

Analysis of soil water chemistry and biogeochemistry of a mountain spruce forest in Achenkirch (Tyrol) with a focus on the nitrogen cycle



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Abstract

The biogeochemical nutrient fluxes (nitrogen, sulfur, calcium, magnesium, and potassium) were quantified for a mature Norway spruce forest in the northern Tyrolean Limestone Alps. The investigation area is situated in a humid, cool climate (MAT 6,4 and MAP 1661mm) with only 25-39% of the incoming water (throughfall) leaving the system via evapotranspiration, while discharge (leachate) counts for 61-75%. Surface run-off fluxes are negligible. The site is assumed to be at risk to become N-saturated due to the high amounts N deposition loads in recent years (up to 16,9 kgN*ha⁻¹*a⁻¹). The soil at the site is mainly classified as 120-160cm deep chromic cambisols and rendzic leptosols with a high content of coarse material. The pH of the soil water is higher than 7 at all depths (5-50cm) and a lot of Mg and Ca are found in the leachate due to the pure dolomitic bedrock. While N inputs via throughfall were about 8 kg N*ha⁻¹*a⁻¹ between 2001 and 2008, sulfur inputs were <3kg*ha⁻¹*a⁻¹. Accordingly S outputs were low (~4kg* ha⁻¹*a⁻¹). The interpretation of soil solution chemistry and the chemistry of the discharging water led to conflicting conclusions on the nitrogen status: (i) The nitrate concentrations in discharge water (leachate) decreased between 2001 and 2008 significantly from 18 to around 1,5 mg/l respectively from 39 to around 3kgN*ha⁻¹*a⁻¹. Generally, concentrations in winter were twice as high as in summer. Since 2004 the nitrate concentrations dropped, indicating that the system changed from an 'N-saturated system' to a 'system in transition', according to the nomenclature of John Aber. ii) Nitrate concentrations and loads at 50cm soil-depth were comparable low and did not decrease between 2001 and 2008. Accordingly the investigation area is not yet nitrogen-saturated.

1 Introduction

Nitrogen (N) is an essential component of proteins, genetic material, chlorophyll, and other key organic molecules. The earth's atmosphere consists of 78 percent nitrogen gas, but most plants and animals cannot use nitrogen gas directly from the air and most terrestrial ecosystems are N limited. As illustrated in Figure 1 the two natural sources of new nitrogen entering this cycle are nitrogen-fixing organisms (bacteria and some algae) and lightning (VITOUSEK ET AL., 1997).

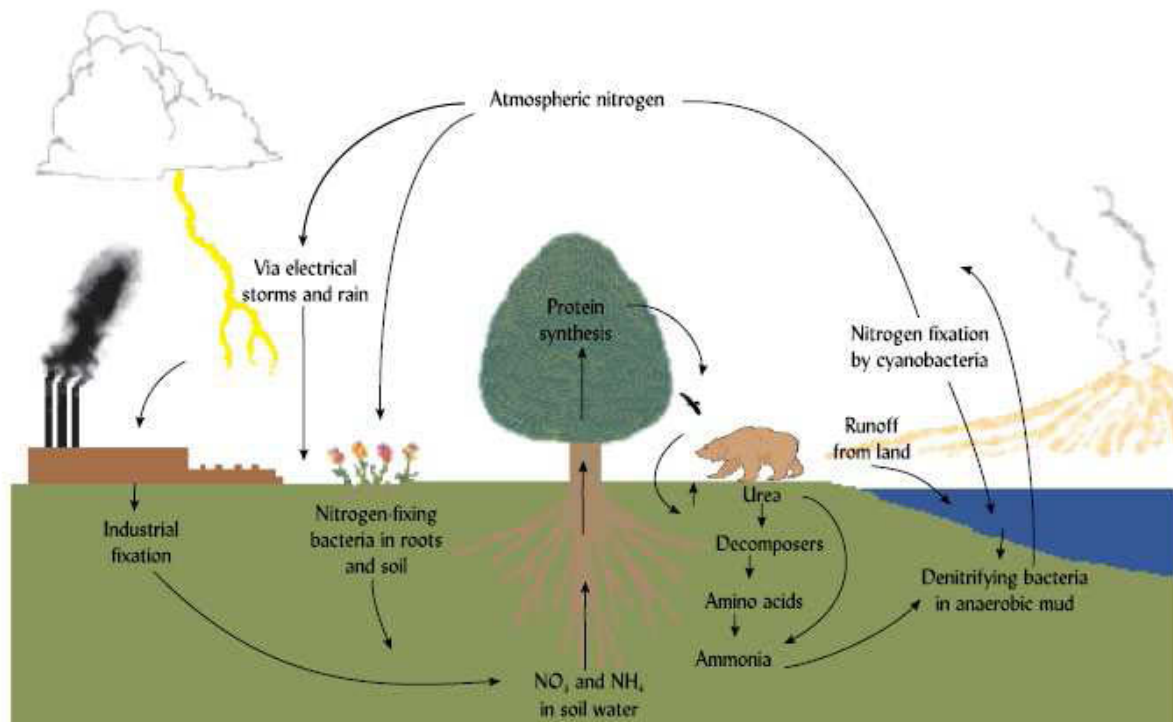


Figure 1: Simplified diagram of the nitrogen cycle

Source: VITOUSEK ET AL., 1997

In the 20th century human driven N input has altered the global N cycle significantly and effectively doubled the annual transfer of nitrogen from the vast but unavailable atmospheric pool to the biologically available forms. The major sources of these additional inputs are industrial N fixation to produce fertilizers, the burning of fossil fuels and the cultivation of N-fixing crops (e.g. soybeans, peas,...). Additionally some land management practices like burning of forests and grasslands, draining of wetlands or land clearing for crops mobilizes N which is stored in the soil (VITOUSEK ET AL., 1997).

Once N enters a forest ecosystem a number of biochemical reactions affect the N cycle (Figure 2). First of all nitrogen can be taken up and put into organic matter. On the other hand organic N can get mineralized. As soon as organic nitrogen is mineralized to Ammonium (NH_4^+) several processes can follow (VITOUSEK AND MELILLO, 1979):

- 1.) Ammonium could be taken up by (re)growing vegetation. This process is mainly influenced by the vegetation type and the stand age.
- 2.) The ammonium released by mineralization could be immobilized by decomposers until the effective C:N ratio is low enough to allow nitrogen release.
- 3.) Ammonium could be converted to nitrite and nitrate. This process occurs most rapidly in base rich, near-neutral soils.
- 4.) The mineralized ammonium could accumulate on cation exchange sites in soils. This process accounts for significant nitrogen retention only if nitrification is very slow. Because foregoing experiments at the Mühleggerköpfl showed high nitrification rates this is unlikely at that site.
- 5.) Ammonium fixation by clays could retain nitrogen in soils. Due to the high amount of coarse material at the site this is not very likely.
- 6.) Ammonia volatilization can be a significant loss of nitrogen from basic or slightly acid soils. Because of the high pH at the site volatile ammonia may be an important factor.

Once ammonium is converted to nitrate it can more easily be leached through soils. Nitrate can be immobilized by microorganisms or taken up by growing vegetation. These processes are important under the same conditions as ammonium immobilization and uptake.

Other processes which can affect nitrate are (VITOUSEK AND MELILLO, 1979):

- 1.) If insufficient water percolates through the soil to leach nitrate below the rooting zone nitrate can be retained and accumulate in the soil.
- 2.) Nitrate can be retained within the soil by anion adsorption. But especially in temperate and boreal forest soils anion adsorption capacity is very low.
- 3.) Denitrification by the dissimilatory pathway can convert nitrate into nitrogen oxides and nitrogen gas.
- 4.) Another possible reduction pathway for nitrate in soils is the nonassimilatory reduction of nitrate to ammonium.

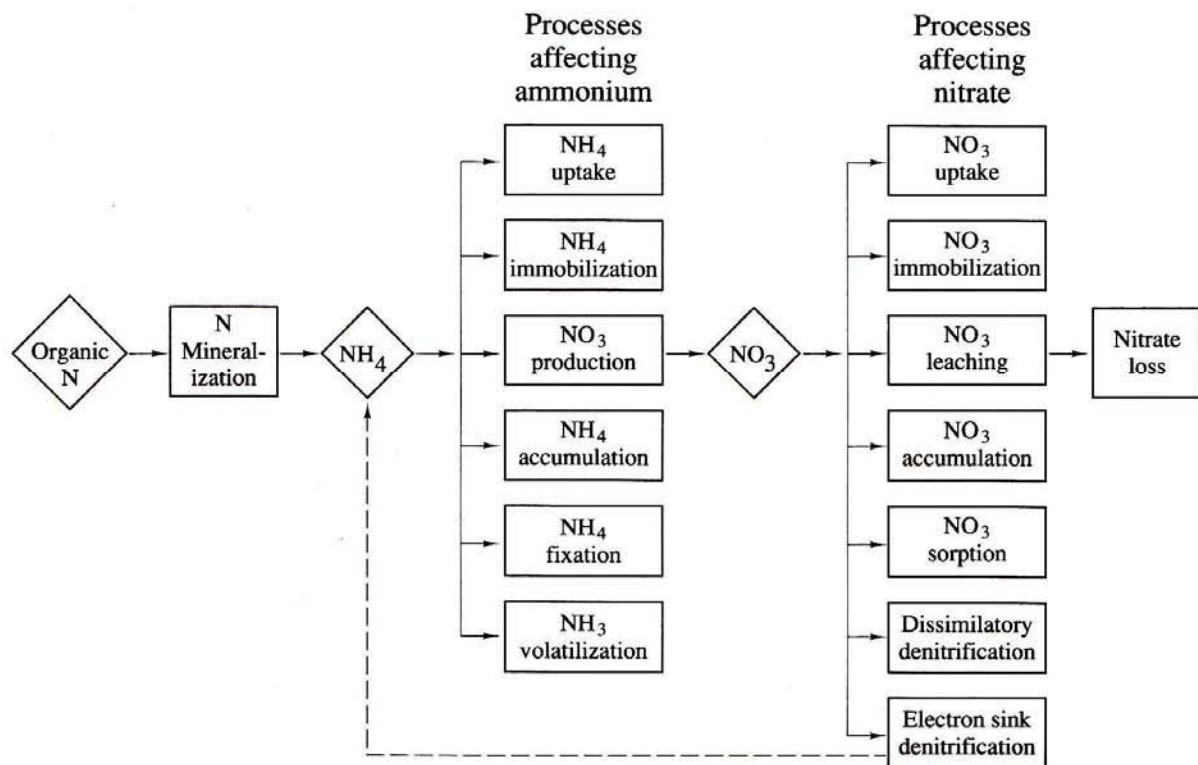


Figure 2: Pathways of mineralization and nitrification of organic nitrogen in the soil

Source: SCHLESINGER, 1991. from VITOUSEK AND MELILLO, 1979.

The main processes of N retention in a forest are immobilization by microbes, uptake by plants and mycorrhizal fungi, abiotic fixation and accumulation of NH_4^+ .

Nitrate leaching and volatilization of gaseous forms of nitrogen (NH_3 , N_2O , N_2) are responsible for losses.

The impacts of elevated N concentrations in ecosystems are manifold

- The forest productivity increases (as long as the system is N limited).
- Outgassing as NO_2^- (which is a highly reactive greenhouse gas).
- N leaching (NO_3^-) into the ground- and stream water increases causing negative consequences for freshwater ecosystems and the cation loss from soils.
- Loss of biodiversity

Thus increasing N inputs can decrease soil fertility and increase soil acidity due to the loss of exchangeable nutrients. Soil acidity also increases because of the N nitrification process. When N gets mineralized bacteria transform the NH_4 into NO_3 and 2H^+ ions are released into the soil ($\text{NH}_4 + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3 + 2\text{H}_2\text{O} + 2\text{H}^+$). So especially at acidified, calcium poor sites N leaching can cause mobilization of toxic aluminum ion concentrations. New supplies of nitrogen showered upon ecosystems can also cause a shift in dominant species and a decline in overall species diversity because only few plants are adapted to take full advantage of high N availability (FRANK ET AL., 2008 AND VITOUSEK ET AL., 1997).

ABER ET AL. (1998) divided the nitrogen saturation process into 4 stages (Figure 3).

Stage 0 is pre-pollution and assumes strong nitrogen limitations on growth.

Stage 1 is characterized by high nitrogen retention and a fertilizer effect of added nitrogen on tree growth.

Stage 2 includes the increase in the nitrification rate and some nitrate leaching, although plant productivity is still high.

In Stage 3 tree growth declines and nitrification and nitrate loss continue to increase while mineralization decreases.

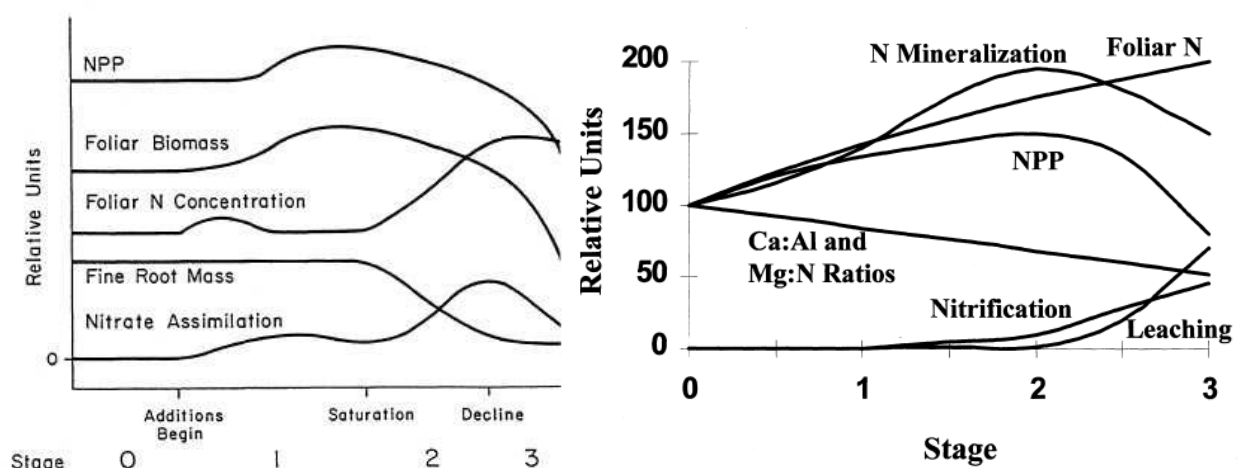


Figure 3: Response of temperate forest ecosystems to long-term, chronic nitrogen additions

Source: ABER ET AL., 1998

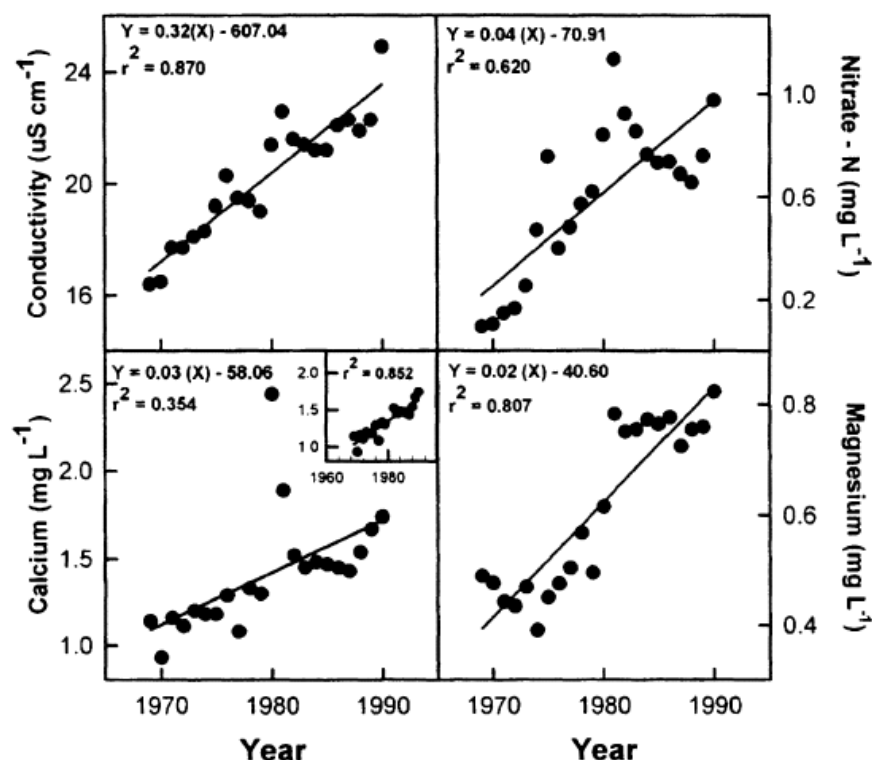


Figure 4: Long term annual average Conductivity, NO_3^- , Ca^{2+} and Mg^{2+} concentrations of a stream water.

Source: PETERJOHN ET AL., 1996

Another symptom can be a seasonal variability in stream water and soil solution nitrate concentration (Fig. 5). In nitrogen limited systems nitrate levels are generally low with little seasonality. As nitrogen limitations diminish, distinct seasonal pattern with

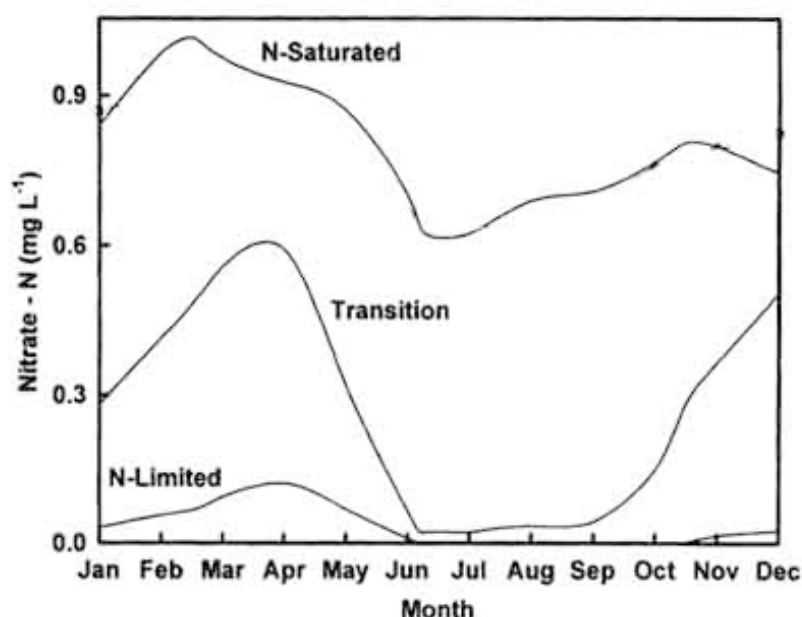


Figure 5: Expected seasonal patterns in stream water and soil solution nitrate concentrations.

Source: ABER, 1992

PETERJOHN ET AL. (1996) identified aquatic symptoms of terrestrial nitrogen saturation such as gradual increases in stream water nitrate and cation concentrations over time due to NO_3^- leaching at forest sites with increased N input (Figure 4).

low nitrate concentrations in the growing season (N uptake by plants) and high concentrations in the dormant season is expected to emerge (Transition). However as the system becomes N-saturated high concentrations and little seasonality are expected to occur (ABER, 1992).

Ecosystems respond differently to changing N inputs. Reliable **indicators** for N saturation are:

NO_3^- leaching (N-Output, Figure 6) is linked with N deposition loads (N-Input). Obviously it is tempting to define critical deposition loads which lead to N-saturation. Critical loads for European coniferous forests are defined between $10\text{--}20 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ (ACHERMAN AND BOBBINK, 2003).

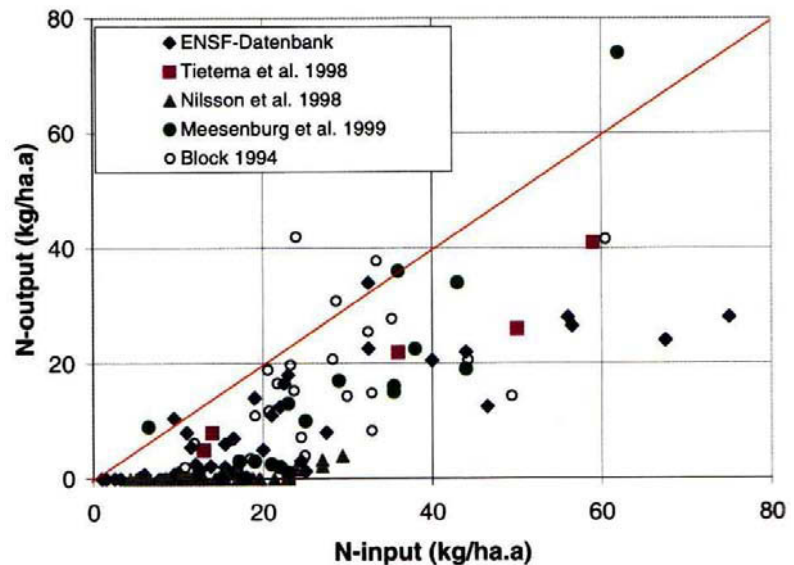


Figure 6: N-input and N-output correlation in forest ecosystems.

Source: HERMAN ET AL., 2001

The NITREX project intended to deduce critical levels of N deposition from a set of European case studies. Measurements of the NITREX-Project showed that Inputs $<10 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ caused little nitrogen leaching from forest ecosystems in Europe. At input fluxes $>10 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ high NO_3^- losses were common. As soon as deposition loads reach values higher than $25 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ nitrate losses are substantial (WRIGHT ET AL., 1995).

AGREN AND BOSSATA (1988) defined a system as being saturated if nitrogen outputs exceed nitrogen inputs over a period of some years (HERMAN ET AL. 2002).

Another indicator parameter which can be used is the C/N ratio in the soil organic matter. GUNDERSEN ET AL. (1998) discovered a relationship between N leaching in forest ecosystems and the C/N ratio of the forest floor. Referring to this observation they created a C/N ratio based classification of ecosystem N status in mature coniferous forests and risk of nitrate leaching (Table 1).

Table 1: Ecosystem N status and nitrate leaching classification based on C/N ratio

Forest floor C/N ratio	>30	25-30	<25
N-status	N-limited	Intermediate	N-saturated
Risk for nitrate leaching*	Low	Moderate	High

* Risk of nitrate leaching relate to cases where the N input > 10kg N*ha⁻¹a⁻¹

Source: GUNDERSEN ET AL., 1998

Because the site seems to be at risk to become N-saturated (chapter 2) this master thesis was initiated to analysis the general biogeochemistry at the site and to analys if the ecosystems N-saturation status changed since the last soil solution samples of this investigation area were analyzed in 2002.

2 Study site

Table 2 summarizes the main characteristics of the investigation plot.

Table 2: Climate, soil properties and stand characteristics at the study site Mühleggerköpfl

Coordinates	11°38'21" East and 47°34'50" North
Elevation	895m
Plot size	0,3ha
Mean annual temperature	6,4 °C (2000-2008)
Mean annual precipitation	1.661mm (2000-2008)
Nitrogen deposition	8 kg N * ha ⁻¹ *a ⁻¹ (2000-2008)
Geology	Dolomitic bedrock
Forest type	90% spruce (<i>Picea abies</i>)
	fir (<i>Abies alba</i>), beech (<i>Fagus sylvatica</i>)
	and maple (<i>Acer pseudplantanus</i>)
Soil types	Mosaic of Chromic Cambisols and Rendzic Leptosols

Source: Modified from JANDL ET AL., 2008

2.1 Geographical position and history of the investigation area

The study site “Mühleggerköpfl” is located in the northern Tyrolean Limestone Alps (Figure 7). The Tyrolean Limestone Alps cover about 380.000 ha of which 68% are covered with forests. In general this area is characterized by cool, humid (precipitation 1100-2200mm) climate with the highest precipitation values in the summer. The dominant tree species are spruce, fir and beech.

