₄) in dry+wet deposition and runoff at KIM catchment (clean rain, CO₂+air temperature), EGIL catchment (acid rain, soil warming) and ROLF catchment (acid rain, reference).

3.3 Dissolved organic carbon and nitrogen

There has been no long-term change in concentrations of total organic carbon (TOC) in runoff from the catchments at Risdalsheia (Figure 11). An exception may be the apparent increase at KIM catchment in 1995-96, the second year of CLIMEX treatment. This increase is statistically significant by the RIA test at the 99% level. TOC concentrations show a regular seasonal pattern with higher levels in the summer and lower levels in the winter, perhaps related to temperature (Figures 12 and 13). The increase at KIM therefore might be an effect of the increased temperature of the CLIMEX treatment, although no such effect has occurred at EGIL catchment (soil warming). Due to the CO₂ enrichment at KIM-C biomass production and thus litterfall have been enhanced. This, too, may have an positive effect on TOC concentrations in runoff.

Concentrations of organic nitrogen (defined as org-N = total N - NO₃ - NH₄ in units μmol/l) closely follow TOC levels, and thus also exhibit clear seasonal pattern with higher concentrations during the summer (Figure 14). The molar C/N ratios (defined as the ratio of TOC concentration μmol/l to organic N concentration μmol/l) is about 40 at all catchments (Figure 15). Apparently the greatly different deposition rates of inorganic N to the catchments do not affect the flux of organic N out of the catchments. Organic N flux appears to be controlled by the TOC flux.

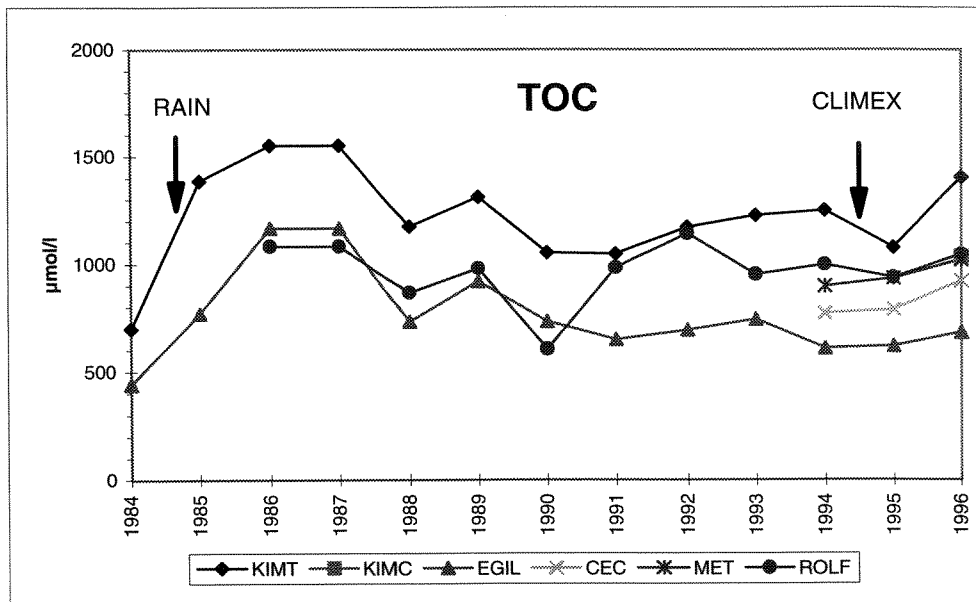


Figure 11. Mean annual volume-weighted concentrations of total organic carbon (TOC) in runoff from catchments at Risdalsheia.

