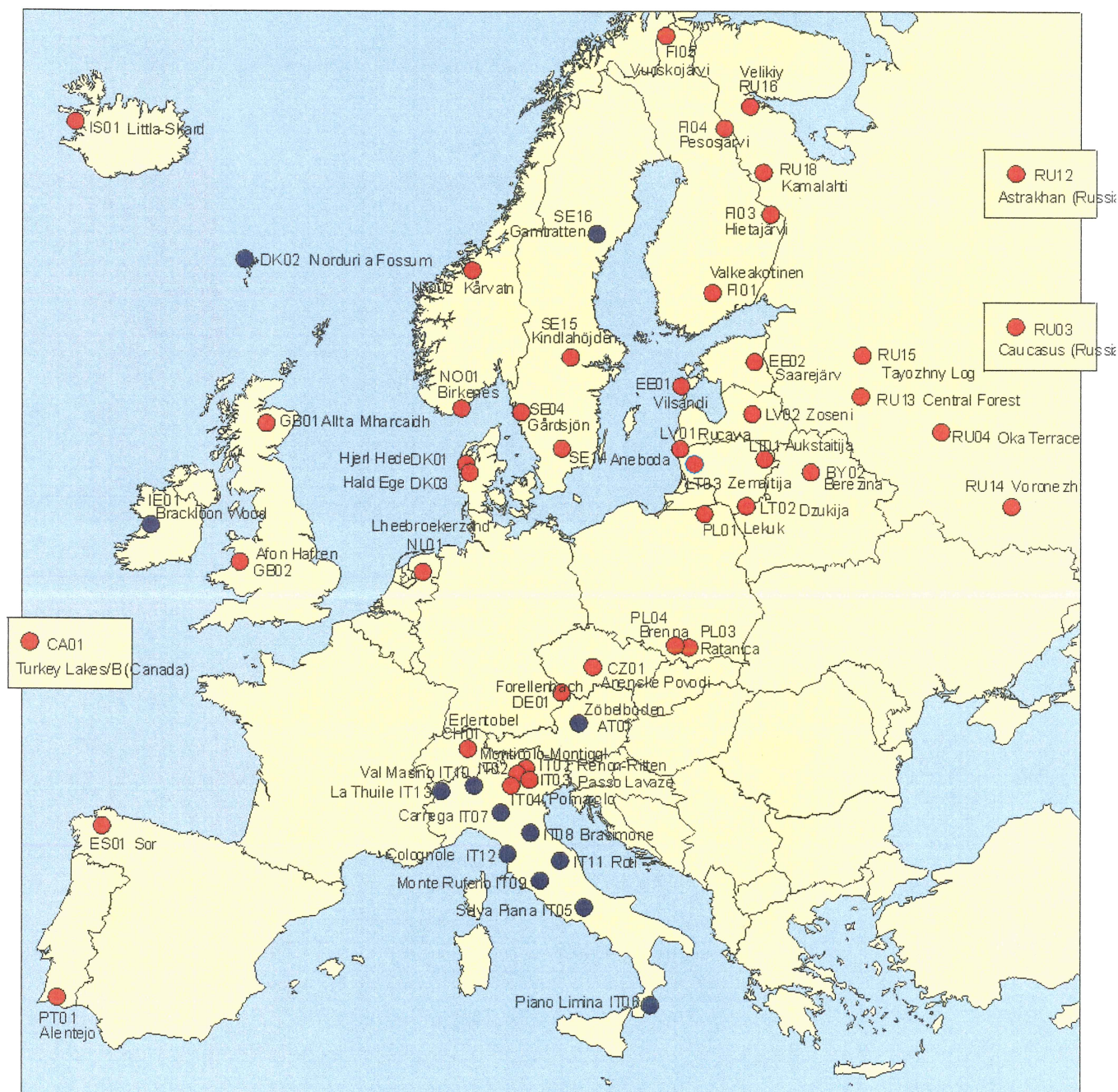## UN-ECE CONVENTION ON LONG-RANGE TRANSBOUNDARY OF AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON INTEGRATED MONITORING ON AIR POLLUTION EFFECTS ON ECOSYSTEMS

Chemistry of atmospheric deposition
at the measurement stations IT01-IT02 in South Tyrol
(co-funded by EU-Reg. 3528/86, 2157/92, 1091/94)

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Chemistry of Atmospheric Deposition in South Tyrol (Italy).

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Atmospheric precipitation chemistry has been recorded in South Tyrol since 1983. Depositions, comprehensive of wet and bulk, throughfall, stemflow and soil water analysis have been investigated in two experimental forest stations since 1994 (at Ritten and Montiggl). Samples were collected at 1 week intervals.

The annual precipitation from 1983 to 1995, recorded at three collection sites (Ritten 1780 m, Montiggl 530 m, Fennberg 1160 m altitude), is shown in Fig. 1. The low amount of precipitation in the province (annual average between 500 and 900 mm in the valleys and up to 1500 mm above 2000 m altitude) is reflected in the deposition values. The distribution of the deposition values during the year shows minimum values in winter and higher values during late spring and summer, which correspond to a similar distribution pattern of the precipitations (Fig. 2).