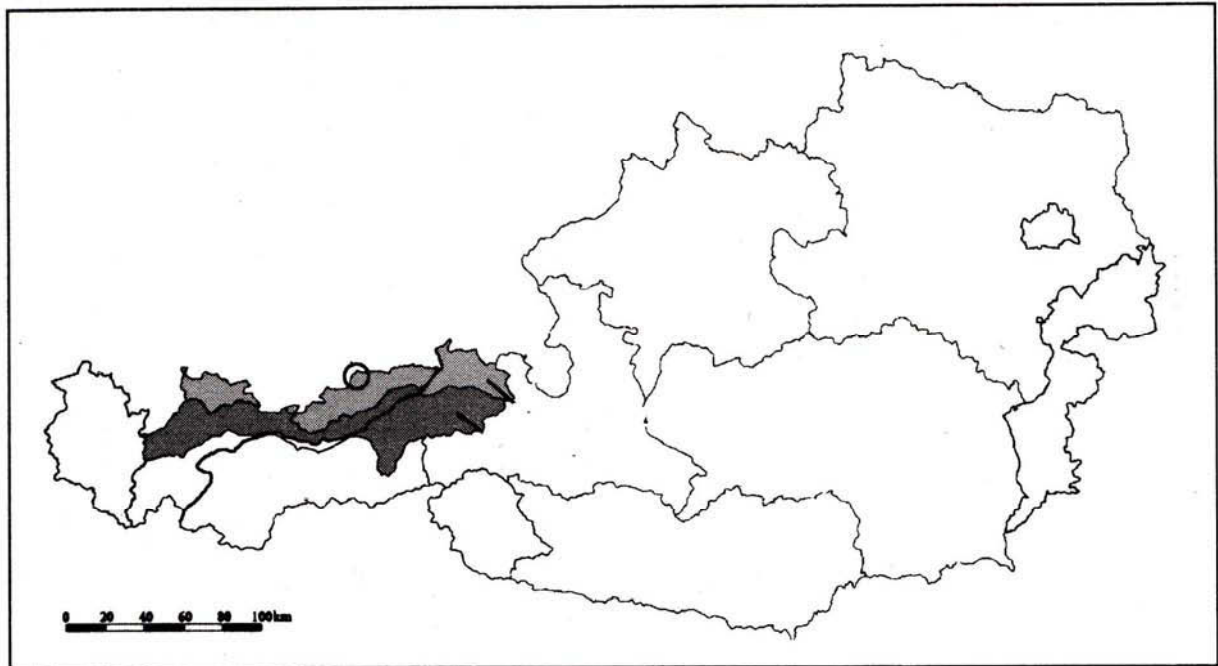


Figure 7: Position of the investigation site within Austria

Source: HERMAN ET AL., 2001

The investigation plot at the “Mühleggerköpfl” itself is an isolated outcrop of dolomitic bedrock in the Achenal which is located at 47° 34' 50" North and 11° 38' 21" East and at an elevation of 895m above sea level (Table 2). The western slope is very steep while the other slopes are gentler (Figure 8). This variability causes a lot of different microclimates within small distances (HERMAN ET AL., 2001).

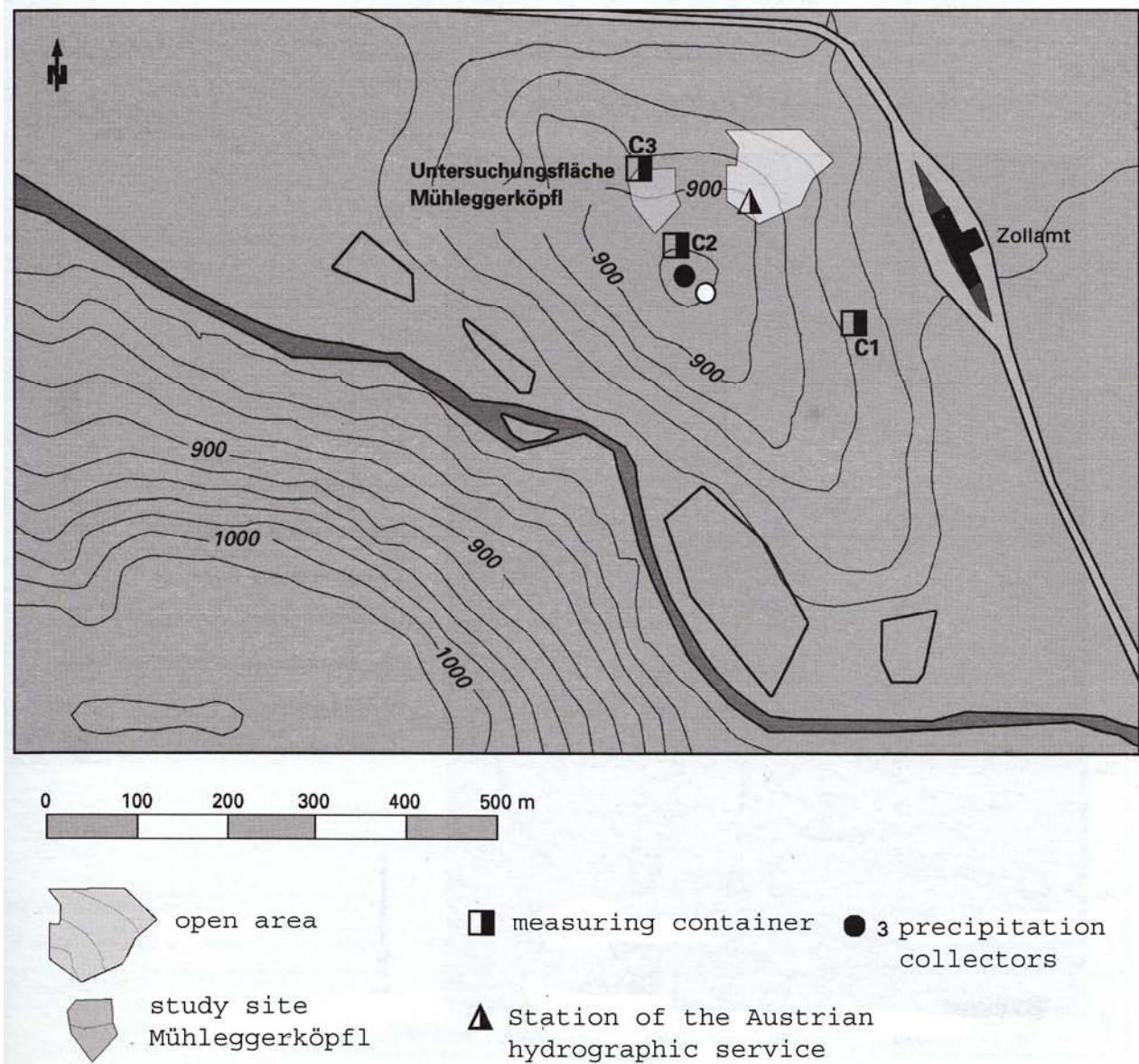


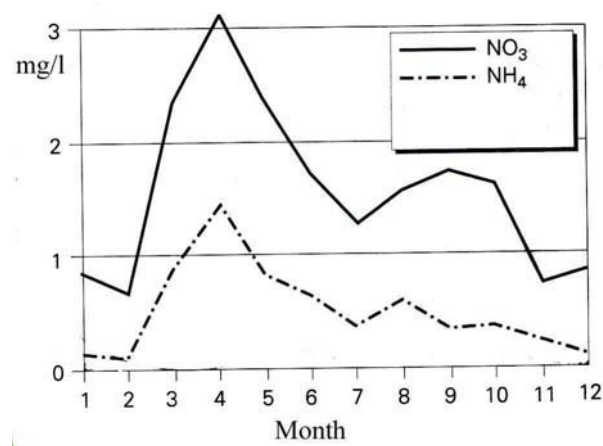
Figure 8: Position of the research monitoring plot

Source: HERMAN ET AL., 2001

In the past centuries this region was intensively used by humans. Pollarding, litter usage, wood pasture and clear-cutting caused nutrient (especially nitrogen) deficiencies. It is assumed that this system became enriched in N and may approach N saturation due to high atmospheric N inputs in the recent past (ENGLISCH, 2001). The reasons for this assumption are the low forest productivity at the site and the porous and rocky soil.

Especially the **northern part of the Austrian Alps and urban areas** are subject to high atmospheric N inputs (e.g. Linz, Vienna woods, Weilhartsforst). Because stationary temperature inversions are very common in the northern Tyrolean Limestone Alps (especially in winter) the thinning of nitrogen oxides is limited and nitrogen oxides from local emissions accumulate in the inversion layers. This leads to an accumulation zone up to a height of about 300m above the bottom of a valley. (HERMAN AND SMIDT, 2004). A second factor for high N inputs in the Northern Alps is the relief. Oncoming air masses are uplifted, which causes frequent rainfall and the absence of prolonged dry periods. Under these conditions even low concentrations of N in the rain lead to a considerable deposition load (JANDL ET AL., 2008). Due to heavy rainfall events the deposited N can be leached through the soil by saturated flow. Because of this exposure elevated N inputs a research plot was established in Achenkirch (Tyrol) at the Mühleggerköpf to investigate if the area is going to be or if it is already N-saturated.

Results from prior research at the plot showed that the annual N Input varies between 9,2 and 16,9 kg N*ha⁻¹*a⁻¹ (1991-1998) with an average of 11,64 kg N*ha⁻¹*a⁻¹.



These loads are in-between the range of critical loads for coniferous forest ecosystems although they can be considered moderate compared to other alpine areas in Austria. It was also found that the NO₃⁻ concentration showed a seasonal pattern (Figure 9) with high concentrations in spring

Figure 9: Average annual NO₃⁻ and NH₄⁺ concentrations (1991-1997) at the Mühleggerköpf.

Source: SMIDT, 2001

The C/N ratio values of the upper soil were between 15-18 (MUTSCH, 2001), which according to the classification by GUNDERSEN ET AL. (1998) indicates a high risk of nitrate leaching. A preliminary analysis indicated that the system was accumulating nitrogen, but not saturated right now as inputs still exceeded the outputs. The system may be approaching nitrogen saturation (HERMAN ET AL. 2002). The capacity of further nitrogen retention remained unknown. Therefore this master thesis was initiated to analysis if the saturation status changed since 2002.

2.2 Climate

The site is located in a very humid, cool climate with absence of prolonged dry periods and with the highest precipitation values in summer (Figure 10 - Figure 11). The mean annual temperature is 6,4°C (2000-2008) and the mean annual precipitation is 1661mm (2000-2008).

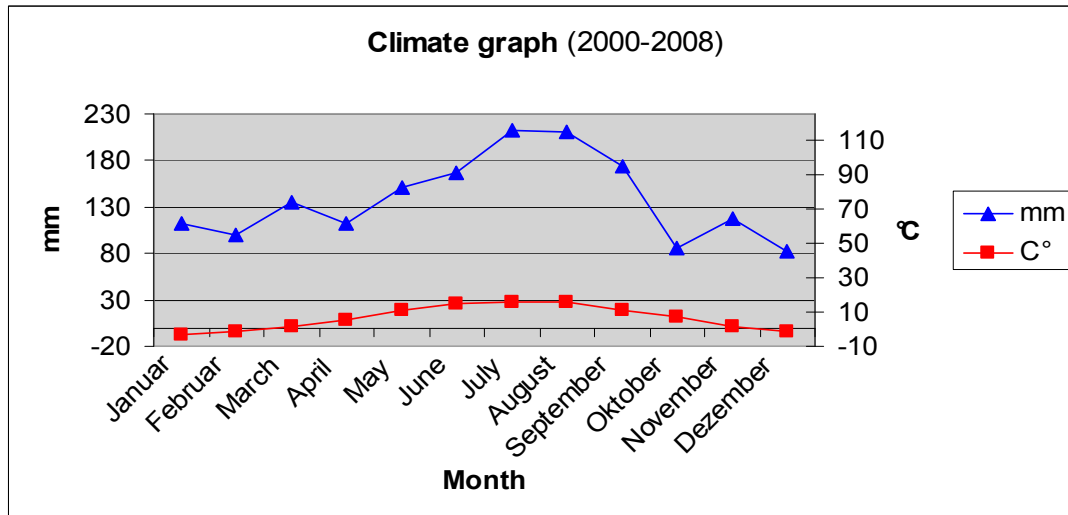


Figure 10: Monthly precipitation and air temperature between 2000 and 2008 (Mühleggerköpfl)

Although 2006 (Figure 11) was a year with relative little precipitation in July, the volumetric water content values in July 2006 were between 37% and 67% at 5cm soil depth. So even at these relatively dry circumstances the soil water content did not reach the permanent wilting point.

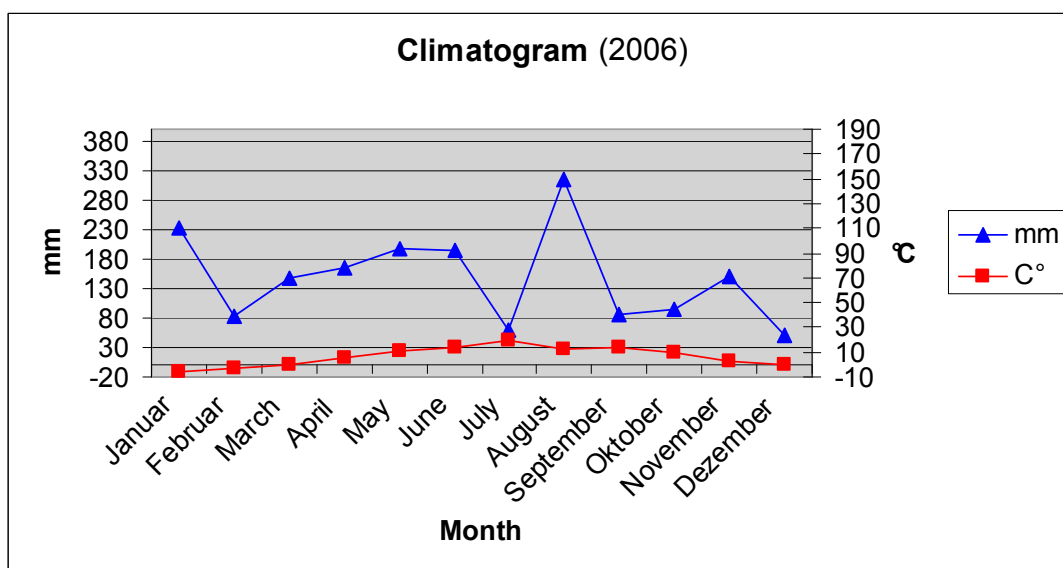


Figure 11: Climatogram of the year 2006 at the Mühleggerköpfl

2.3 Vegetation

The area is covered by a mature (125 years) forest. Spruce (*Picea abies*) accounts for about 90% of the trees on the site. Other species are fir (*Abies alba*), beech (*Fagus sylvatica*) and maple (*Acer pseudoplatanus*). In the years 2003, 2004 and 2005 some mature spruces were infested by bark beetle and were removed. Since 2005 beetle-traps are set up. As a result of these disturbances gaps in the canopy were created. In the gaps a rich regeneration of maple and beech occurred. The maples even dominate the understory vegetation.

This increasing dominance of deciduous species is a general pattern which is occurring in northern Tyrol for about a decade. This observation was confirmed by the Forest Service Tyrol.

The high coarse material content in the soil and the shallow rooting depth of spruce limits the rooting space. About 60% of the roots appear in the Ahb-horizon. Only some roots are encountered in the Bvrel-horizon and there are no roots in the C-horizon. The shallow rooting depth limits the nutrient uptake to the upper 40-50cm with a focus on the upper 20cm (ENGLISCH, 2001).

2.4 Soil distribution and soil characteristics

2.4.1 Soil types and soil physics

The main soil types within the study area are Chromic Cambisols and Rendzic Leptosols. Figure 12 shows a typical soil profile. The soil depth ranges from 120cm to 160cm. Soils are a mosaic of Cambisols and Leptosols within a very small area. While at the left part of the picture are almost entirely Rendzic Leptosols with a very thin AhbB-horizon, the right part is dominated by Cambisols with deep AhbB and Bvrel horizons. In the entire profile there is a dominant Cv-horizon ranging in depths from 50 to 110cm.

As is common for Rendzic Leptosols the soil profile shows a high organic matter content (ENGLISCH, 2001). The Humus layer is classified as Mull (F) and is only very thin.

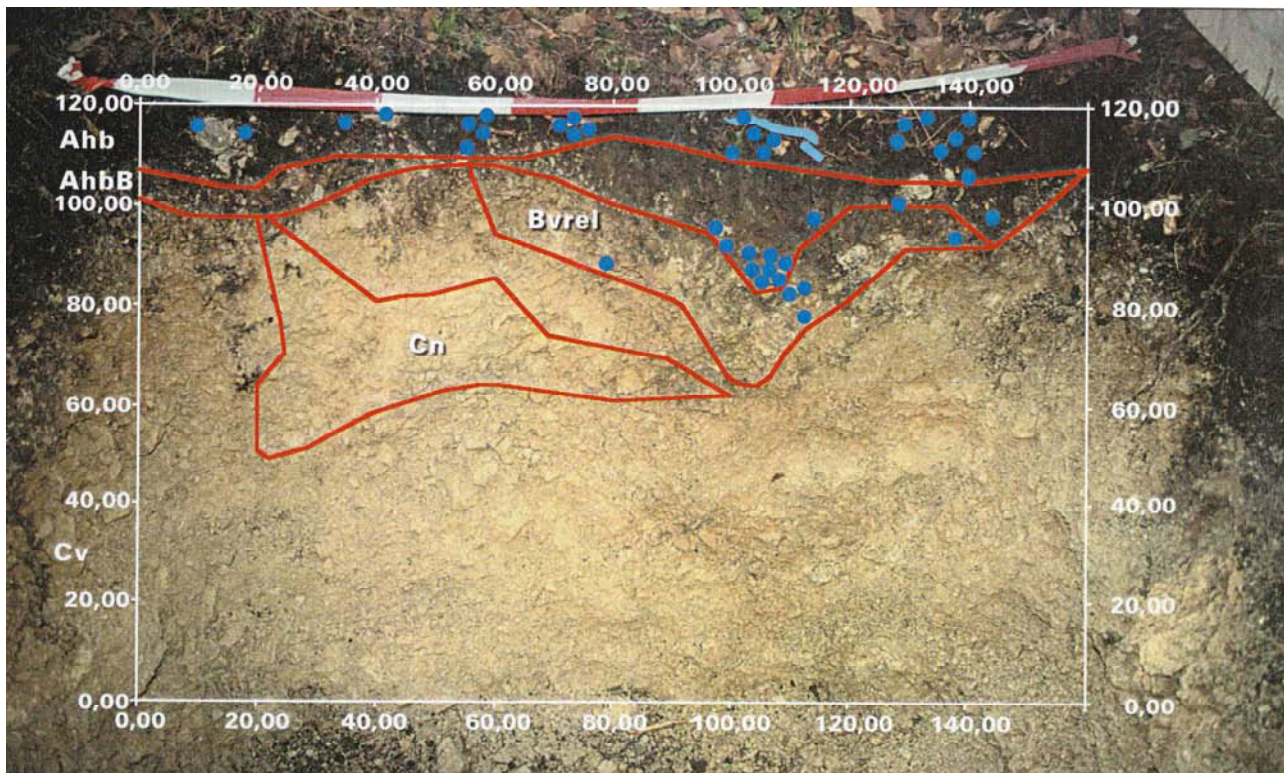


Figure 12: Typical soil profile at the research area Mühleggerköpfl

Source: ENGLISCH, 2001

In general the **soil depth** (Figure 13) of the Cambisols is between 30 and 60cm although there are some deeper (60-120cm) parts. The Rendzic Leptosols reach downs between 15 and 30cm. In the northern part of the area weak symptoms of water logging were found (ENGLISCH, 2001).

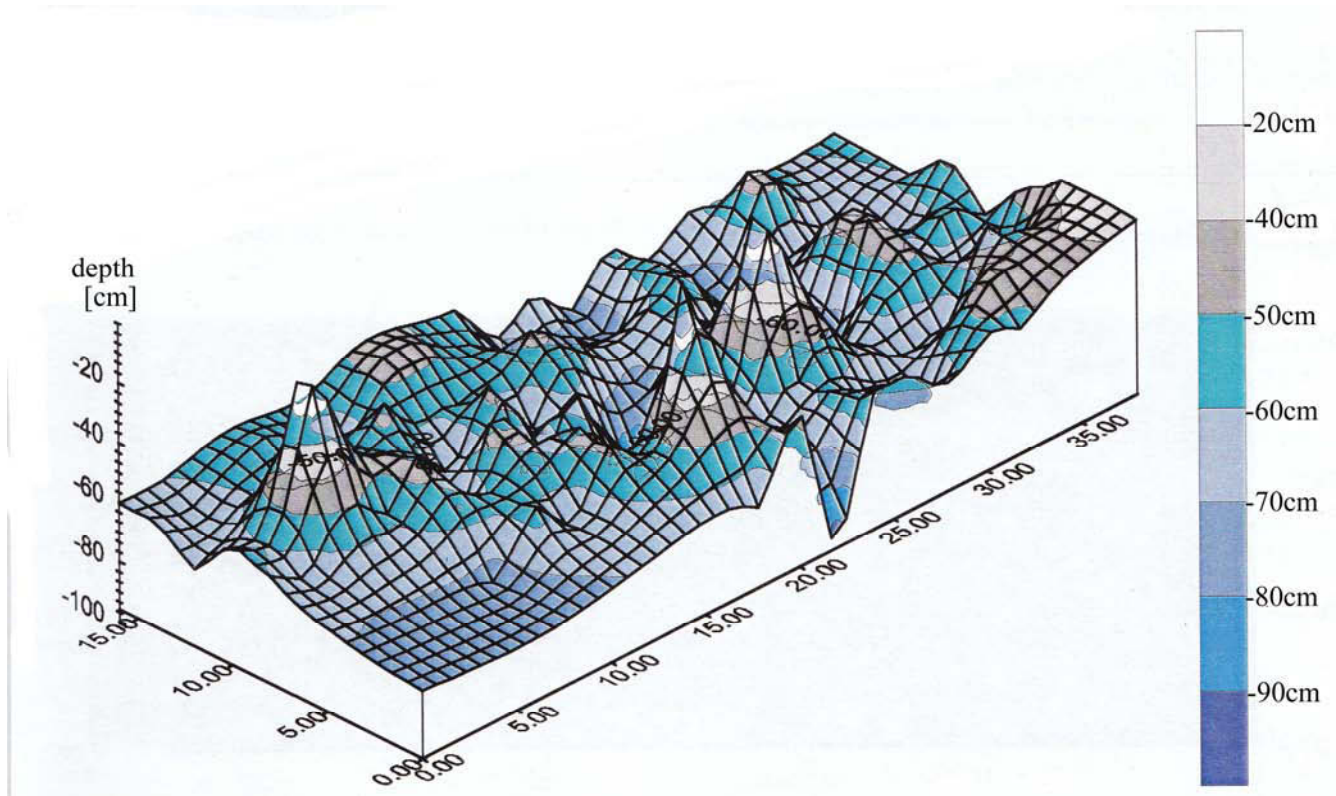


Figure 13: Small scale variability of the soil depth at the Mühleggerköpfl

Source: ENGLISCH, 2001

The **texture** is less variable and comprises loams and loamy clays and becomes somewhat coarser with increasing soil depth (Table 3).

Table 3: Soil texture at the Mühleggerköpfl

Depths	C org	Texture	Coarse material
0-15 cm	89 mg/g	loamy clay	0%
15-20 cm	69 mg/g	loamy clay	60%
20-30 cm	36 mg/g	loamy clay	80%
30-60 cm	14 mg/g	loam	80%
60-80 cm	12 mg/g	sandy loam	80%
loamy clay = 45% clay, 30% silt and 25% sand loam = 30% clay, 30% silt and 40% sand sandy loam = 20% clay, 30% silt and 50% sand			

Source: Modified from ENGLISCH, 2001 AND MUTSCH, 2001

The **field capacity** is defined as the water quantity in the soil which is left 3 days after complete saturation of the soil. Thus it describes the soil's ability to retain and store water against gravity. The field capacity mainly depends on the pore size distribution. While the water flows down in the big pores, water is retained by capillarity in smaller pores. However, the water which is stored in pores $<0,2\mu\text{m}$ is not plant available because the tension is too high (about 15000hPa). This is called the permanent wilting point because the plants are not able use the left soil water.

The relationship between **tension and water content** in a depth of 5cm is illustrated in Figure 14. The relationship was determined in the laboratory and at the field.

The field capacity values at the Mühleggerköpfl are between 45-115mm (Rendzic Leptosols) and 54-61mm (Chromic Cambisols) (ENGLISH, 2001).