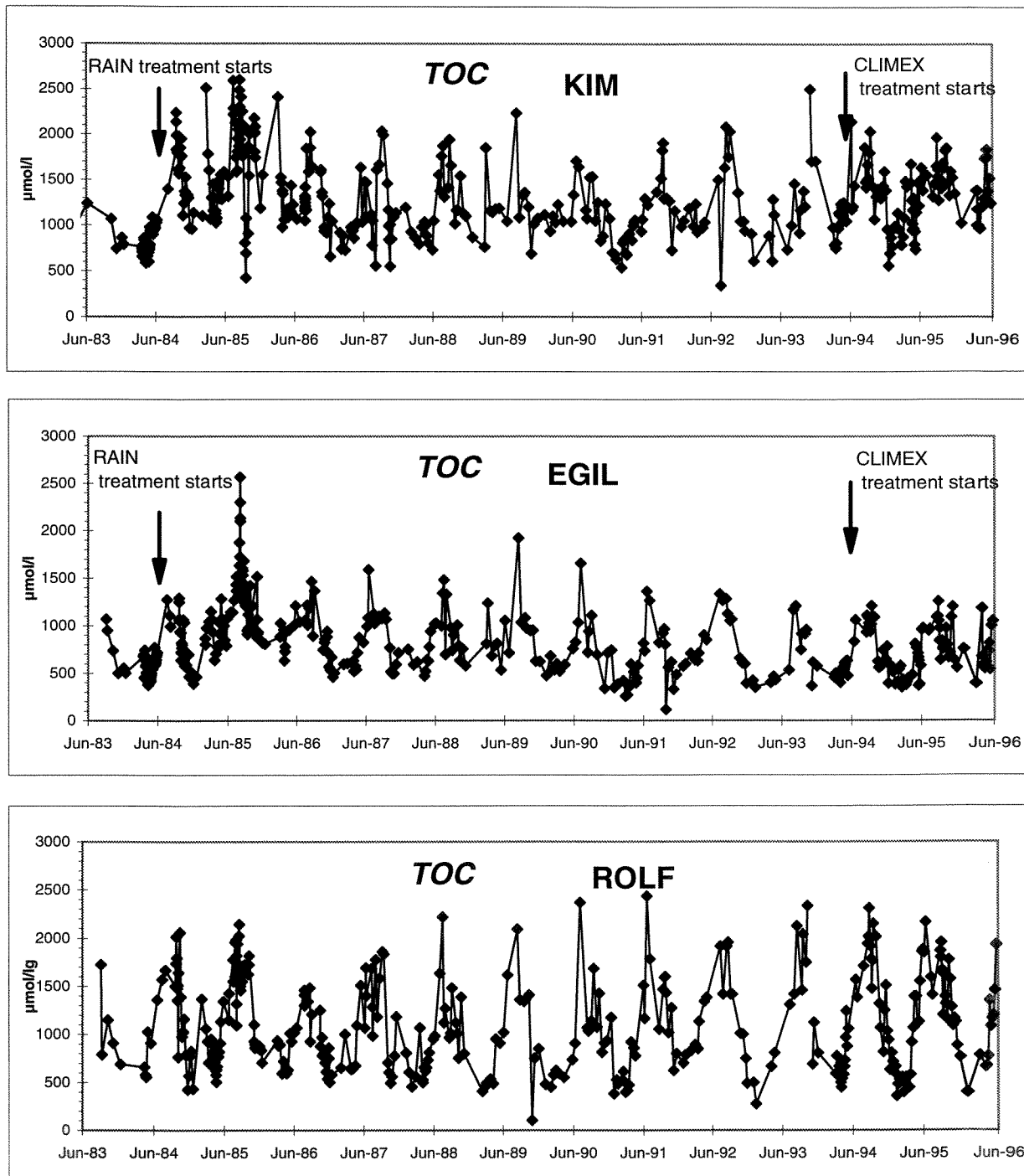


Figure 12. Concentrations of total organic carbon (TOC) in individual samples of runoff at KIM catchment (roof, clean rain; CO_2 and temperature), EGIL catchment (roof, acid rain; soil warming), and ROLF catchment (untreated reference) for the 13-year period June 1983 - June 1996.