The three main factors influencing precipitation chemistry are anthropogenic air pollution, mineral dust and sea spray. The low concentrations of sodium and chloride, both with a median concentration, in the wet samples, around 5 μmol L^{-1} show the little influence in South Tyrol of sea spray (seasalt). Alkaline dust, transported by air masses from the Sahara, is relatively frequent in the precipitations of the province, influences mostly the calcium concentrations and has a buffering action on the acidity of depositions. H^+, SO4 and NO3 and heavy metals are generally linked with air pollution. Different sources, natural and anthropogenic, contribute to the emission of ammonia.

The annual proton input due to open bulk precipitation was in South Tyrol, during 1995, equal to 0.06 kmol ha^{-1} a^{-1} in Montiggl, 0.07 at Ritten and 0.09 in Fennberg. This annual proton input is 1/10 of the value found in Lange Bramke (D) equal to 0.72 kmol ha^{-1} a^{-1} (Hauhs, 1989) and much lower than the value found in other sites in central Europe, southern Norway or Netherlands (Paces (1985), Abrahamsen et al. (1989), Mulder et al. (1987)). The development of pH median values in bulk precipitation at the three sampling sites is shown in Fig. 3. The median values in wet precipitation are generally up to 0.1 unit lower than in bulk. The annual median pH values registered in South Tyrol during the last eleven years, ranging between 4.8 and 5.4, show that on annual basis the precipitation in the province has low acidity. pH median values in north-western Italy (Piedmont and Lombardy) and in Canton Ticino, Switzerland range from slightly above 4.0 to 4.3-4.4 (Mosello & Marchetto, 1996). All these pH median values are obtained from weekly samples and are therefore generally higher than those obtained from single events because small events rich in acidic substances are diluted with the others events during the week.

Acidity of depositions in South Tyrol, as in all the others parts of Italy and to a minor extent also in the regions located north of the Alps mountain chain, is mitigated by relatively frequent episodes of precipitation with pH higher than 6.0 due to the transport of alkaline dust, transported by air masses from the Sahara. In this respect a decrease of the calcium input was registered in 1995 (Fig. 4). This decrease produced a higher acidity of precipitation despite a further decrease of the sulphur and also a decrease, for this year, of the nitrogen compounds.

The mean sulphate deposition in South Tyrol during the period 1983-95 was around 0.19 kmol ha^{-1} a^{-1}. The mean sulphate deposition in the Solling area in Germany was 0.72 k mol ha^{-1} a^{-1} for open bulk precipitation and 2.60 kmol ha^{-1} a^{-1} for throughfall under spruce forest (Matzner, 1989). Mean deposited amounts of sulphate in the Netherlands are 0.465 kmol ha^{-1} a^{-1} and similar in Japan (0.48 kmol ha^{-1} a^{-1} (Hara, 1991). The mean nitrate deposition in South Tyrol during the same period was 0.3 kmol ha^{-1} a^{-1}, while in the Solling area in Germany ranged between 0.43 and 0.86 kmol ha^{-1} a^{-1} (Matzner & Meiwes, 1994).

Nitrogen dioxide (nitrate deposition) has, in relation to sulphur dioxide (sulphate deposition), a relevant relative role in South Tyrol. Nitrate deposition levels showed a steadily increasing relative share against a continuing decreasing importance of sulphate. The molar ratio of sulphate input to nitrate input in South Tyrol has decreased from around 0.8 in the period 1985-88 to around 0.5 in the period 1991-95. Sulphate depositions have decreased greatly during the last six years (Fig. 5), whereas nitrate depositions rather show a light tendency toward increase. Ammonia depositions instead did not change significantly during the period 1983-95 (Fig.5).

Concentration relationships of H^+ to sulphate and nitrate and between sulphate and calcium have been evaluated using weekly data from the last three years (1993-95). H^+ is better correlated with nitrate (r=0.62, n=102) than with sulphate (r=0.31, n=102) in the station Ritten located north of the town, while no significant correlation is found between H^+ and both nitrate and sulphate in the two locations of Montiggl and Fennberg probably because of a higher content of calcareus dust in the local soil. A very good correlation is instead found between calcium and sulphate for all sampling sites and particularly for the bulk samples (r= 0.73-0.80). This suggests either that alkaline dust is reacting with the acidic atmospheric substances or an influence of wind-blown dust containing $CaSO_4$ minerals, such as gypsum, which provides a natural nonacidic source for the precipitation of sulphate ions. Also the relatively weak correlation between SO_4 and H^+, with many sulphate concentrations values present consistently with low concentrations of protons could confirm one or both of the two buffering phenomenon suggested above. A good correlation also exists between sulphate and magnesium and between calcium and magnesium. The relationships of sulphate and calcium concentrations between wet and bulk precipitation show the influence of dust dryfall collected in the bulk collectors, which is greater for calcium than for sulphate (Fig. 6). Sodium and chloride concentrations in wet samples show a good correlation (r=0.72).

Tab. 1: Median values of the monthly weighted mean values for stemflow, throughfall, soil water, bulk and wet samples for the collection sites of Ritten and Montiggl during 1994-95.