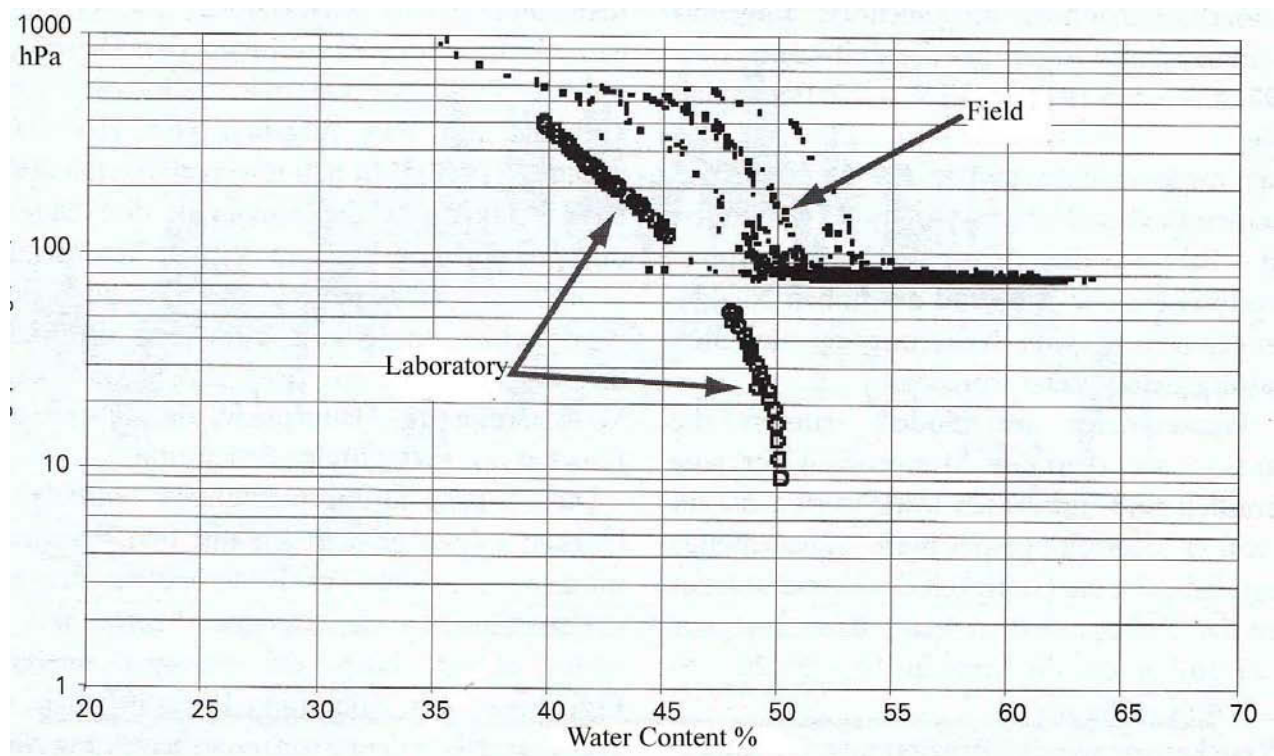


Figure 14: Water Content - water tension relationship at the Mühleggerköpfl in 5cm depth

Source: FEICHTINGER AND SCHEIDL, 2001

2.4.2 Chemical characteristics of the soil

2.4.2.1 The solid phase

The nutrient concentrations and C/N ratios given in

Table 4 were determined for the mineral soil only and not the humus layer.

Table 4: Chemical characteristics of the solid phase at the Mühleggerköpfl

	Carbonat*** [g/kg]	Organic matter [g/kg]	N tot [g/kg]	C/N ratio	N pool* [kg/ha]	Ca [g/kg]	Mg [g/kg]
Upper 15 cm	19-236	153-361	5,4-11,9	15-18	15.500	10-103	9-52
Lower mineral soil	>800	2-60	<1**	10-40		20-213	14-121

Source: Modified from MUTSCH, 2001

* N pool: The pool is calculated to a depth of 40 cm (rooting zone) and varies between 12.900 and 17.500 kg/ha (4 soil samples).

** In profiles 3 and 4 Ntot was around 3,4 and 5,25 to a depth of 30 and 50cm.

***Carbonat refers to Calcit and Dolomit (similiar values were obtained for these two C reservoirs)

The organic carbon content decreases with the depth. Humus (OC*1,72) concentrations between 361 and 153 g/kg were obtained in the upper soil while the lower soil contains only around 15 g/kg humus.

Total nitrogen content correlates with the soil organic carbon content. Highest N-Tot values are in the upper soil (5,4 and 11,9 g/kg) and decrease to <1g/kg in the lower soil. The nitrogen pool between 0 to 40cm ranges from 12.900 to 17.500 kg/ha with an average amount of 15.500 kg/ha.

The C/N ratios of 15-18 in the upper 15cm indicate favorable environmental conditions for soil organisms (MUTSCH, 2001), which agrees with the humus layer classification of Mull.

2.4.2.2 Ion Concentrations in the water samples

Measured ions in solution are Cl^- , NO_3^- , NH_4^+ , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} and Ca^{2+} .

In general the highest concentrations were found in the surface run-off samples while the throughfall concentrations were low for every ion measured. Soil solution concentrations were similar for different depth although some variability existed.

Most pronounced differences were in magnitudes between soil solution and discharge samples. For example the NO_3^- concentrations in the discharge were much higher while the NH_4^+ concentrations were lower.

Table 5 gives an overview of the measured concentration values of different constituents.

The *pH* was rather low in the throughfall (4,8 on average) and increased significantly in water samples taken from the surface or in the soil (7,5 – 8,2 in average).

The mean concentrations of *nitrate* in the soil solution were low (1,5-5 mg/l) compared to the discharge and surface run-off values (12 and 47 mg/l). The higher concentrations were found in the upper mineral soil (5-15cm). Especially the surface run-off concentrations in particular had a high standard deviation due to high mineralization rates in summer.

The NH_4^+ concentrations in soil solutions and discharge were always very low with the highest mean concentrations at 15 cm (0,38mg/l)

The mean concentrations of Mg^{2+} and Ca^{2+} were very high within the whole soil profile. Mg^{2+} reached concentrations between 15 mg/l (15cm) and 22 mg/l (discharge) while Ca^{2+} values were within a range between 24 mg/l (25cm) and 38 mg/l (discharge).

The mean *sulfate* concentrations reached values around 2-3 mg/l. But individual measurements, probably outliers, differed greatly. The highest value of 37 mg/l was obtained at 25cm.

The mean concentrations of K^+ and Na^+ were low in all samples. While K^+ concentrations were similar in the throughfall and the soil solution samples, Na^+ concentrations were higher in the soil.

Cl^- reached concentrations smaller than 1 mg/l in average. Only the mean surface run-off concentration was about 2 mg/l.

Table 5: Arithmetic mean concentration values in different depths (2000-2008).

Variable	Depth	N	Mean [mg/l]	Std. deviation	Minimum [mg/l]	Maximum [mg/l]
pH	troughfall	213	4,81	0,43	3,90	6,50
	surface run-off	124	7,51	0,62	5,96	8,80
	5cm	217	8,20	0,25	6,68	8,70
	15cm	196	8,18	0,25	6,98	8,60
	25cm	199	8,21	0,23	7,00	8,65
	50cm	200	8,19	0,25	6,94	8,70
	discharge	165	8,20	0,42	5,30	8,90
Cl ⁻	troughfall	213	0,25	0,24	0,00	1,70
	surface run-off	129	2,02	1,57	0,08	8,06
	5cm	224	0,90	1,76	0,03	25,49
	15cm	198	0,91	1,95	0,00	19,44
	25cm	204	0,62	2,23	0,00	32,01
	50cm	203	0,88	1,42	0,02	13,51
	discharge	165	0,51	0,27	0,00	1,94
NO ₃ ⁻	troughfall	213	1,41	0,86	0,00	6,31
	surface run-off	129	46,58	66,03	0,07	366,19
	5cm	224	4,94	7,01	0,00	45,15
	15cm	201	5,08	5,30	0,02	26,28
	25cm	204	1,56	1,82	0,00	9,95
	50cm	203	2,72	6,89	0,00	50,85
	discharge	165	11,67	8,52	0,00	40,19
NH ₄ ⁺	troughfall	213	0,26	0,26	0,00	1,28
	surface run-off	129	0,39	0,78	0,00	4,84
	5cm	224	0,05	0,21	0,00	2,43
	15cm	201	0,38	0,57	0,00	3,45
	25cm	205	0,10	0,54	0,00	6,85
	50cm	203	0,12	0,45	0,00	4,29
	discharge	165	0,02	0,04	0,00	0,36
SO ₄ ²⁻	troughfall	213	0,60	0,34	0,03	1,85
	surface run-off	129	2,74	2,31	0,00	14,09
	5cm	224	2,62	2,07	0,00	14,42
	15cm	201	3,85	4,03	0,06	22,79
	25cm	203	1,75	2,81	0,00	36,92
	50cm	203	1,83	2,38	0,00	24,89
	discharge	165	1,50	0,74	0,11	4,19
Na ⁺	troughfall	213	0,15	0,14	0,00	1,21
	surface run-off	129	0,50	0,31	0,03	1,84
	5cm	224	0,25	0,12	0,00	0,87
	15cm	201	0,31	0,28	0,03	1,98
	25cm	205	0,25	0,15	0,00	1,00
	50cm	203	0,35	0,17	0,00	1,17
	discharge	165	0,19	0,13	0,00	1,27
K ⁺	troughfall	213	0,11	0,21	0,00	1,61
	surface run-off	129	2,02	1,42	0,00	7,40
	5cm	224	0,09	0,17	0,00	1,48
	15cm	201	0,10	0,20	0,00	1,68
	25cm	205	0,10	0,22	0,00	2,13
	50cm	203	0,15	0,34	0,00	4,03
	discharge	164	0,05	0,06	0,00	0,31
*Mg ⁺⁺	troughfall	98	0,15	0,42	0,00	3,65
	surface run-off	46	20,67	13,26	0,58	73,12
	5cm	99	17,44	3,09	8,37	23,42
	15cm	99	16,37	2,48	9,76	23,99
	25cm	96	14,56	3,18	3,12	22,99
	50cm	94	17,19	4,53	7,88	29,74
	discharge	66	22,12	4,82	0,18	31,89
*Ca ⁺⁺	troughfall	97	0,34	0,68	0,02	6,52
	surface run-off	45	30,68	16,29	0,00	74,06
	5cm	98	29,09	5,59	13,87	46,19
	15cm	98	27,98	4,71	16,36	50,92
	25cm	95	23,60	5,73	5,70	41,86
	50cm	93	26,84	8,38	13,50	61,18
	discharge	66	38,15	9,30	0,45	69,09

* Only measured values between 2005 and 2008 included because earlier data do have a bias due to measurement techniques.

2.5 Suitability as investigation plot to analyse soil water chemistry

The site position guarantees that the plot is not influenced by backwater, non-local surface flows and non-local litter input (ENGLISCH, 2001). Additionally the site position in the northern Alps, which causes high N and S deposition loads, makes the site suitable.

The high variability of soil types and soil characteristics makes it difficult to analyze the investigation area but because this variability and the obtained soil characteristics are typical for the Tyrolean Limestone Alps it would not be appropriate to analyze a smooth area which is easier to analyze.

3 Methods

The following sections describe measurement and analysis methods for temperature, precipitation, throughfall, surface run-off, soil solution, discharge soil water content and tension (Table 6). The samples were taken between 1998 and 2008.

3.1 Measurement techniques and experimental set-up

Table 6 summarizes the parameters and their measurement frequency at the research area. While temperature, precipitation, water content and tension are measured and recorded automatically, the water samples (throughfall, surface run-off, soil solution and discharge) are collected on a biweekly basis. The collected water samples are shipped to the BFW for chemical analysis where pH and Cl^- , NO_3^- , NH_4^+ , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} and Ca^{2+} concentrations (mg/l) are measured. Soil solution concentrations, water content and soil tension are measured at a depth of 5, 15, 25 and 50cm.

Table 6: Measured parameters at the investigation area

Parameter	Measured components	Method	Interval
Temperature	°C		daily
Precipitation	mm	Tipping bucket	daily
Throughfall	l/ha, pH, Cl^- , NO_3^- , NH_4^+ , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+}	Bulk sampler	2 weeks
Surface run-off	ml, pH, Cl^- , NO_3^- , NH_4^+ , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+}	Gutter	2 weeks
Soil solution	pH, Cl^- , NO_3^- , NH_4^+ , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+}	Suction cups	2 weeks
Discharge	ml, pH, Cl^- , NO_3^- , NH_4^+ , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+}	Lysimeter	2 weeks
Water content	Volumetric %	FDR, Capacity probe	daily
Tension	hPa	Gypsum block	daily

3.1.1 Temperature and precipitation

Precipitation is measured by a weather station of the Austrian institution “Hydrografischer Dienst” around 50m below the study site (Figure 8). The precipitation is measured by tipping buckets. Precipitation and temperature values are logged every half an hour and are averaged to daily values.

3.1.2 Throughfall



Figure 15: Bulk sampler used to Collect throughfall.

The throughfall is measured by 15 bulk samplers (Figure 15), each with a diameter of 18cm. Because spruce is the dominant tree at the site stem flow volumes are expected to be small and can be neglected in the flux calculations.

As are all water samples the collected throughfall is analyzed every 2 weeks for l/ha, pH and Cl^- , NO_3^- , NH_4^+ , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} and Ca^{2+} concentrations.

3.1.3 Surface run-off, soil solution samples, water content and tension

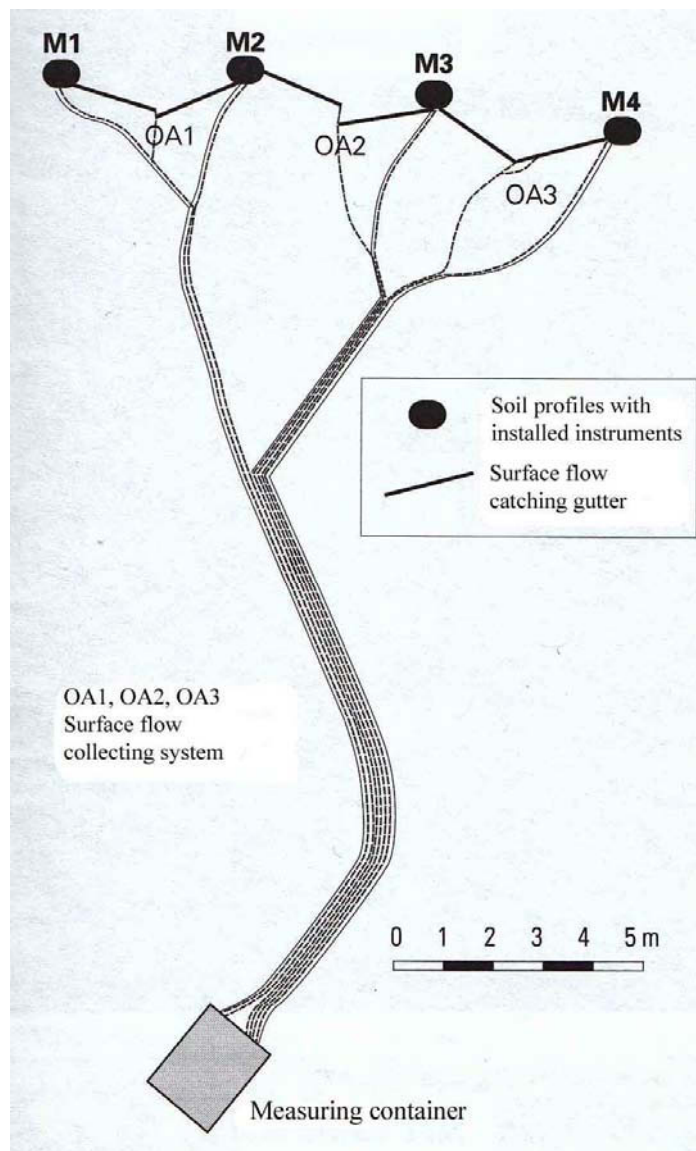


Figure 16 illustrates the experimental set-up. Gutters were installed between the 4 soil profiles (M1-M4) to collect **the surface run-off**. The run-off is collected by OA1, OA2 and OA3. The collected water samples are transported downhill to the measuring container by tubes (~20m) which are installed 30-50 cm under the surface (FEICHTINGER AND SCHEIDL, 2001). Afterwards the collected samples are shipped to the BFW for chemical analysis. The instruments that collected soil solution and measure water content and tension in the soil (Table 6) were installed at the 4 soil profiles (Figure 17).

Figure 16: Experimental set-up to quantify soil water content, soil temperature, surface run-off and soil solution

Source: FEICHTINGER AND SCHEIDL, 2001

Figure 17 shows the 4 soil profiles (location shown in Figure 16) where suction cups, the gypsum blocks and the FDR sensors were installed (described below).

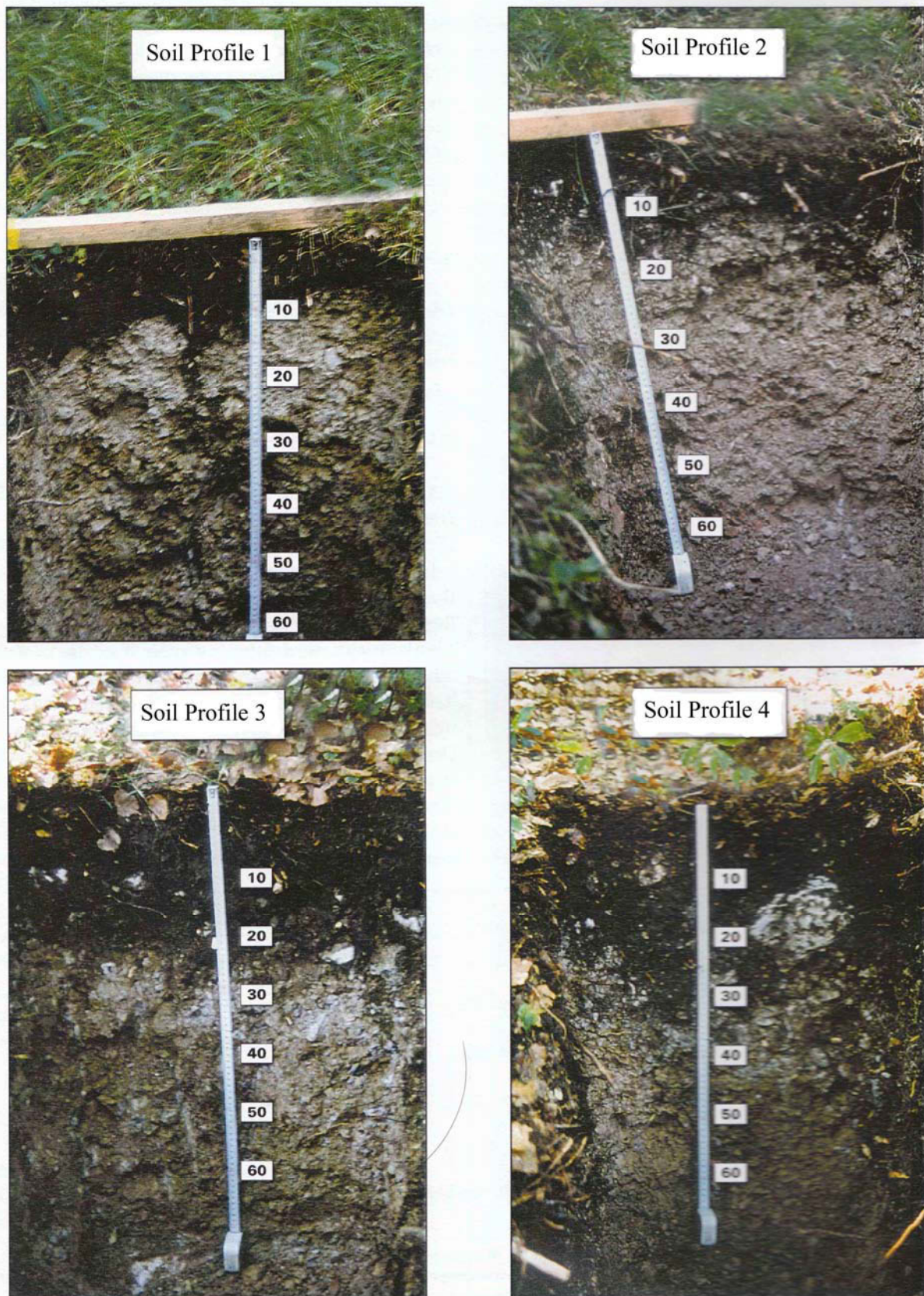


Figure 17: 4 soil profiles (M1-M4) at which the instruments are installed

Source: FEICHTINGER AND SCHEIDL, 2001

The **soil solution samples** are collected by suction cups (company ROBU-Glas). The cups were installed at all 4 soil profiles and collect water samples at 5, 15, 25 and 50cm (FEICHTINGER AND SCHEIDL, 2001). The sum of the samples are analyzed every two weeks in a laboratory in Tyrol. Consequently 4 concentrations were measured for 5, 15, 25 and 50cm.

The **soil water content** is measured as a function of the dielectric constant (wave reflection speed of electromagnetic waves) which differs between water, air and the solid phase. The constant values are 1 (air), 2-4 (water) and 80 (solid phase). There are different techniques such as TDR (Time Domain Reflectometry), FDR (Frequency Domain Reflectometry) and capacitance probes. The used techniques in this study are FDR Sensors (Theta-Sensors) and capacitance probes (Vitel –Sensors). The sensors were installed at all 4 soil profiles and measure the daily water content at 5, 15, 25 and 50cm soil depth (FEICHTINGER AND SCHEIDL, 2001).

The **tension** is measured by gypsum blocks. Two different types were installed at the site. Gypsum blocks of the trademark Watermark were used for the measurement range between 50-1500hPa whereas gypsum blocks of the trademark Waterwise were used for the measurement range between 400-15000hPa. Both types were installed at all 4 soil profiles and measure the daily tension at 5, 15, 25 and 50cm soil depth. In addition tension is measured by the same tensiometers used to measure water content. (FEICHTINGER AND SCHEIDL, 2001).

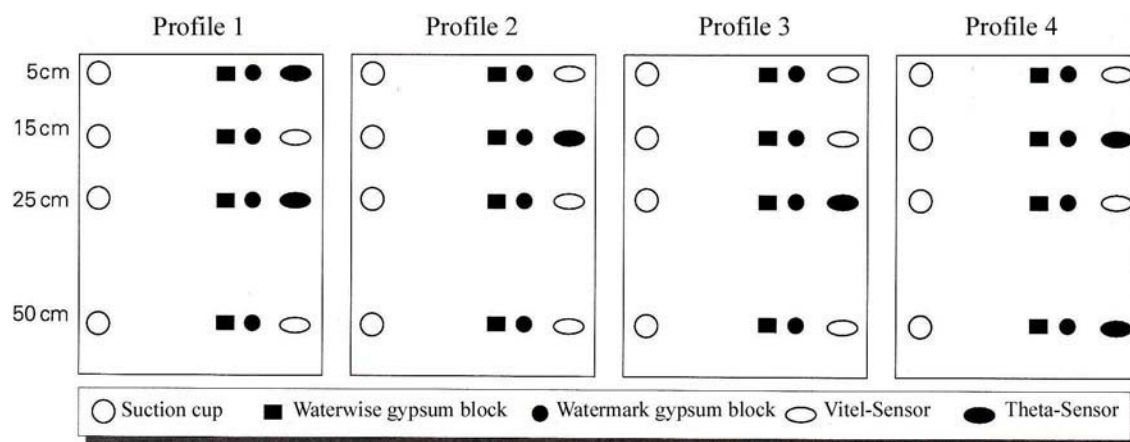


Figure 18: Installation draft for the instruments at the 4 soil profiles

Source: (FEICHTINGER AND SCHEIDL, 2001).

3.1.4 Discharge

The **discharge** is measured by a completely enclosed lysimeter with a size of $0,5\text{m}^2 \times 0,65\text{m}$ (Figure 19) which was installed in 1998. The lysimeter is circular and the depth of 65cm corresponds to the maximum soil depth at the investigation area. The soil monolith is lined by a water proof synthetic ring to avoid the influence of lateral water flow. A perforated steel panel at the bottom ensures that water can flow into the water collecting pan and then into the storage tank. To avoid the loss of soil into the pan a sand filter was installed. This device provides a measurement of the deep water discharge with minimal disturbance of the soil (KRENN ET AL., 2001).