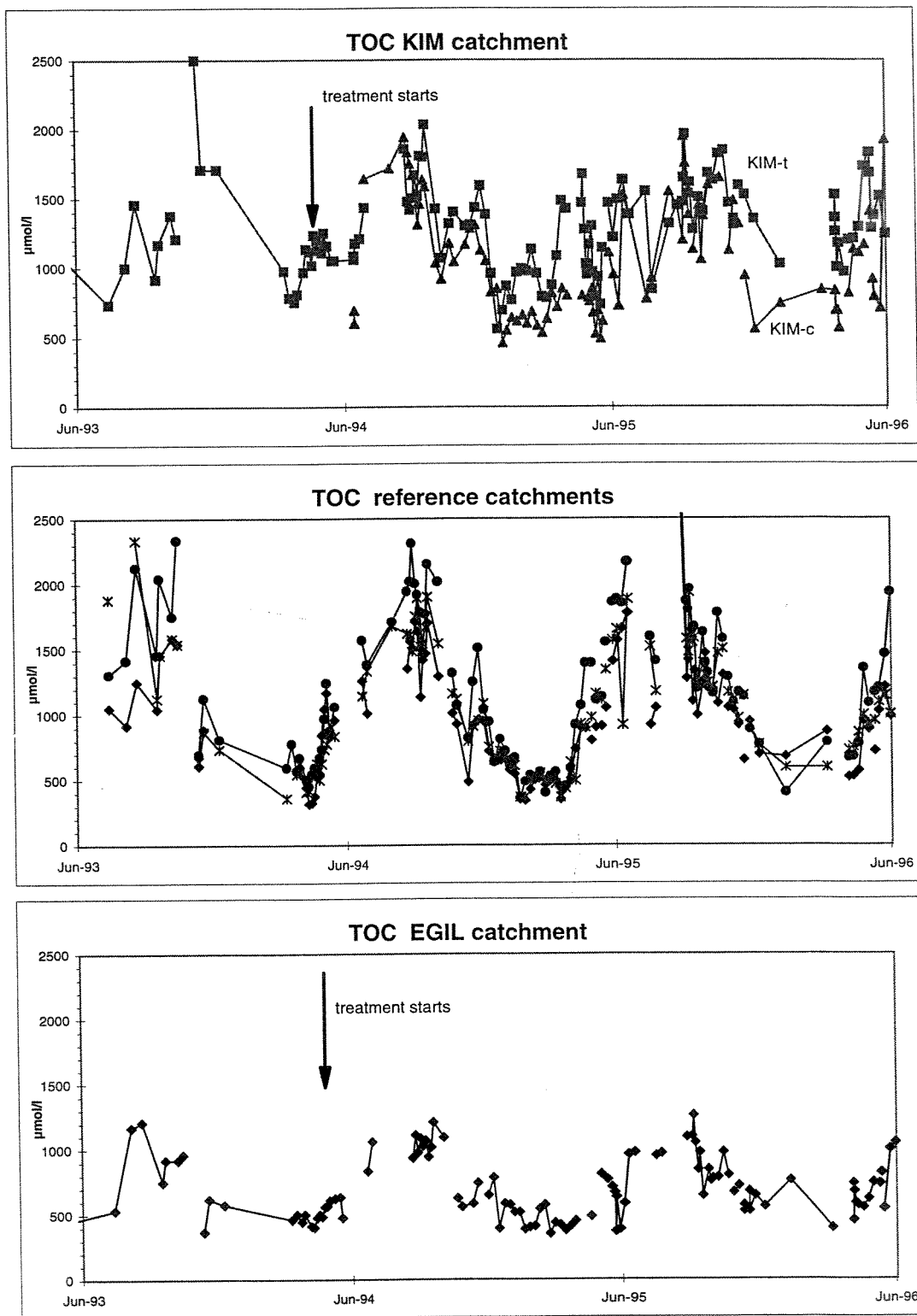


Figure 13. Concentrations of total organic carbon (TOC) in individual samples of runoff at KIM-T catchment (roof, clean rain; CO_2 and temperature), KIM-C catchment (roof, clean rain; control), EGIL catchment (roof, acid rain; soil warming), and CECILIE, METTE and ROLF catchments (untreated references) for the 3-year period June 1993 - June 1996 (CLIMEX pre-treatment year and treatment years 1 and 2).