	Ritten Stemflow	Ritten Throughf.	Ritten Soil	Ritten Bulk	Ritten Wet	Montiggl Stemflow	Montiggl Throughf.	Montiggl Soil	Montiggl Bulk	Montiggl Wet
pH	5.8	5.2	5.6	5.0	5.1	6.0	6.0	5.6	5.1	5.0
Ca mg l^{-1}	2.3	1.2	0.9	0.3	0.2	4.4	2.6	2.4	0.6	0.3
Mg mg l^{-1}	0.8	0.5	0.3	0.1	0.0	1.0	0.9	1.0	0.1	0.1
K mg l^{-1}	12.1	5.0	1.0	0.1	0.1	13.0	6.3	1.0	0.2	0.1
N-NH4 mg l^{-1}	2.6	0.4	0.0	0.4	0.3	0.7	1.2	0.0	0.4	0.3
N-NO3 mg l^{-1}	0.4	0.7	0.1	0.4	0.4	0.8	1.0	0.0	0.6	0.5

Precipitation over a forested ground is altered by interaction with plant surfaces which act as a filter for airborne gases and particles. This results in a transfer to the forest floor of material captured, washed, and leached from the forest canopy. Hydrogen ion concentration was found to be dependent on tree species, with coniferous canopies decreasing pH and decidous increasing pH (Johannes et al., 1985). The monthly means of pH for throughfall and stemflow are higher than for bulk both in the deciduous forest experimental area of Montiggl and in the coniferous forest of Ritten (Fig. 7), the difference becoming greater for some months of the year. In this latter site particularly high pH values were registered for stemflow. These higher pH values suggest the excretion of base cations rather than the washout of acidic substances from the foliage and stem of the trees.

The calcium inputs from the stemflow and throughfall were higher than in the bulk samples reflecting the washout and excretion (Tab. 1). The magnesium monthly input was also greater than in bulk and also the sulphate input exceeded that from bulk precipitation. The monthly

inputs of potassium and nitrate with throughfall and stemflow and in the soil water are shown in Fig. 8 and 9. Potassium concentrations are much greater in throughfall and stemflow than in wet and bulk precipitation, where concentrations remain low throughout the year (Tab. 1). Monthly mean concentrations of nitrate for throughfall and stemflow and their difference in relation to the levels recorded in the bulk and wet samples show different behaviour in the two years of study. Particularly high values were recorded in some single months for throughfall, stemflow and soil water in the coniferous forest of Ritten. Ammonium inputs from throughfall were higher than those from open bulk inputs, during summer, and particularly for the deciduous forest of Montiggl. Ammonium concentrations in stemflow were instead higher for the coniferous forest of Ritten. No nitrogen either as ammonia or as nitrate is present in the soil water. The interaction of the canopy on the nitrogen flow is dependent of its biological activity (time of the year) and of the nitrogen deposition level. An adsorption of the deposited N in the canopy is registered when the deposition level is low, whereas, in more polluted areas, a higher N flow is measured in the troughfall than in the precipitation. The uptake from the canopy recorded during summer 1995 (Fig. 9) did not take place the year before, perhaps because of the different levels of N deposition in the two years (Fig. 5).

The impact of acid deposition has not induced serious damages to lakes in the province. A remarkable increase of the concentrations of calcium, sulphate and alkalinity was registered during the period 1988-96 for the lake „Milchsee", one of the better monitored high altitude remote lakes of the province. This increase together with a similar increase of dissolved silica suggests that within the watershed takes place a progressive increase of the weathering, perhaps because of the increased air temperatures: a decrease of the period of snow covering of lake and watershed causes an increased weathering, which exerts an increased buffering action on the deposited acidic substances.