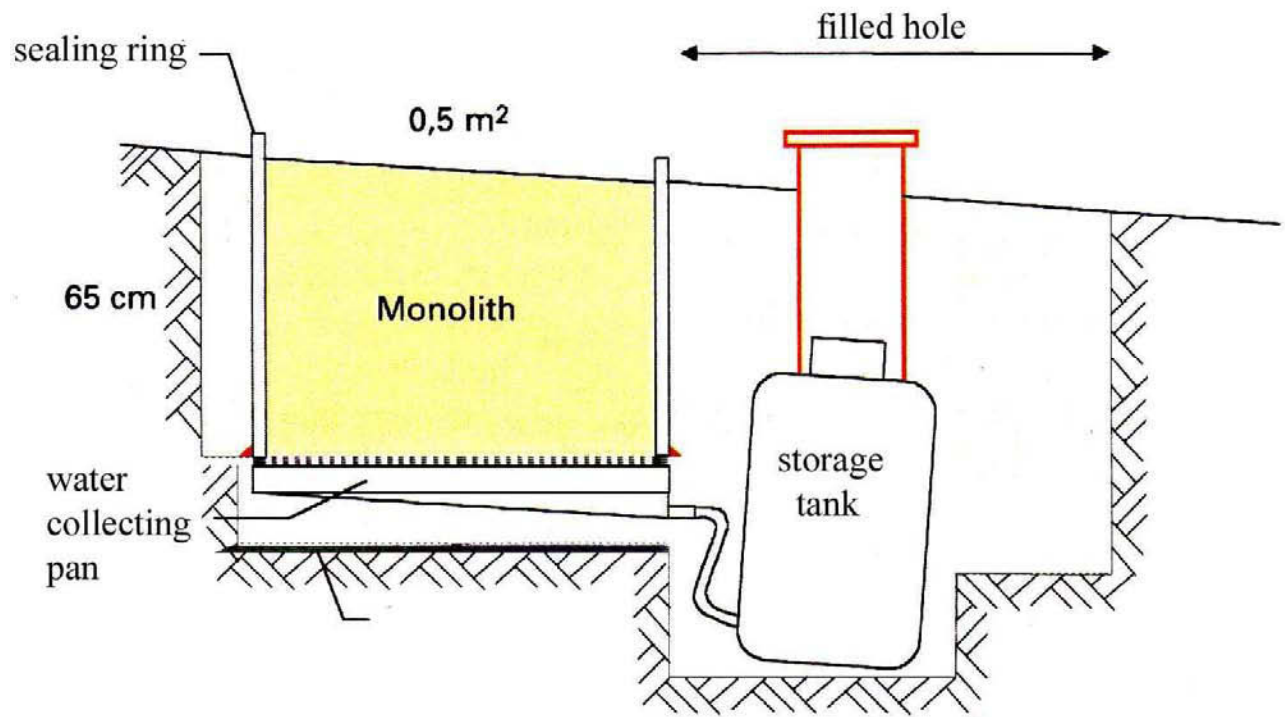


Figure 19: Lysimeter for the collection of soil water leaching through the profile
Source: KRENN ET AL., 2001

3.2 Data processing

3.2.1 Statistics

Statistics were performed the cleaned dataset (chapter 3.2.2 and 4.1) using the statistic program SAS 9.1.

In order to identify if statistically significant differences between throughfall (1), surface run-off (2), soil solution samples at 5, 15, 25 and 50cm and discharge (75) concentrations (Cl^- , NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , K^+ , Mg^{2+} , Ca^{2+}) exist, a General Linear Model (**comparison of means**) was used.

The data was tested with the Student-Newman-Keuls-Test (SNK) and the Duncans multiple range test.

In these tests all measurements of one element, which are collected by the same technique (e.g. throughfall bulk sampler, suction cups at 15cm,...), are put together and grouped (A,B,C,D,E,F). If means of two different techniques (e.g. suction cups at 15 and 25cm) are identified with the same letter there are no significant statistical differences between them ($\alpha=0,05$). For example this situation appears for the techniques 15, 5, 50, 25 and 1 in Table 7. It is also possible that samples of one technique are classified with two letters (e.g. AB). In this case the samples fit into category A and B. Means are always sorted from the highest (A) to the lowest (F) value.

Correlations and regressions were calculated between ion concentrations of diverse elements at a given collection depth; especially between nitrate and cation (Mg^{2+} , Ca^{2+} , K^+ and $\text{Mg}^{2+}+\text{Ca}^{2+}+\text{K}^+$) concentrations because high amounts of NO_3^- leaching brings cationic ions with it. Additionally, correlations between nitrate and water fluxes were computed to investigate if the leaching nitrate is mainly caused by water fluxes or if other processes determine nitrate fluxes.

Table 7: Student-Newman-Keuls-Test (SNK) results for different NO_3^- sampling techniques.

SNK grouping	Arith. mean	N	Techn.
A	46.576	129	2
B	11.670	165	75
C	5.077	201	15
C			
C	4.944	224	5
C			
C	2.722	203	50
C			
C	1.556	204	25
C			
C	1.411	213	1

3.2.2 Data check

Before the recorded data are analyzed statistically it is necessary to check it for errors. In general, two types of errors are discerned in chemical analyses:

Precision or statistical errors, which reflect random fluctuations in the analytical procedure. When standard deviation is small (upper illustration of Figure 20) measurements are very precise but the result may not be accurate.

Accuracy or systematic errors are displaying systematic deviations due to faulty procedures or interferences during analyses. (APPELO AND POSTMA, 1996).

The lower illustration shows a very precise and accurate sample.

Errors can also occur due to mistakes in the data input and data transmission.

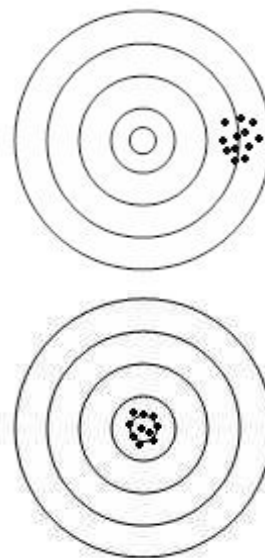


Figure 20: Accuracy and precision of chemical analysis

The first requirement to get good data that there are laboratory internal control mechanisms in place such as inclusion of control or blank samples, the measurement of standard solutions and the use of internal standards.

Once the data have been obtained from the laboratory the data has to be checked for veracity. In example are the values obtained plausible or realistic. To that end three methods were used:

- Charge Balance
- Analysis of temporal trends of element fluxes
- Correlations between measured concentrations

3.2.2.1 Charge Balance

The electric charge of a chemical solution always has to be in balance. A chemical system is not electrical charged and chemical reactions do not build up or dissipate electrical charges.

$$\sum \text{Cations} = \sum \text{Anions}$$

The unit of measurement of the measured soil water solution concentrations (NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} and NO_3^-) is mg/l what does not reflect the number of electrical charges but the weight of the analyzed ions. To calculate the charge balance the unit has to be transformed into mmol/l and then into mol equivalents to account for differences in valence among the major ions (Table 8).

Table 8: Calculation of meq/l for the throughfall solution sample week 13 in the year 2000

	mg/l		Form. wght		mmol/l		Charge		meq/l
NH_4^+	0,2	/	18,04	=	0,01108742	*	1	=	0,0111
Na^+	0,1	/	22,99	=	0,00434976	*	1	=	0,0043
K^+	0	/	39,10	=	0	*	1	=	0,0000
Mg^{++}	0	/	24,31	=	0	*	2	=	0,0000
Ca^{++}	0,5	/	40,08	=	0,01247567	*	2	=	0,0250
				=		*		=	
Cl^-	0,1	/	35,45	=	0,00282064	*	1	=	0,0028
SO_4^{--}	1,1	/	96,06	=	0,01145087	*	2	=	0,0229
NO_3^-	1,1	/	62,00	=	0,01774053	*	1	=	0,0177

HCO_3^- concentrations are not routinely analyzed. Because they have an important influence to the charge balance (especially in samples with a high pH) the actual HCO_3^- concentrations have to be derived indirectly.

Atmospheric CO_2 gas dissolves in the rainwater or soil water. Gaseous $\text{CO}_{2(g)}$ forms aqueous $\text{CO}_{2(aq)}$, which associates to some extent with water molecules to form carbonic acid, H_2CO_3^* (H_2CO_2^* is the analytical sum of $\text{CO}_{2(aq)}$ and the true carbon acid H_2CO_3). Carbonic acid can dissociate in two steps from releasing one proton (H^+) in each step (APPELO AND POSTMA, 1996):

- 1.) $\text{CO}_{2(g)} \rightarrow \text{CO}_{2(aq)}$
- 2.) $\text{CO}_{2(aq)} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3^*$
- 3.) $\text{H}_2\text{CO}_3^* \rightarrow \text{H}^+ + \text{HCO}_3^-$
- 4.) $\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{--}$

The relative mass action constants that are needed to calculate the composition of the solution (at a temperature of 25°C) are given in Table 9.

Table 9: Equilibrium constants for dissolved CO₂ species at 25°C

$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3^*$	$\text{KH} = [\text{H}_2\text{CO}_3^*]/\text{pCO}_2$	$\text{KH} = 10^{-1,5}$
$\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$	$\text{K}_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3^*]$	$\text{K}_1 = 10^{-6,3}$
$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{--}$	$\text{K}_2 = [\text{H}^+][\text{CO}_3^{--}]/[\text{HCO}_3^-]$	$\text{K}_2 = 10^{-10,3}$

SOURCE: APPELO AND POSTMA, 1996

The associated H_2CO_3^* content is calculated by a simple multiplication of the Henry's Law constant ($10^{-1,5}$) with the CO_2 partial pressure in the atmosphere ($10^{-3,5}$). The HCO_3^- concentration of soil solution samples was calculated and the charge balance was analyzed with a partial pressure of 400 and 800 ppm because no CO_2 partial pressure values within the soil are available.

Table 10: Multiplied equilibrium constants

To calculate the next two dissociation steps it is necessary to remember that the addition of two reactions requires multiplication of the two mass action constants and that subtraction requires division. With this information these constants can be add together like shown in Table 10.

Components	Log K (25°C)
H_2CO_3^*	-1,5
HCO_3^-	-7,8
CO_3^{--}	-18,1

Source: SIGG AND STUMM, 1996

Beside the equilibrium constants the pH value and the partial pressure (pCO_2) are the mainly factors influencing the HCO_3^- and CO_3^{2-} concentration in an open system (influence of pH illustrated in Table 9). With a pCO_2 of 350ppm the calculation works this way (SIGG AND STUMM, 1996):

1.)	$\text{H}_2\text{CO}_3^* = \text{KH} * \text{pCO}_2$	
	$\text{H}_2\text{CO}_3^* \rightarrow 10^{-1,5} * 10^{-3,5}$	$\log \text{H}_2\text{CO}_3^* = -5$
2.)	$\text{HCO}_3^- = 10^{-7,8} * [\text{H}^+]^{-1} * \text{pCO}_2$	
	$\text{HCO}_3^- \rightarrow 10^{-11,3} * [\text{H}^+]^{-1}$	$\log \text{HCO}_3^- = -11,3 + \text{pH}$
3.)	$\text{CO}_3^{--} \rightarrow 10^{-18,1} * [\text{H}^+]^{-2} * \text{pCO}_2$	
	$\text{CO}_3^{--} \rightarrow 10^{-21,6} * [\text{H}^+]^{-2}$	$\log \text{CO}_3^{--} = -21,6 + 2\text{pH}$

Figure 21 illustrates the relative change in concentration of carbonic acid and its derivatives as a function of the pH using the formulas listed above. With rising pH the content of carbon increases. Total concentrations can change this way because the system is open whereby atmospheric CO_2 can interact with the solution.

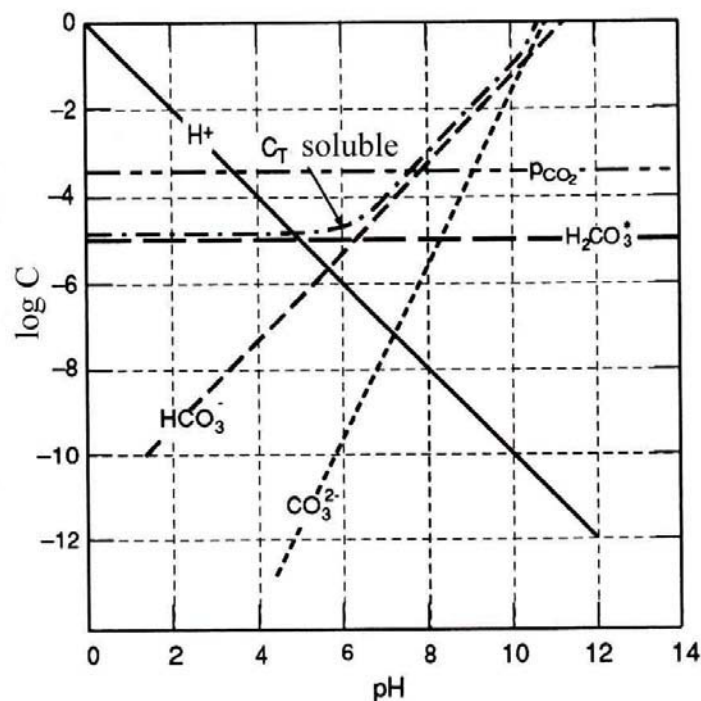


Figure 21: The activity of CO_2 species in water as function of pH at a constant CO_2 pressure of 350ppm. $\text{CT soluble} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$

Source: SIGG AND STUMM, 1996

Changes of carbonic acid concentrations due to lower temperature were not included. This makes the results conservative, because the concentration would increase with the lower solution temperatures that are expected to appear at this site.

Because the pH value is an alternative representation of H^+ concentration it is easy to calculate the H^+ and the OH^- concentration. For example a pH of 5,5 presents a concentration of $10^{-5,5}$ mol H^+ /l. Because $[\text{mol H}^+][\text{mol OH}^-] = 10^{-14}$ the OH^- value at a pH of 5,5 is $10^{-(14-5,5)}$ mol OH^- /l.

The calculated concentrations were put into the charge balance as illustrated in Table 11.

To put the charge balance into perspective the charge balances ($\sum \text{Cations} - \sum \text{Anions}$) as a % of sum cations are calculated for every single sample taken. The compilation of all steps involved is illustrated in Table 11.

Table 11: Charge Balance for the throughfall solution sample week 13 in the year 2000

	mg/l		Form. weight	=	mmol/l	*	Charge	=	meq/l
NH ₄ ⁺	0,2	/	18,04	=	0,011087421	*	1	=	0,0111
Na ⁺	0,1	/	22,99	=	0,004349761	*	1	=	0,0043
K ⁺	0	/	39,10	=	0,000000000	*	1	=	0,0000
Mg ⁺⁺	0	/	24,31	=	0,000000000	*	2	=	0,0000
Ca ⁺⁺	0,5	/	40,08	=	0,012475672	*	2	=	0,0250
H ⁺					0,063000000	*	1	=	0,0063
							Σ	=	0,0467
Cl ⁻	0,1	/	35,45	=	0,002820636	*	1	=	0,0028
SO ₄ ⁻⁻	1,1	/	96,06	=	0,011450866	*	2	=	0,0229
NO ₃ ⁻	1,1	/	62,00	=	0,017740533	*	1	=	0,0177
OH ⁻					0,000001585	*	1	=	0,0000
HCO ₃ ⁻					0,000794328	*	1	=	0,0008
CO ₃ ⁻⁻					0,000000006	*	2	=	0,0000
							Σ	=	0,0443
Charge balance ($\sum \text{Cations} - \sum \text{Anions}$)				=	0,00243				
Deviation in % of sum cations*				=	5,2				

* Maximum acceptable deviation according to APPELO AND POSTMA (1996) is 10% for measurements with $\sum \text{Cations}$ or $\sum \text{Anions} < 2 \text{ meq/l}$ and 4% for measurements with $\sum \text{Cations}$ or $\sum \text{Anions} > 2 \text{ meq/l}$.

In this particular example (Table 11) organic acids in this sample had no big influence to the charge balance, because in general throughfall samples consists of distilled water that is enriched with aerosols, gas and dust. But in soil solution samples organic acids may play a major role.

Sometimes elements other than the main ions Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, NO₃⁻ and HCO₃⁻ contribute significantly, like for example Fe⁺⁺ and NH₄⁺ in reduced groundwater, or H⁺ and Al³⁺ in acid water (APPELO AND POSTMA, 1996). The specific circumstances needed do not exist at the study site, therefore the influence of metal concentrations can be neglected.

3.2.2.2 Analyses of *time courses* of element fluxes

Analyzing temporal trends is a powerful data check method for outliers. Specific ion concentration values, which are not reasonable but otherwise do not influence the charge balance can also be identified this way. These outliers can occur for different reasons such as writing errors and sample contamination. Common outliers are too high NaCl concentrations (NaCl is present in laboratory detergents and sweat) and elevated CaMgCO_3 concentrations (If a dolomite grain dissolves in the solution sample).

But high concentration values are possible. For example a small amount of rain after a long dry period can wash down a lot of dust, which is sitting on the needles thus causing a concentration spike. Such accumulation effect is unlikely at this site, because of the absence of prolonged dry periods.

In this thesis measured concentrations were treated in a very conservative way to avoid overly subjective manipulations to the original data. Figure 22 shows a typical *time course* without outliers.

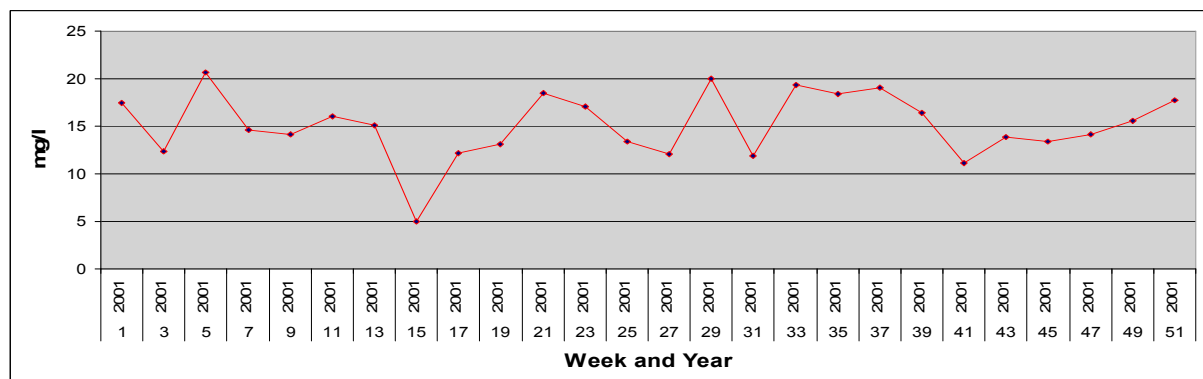


Figure 22: Typical time course of NO_3^- concentrations in the discharge (2001) without outliers.

3.2.2.3 Water chemical correlations

A high or low concentration of one ion is often associated with high or low concentrations of another ion because some ion concentrations are highly intercorrelated. By calculating simple ratios between two or more ions it is possible to test if the measured concentrations correspond to the anticipated concentrations. This analysis was used if a measurement showed an irregularity in one of the other two data check methods described above.

NO_3^- is a good indicator for this purpose as high amounts of NO_3^- leaching must have cationic ions associated with it. Ca^{++} and Mg^{++} correlate where the bedrock is dolomitic.

Consequently ratios used were $\text{Ca}^{2+}:\text{NO}_3^-$, $\text{Mg}^{2+}:\text{NO}_3^-$, $\text{K}^+:\text{NO}_3^-$, $\text{Ca}^{2+}+\text{Mg}^{2+}+\text{K}^+:\text{NO}_3^-$ and $\text{Ca}^{2+}:\text{Mg}^{2+}$.

3.2.3 Calculating Evapotranspiration

The potential Evapotranspiration (ET_0) was calculated with the Thornthwaite formula (empirical formula). This formula is based mainly on temperature, with an adjustment for the number of daylight hours. The ET values can only be calculated on a monthly basis (mm/day for every month) because this formula does not use a lot of input variables (KARLSSON AND POMADE, S.A). Due to the absence of other climate parameters, it was not possible to use another formula that provides better results but typically uses more input variables.

To calculate the ET_0 following parameters have to be included:

- T_m = Mean temperature within the whole month [$^{\circ}C$]
- N = Mean daily duration of maximum possible sunshine hours per day within the specific month [h/d] (Table 12)
- d = Number of days within the specific month [d]
- t = Mean monthly temperature over period of years [$^{\circ}C$]

These parameters are used to calculate following factors and indexes:

- Correction factor [f] = $N \cdot d / 12 \cdot 30$ per month
- Standard value of the mean monthly temperature [i] = $(t/5)^{1,514}$
- Temperature index [I] = $\sum i$ per year on monthly basis
- Empirical factor [a] = $(0,0675 \cdot I^3 - 7,71 \cdot I^2 + 1792 \cdot I + 49239) \cdot 10^{-5}$

Ultimately these values get combined to calculate ET_0 as follows:

- $ET_0 = 0,533 \cdot f \cdot (10 \cdot T_m / I)^a$ [mm/day]

Compared to other formulas (e.g. the Penman formula), Thornthwaite values tend to overestimate the potential evaporation. This is particularly marked in the summer months with the high temperatures affecting the Thornthwaite computation, whereas the Penman estimate takes into consideration other meteorological factors (KARLSSON AND POMADE, S.A).

ET_0 is calculated assuming an area with unrestricted availability of water and nutrients, which is covered by 12cm high grassland. So in arable land-use it is necessary to calculate the influence of different crops, because there are periods without vegetation cover and variations in water use efficiencies. Therefore a crop specific coefficient (k_c) is multiplied with the calculated ET_0 values. In a second step the limited water availability in drought periods are taken into account (k_{adj}). Like the k_c factor the k_{adj} factor is multiplied with the previous result.

For the calculation of the ET_{nat} at the study site no k_c factor was used, because spruce forests do have a vegetation cover all year long. It was further assumed that spruce ecosystems evaporate and transpire as much as grasslands do. Also no k_{adj} factor was included, because there was no evidence for the occurrence of prolonged drought periods.

Table 12: Mean daily duration of maximum possible sunshine hours for different month and latitudes.

Northern Latitudes	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
50	8,5	10,1	11,8	13,8	15,4	16,3	15,9	14,5	12,7	10,8	9,1	8,1
48	8,8	10,2	11,8	13,6	15,2	16,0	15,6	14,3	12,6	10,9	9,3	8,3
46	9,1	10,4	11,9	13,5	14,9	15,7	15,4	14,2	12,6	10,9	9,5	8,7
44	9,3	10,5	11,9	13,4	14,7	15,4	15,2	14,0	12,6	11,0	9,7	8,9
42	9,4	10,6	11,9	13,4	14,6	15,2	14,9	13,9	12,6	11,1	9,8	9,1
40	9,6	10,7	11,9	13,3	14,4	15,0	14,7	13,7	12,5	11,2	10,0	9,3

Source: Calculated from FAO, 1998

3.2.4 Hydrological Balance

3.2.4.1 Method used to calculate the hydrological balance

For further calculations it is necessary to calculate the hydrological balance at the site. In general this is calculated by the formula:

$$\text{Precipitation} + \text{Capillary rise} = \text{ET} + \text{Discharge} + \text{Surface run-off} \pm \text{change of soil water content}$$

The components of this calculation are illustrated in Figure 23.