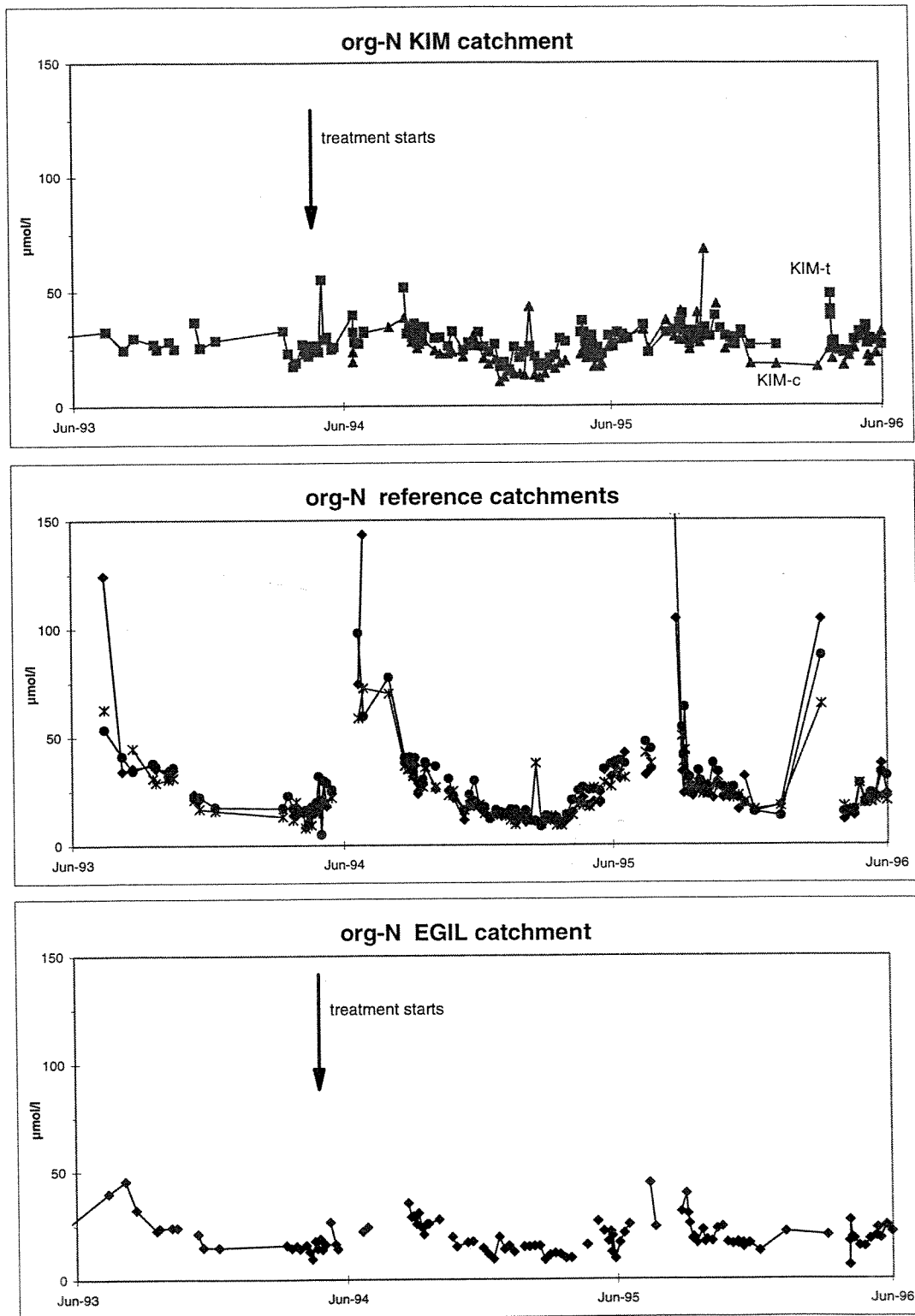


Figure 14. Concentrations of organic nitrogen in individual samples of runoff at KIM-T catchment (roof, clean rain; CO_2 and temperature), KIM-C catchment (roof, clean rain; control), EGIL catchment (roof, acid rain; soil warming), and CECILIE, METTE and ROLF catchments (untreated references) for the 3-year period June 1993 - June 1996 (CLIMEX pre-treatment year and treatment years 1 and 2).