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Wathne, B.M., Patrick, S. T., Monteith, D., Barth H. (Editors - 1995). AL:PE 1 Report. E.C. *Report EUR 16129 EN*, pp. 292.
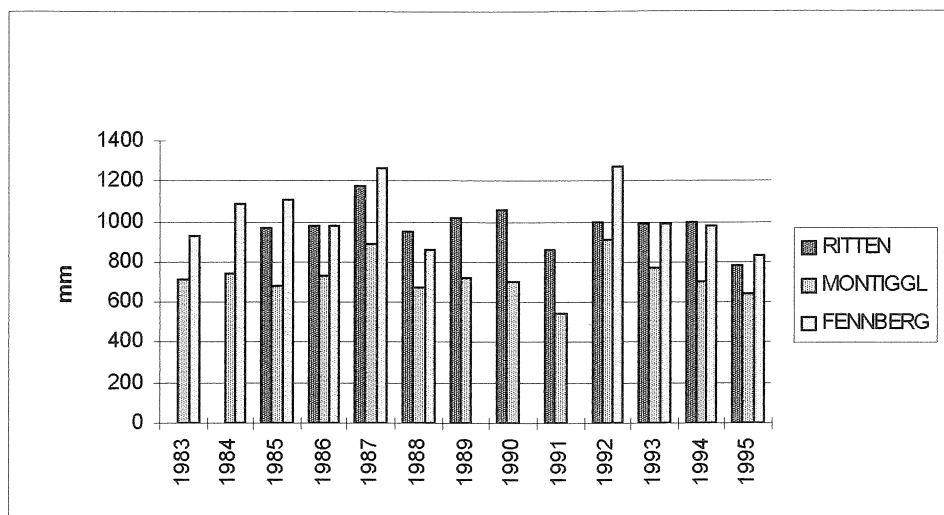
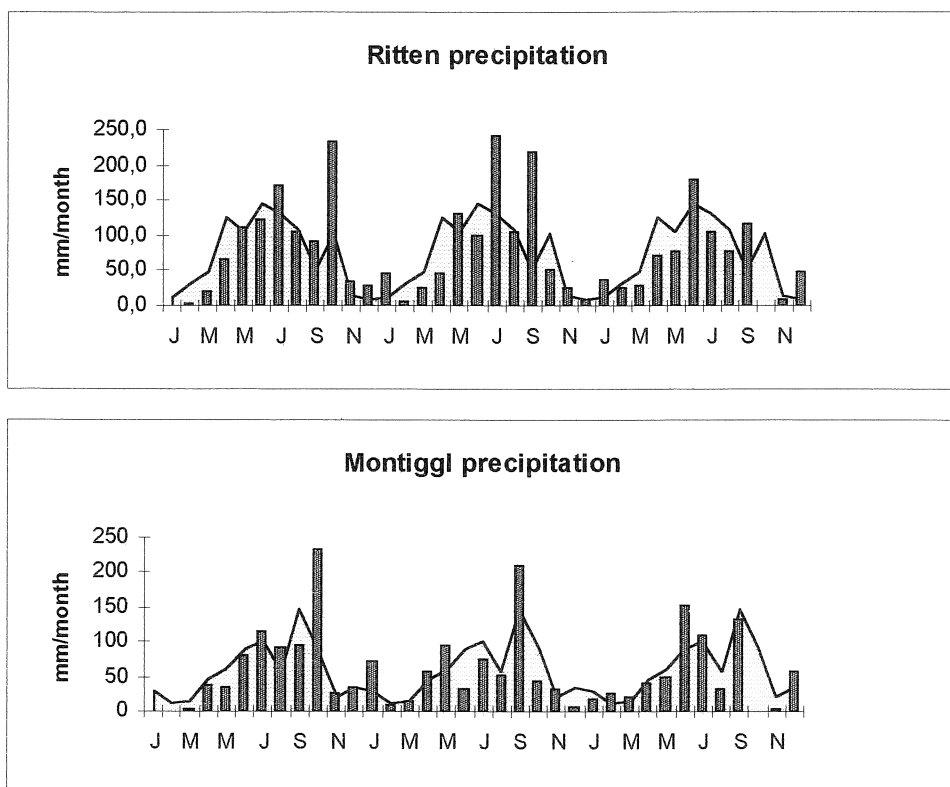Fig. 1: Yearly precipitation at the collection sites Ritten, Montiggl, Fennberg.