The change of soil water content (WC) was negligible as the hydrological balance was computed on annual basis. If the balance is calculated on annual basis and the change of water content is negligible because the soil will always reach FC at the end of the year (winter). Likewise capillary rise was not included because it is not likely that a lot of water is rising at such a moisture site with a very high content of coarse material (i.e. water movement is mainly downward). Therefore the formula was simplified to:

$$\text{Precipitation} = \text{ET} + \text{Discharge} + \text{Surface run-off}$$

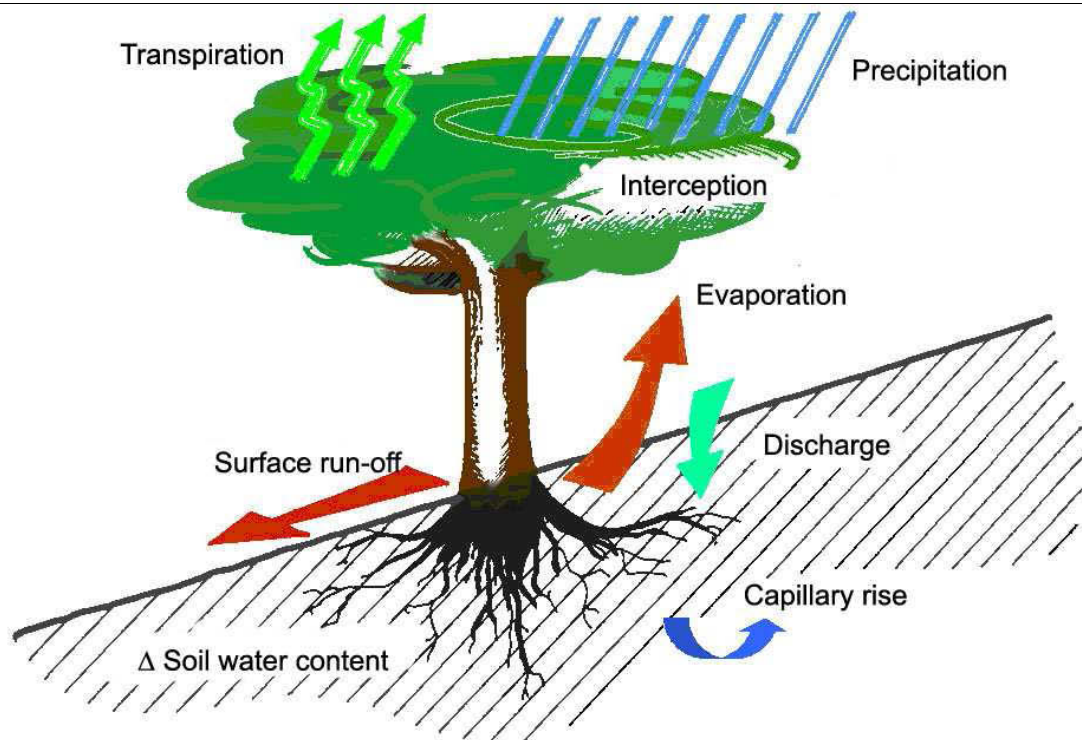


Figure 23: Hydrological Balance

Source: Modified from OASIFICATION, 2009

In the calculation of the total discharge, precipitation was replaced by throughfall fluxes. The calculated ET values (which implicitly include interception losses) had to be modified because the throughfall water fluxes already accounted for the amount of precipitation that was held back by interception (I). The amount of Interception was assumed to be 20% of the entire Evapotranspiration. Therefore the ET value was scaled down by 20%. This value of 20% may seem to be low compared to values obtained in other spruce stands. For example STANISLAW MALEK (2009) obtained interception rates of 35-41% (% of precipitation) in mature spruce stands in southern Poland. In this study, relatively low interception was used, because heavy rainfall events are common and generally lead to cause low interception rates. Another reason was the assumption of relatively high water input by fog deposition. WRZESINSKY ET AL. (2004) for example obtained a fog water deposition of about 4,5% of total water input in a similar mature Norway spruce forest site in Weidenbrunn, Germany.

The surface run-off was collected by long gutters spanning a length of 11,5m (chapter 3.1.3). To get m³/ha values the area where surface run-off took place was assumed to be a 100m*100m square. So the front from which water can leave the system was 100m long. Based on these assumptions the measured fluxes had to be extrapolated to a length of 100m.

Since throughfall and the surface run-off samples were collected every two weeks. So the discharge was calculated over two week intervals and summed up to an annual value. Using this approach, individual weeks could yield a negative discharge value because the change (decline) in soil water content within the soil was not accounted for.

ET had a temporal resolution of one month (same daily value for every single day within one month) because ET was calculated with the Thornthwaite formula. If a two weeks sample straddled two months the arithmetic mean of the two monthly ET values was used. This procedure was applied for the samples collected in weeks 1, 19, 23, 27, 45 and 49.

No surface-run off data were available for the year 2002. Due to the extreme low amount of surface run-off (<0,1% of throughfall). The expected error in the water balance was considered negligible.

In the calculation of nutrient fluxes, however this error was a bigger problem because of the very high concentrations measured in the surface run-off.

The nutrient discharge was calculated using the results of the water balance. Therefore a volume-weighted approach was used in which the calculated water flux (2 week time interval) was multiplied by the nutrient concentrations in the lysimeter samples. Afterwards the results were summed up to an annual flux.

3.2.4.2 Comparison of measured and calculated discharge to evaluate the results quality

The computed discharge was validated with the measured discharge (lysimeter) on an annual basis. The deviation was calculated using the measured discharge as the basis discharge:

$$\text{Deviation} = (\text{calculated discharge} - \text{measured discharge}) / \text{measured discharge} * 100$$

The deviation thus calculated was highest possible deviation gained with calculated discharges as base values because the measured discharge was smaller than calculated discharge in most cases. If the deviation was negative the measured value was higher. In this case the calculated deviation was lower than if the calculated values were used as base values.

The same procedure was used for the calculated and the measured nutrient fluxes. A bad result for the comparison of nutrient fluxes would indicate an error in the temporal resolution of the hydrological balance, even though the balance fits on annual basis. Due to the coarse temporal resolution of the ET calculation this error is assumed to be high.

3.2.5 Estimating the sites risk to leach nitrate

The site is prone to leach nitrate due to the physical characteristics of the soil (high content of coarse material) and the very humid climate, allowing for more and faster water percolation. One method to determine a sites risk to leach nitrate is to estimate the **exchange rate of the soil** water at field capacity (GÄTH AND WOHLRAB, 1988). It describes how often the soil water content (at field capacity) turns over within one year.

The exchange rate (Ns) is determined by the parameters field capacity (FC) in mm and the annual discharge (As= Precipitation – Evapotranspiration). Surface run-off is not taken into account in this formula and can be neglected due to low values at the site.

$$Ns = As/FC$$

Because the soils field capacity is very variable the exchange rate were calculated using three different FC values (100mm, 75mm and 50mm) which stand for very high, intermediate and very low field capacity assumptions at the site.

The exchange rates were interpreted according to the classification by GÄTH AND WOHLRAB (1988) (Table 13).

Table 13: Evaluation of obtained water exchange rates

Risk	Exchange rate [1*a ⁻¹]
Very low	< 0,7
Low	0,7 - 1
Medium	1 - 1,5
High	1,5 - 2,5
Very High	> 2,5

Source: GÄTH AND WOHLRAB, 1988

In addition, the sites risk was determined using the classification system of GUNDERSEN ET AL. (1998). Gundersen et al. discovered the C/N – N leaching relationship for **C/N ratios in the forest floor** (Table 14). While C/N ratios in the mineral soil at the Mühleggerköpfl are very high, it can be assumed that this relationship may be applicable at this site also because some parts of the upper mineral do have organic matter contents > 300g/kg and so by definition they would have to be classified as humus layer. It is assumed that the C/N ratio is very low in the humus layer.

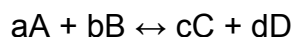
Table 14: Forest floor C/N ratio as a rough indicator of ecosystem N status in mature coniferous forests. Risk of nitrate leaching relate to cases where the forest receive more than 10 kg N*ha⁻¹a⁻¹ in deposition.

Forest floor C/N ratio [g/g]	>30	25-30	<25
N-status	N-limited	Intermediate	N-saturated
Risk for nitrate leaching	Low	Moderate	High

Source: GUNDERSEN ET AL. 1998

3.2.6 The chemical equilibrium

Fundamental to any description of equilibria in water is the **law of mass action**. It states that for a reaction of the generalized type:



The distribution at equilibrium between the species at the left and right is described by:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The equilibrium constant K e.g. determines how much of the initial elements dissolve/precipitate, build complexes, or how gaseous elements dissolve. So every single reaction has its own equilibrium constant (APPELO AND POSTMA, 1996).

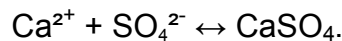
When a soil solution sample is analyzed in the laboratory the total amount of e.g. Ca^{2+} within the solution sample is determined. This does not give information as to how many of this Ca^{2+} exists as free Ca^{2+} ions and how many of them build complexes or precipitate. This may have a big influence to soil water chemistry, because the same element can behave very differently in the presence of other elements or if it precipitates. Therefore some corrections for solubility calculations were necessary.

3.2.6.1 Corrections for solubility calculations

Total concentration values had to be corrected for the effect of aqueous complexes and precipitation. Further, the reactivity of ions is influenced by the ionic strength ($0,5 \cdot \sum \text{charge of ion} \cdot \text{mol/l}^2$) and the water temperature.

Activities which appear in solubility products reflect the chance that two ions react and form a precipitate. In pure water an ion such as Ca^{2+} is surrounded by a shield of water molecule dipoles. In the presence of **charged solutes** additional electrostatic shielding occurs, and the reactivity of the ion is reduced. The activity of the ion approaches its molar concentration as the concentration of all solutes approaches zero. The activity coefficient is influenced by temperature with (in general) a higher activity at a higher temperature (APPELO AND POSTMA, 1996).

The reactivity of ions in solution is further reduced by the presence of ion pairs or aqueous **complexes**. One complex occurring is for example:



Its distribution is simply obtained by applying the law of mass action.

$$10^{2,5} = \frac{[\text{CaSO}_4]}{[\text{Ca}^{++}][\text{SO}_4^-]}$$

Where CaSO_4 is by definition equal to 1. In this case the mass action constant is a stability constant because the reaction is written as an ion-association reaction. If the reaction is written as a dissociation reaction (simply the reverse equation) dissociation constant has to be used.

In reality, numerous other reactions besides this CaSO_4 ion-association reaction take place simultaneously. Simply stated Ca^{++} can form a lot of different complexes (e.g. CaF^+ , CaOH^+ , and so on) depending on what elements are surrounding the ion. To obtain a rough picture of what complexes might appear in the solution it is necessary to compute the equations of all possible reactions from the initial analytical data. This yields a new dataset including molar concentrations of the complexes. With this data, equations have to be calculated again. This iterative process has to be continued until no further significant improvement is obtained (APPELO AND POSTMA, 1996).

An approach to calculate the **state of saturation Ω** of a soil solution sample, is to compare the solubility product K_{sp} (the solubility constant for the specific solid at equilibrium) with the analogue product Q of activities derived from the water analyses. The saturation state Ω can be expressed as the ratio between Q and K_{sp} .

$$\Omega = Q/K_{sp}$$

Thus for $\Omega = 1$ there is equilibrium, $\Omega > 1$ supersaturation and $\Omega < 1$ subsaturation. In the case of large deviations from equilibrium, a logarithmic scale such as the saturation index (SI) can be useful. Thus, for $SI = 0$ there is equilibrium, $SI > 0$ supersaturation and $SI < 0$ subsaturation.

$$SI = \log(Q/K_{sp})$$

For subsaturation dissolution is expected while supersaturation suggests precipitation (APPELO AND POSTMA, 1996).

3.2.6.2 Calculating the chemical equilibrium with MineQL+

The calculation of the chemical equilibrium is unbelievably time consuming because all these processes are so complex, it requires a computer program. The program used in this thesis is MineQL+ (version 4.5 2001).

The chemical equilibrium was calculated on an annual basis using the arithmetic mean concentration of the different elements and pH for every year (2000-2008). The water temperature was set at 6,4°C (MAT). This approach may seem somewhat rudimentary, but the intention was to get an overview first and explore details further when unusual results were obtained.

To calculate the equilibrium some assumptions had to be made:

No ionic strength correction was included.

The CO₂ partial pressure (pCO₂) was assumed to be 380ppm in the throughfall and the surface run-off samples, while a pCO₂ of 400 ppm was used for the upper 5cm of the mineral soil. For the lower mineral soil a pCO₂ of 500ppm was assumed. The 400ppm value in the upper soil was chosen because of a relatively good air exchange.

The pCO₂ is an important factor because it has a great influence on the chemical system highly (chapter 3.2.2.1). For example the pCO₂ mainly influences the solubility of Ca²⁺ (Figure 24).

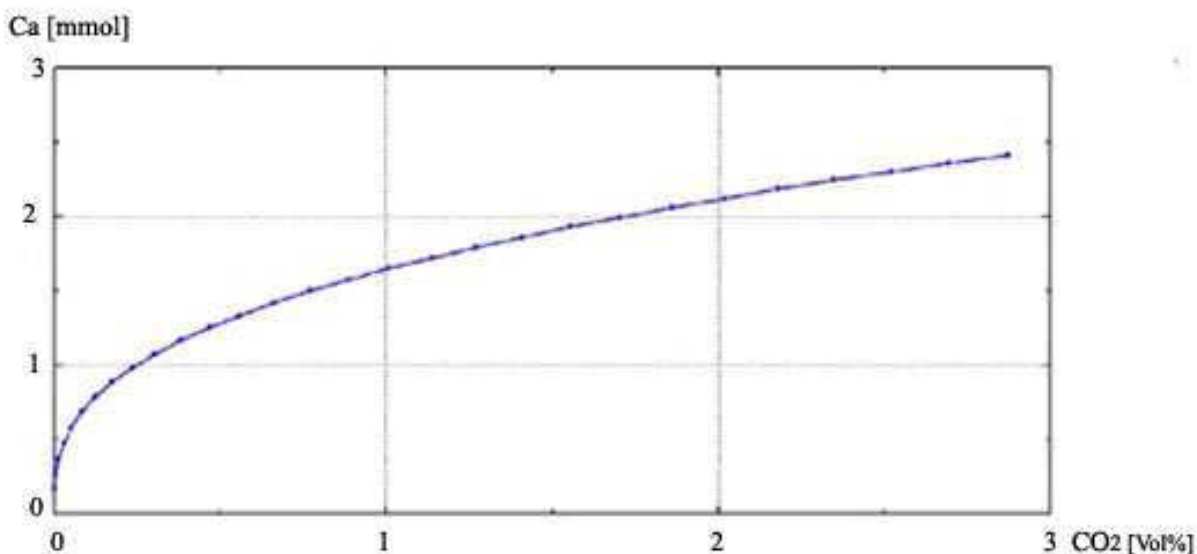


Figure 24: Dissolution of Ca²⁺ with a rising pCO₂ (Calcite Equilibrium)

The chemical equilibrium of every single depth was calculated two times. Once excluding the solid phase (precipitation) and another time including the solid phase. This was done because the solution samples definitely did not show any precipitation when they entered the suction cups. However, it is possible that the system is highly saturated with an element that can precipitate at specific places within the soil (e.g. if water loss increases the concentration) or after the soil water leaves the system (e.g. because the water leaves the system before the precipitation process is finished). The solids which were taken into account were Dolomite (ordered and disordered), Calcite, Aragonite, Anhydrit, Magnesite and $\text{Mg}(\text{OH})_2$. These solids were selected because they are likely to be found in the pure dolomitic bedrock, typical of the research site. In a first step only dolomite (ordered and disordered) was included in the calculation; afterwards others solids were also considered.

The outcome of such calculations is not perfect because not all elements are included as some were not analyzed. Nevertheless this calculation considered the main elements. In addition, the temporal resolution of one year causes some uncertainty as seasonal differences can not be analyzed this way. In summary, the result provided a general indication of the state of the system, yet there are periods and places (within the soil) at which the calculated conditions are different to the real ones. Consequently, while the results of these calculations can be trusted in a general sense, it is necessary to carefully interpret and scrutinize the results detect the processes involved.

3.2.7 Calculation of concentration allocations and fluxes

3.2.7.1 Analysis of patterns in the concentration data

The measured concentrations were analysed in two ways:

- Graphs
- Correlations

Plots of the data were used to identify temporal patterns in the distribution of elements using weekly, seasonal and yearly time scales. During these time spans the different element concentration data were plotted for different depths (throughfall, surface run-off, soil water and discharge). To get an overview, annual patterns were investigated first to see if there were inner-annual changes between 2000 and 2008. The next step was to see if there were seasonal patterns and finally the data was examined for weekly patterns.

Correlations were used to determine elements which are interacting with each other that could help in interpreting our results..

3.2.7.2 Analysis of elemental fluxes

The **data used for these calculations** were *throughfall* (bulk sampler), *discharge* (lysimeter) and the *suction cups at 50cm*.

To estimate changes of nitrogen deposition loads over a longer period of time the data collected by bulk sampler (*throughfall*) between 2000 and 2008 was completed with the wet-only open-land deposition (WADOS) measurements of SMIDT (2002). These two methods were used simultaneously in the year 1998. The comparison of these two measurement methods in 1998 showed that this data was similar. In 1998 N-total loads of the WADOS measurements were 12,48 kg N*ha¹*a¹ while the bulk sampler collected 12,97 kg N*ha¹*a¹.

To calculate the *discharge*, the amount of water which was collected in the lysimeter was used and multiplied with the associated nutrient concentrations. The influence of the changed matric potential exerted on the bottom soil layer of the lysimeter was considered negligible due to the high content of coarse material and due to the fact that the Mühleggerköpfl is a very wet site. Furthermore it was not possible to calculate a water balance to the desired level of accuracy because of insufficient climatic data. Also, there was not enough data available to calculate water fluxes based on water content and tension. Despite these limitations, the water balance calculated with the Thornthwaite formula indicated that the lysimeter values are useful in our case (chapter 4.2). One problem with lysimeter-derived water fluxes is that lateral fluxes are not taken into account. This problem is unlikely at the research area (chapter 2.5). The main problem with this approach was the high number of missing lysimeter data between 2006 and 2008 (chapter 4.2).

A second approach for calculating the discharge loads was to combine concentration values of the *suction cups at 50cm* with the water fluxes obtained in the lysimeter. described in section 3.1.4. To that end the arithmetic mean concentrations of the four suction cup samples were multiplied with the associated water fluxes of the lysimeter.

The throughfall and discharge fluxes were calculated for all elements analysed in the laboratory between 2001 and 2008. In this first step, missing values were ignored which caused an underestimation of specific fluxes.

In a second step, some of the fluxes were recalculated as described below.

Patterns obtained in concentration data were compared to patterns in fluxes.

Two approaches were used:

- Analysis of fluxes as concentrations were analysed (chapter 4.6.1)
- Analysis of the influence of water fluxes on changing concentrations (e.g. dilution effects).

The influence of water fluxes on loads was characterized by the correlation between water fluxes [m^3/ha] and nitrate fluxes [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]. Correlations were calculated separately for the discharge (lysimeter) data between 2001 and 2003 and the data between 2004 and 2008. This was necessary to take the change of discharge (lysimeter) nitrate concentrations in 2004 (chapter 4.6.1) into account. In addition, a ratio of annual water [$\text{m}^3\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$] and nitrate [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$] fluxes was computed to check if the amount of nitrate leaching in the lysimeter was always associated with the same amount of water or if there was a change over years.

A change in input loads may lead to changes in nitrate concentrations in the lysimeter-discharge samples (chapter 4.6.1). Therefore annual deposition loads ($\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the throughfall) were calculated. Furthermore, deposition loads for different weeks between 2001 and 2008 were calculated to determine if the input occurs mainly in summer as is expected.

A final reason to calculate deposition loads was to determine if critical loads were reached.

3.2.7.3 Determination of the ecosystem's nitrogen status by comparisons of input and output fluxes

To determine the nitrogen saturation status of the ecosystem an N-release index was calculated. This index is a simple comparison of the annual input (throughfall) and output (lysimeter and suction cups at 50cm) N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) fluxes:

$$\text{The N release Index} = \text{Output/Input}$$

The N release Index describes how much of the incoming nitrogen (via throughfall) leaves vs is retained by the ecosystem.

The N release Index was calculated based on two different output assumptions:

- Annual output measured in the lysimeter samples
- Annual output calculated by a multiplication of lysimeter water fluxes with the arithmetic mean of the weekly concentration values of the four suction cups at 50cm.

For the interpretation of the results a classification developed by the BUNDESMINISTERIUM FÜR ERNÄHRUNG, LANDWIRTSCHAFT UND FORSTEN (2000) was used.

In order to calculate the N release Index the missing concentration values for outfluxes had to be estimated. The output was underestimated and caused too low N release Indexes due to the high number of missing concentrations (2006-2008) in the lysimeter samples. To bring this error into perspective, the missing values were taken into account in a second step: The calculated output [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$] was summed up with the calculated output * % of missing concentrations values.

In July 2008, there was a high amount of deposited nitrogen that could not be directly quantified by the throughfall collection data due to 4 weeks without measurements (chapter 4.2). To obtain this missing N input, the calculated N input of 2008 was multiplied by 0,31 to reflect the observation that in July 2008 precipitation was about 31% of the rest of the year. Yet this approach too may still have underestimated the deposition load of 2008 as a greater portion of annual N input tends to occur in summer (chapter 4.6.2.1)

Since lysimeter discharge showed much higher concentration values than the soil solution samples and there was no evidence of other nitrogen sources (e.g lateral fluxes or high amounts of organic matter mineralized at a depth of 50 cm), the N release Index was also calculated with an output based on the 50 cm suction cups concentrations and the lysimeter water fluxes. It was assumed that there was only limited N uptake in the lysimeter. Although there were few missing concentration values in the suction cup samples between 2006 and 2008, a lot of water fluxes were missing in the lysimeter measurements.

The same input data were used to calculate the N release Index based on lysimeter or suction cup concentrations.

4 Results and Discussion

4.1 Data check

4.1.1 Overview of deleted values and the way results were interpreted

The data quality differs depending on the sampling method. The data check in general showed good quality for temperature, precipitation, throughfall, surface run-off and discharge data while the charge balances of the suction cup samples were worse. Table 15 illustrates the number of samples where measured data had to be deleted. In most cases only one specific ion concentration value had to be deleted. Especially if the charge balance did not fit the whole sample (all ion concentration values within the sample) had to be deleted.

Table 15: Overview of deleted values (2000 and 2008) based on the data check results.

	Deleted ion values	Samples deleted	Explanatory notes
Throughfall	1	0	14 weeks with missing values in 2000
Surface run-off	6	0	No values available for 2002
5 cm	2	0	
15cm	9	1	
25cm	14	1	
50 cm	9	1	
Discharge	0	0	No values available for 2000
Sum	41	3	

If the interpretation of unusual patterns in specific ion concentrations or of a whole sample was not obvious, the measurement was kept in the database to avoid a disproportionate rounding of the data. Thus the data erasing was done in a conservative way.

Figure 25 shows a clear NaCl outlier which is likely caused by contamination by sweat or laboratory detergents.

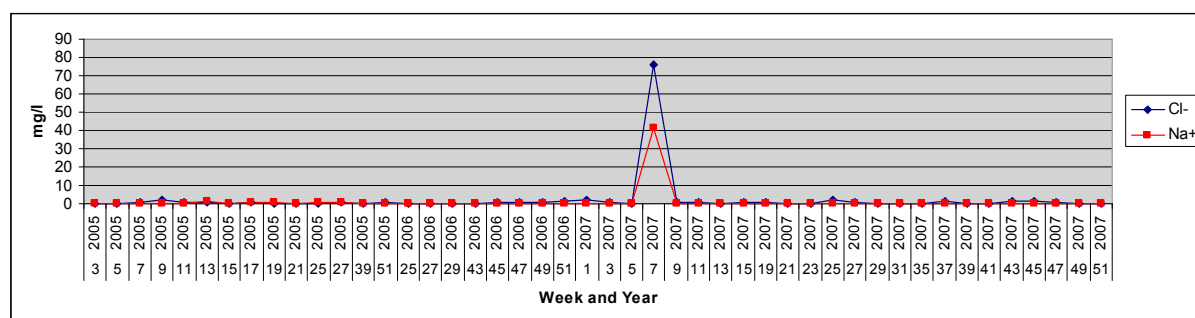


Figure 25: Measured Na⁺ and Cl⁻ concentrations in the years 2006 and 2007 at the suction cup B09 which is installed at a depth of 25cm.

Figure 26 illustrates an Mg²⁺ and a Ca²⁺ outlier in obtained throughfall concentrations. It is assumed that these concentrations were measured due to a dolomite grain which got into the sample. There were no similar values between 2000 and 2008.

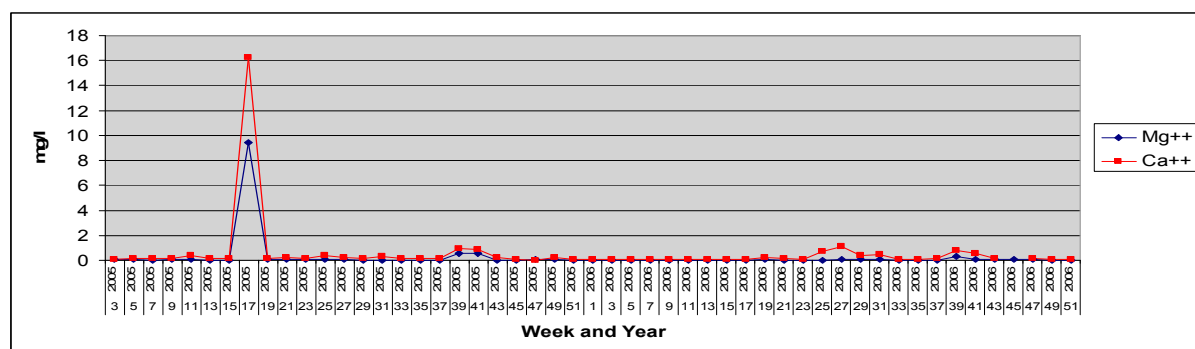


Figure 26: Measured throughfall Mg⁺⁺ and Ca⁺⁺ concentrations in the years 2005 and 2006.