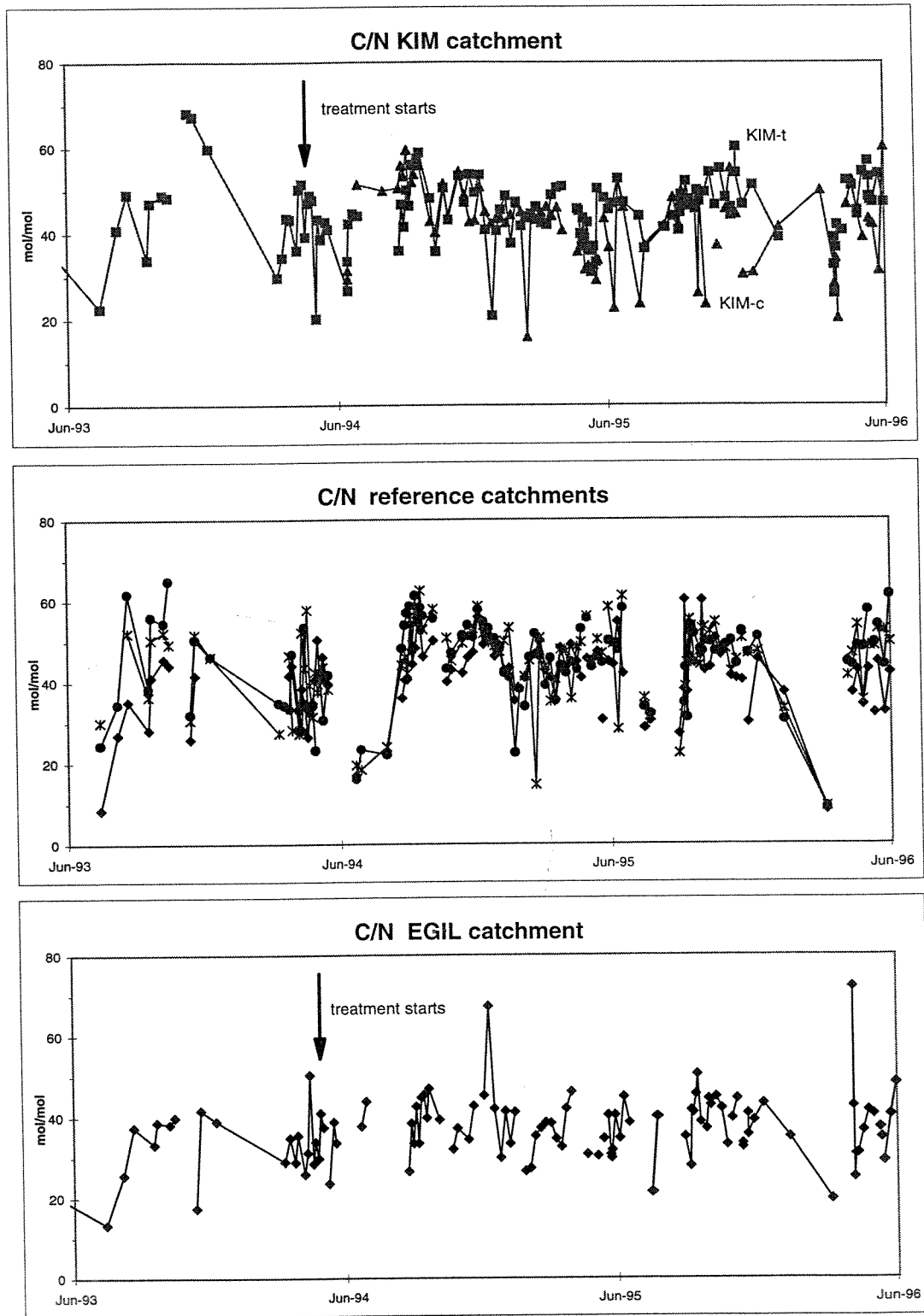


Figure 15. Molar C/N ratios (TOC/org-N) in individual samples of runoff at KIM-T catchment (roof, clean rain; CO₂ and temperature), KIM-C catchment (roof, clean rain; control), EGIL catchment (roof, acid rain; soil warming), and CECILIE, METTE and ROLF catchments (untreated references) for the 3-year period June 1993 - June 1996 (CLIMEX pre-treatment year and treatment years 1 and 2).

4. Discussion

The CLIMEX treatment at KIM catchment (increased CO₂ and temperature) has caused small but important changes in runoff chemistry and flux of solutes from the catchment. Most striking is the decrease in sulphate levels, most probably due to the enclosure of the catchment and thus reduction of dry deposition of sulphur gases and particulate. Sulphate concentrations in runoff at KIM catchment are now at levels similar to those in lakes in pristine areas such as north-western Norway (Henriksen et al. 1988).