Fig. 2: Monthly precipitations during the years 1993,1994,1995 (bars) and monthly means of the same three years (shaded area).
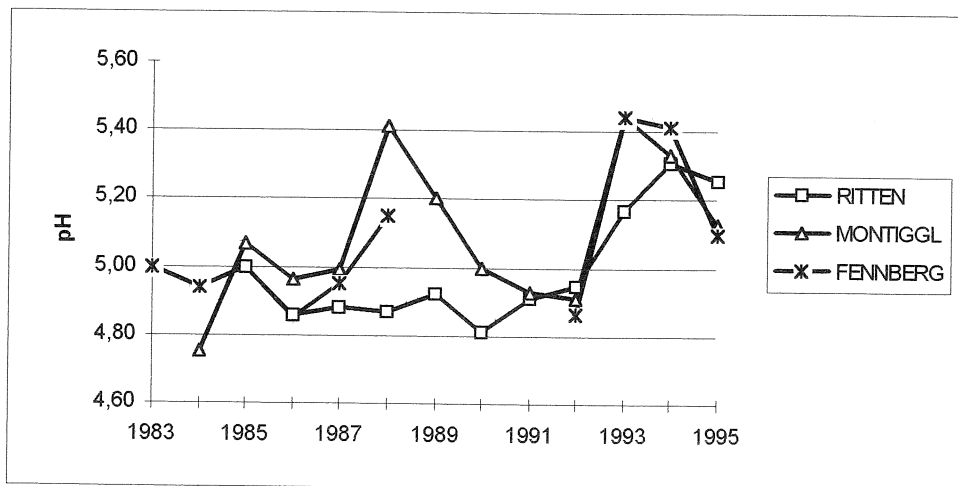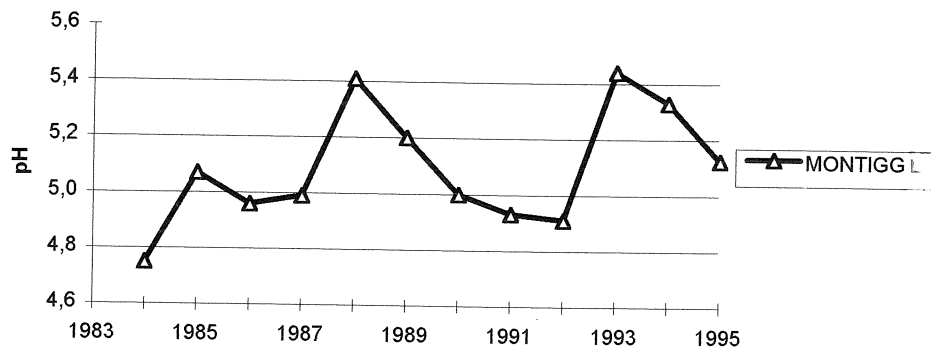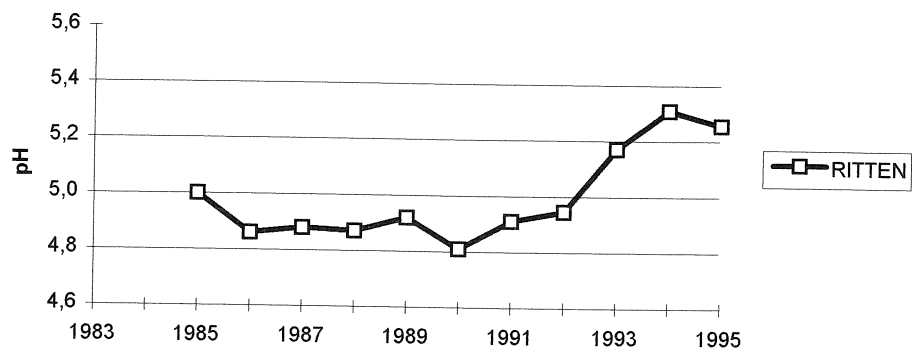
Fig. 3: Development of pH median bulk values in the stations Ritten, Montiggl and Fennberg.