In general the data for throughfall, surface run-off and discharge passed the quality thresholds. Samples from suction cup samples showed high charge balance errors. The margins for data acceptance were defined as 100%, that is wider than suggested by APPELO AND POSTMA (1996) in order to retain a sufficient size of the dataset (chapter 3.2.2.1). Charge balance values (in % sum of cations) of 700% appeared several times. If such a high error occurred the entire record was deleted as re-analysis of the samples was impossible.

4.1.2 Erased data of the years 1998 and 1999

The solution samples collected between 1998 and 1999 were not considered for further analysis because they showed very high concentration variability and a poor charge balance. The charge balance values after 1999 (Figure 28) generally approach 100% because the Mg^{2+} and Ca^{2+} measurements in this period of time are too high (see chapter 4.1.3.). The throughfall values were used in Figure 27 and Figure 28 to illustrate deviations because their smaller concentrations accentuate the error visually.

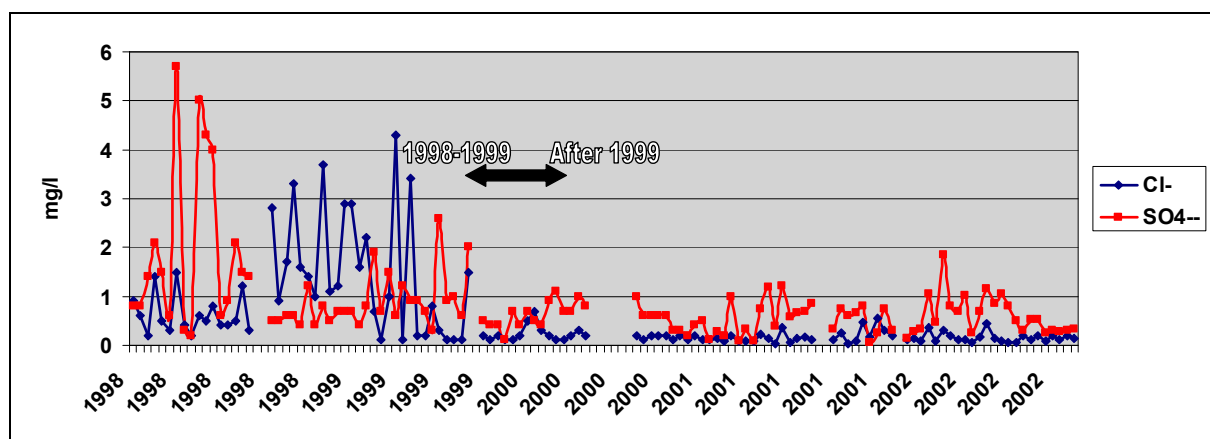


Figure 27: Cl^- and SO_4^{2-} throughfall concentration values between 1998 and 2001

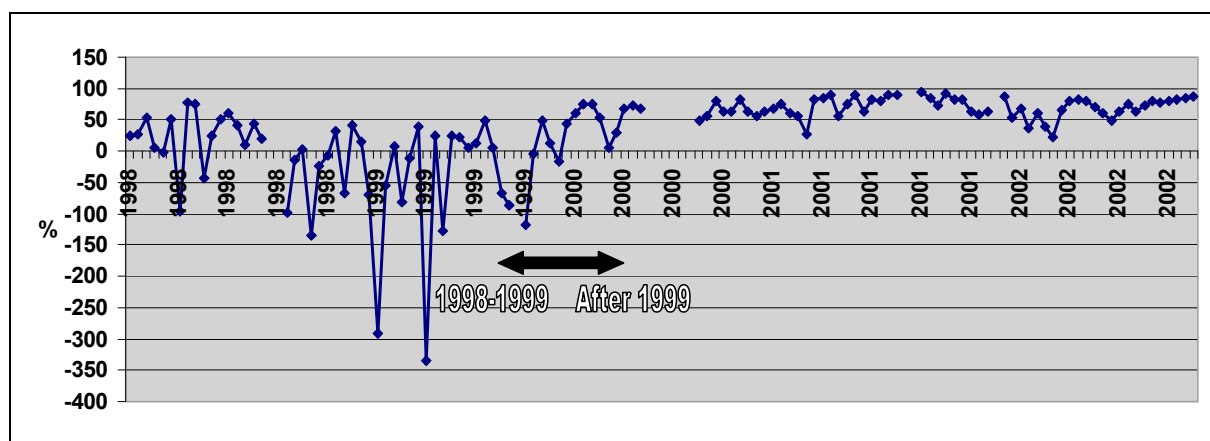


Figure 28: Throughfall charge balance values in % sum of cations between 1998 and 2002

4.1.3 Too high Mg^{2+} and Ca^{2+} concentrations between the years 1998 and 2004

The Mg^{2+} and Ca^{2+} concentrations obtained between 1998 and 2004 are much higher than in the following 4 years to 2008. This is the result of lab protocol that leads to a systematic error that was not immediately noticed. In subsequent years the lab procedure was modified, and the data analyzed after 2004 passed the quality requirements.

Table 16 shows the average throughfall concentrations (Mg^{2+} , Ca^{2+}) between 2000 and 2004. The concentrations were 0,22 Mg^{2+} and 2,13 mg Ca^{2+} /l but only 0,06 Mg^{2+} and 0,22mg Ca^{2+} /l the following 3 years..

Table 16: Average annual Mg^{2+} and Ca^{2+} concentrations in the throughfall

Concentrations (mg/l)	2000	2001	2002	2003	2004	2005	2006	2007
Mg^{2+}	0,14	0,149	0,169	0,26	0,385	0,0833	0,038	0,06
Ca^{2+}	1,265	1,756	1,576	2,387	3,66	0,24	0,251	0,171

This change in concentrations in 2004 was found again in deposition loads (Figure 29), indicating that the higher concentration values were not caused by dilution effects which would have changed the concentration but not the amount.

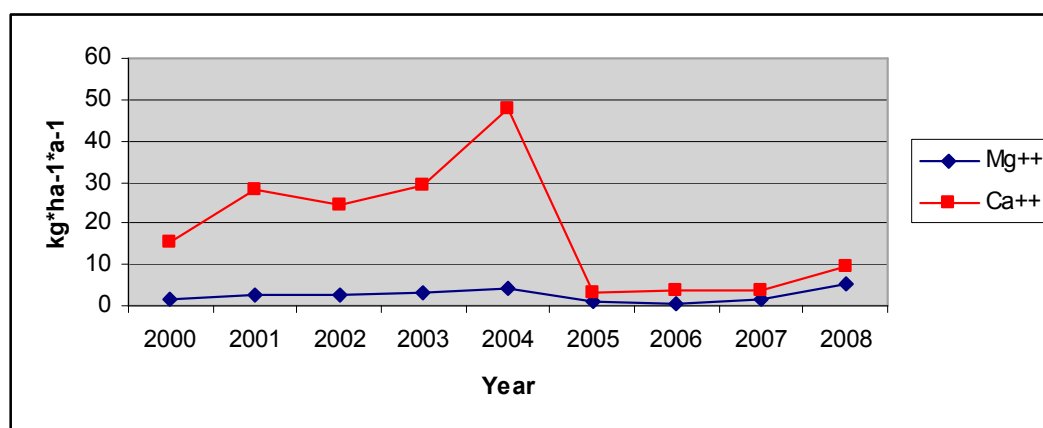


Figure 29: Mg^{2+} and Ca^{2+} annual deposition loads

*2000: In the year 2000 there were 12 weeks without any measurement what explains the relatively small amount of deposited Mg^{2+} and Ca^{2+} .

This correction in Mg^{2+} and Ca^{2+} concentrations had to be considered in the interpretation of the charge balance results because Mg^{2+} and Ca^{2+} play a major role as divalent ions which appear in a high concentration.

Since Mg^{2+} and Ca^{2+} are very important for the soil solution chemistry they can not be neglected due. So the data was kept in the data set and used for further calculations.

The Mg^{2+} and Ca^{2+} concentrations in the soil are much higher than in the throughfall. For example the average concentrations at 5cm (2005-2008) were 17,44mgMg/l and 29,09mgCa/l. The obtained measurement error obtained in the throughfall data (<0,3mg/l) is too small to influence the accuracy of the soil solution analyses in a relevant magnitude due to the very high Mg^{2+} and Ca^{2+} concentrations in soil solution.

Related to the obtained measurement error of not more than 0,3 mg/l in the throughfall data, this error does not change the results of soil solution analysis . One more reason why the data should be kept in the dataset is that the input (throughfall) is not very important for the Mg^{2+} and Ca^{2+} cycle because the mineralization of litter is assumed to be the main source for these elements at that site.

4.1.4 Missing values

For a variety of reasons the dataset has a lot of missing values. For example, in 2000 there are no concentration and water flux values for the discharge and in the year 2002 surface run-off values are missing. Apart from these complete blackouts, measurements of specific weeks within a year are frequently missing. Especially the discharge database showed numerous data gaps in the years between 2006 and 2008.

Some data were relocated in the database after the data check showed that they have been lost in data translation. In most cases, data were simply not measured. Reasons for this were for example blocked suction cups, too high suction power within the soil, erased values (data check) or lack of collection of the samples.

One approach to reconstruct these missing values would be to interpolate between existing data. This was not done because it would have been a data manipulation which should be avoided. Consequently every single result used in further calculations had to be assessed for the potential influence of missing values.

The quantity of these missing values were relatively small compared to the large amount of available data

4.1.5 Unusual and unexplained concentrations

The average annual Mg^{2+} and Ca^{2+} concentration values in 2002 were unusual (Figure 30). The Mg^{2+} and Ca^{2+} concentrations are commonly correlated because the initial source of both is the dolomitic bedrock. In this particular year the Ca^{2+} concentration increased while the Mg concentration decreased.

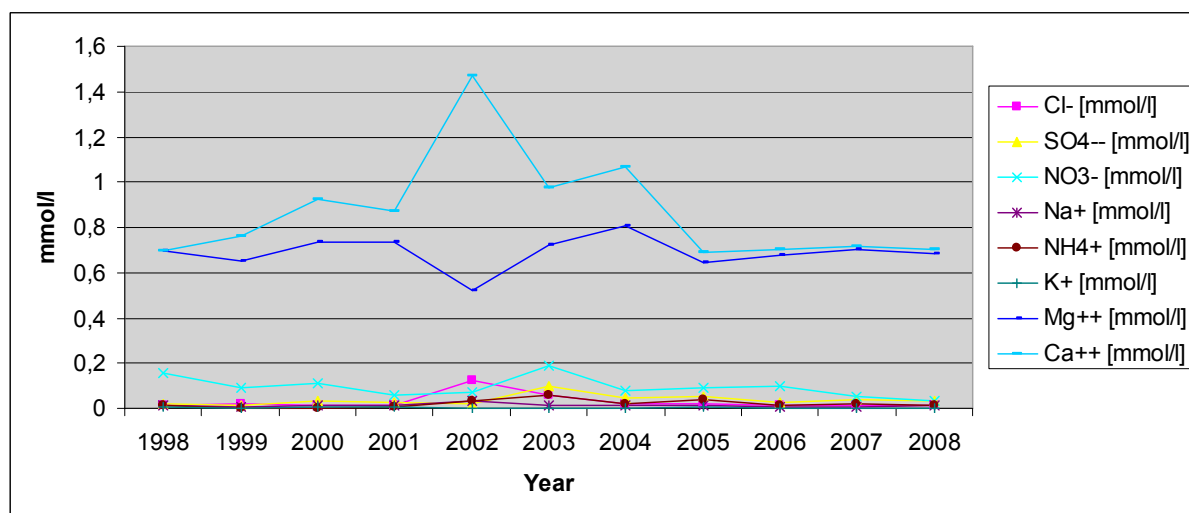


Figure 30: Annual average concentrations at a depth of 15cm in mmol/l

Soil solution concentrations in week 19 in 2003 are very different from all other measured concentrations, even though the charge balance did not show any unusual results. A systematic laboratory error was unlikely because throughfall, surface run-off and discharge concentrations, which were likely analyzed at the same time, were normal.

Especially the Cl^- concentrations seemed much too high. SO_4^{2-} and NH_4^+ concentrations were also elevated. On the other hand Mg^{++} concentrations were low, while Ca^{2+} , NO_3^- , K^+ and Na^+ concentrations were within their normal range. In all these samples the pH declined from about 8 to 7. This observation applied for every depth, in least one of the 4 soil profiles. At most soil depths the same pattern was observed in at least 3 of 4 soil profiles. Because this pattern showed in so many

different samples, but not in all (especially not in the throughfall, surface run-off and discharge concentrations) it is unlikely that the values were the result of laboratory errors. Because of this consistent pattern, the values were kept in the dataset.

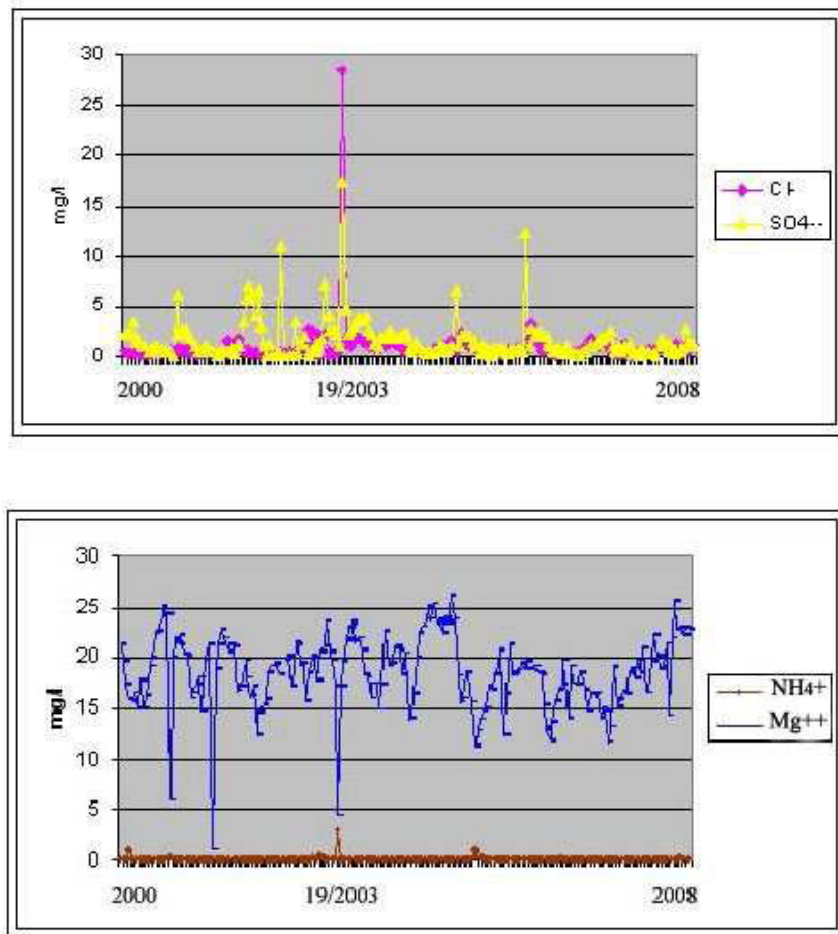


Figure 31: Mg^{2+} , NH_4^+ , Cl^- and SO_4^{2-} concentrations time courses between 2000 and 2008.

4.2 Statistics

Based on the Student-Newman-Keuls-Test (Table 17) there were no general and consistent statistically significant differences between sampling methods, but specific differences for single elements were detected.

There was a significant enrichment in Cl^- concentrations from the throughfall to the surface run-off. Soil solution and discharge samples all had similar concentrations.

Surface run-off and discharge NO_3^- concentrations were also significantly different while all other sampling levels yielded similar concentrations.

While all NH_4^+ soil solution and discharge samples except soil solution at 15cm (A) had the lowest concentrations, there were significant differences between throughfall (B) and run-off (A) concentrations.

The K^+ concentration in all samples was similar except in run-off where concentrations which were much higher.

Mg^{2+} concentrations showed a clear pattern: Low in throughfall (D), somewhat higher in run-off (C) and highest in discharge (A), while all soil solution samples except 25cm (C) had intermediate concentrations (B).

SO_4^{2-} , Na^+ and Ca^{2+} sample concentrations did not show any specific pattern.

Table 17: Results of the Student-Newman-Keuls-Test

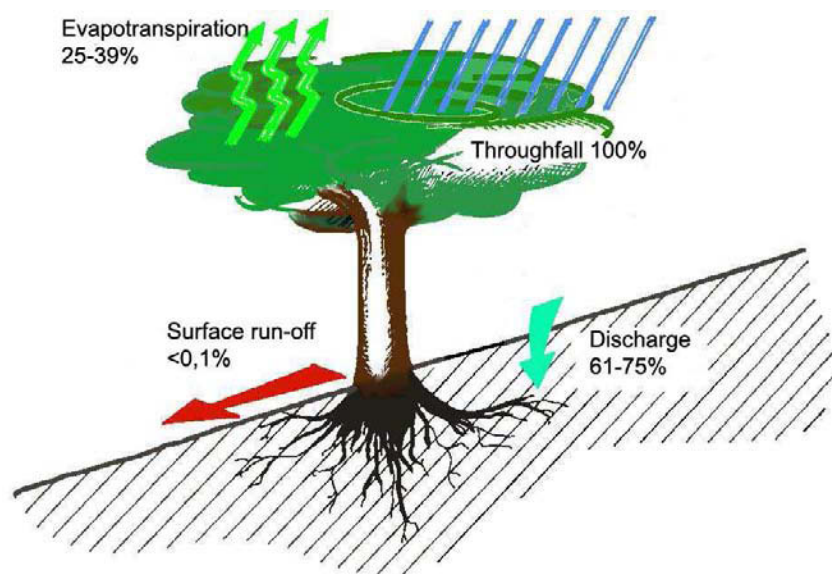
	Cl^- [mg/l]	NO_3^- [mg/l]	NH_4^+ [mg/l]	SO_4^{++} [mg/l]	Na^+ [mg/l]	K^+ [mg/l]	Mg^{++} [mg/l]	Ca^{++} [mg/l]
Throughfall	0,25 [C]	1,41 [C]	0,26 [B]	0,60 [D]	0,15 [F]	0,11 [B]	0,19 [D]	1,31 [F]
Surface run-off	2,02 [A]	46,58 [A]	0,39 [A]	2,74 [B]	0,50 [A]	2,02 [A]	15,07 [C]	25,63 [E]
Solution at 5cm	0,90 [B]	4,94 [C]	0,05 [C]	2,62 [B]	0,25 [D]	0,09 [B]	18,00 [B]	32,52 [C]
15cm	0,91 [B]	5,08 [C]	0,38 [A]	3,85 [A]	0,31 [C]	0,10 [B]	16,89 [B]	34,65 [B]
25cm	0,62 [BC]	1,56 [C]	0,10 [C]	1,75 [C]	0,25 [D]	0,10 [B]	15,62 [C]	28,19 [D]
50cm	0,88 [B]	2,72 [C]	0,12 [C]	1,83 [C]	0,35 [B]	0,15 [B]	17,98 [B]	31,96 [C]
Discharge	0,51 [BC]	11,67 [B]	0,02 [C]	1,50 [B]	0,19 [E]	0,05 [B]	20,30 [A]	37,97 [A]

The Duncan test identified some other statistical differences between specific elements at various sampling levels. So Cl^- throughfall and discharge concentrations were classified into group D and CD. NH_4^+ concentrations at 5 and 25cm were classified as CD, while discharge concentrations were put into an own group D. Also some more differences were identified for Mg^{2+} concentrations: 15cm were classified as part of group C, while surface run-off and 25cm concentrations were put into group D. So throughfall was displaced into group E due to the shift of the surface run-off into group D.

The results of correlation and regression analyses are presented in the applications where they were used to analyse the data.

4.3 Hydrological Balance

The calculated water balance for the years 2000-2008 showed that surface run-off



was negligible (Figure 32). ET and discharge accounted for respectively 25-39% and 61-75% of the incoming throughfall. Interception of rain in the canopy is not shown because throughfall rather than precipitation was used.

Figure 32: Calculated water balance for the period 2000-2008

4.3.1 Water balance

Detailed information's about the water balance in individual years are given in Table 18. Only in the year 2008 interception was included in the calculation of ET because the water balance was computed based on precipitation. This approach was necessary because of the two missing throughfall values during a period with high precipitation.

Table 18: Calculated water balance for single years between 2000 and 2008.

Year	Throughfall		Surface run-off***		ET*		Discharge	
	[m ³ /ha]	%	[m ³ /ha]	%	[m ³ /ha]	%	[m ³ /ha]	%
2000	17.926	100	0,27	<0,1	4.537	25	13.389	75
2001	16.512	100	0,31	<0,1	4.335	26	12.177	74
2002	16.121	100		<0,1	4.578	28	11.543	72
2003	12.135	100	0,31	<0,1	4.780	39	7.355	61
2004	13.441	100	0,05	<0,1	4.281	32	9.159	68
2005	14.489	100	0,12	<0,1	4.283	30	10.206	70
2006	14.805	100	0,02	<0,1	4.644	31	10.161	69
2007	15.725	100	0,05	<0,1	4.491	29	11.234	71
**2008	12.223	100	0,04	<0,1	4.620	38	7.603	62

* ET values excluding Interception because throughfall was used as basis

** In 2008 missing throughfall values occurred for which reason the equation had to be calculated with precipitation values. Therefore the calculated ET value for 2008 includes interception.

*** Many missing values in the surface-run off values which are negligible due to the low amount of surface run-off

To test the reliability of these results the calculated discharge values were compared with the values obtained from the lysimeter (Table 19).

Table 19: Comparison of calculated and measured discharge.

Discharge Year	Calculated $\text{m}^3 \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$	Missing values (Throughfall)	Measured $\text{m}^3 \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$	Missing values (Discharge)	Deviation %
2000	13.389	0 of 26 (0%)	No value	No values	No value
2001	12.177	2 of 26 (7,7%)	11.402	0 of 26 (0%)	6,798
2002	11.543	1 of 26 (3,8%)	12.053	1 of 26 (3,8%)	-4,235
2003	7.355	4 of 26 (15,4%)	8.477	2 of 26 (7,7%)	-13,24
2004	9.159	3 of 26 (11,5%)	9.111	2 of 26 (7,7%)	0,534
2005	10.206	1 of 26 (3,8%)	9.121	4 of 26 (15,4%)	11,896
2006	10.161	1 of 26 (3,8%)	8.533	10 of 26 (38,5%)	19,077
2007	11.234	2 of 26 (7,7%)	7.350	12 of 26 (46,2%)	52,851
2008	7.603	2 of 26 (7,7%)	4.710	14 of 26 (53,8%)	22,864

This comparison showed that the calculated and measured data fit well in the years 2001-2005 (Deviation between -13 and +12 %). After 2005 the deviation increased significantly which suggests an error in calculation. The likely reason is a high number of missing values (19-54%) in the measured discharge fluxes, resulting in smaller measured values than the calculated ones. This explanation cannot explain results in 2008 when the highest number of missing data occurred (54%), yet the deviation between calculated and measured values was “only” 23%. Here, the explanation lies in the two missing throughfall values (6th to 31st of July) in 2008 during a period of heavy rainfall events (in this period the rainfall was 227mm). The discharge of 2008 was therefore recalculated using precipitation values in this period, and the ET used now had to include interception losses. After this amount was taken into account the deviation increased to 61%, what was more in line with the high number of missing values.

On annual basis the comparison indicated a good quality of calculated water balance. This result suggests that it is possible to use the measured lysimeter concentrations and water fluxes for further calculations. This is reasonable because the temporal resolution and quality of the calculated water balance is not adequate because of the relatively coarse estimation of the ET values (4.3). So it was assumed that lysimeter was appropriate to measure loads although the lower boundary condition was open to the atmosphere. So free drainage was assumed what was

reasonable due to the appearance of heavy rainfall events, very high contents of coarse material within the soil (80%) and the absence of non-local flows.

The deviation calculated and measured data at specific two week intervals was high due to the low temporal resolution of the calculated evapotranspiration (1 month).

A general pattern observed was that in the summer weeks with high ET, the deviation $[(\text{output calculated} - \text{output measured})/\text{output measured} \cdot 100]$ often showed high negative values (maximum was -13.600%). This happened because a negative water balance in this 2 week time period was calculated because a relatively heavy rainfall event within these two weeks caused a little amount of discharge, meaning that there was soil water recharge (=increase in soil water content) for the whole 2 week period, compared to a low positive balance obtained in the lysimeter. Such high differences indicate that it is definitely more appropriate to use measured output for further calculations.

To calculate fluxes more precisely soil physics would have to be analyzed in detail to calculate water fluxes based on changes in measured water content and tension.