At KIM catchment the significant increase in TOC may be explained by the 3-5 °C increase in temperature of the treatment and an enhancement of biomass production (e.g., litterfall) due to CO₂ enrichment. Higher temperature should cause an increase in the rate of decomposition of organic matter, both new litter and older soil organic matter. This decomposition could potentially release a number of chemical compounds to soil solution, in particular NO₃ and NH₄ as well as TOC and organic N. At KIM catchment the RIA test does not reveal significant changes in either NO₃ or NH₄. For these components, however, RIA is a weak test because of the large pre-treatment difference in NO₃ and NH₄ levels between KIM catchment (clean rain) and the other catchments (ambient rain). And unfortunately there are no pre-treatment data from KIM-C to compare with KIM-T. KIM-C has very similar runoff chemistry to KIM-T for major components such as SO₄, SBC and ANC (Figure 2), but quite different levels of NO₃ and NH₄ (Figure 5). It is tempting to ascribe these differences to the CLIMEX treatment at KIM-T, but the lack of pre-treatment data preclude the statistical test of this hypothesis.

At EGIL catchment RIA indicates that soil warming has caused statistically significant increases in NO₃ and NH₄ concentrations relative to the reference catchment ROLF (Figures 8 and 9). These increases were apparent already after 1 year of treatment, and are ascribed to increased decomposition of soil organic matter due to the increased soil temperature (Lükewille and Wright, in press).

There are 2 factors which may account for higher concentrations of NO₃ and NH₄ at EGIL but not at KIM. At EGIL catchment the external supply of nitrogen is high; ambient nitrogen deposition is 14 kgN/ha/yr. At KIM catchment, on the other hand, the external supply has been < 2 kgN/ha/yr for 13 years. EGIL catchment (and the reference catchments) release significant concentrations of inorganic N most of the year, while at KIM catchment concentrations in runoff are much lower and generally near zero during the growing season. EGIL catchment is apparently N saturated, whereas KIM is not. Thus N released at KIM might be more completely immobilised by soil micro-organisms, whereas at EGIL the N requirement for microbial immobilisation is already met. Secondly the treatment at KIM catchment warmed the air as well as the soil, whereas at EGIL only the below-ground part was affected. At KIM catchment both the increased temperature and increased CO₂ tend to promote plant growth and thus plant demand for nitrogen. N released from enhanced decomposition might therefore be taken up by plants and not appear in runoff. At EGIL

catchment on the other hand, the air is not affected and plant growth is not increased except for species with bulbs or other below-ground growth points.

The changes in runoff chemistry caused by the CLIMEX treatments at KIM and EGIL catchments suggest that the internal cycling of nutrients in these forest ecosystems has only been moderately affected during the first 2 years. There are indications that the effects are increasing over time at KIM catchment in that the second year of treatment at KIM catchment resulted in larger changes than exhibited during the first year. Further years of treatment will reveal whether the changes in chemical fluxes in runoff are transient or long-lasting.

Although the changes may be small with respect to the forest ecosystem, the increased concentrations of NO_3 and NH_4 may have significant impact on aquatic ecosystems downstream. At EGIL catchment the concentrations of NO_3 rose from an average 34 $\mu\text{eq/l}$ for the 3 years prior to treatment to 42 $\mu\text{eq/l}$ for the first 2 years of treatment. This 20% increase represents a significant increase in concentrations of strong acid anions. In acid-sensitive freshwaters, this leads to acidification, with increased concentrations of H^+ and inorganic-Al and decreased ANC.

If the CLIMEX results can be extrapolated in time and space, large-regions of southern Norway and other parts of northern Europe and eastern North America potentially can be adversely affected by nitrate release. It is as yet unknown whether a long-term increase in temperature due to global change will result in widespread rise in N leaching due to increased mineralisation of soil organic matter. And it is also unknown whether increased leaching of N will be limited to those ecosystems that receive significant N deposition. Certainly the organic soils typical of the boreal region contain N stores equivalent to many decades of N deposition, and loss of only a small fraction can cause significant effects on soils and waters (Hessen and Wright 1993).

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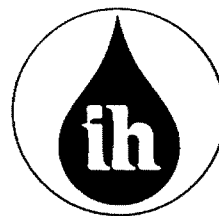
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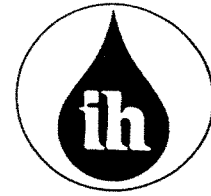


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