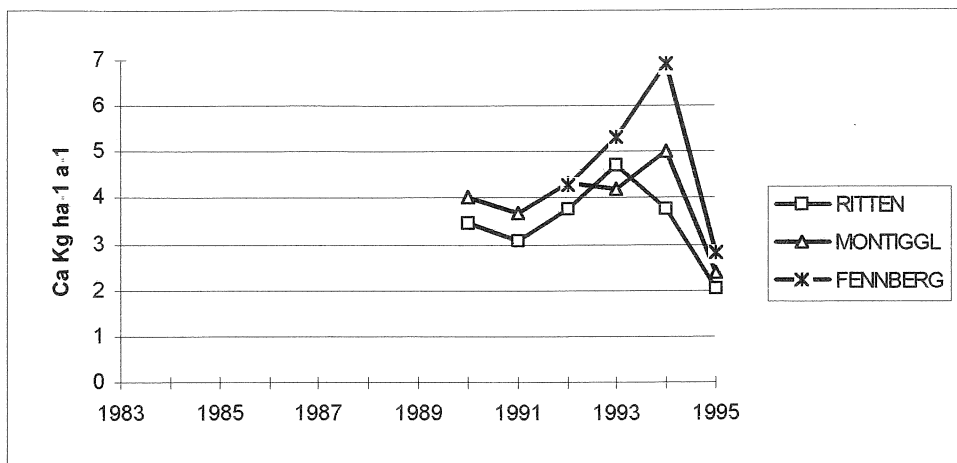
Fig. 4: Development of calcium fluxes with bulk precipitation in the stations Ritten, Montiggl and Fennberg.
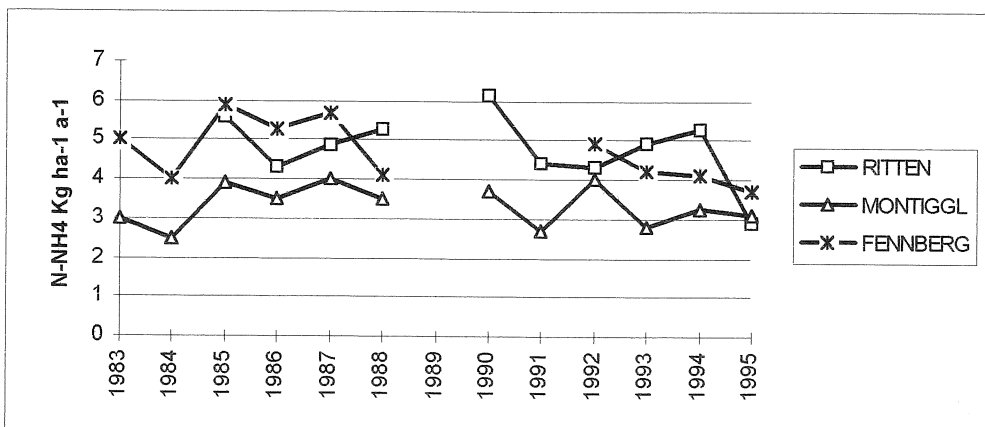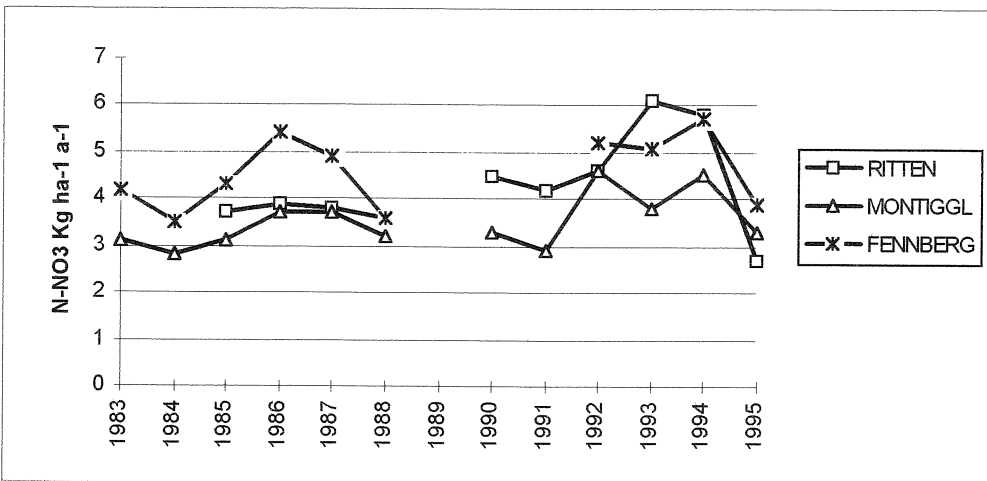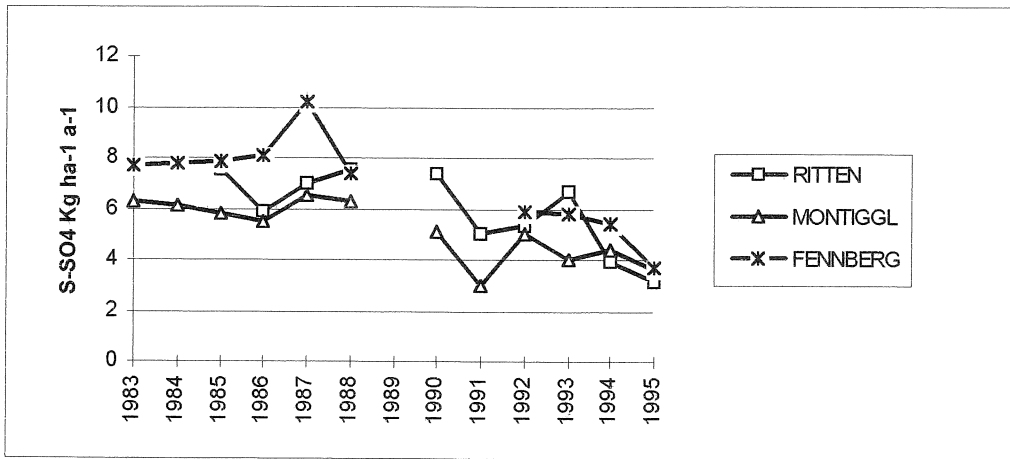