The relationship between Precipitation and Evapotranspiration (Figure 33) shows the absence of prolonged dry periods at the site.

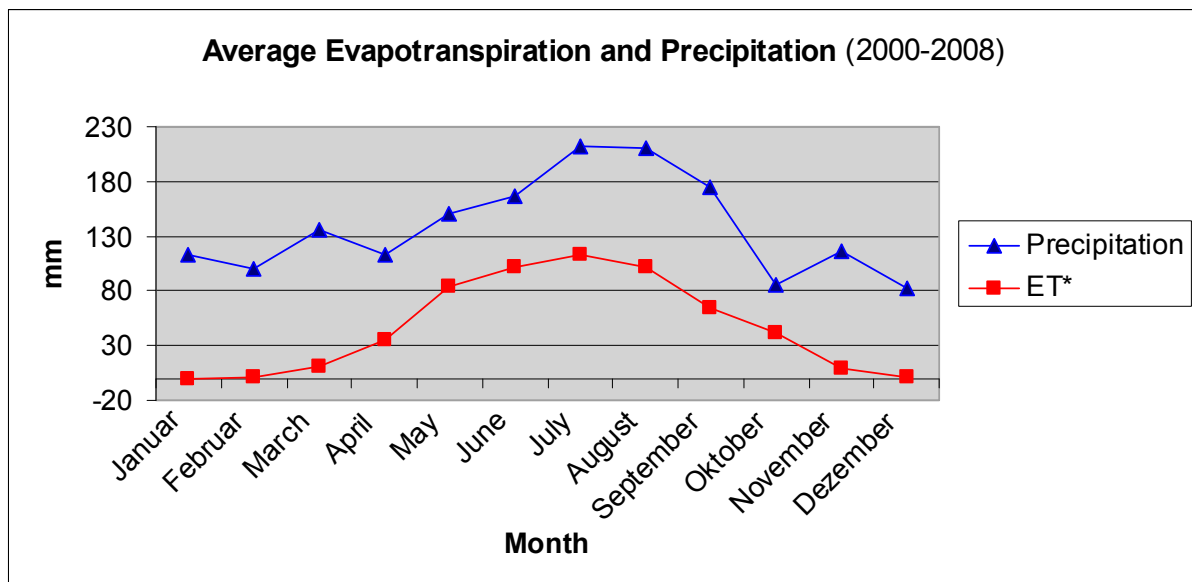


Figure 33: Average monthly Evapotranspiration and Precipitation at the Mühleggerköpf between 2000 and 2008.

* Potential ET calculated with Thornthwaite formula

4.3.2 Nutrient Discharge

Table 20 shows the amount of the calculated and measured nutrient discharge fluxes for the period 2000-2008. The fluxes summarized in this table were considered underestimates because water fluxes were only multiplied by the available concentration values. Due to a lot of missing discharge values (especially after 2005) there were many calculated water fluxes without associated concentration values.

Table 20: Calculated and measured nutrient fluxes between 2000 and 2008

Output calculated	Cl^-	NH_4^+	SO_4^{--}	Na^+	NO_3^-	K^+	Mg^{++}	Ca^{++}
Year	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]
2000	No value	No value	No value	No value	No value	No value	No value	No value
2001	5,12	0,42	18,97	1,81	174,61	0,42	207,17	423,97
2002	5,11	0,06	14,85	1,76	149,82	0,47	225,06	433,3
2003	3,37	0,18	16,19	0,96	127,07	0,18	128,86	259,49
2004	6,01	0,13	20,54	1,81	93,02	0,42	186,69	374,34
2005	6,04	0,48	12,18	2,75	125,08	0,57	223,54	405,82
2006	2,43	0,07	7,74	0,89	55,8	0,13	119,72	203,05
2007	4,48	0,03	5,27	1,42	18,31	0,21	157,99	256,78
2008	2,08	0,01	5,18	1,17	9,30	0,35	96,1	177,18

* Values 2008 are calculated like in Table 18 (7603m³/ha).

Output measured	Cl^-	NH_4^+	SO_4^{--}	Na^+	NO_3^-	K^+	Mg^{++}	Ca^{++}
Year	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]	[kg/ha]
2000								
2001	4,9	0,45	19,97	1,64	169,59	0,24	193,51	396,2
2002	5,7	0,12	15,55	2,11	162,56	0,59	236,03	458,11
2003	3,83	0,24	19,45	1,26	150,55	0,23	150,74	299,49
2004	5,53	0,13	18,16	1,61	94,92	0,45	199,09	395,87
2005	5,83	0,46	12,26	2,77	100,75	0,41	209,23	377,48
2006	4,43	0,12	10,17	1,67	69,26	0,6	148,46	251,38
2007	5,61	0,06	6,59	1,58	24,65	0,3	171,16	289,98
2008	2,21	0,04	4,15	1,3	8,15	0,46	102,19	186,03

As expected, the results of the deviations calculated and measured nutrient fluxes were not as smooth as the water balance deviations (Table 21). All fluxes were calculated using a volume weighted mean concentration that included only those samples for which both measured concentration values and calculated 2-week water discharge values were available. As explained in the previous chapter these calculated 2 week water discharge values were not as good as the measured water balance. The fact that the change of soil water content was not taken into account caused the main error in this calculation.

The problem of missing discharge (lysimeter) values obtained in the water balance did not influence the result as much as in the water balance because periods with missing discharge values were not included in the calculated fluxes either.

Especially the molecules occurring in low concentrations (K^+ and NH_4^+) exhibited high deviations.

Table 21: Deviation calculated and measured nutrient fluxes in the period of 2000-2008

Deviation of nutrient fluxes								
Year	Cl^-	NH_4^+	SO_4^{--}	Na^+	NO_3^-	K^+	Mg^{++}	Ca^{++}
2000	No value	No value	No value	No value	No value	No value	No value	No value
2001	4,49	-6,67	-5,01	10,37	2,96	75,00	7,06	7,01
2002	-10,35	-50,00	-4,50	-16,59	-7,84	-20,34	-4,65	-5,42
2003	-12,01	-25,00	-16,76	-23,81	-15,60	-21,74	-14,52	-13,36
2004	8,68	0,00	13,11	12,42	-2,00	-6,67	-6,23	-5,44
2005	3,60	4,35	-0,65	-0,72	24,15	39,02	6,84	7,51
2006	-45,15	-41,67	-23,89	-46,71	-19,43	-78,33	-19,36	-19,23
2007	-20,14	-50,00	-20,03	-10,13	-25,72	-30,00	-7,69	-11,45
2008	-6,07	-67,15	24,73	-10,05	14,13	-22,89	-5,95	-4,76

4.4 Estimation of the sites risk to leach nitrate

The calculated **exchange rates** reached values from 10,9 (FC=100mm) to 21,8 (FC=50mm), indicating very fast soil water turnover and a very high risk of nitrate leaching (Table 22).

The reasons for this high risk are the high amount of precipitation at the site combined with the high content of coarse material in the soil which causes low field capacity, leading to rapid water flow through.

Table 22: Evaluation of obtained exchange rates at the Mühleggerköpfl

Risk	Exchange rate [1*a ⁻¹]	Value at FC = 50mm	Value at FC = 75mm	Value at FC = 100mm
Very low	< 0,7			
Low	0,7 - 1			
Medium	1 - 1,5			
High	1,5 - 2,5			
Very High	> 2,5	21,8	14,6	10,9

Source: GÄTH AND WOHLRAB, 1988

With a **C/N ratio <30 and atmospheric N inputs >10kg*ha⁻¹*a⁻¹** a site is at risk to leach N according to GUNDERSEN ET AL. (1998).

In the recent years atmospheric nitrogen inputs via throughfall were only about 8 kg*ha⁻¹*a⁻¹ between 2001 and 2008 (chapter 4.6.2.1). With inputs lower than 10kg*ha⁻¹*a⁻¹ the site dropped out of the risk category. But with C/N ratios of 15-18 in the upper 15cm of the mineral soil (chapter 2.4.2.1) there may be some risk based on the classification of GUNDERSEN ET AL. (1998).

Collectively, these indicators show that the site is at a threshold of increasing nitrate leaching risk.

4.5 Chemical Equilibrium

While throughfall, surface run-off and the soil solution samples showed similar chemical reactions, discharge was different (Table 23 and Table 24). According to the MineQL+ runs (See section 3.2.6), solids precipitated only in the soil solution samples and not in the aboveground ones. The results are illustrated in % of initial concentration which was measured in the laboratory. An element was declared inert if less than 1% of the initial concentration reacted with other elements. The soil solution samples of all 4 depths were analyzed as a single group because they were similar, and it was thus possible to present the results more clearly. The data for every single depth can be found in Appendix B

Table 23: Chemical equilibrium of different water depths without solids included into calculation.

No solids	Throughfall	%	Surface run-off	%	Soil solution	%*	Discharge	%
Cl^-	inert		inert		inert		inert	
SO_4^{2-}	$\text{CaSO}_4, \text{MgSO}_4$	71,12	$\text{CaSO}_4, \text{MgSO}_4$	46,53	$\text{CaSO}_4, \text{MgSO}_4$	56,44	NH_4SO_4^-	88
NO_3^-	CaNO_3^+	8	CaNO_3^+	51	CaNO_3^+	74	inert	
NH_4^+	inert		NH_3	8	$\text{NH}_3, \text{CaNH}_3^{2+}$	22,2	$\text{NH}_3, \text{NH}_4\text{SO}_4^-$	27,2
Na^+	inert		inert		inert		NaSO_4^-	1
K^+	inert		inert		inert		KSO_4^-	1
Mg^{++}	MgSO_4	13	MgSO_4	2	inert		MgSO_4	24
Ca^{++}	$\text{CaNO}_3^+, \text{CaSO}_4$	6,15	CaNO_3^+	34	CaNO_3^+	5	$\text{CaNO}_3^+, \text{CaSO}_4$	37,17

* Mean of 4 soil depth (values for every single depth can be found in Appendix B)

If precipitation reactions were excluded, Cl^- , Na^+ and K^+ were inert elements. While Cl^- stayed inert over the full range of solution samples, Na^+ and K^+ could form complexes in the discharge only, with 1% of the initial Na^+ and K^+ forming NaSO_4^- and KSO_4^- complexes.

Between 46 and 88% of the initial SO_4^{2-} existed in a complexed form in all different solution samples, and SO_4^{2-} can be considered a highly reactive complex. The main complexes were CaSO_4 (46-71%) and MgSO_4 (12-44%). The discharge solutions were somewhat different by the absence of these complexes but the dominance of NH_4SO_4^- (88%). The reason for this outcome was the elevated NH_4^+ concentrations in the discharge (compared to the soil solution samples). The high concentration of NH_4SO_4^- in the discharge shows that SO_4^{2-} leaching takes a lot of NH_4^+ with it. The nitrogenous complexes (NO_3^- and NH_4^+) were not as reactive as SO_4^{2-} . NO_3^- mainly appeared as CaNO_3^+ (8-71%), while the NO_3^- in the discharge was 100% inert. NH_4^+

in the throughfall was generally inert, but a lot of NH_3^+ (8-27%) appeared in the other samples, explained by the very high pH values at the site.

Mg^{2+} and Ca^{2+} reacted especially with the anions SO_4^{2-} and NO_3^- . Mg^{2+} formed complexes with SO_4^{2-} (MgSO_4) in all samples except in the soil solution samples where it was relatively inert (2-24%). Ca^{2+} also reacted with NO_3^- to form CaNO_3^+ (5-37%) at all sampling levels. CaSO_4 (15-17%) existed only in the throughfall and the discharge. It is clear that complexation was limited by the amount of anions available relative to the extremely high Mg^{2+} and Ca^{2+} values.

The observation of anions (SO_4^{2-} and NO_3^-) mainly reacting with Mg^{2+} and Ca^{2+} showed that the leaching anions carry the base cations Mg^{2+} and Ca^{2+} with them. This was expected because of the high amount of these cations within the system and suggests that as expected; the system is unlikely to acidify.

When the possible precipitation of Ca^{2+} and Mg^{2+} into dolomite was taken into account, some reactions changed (Table 24). These results are only illustrated for the soil solution and the discharge because there was no influence of the solid phase on above-ground solution samples. While the discharge data did not show any dolomite precipitating, all available Mg^{2+} and the associated Ca^{2+} precipitated in the soil solution, leaving little residual Mg^{2+} in solution (in reality a small amount of Mg^{2+} is left within the system because there must be at least as much left as the stability constant determines), 90% of the initial Ca^{2+} was formed into dolomite.

Due to this projected precipitation loss of Mg^{2+} and Ca^{2+} , the part of SO_4^{2-} and NO_3^- exiting as CaNO_3^+ and MgSO_4 decreased from 74 to 18% and 44 to 0%, respectively. The part of SO_4^{2-} reacting to form CaSO_4 did not decrease.

The SI of dolomite in the discharge was 0 with no solid precipitating, indicating discharge was in equilibrium.

Table 24: Chemical equilibrium of different water depth with dolomite included into calculation

Solids incl.	Soil solution*				Discharge		
	Complexes	%	Solids	%	Complexes	%	Solids
Cl⁻	inert		no		inert		no
SO₄²⁻	CaSO ₄	89	no		NH ₄ SO ₄ ⁻	88	no
NO₃⁻	CaNO ₃ ⁺	18	no		inert		no
NH₄⁺	NH ₃ , NH ₄ SO ₄ ⁻	23,1	no		NH ₃ , NH ₄ SO ₄ ⁻	27,2	no
Na⁺	inert		no		NaSO ₄ ⁻	1	no
K⁺	KSO ₄ ⁻	1/2	no		KSO ₄ ⁻	1	no
Mg⁺⁺	no		Dolomite (ordered)	100	MgSO ₄ , MgHCO ₃ ⁺	24,1	no
Ca⁺⁺	CaSO ₄ , CaNO ₃ ⁺	2,1	Dolomite (ordered)	90	CaNO ₃ ⁺ , CaSO ₄	37,17	no

* Mean of 4 soil depth (values for every single depth can be found in Appendix B)

If dolomite was taken into account, the SI for the soil solution samples was positive for Aragonite and Calcite. The SI of single years also showed positive values for Anhydrite, Magnesite, Huntite and Mg(OH)₂. These solids were taken into account in a second step due to this obvious over-saturation. In that case, almost the whole remainder of dissolved Ca²⁺ precipitated into Calcite. Under these circumstances the CaNO₃⁺ content vanished while the CaSO₄ content decreased to a value of about 8% of initial SO₄²⁻ concentration. The main difference between the two elements was that NO₃⁻ stayed inert while SO₄²⁻ molecules reacted with Na⁺ to form NaSO₄⁻ (5% of initial SO₄²⁻).

4.6 Concentration allocations and fluxes

Main results of the analysis of concentrations:

- The concentrations of SO_4^{2-} und NO_3^- in the discharge water declined from 2000 to 2008.
- On a seasonal basis, the surface run-off samples showed high concentrations in summer. This was explained by high mineralization rates in the forest floor, couple to low uptake because the ions leached before they could interact with plant roots. Due to this, correlations between different elements appeared primarily in the surface run-off because roots were not able to interact with the water.
- The soil solution samples had low NO_3^- concentrations in summer. This pattern appeared in all years between 2000 and 2008, with the exception of the year 2003.
- The discharge NO_3^- concentrations were consistently high in winter but did not show low concentrations in summer till 2004. While there weren't low concentration values in summer between 2000 and 2003 this seasonal pattern started to emerge in 2004 and became clearer till 2008.
- The discharge concentrations measured in the lysimeter samples were much higher than the concentrations in suction cups at lower depth. Since there is no evidence for additional nitrogen sources (chapter 2.5) from lateral fluxes or other sources this pattern could not readily be explained.

At Mühleggerköpfl the high discharge concentrations and the change of discharge concentrations in 2004 could potentially be explained by:

- Change in deposition loads
- Change of tree species and stand maturity
- Change in solution- root interactions within the lysimeter
- A decrease in the disturbance effect caused by the installation of the lysimeter

Main results of the analysis of deposition loads:

- The analysis of deposition loads between 2001 and 2008 (Figure 40) did not indicate a change of deposition loads within these eight years; however, loads were lower than in preceding years (1991-2000).
- Critical N deposition loads were not reached in the observation period (2001-2008).
- Deposition of nitrogen peaked in summer and was low in the dormant season

Main results of the analysis of discharge loads:

- NO_3^- , SO_4^{2-} and NH_4^+ discharge loads decreased considerably between 2001 and 2008.
- NO_3^- discharge fluxes were high all year long between 2001 and 2003. In 2004 loads started to decrease during the vegetation period, while remaining high in the dormant season.
- After 2005 much less nitrate leached despite similar water flux.
- Since 2004 the correlation between water and nitrate fluxes became less pronounced, indicating some kind of alteration of the nitrogen cycle since 2004.
- Nitrate leaching losses were lower if discharge was calculated with the suction cup's concentrations.

Main results of the analysis of the N release Index:

- N leaching losses based on the discharge fluxes indicated extreme high N releases. Only 2008 was classified as non-saturated, with N release values commonly found in disturbed ecosystems only.
- If the discharge was calculated with the concentrations at 50cm depth the system retained nitrogen in most of the years. According to these findings the research area may be approaching N saturation and remains at a very labile equilibrium between release and retention of nitrogen.

4.6.1 Patterns in the distribution of measured concentrations

4.6.1.1 Temporal trends

Concentrations plotted over time illustrated temporal patterns of different concentrations. This analysis identified some patterns:

The ions Mg^{2+} , Ca^{2+} , Cl^- , Na^+ and K^+ did not show temporal patterns while the anions NO_3^- and SO_4^{2-} did. Their concentrations in the discharge decreased between 2001 and 2008 (Figure 34), while the input concentrations (throughfall) did not change for NO_3^- and SO_4^{2-} (Table 25). Concentrations of NO_3^- and SO_4^{2-} in the soil solution samples did not decrease between 2001 and 2008.

Table 25: Annual mean SO_4^{2-} and NO_3^- concentrations [mg/l] in the throughfall (2000–2008)

	2000	2001	2002	2003	2004	2005	2006	2007	2008
NO_3^-	1,28	1,3	1,36	1,27	1,67	1,54	1,49	1,3	1,47
SO_4^{2-}	0,63	0,54	0,6	0,66	0,69	0,62	0,61	0,47	0,62

Table 26: Seasonal mean concentrations [mg/l] of SO_4^{2-} and NO_3^- in the discharge (2001-2008)

Season	SO_4^{2-}	NO_3^-
Spring	1,68	11,50
Summer	1,21	8,76
Fall	1,38	9,84
Winter	1,71	17,16

On a seasonal scale, the plots indicated highest anion concentrations in winter and spring as illustrated in Table 26, while concentrations in other seasons are also high. While the seasonal

pattern of NO_3^- is very strong, with a mean concentration in winter twice that of the mean summer value, the pattern of SO_4^{2-} is much weaker. The same pattern was also observed when the data were evaluated on weekly basis (Figure 35). There were very high discharge NO_3^- concentrations obtained in the first 15 weeks of the year. The seasonal pattern for NO_3^- may have been due to vegetation uptake of NO_3^- through the growing season and not in the dormant season. The more attenuated pattern for SO_4^{2-} may reflect that this anion was not taken up in the growing season at the same rate as NO_3^- was. Considering the fact that the soil water content in winter was rather high and that SO_4^{2-} did not show the same pattern as NO_3^- , it is unlikely that the seasonal pattern was caused by dilution effects by increasing water contents. Collectively this indicates that NO_3^- mainly leached in winter similar to observations by VAN MIEGROET ET AL. (2001) in an N-saturated forest catchment in the Smoky

Mountains, and the eastern US. There they obtained high inorganic N deposition loads from April to September and high inorganic N leaching from November to March. Figure 35 also illustrates that discharge concentrations in summer were especially high from 2001-2003 (about week 20-40). In 2004 high concentrations were obtained in fall but not in summer. From 2005-2008 NO_3^- concentrations were low except in winter.

The NO_3^- concentrations in soil water collected at a depth of 50cm were much lower than in the discharge solutions (Table 27). Since the main rooting zone of spruce is in the top 30cm, the 50cm and the discharge concentrations should be similar; yet they were not. The temporal pattern, however, was similar with low NO_3^- concentrations in summer and relatively high concentrations in the dormant season. Only in 2003 were extremely high NO_3^- concentrations measured in summer and spring, possibly due to some kind of disturbance at the research area. This pattern was obtained in other depths too.

On an annual basis, NO_3^- concentrations did not decrease between 2001 and 2008 as the discharge concentrations did.

Table 27: Seasonal mean NO_3^- concentrations [mg/l] at 50cm depth

Season	2000-2008	2000-2008 without 2003	2003
Spring	2,25	1,14	14,65
Summer	4,03	0,44	45,19
Fall	2,13	2	2,99
Winter	2,9	2,9	2,91

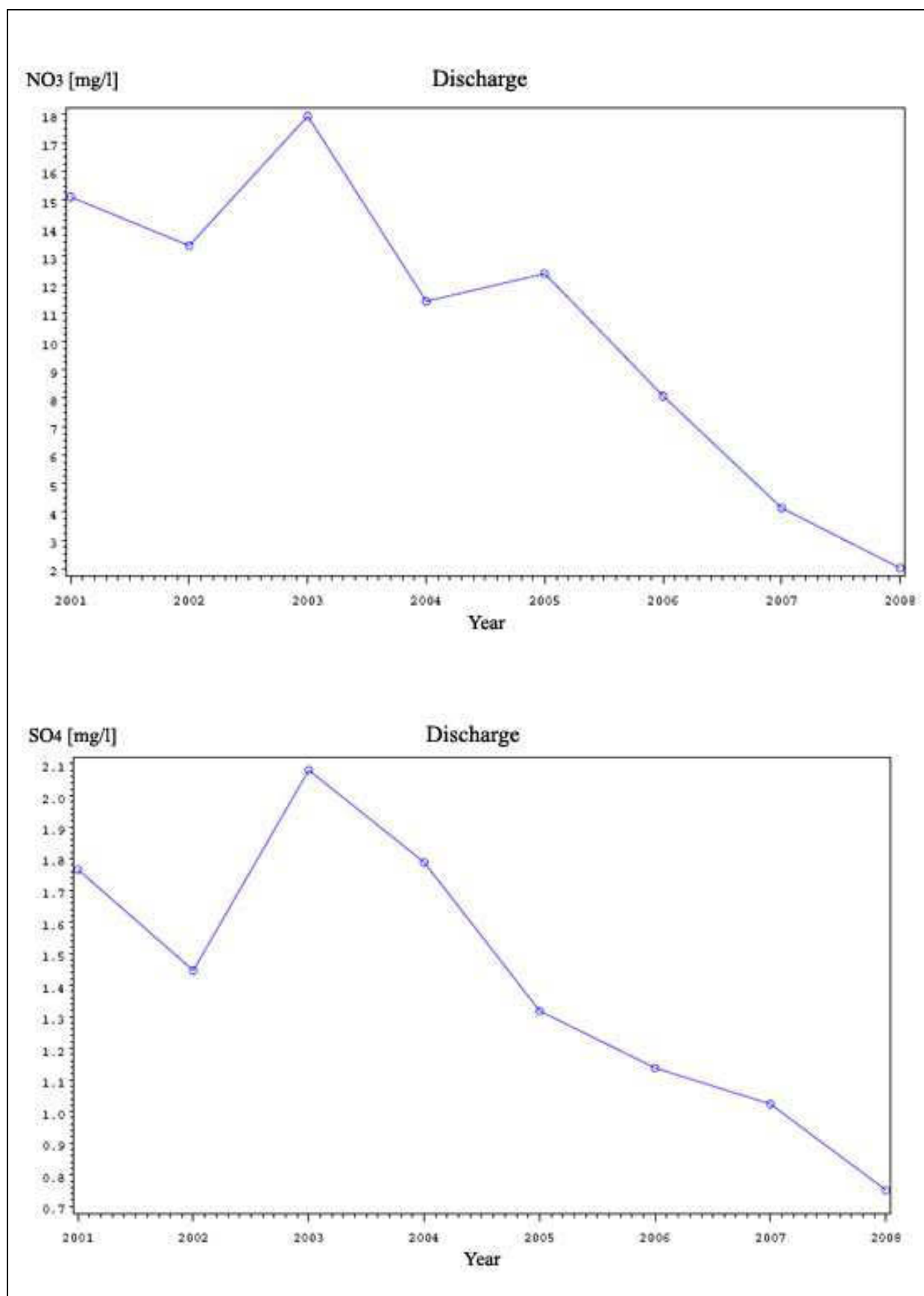


Figure 34: Average annual NO_3^- and SO_4^{2-} concentrations in the discharge (2001-2008)