Fig. 5: Development of sulfate, nitrate and ammonia fluxes with bulk precipitation in the stations Ritten, Montiggl and Fennberg.
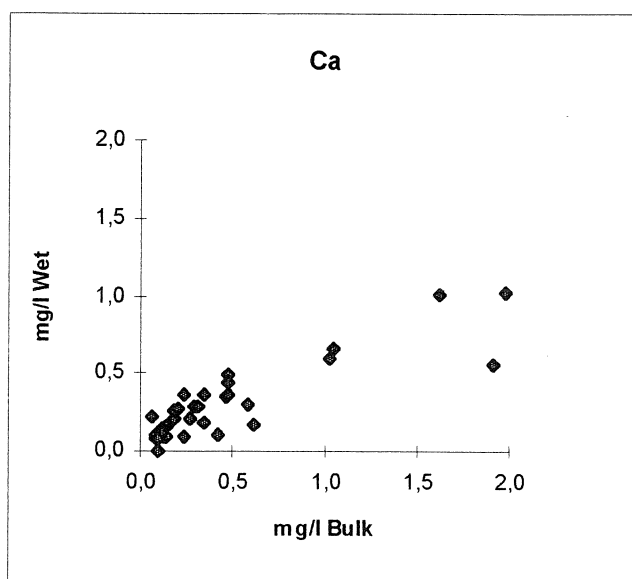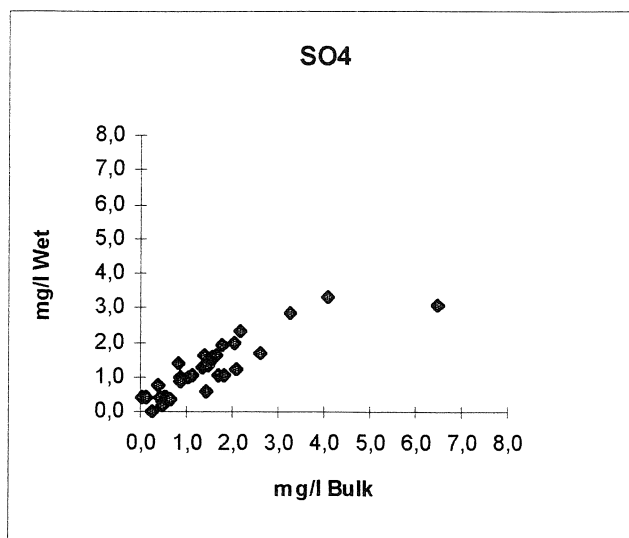
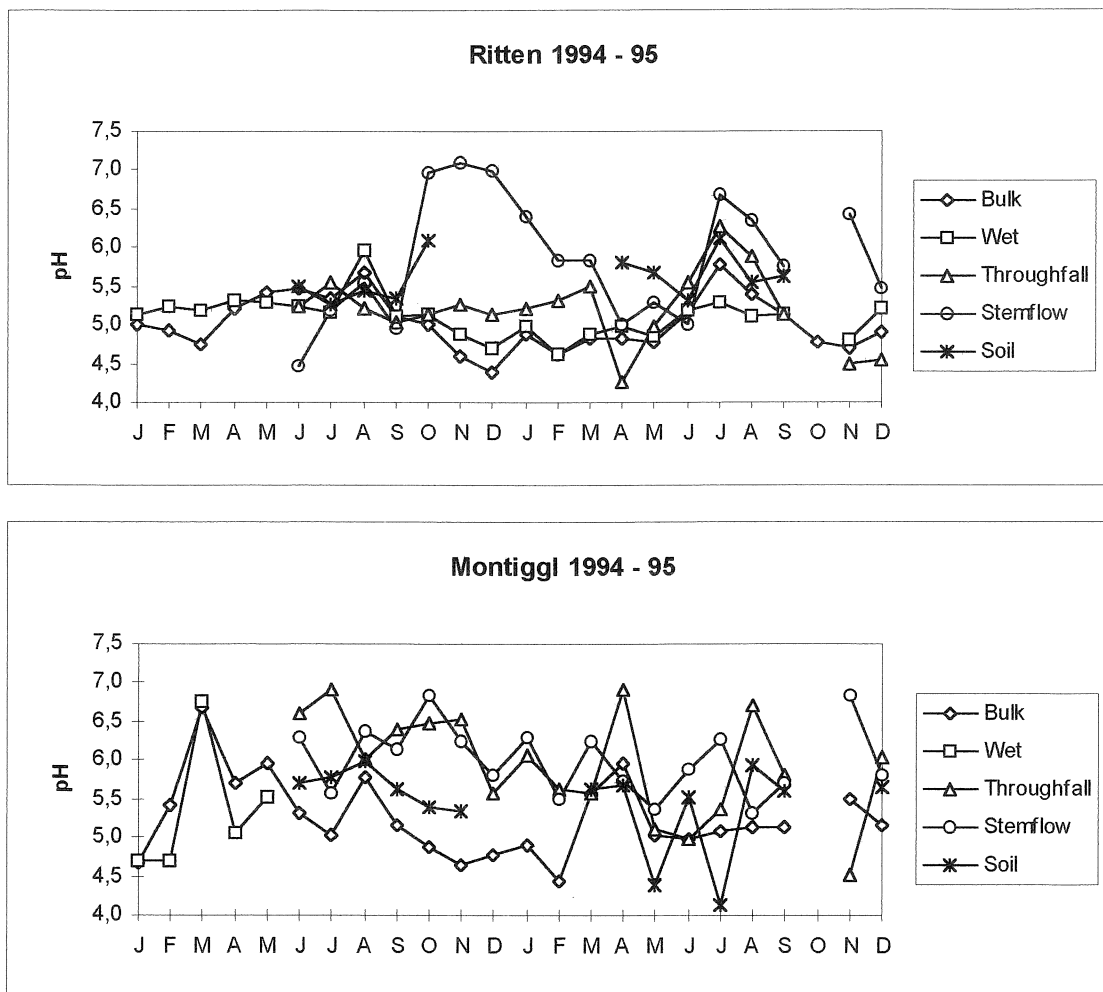Fig. 6: Relationship of sulphate and calcium between bulk and wet precipitation at Ritten in 1995.

Fig. 7: pH of bulk and wet precipitation, throughfall, stemflow and soil water at Ritten and Montiggl.
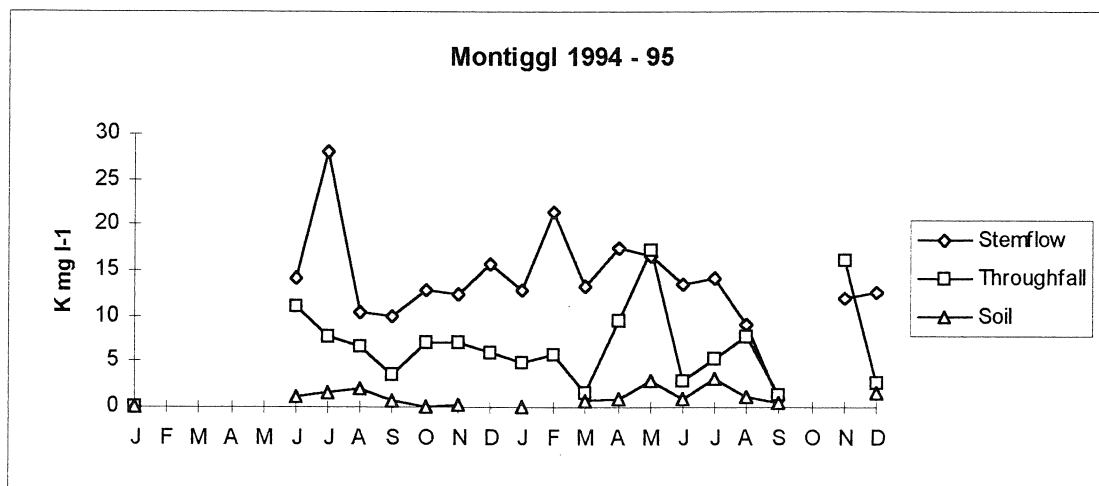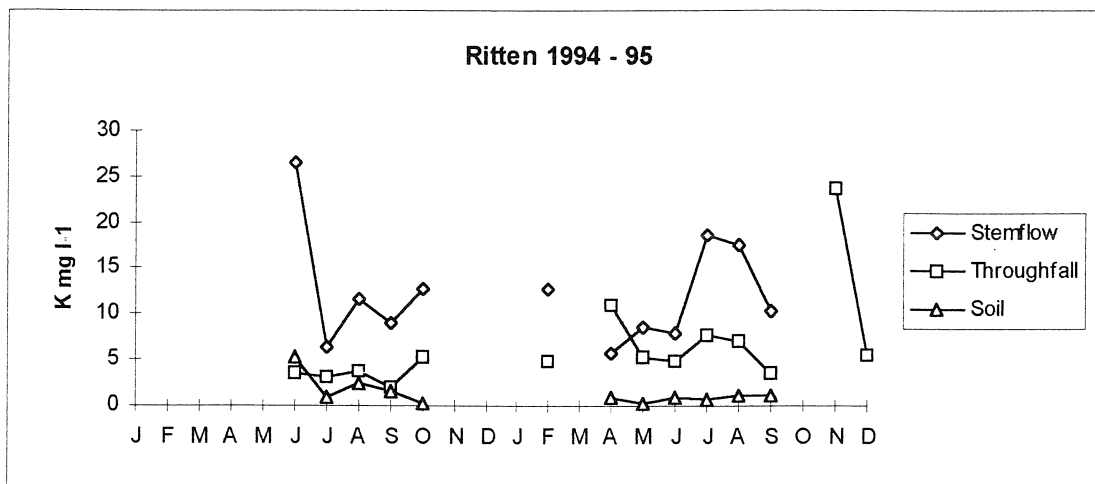
Fig. 8: Development of potassium fluxes with stemflow, throughfall precipitation and in soil water. Bulk and wet fluxes are too low to be represented here.
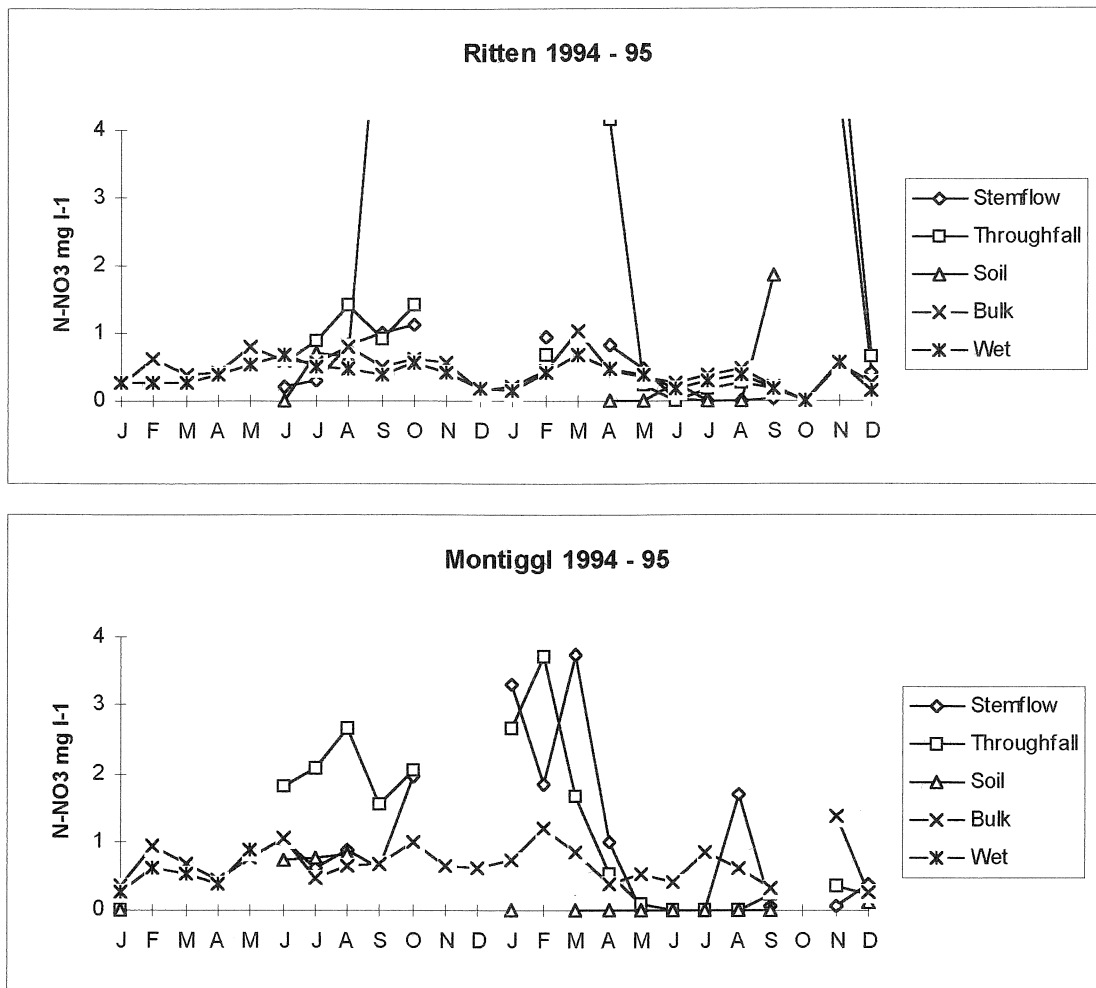
Fig. 9: Development of nitrate fluxes with stemflow, throughfall, soil water, bulk and wet precipitation and in soil water.