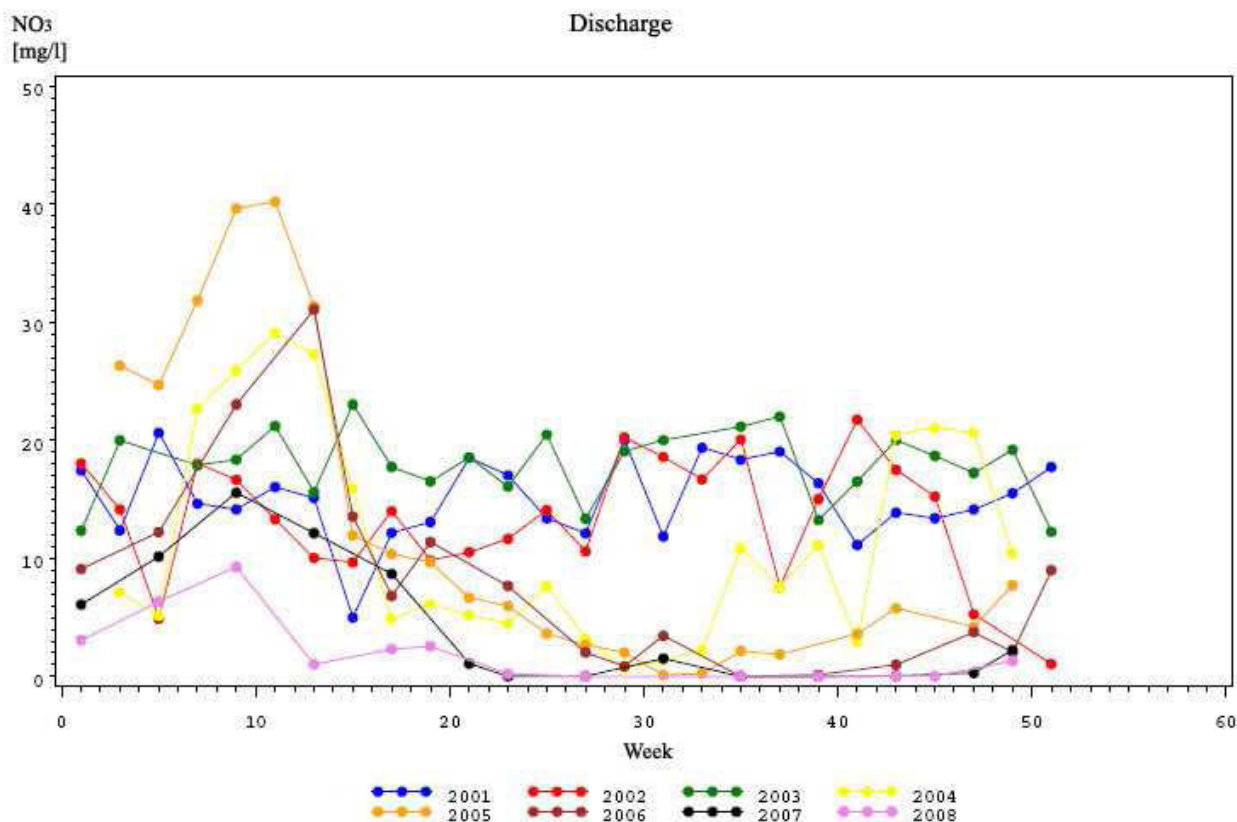


Figure 35: Weekly NO_3^- concentrations in the discharge (2001-2008)

The seasonal pattern for NO_3^- and SO_4^{2-} observed in the discharge was much more pronounced in the soil solution samples (Figure 36). For example, the solution samples at 15cm depth had very low concentrations in summer. On the other hand there were a considerable number of outliers in the summer of 2003 at all soil depths, although least distinctive at 25cm. These outliers were likely caused by temporary and locally high mineralization rates (so-called “hotspots”). That such outliers were not observed in the discharge samples and seasonal patterns were less pronounced suggests that large amounts of available nitrogen were reduced by uptake within the rooting zone or that discharge solutions integrated this spatial variability in process rates.

On the other hand, the surface run-off samples showed high NO_3^- concentrations in summer (Figure 36) and low concentration values in the dormant season. Since nitrogen levels within the surface run-off could not be influenced strongly by vegetation uptake, the mineralized nitrogen appeared at high concentrations in summer. In the dormant season mineralization was low what caused lower concentrations in the surface run-off.

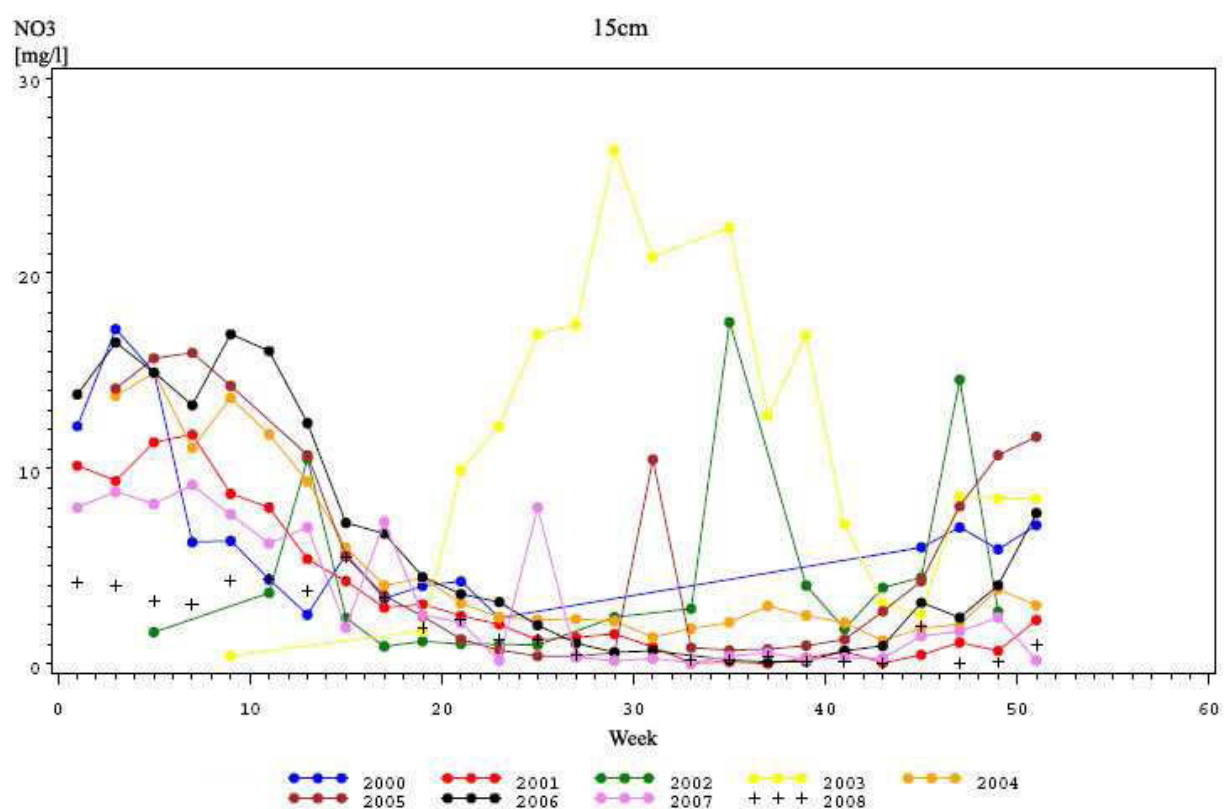
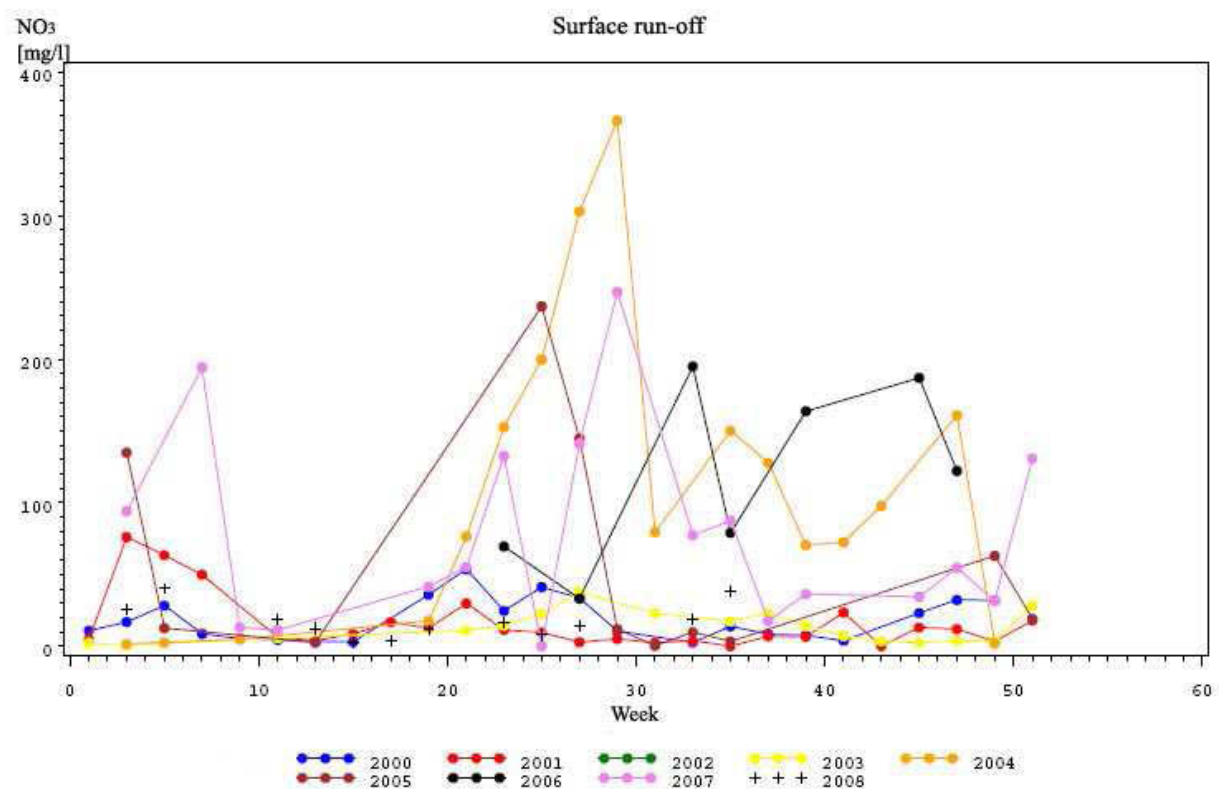


Figure 36: Weekly NO₃⁻ concentrations in the surface run-off and in 15cm (2000-2008)

The mean annual NO_3^- concentration in the discharge decreased between 2001 and 2008 (Figure 35). Presenting these data in a high temporal resolution (Figure 37), this trend remained, but another pattern appeared additionally. While NO_3^- concentrations in the discharge were high all year long between 2001 and 2003, this system changed in 2004. After 2004 the temporal pattern obtained in the soil solution samples (Figure 36) appeared in the discharge too. According to ABER (1992) this pattern indicates that the system changed from an N-saturated system to a system in transition towards a more N-limited status in the near future. In 2008 there were no high NO_3^- concentration values anymore. The concentrations in winter were already very low compared to the concentrations obtained in the previous years.

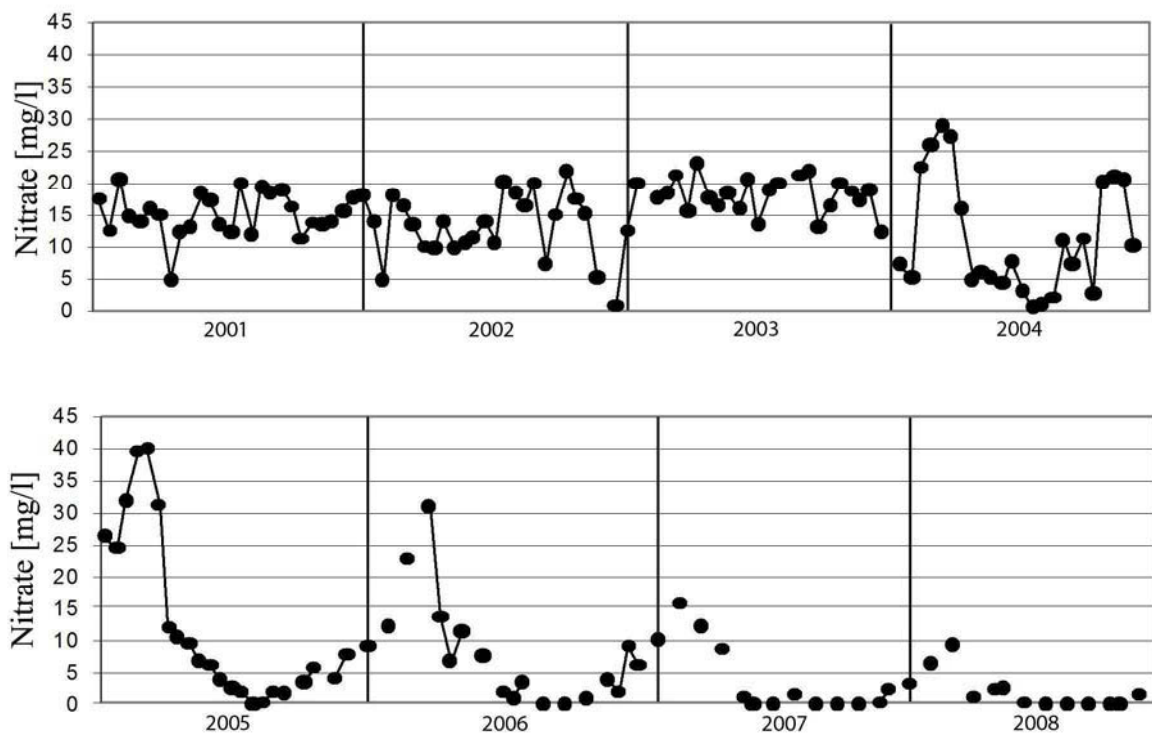


Figure 37: Measured NO_3^- concentrations in the discharge (2001-2008)

This progressive change in temporal pattern mimics perfectly with the ones PETERJOHN (1996) observed at Fernow, West Virginia, albeit in reverse order (Figure 38). Compared to his data the temporal pattern obtained here was much more pronounced. Peterjohn interpreted the system as being saturated with $\text{NO}_3\text{-N}$ concentrations of about 1mg $\text{NO}_3\text{-N}$ in stream water (1983-1994) throughout the whole year. The solution concentrations reached around 3,3 mg/L in the Mühleggerköpfl discharge water between 2001 and 2003.

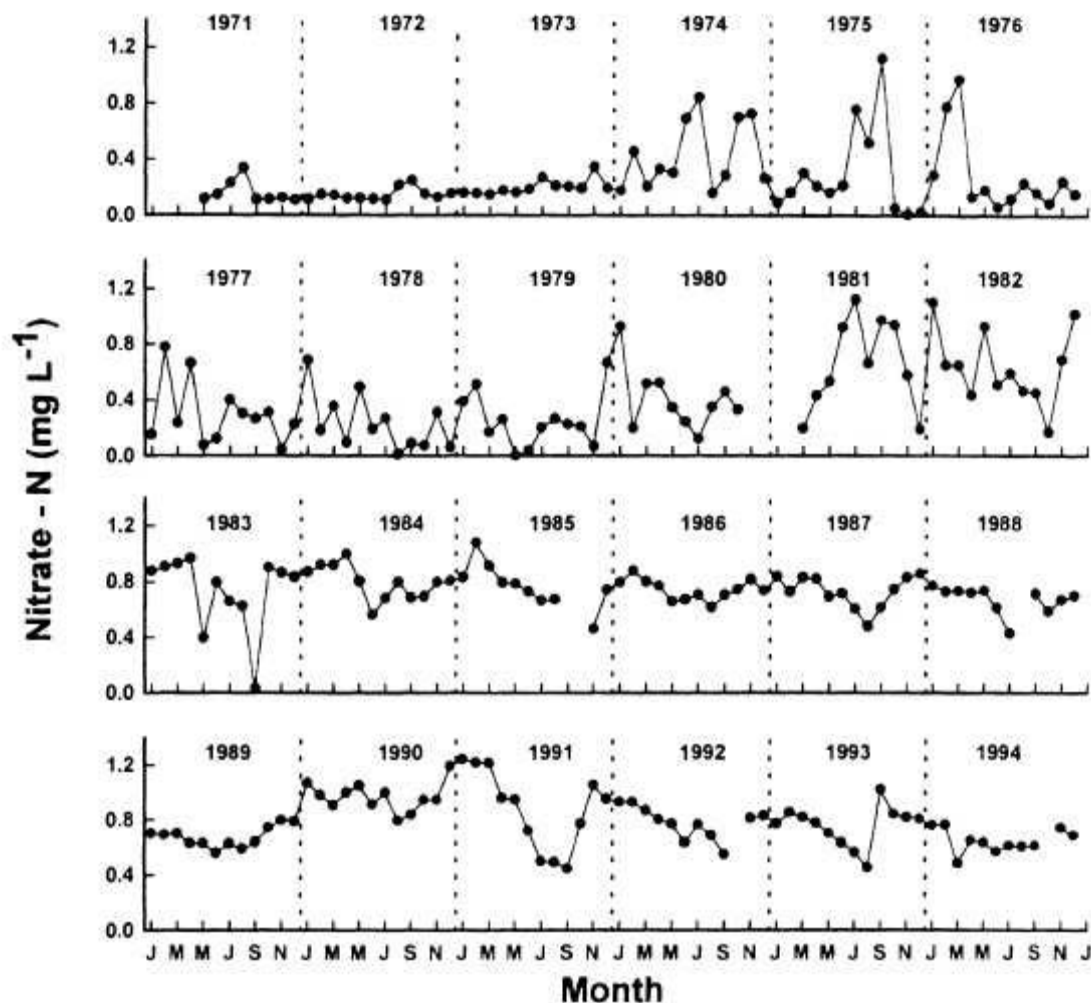


Figure 38: Long-term record of the volume-weighted average monthly nitrate concentrations for watershed 4 at the Fernow Experimental Forest.

Source: PETERJOHN ET AL., 1996

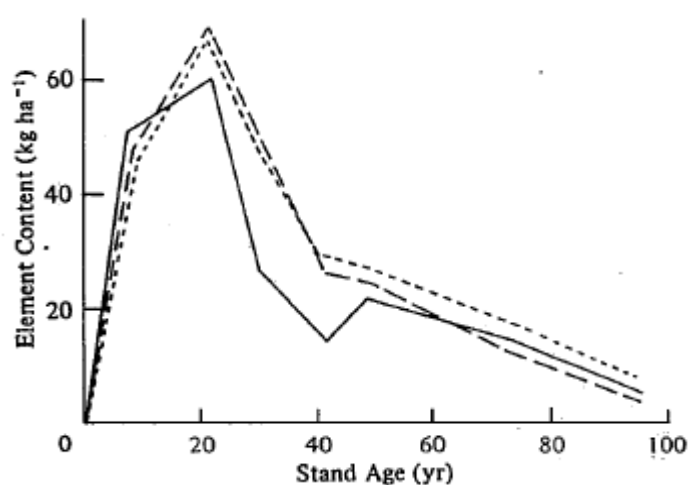
At Mühleggerköpfl the following explanations are reasonable:

- Change in deposition loads.
- Change of tree species and stand maturity.
- Change in solution-root interactions within the lysimeter.
- A decrease in the disturbance effect caused by the installation of the lysimeter.

In contrast, the **throughfall concentrations** did not decrease between 2000 and 2008. It is possible that there was less rainfall in the last years that could lower N inputs. Additionally it was necessary to compare the input fluxes of this study with earlier measurements at the site to find out if there was a change before 2000. If there was no change of input fluxes it is likely that the observed decline in the discharge N flux was caused by the shift from a mature to an aggrading forest.

The reduced productivity of the remaining forest after the bark beetle attack in 2003 and 2004 and the subsequent growth of an aggrading forest could account for this pattern. Such **systematic changes in elemental cycling associated with stand maturity** were illustrated by COLE AND RAPP (1998) when they followed the nutrient cycling patterns in spruce forests ranging in age from 22 to 138 years. They found increasing uptake to a maximum at age 65 years, which decreased slowly afterwards. With the opening of the forest canopy at an age of 70 years they assigned an increasing role of the understory vegetation in the nutrient dynamics that increased the nutrient uptake of the stand. Such an opening of the canopy happened when bark beetle infected trees were harvested.

Similarly, TURNER (1975) found that young aggrading forests take up a lot of nitrogen



within their first 15 years (Figure 39). With canopy closure the role of understory vegetation decreases. This also supports the theory that the harvesting of bark beetle trees could have increased the stand's nutrient uptake.

Figure 39: Accumulation of nitrogen (---), potassium (—) and calcium (— —) in the understory vegetation of various aged stands of Douglas fir.

Source: TURNER, 1975

The shift from spruce to mainly deciduous trees which occurred in the understory could also have increased the nitrogen uptake. While coniferous forests have higher nitrogen use efficiencies (NUE), deciduous forests have higher uptake rates and deeper rooting depth than spruce forests (COLE AND RAPP, 1996).

Furthermore, deciduous forests cause much higher soil water depletion in summer than spruce forests (SCHUME, 2003). As a consequence less water is percolating into deeper horizons in summer which decreases the nitrate leaching risk.

Apart from the change in nitrogen fluxes associated with the woody understory, herbaceous vegetation may have influenced nitrogen fluxes as well. According to MOORE ET AL. (2007) the herbaceous vegetation plays a major role in the nutrient cycle because this stratum contains a far greater proportion of N-rich foliage and

green stems. They found nitrogen contents of 4,7-7,7% of the total N pool stored in the herbaceous layer of a spruce-fir stand following fir mortality and spruce windthrow. According to MOORE ET AL. N uptake by understory can exceed that of overstory. So the herbaceous vegetation becomes a very important nitrogen sink if the site gets thinned out.

ABER ET AL. (1998) argue that under undisturbed, mature, or steady state conditions, all forests should be near the middle of stage 2 (Figure 3), where nitrogen losses balance nitrogen deposition inputs .

On the other hand, some scientists also have observed increased nitrogen leaching losses after harvesting, especially after clear-cutting (LEWIS AND LIKENS, 2007). Since only single trees were cut and the understory was not harmed it is unlikely that this is responsible for the pattern observed at the Mühleggerköpfl, especially since it was not observed in the lysimeter data. But this could have caused the high concentrations in the suction cup samples in 2003 (Figure 36).

Another interpretation for the very high nitrate concentrations in the discharge between 2001 and 2003 and compared to the soil solution samples was that the soil within the lysimeter has only a low **root density**. The lysimeter contains no tree roots and only some roots of the sparse herbaceous vegetation that has developed since the construction of the lysimeter in 1998. Consequently, there may have been no plant uptake contributing to NO_3^- retention until 2004. Additionally to the natural growth the bark beetle diseases could have influenced the understory which may have started to explore this part of the soil due to the increased sunlight at the forest floor.

It is also possible that the **soil disturbance** by the installation of the lysimeter what caused high concentrations in the discharge of the following years. Since 2004 these concentrations would be declining due to the systems recovery.

4.6.1.2 Correlations between different ions at specific depths

There were only few significant correlations found between ion concentrations of different elements at specific depths. Especially in the soil solution samples no significant correlation was found. On the other hand in the surface run-off almost every element correlated with each other. A reason for this may have been that the mineralized elements in the surface run-off were not as influenced by uptake and microbial interactions as the soil solution samples. The only elements which were correlated at every depth were Mg^{2+} and Ca^{2+} . Indicating that they have dominantly the same origin, i.e. dissolution of dolomite.

In the discharge the anions NO_3^- and SO_4^{2-} and the cations Mg^{2+} and Ca^{2+} correlated with correlation coefficient values of 0,5 and 0,92. A correlation of anions with cations was not found.

On the other hand MineQL+ indicated that high amounts of Ca^{2+} and Mg^{2+} that leached left the system associated with the anions NO_3^- and SO_4^{2-} . According to MineQL+ Ca^{2+} have left mainly as CaNO_3^+ (37% of total Ca^{++}) and CaSO_4 (17%) while Mg^{2+} as MgSO_4 (24%).

4.6.2 Elemental fluxes

When fluxes were calculated it was important not to forget the number of missing values because they affect the amount. Details about them were explained in chapter 4.2. Another important fact is that in the period of the two missing throughfall values in 2008 (July) high precipitation occurred (31% of the precipitation of the rest of the year). Since nitrogen input was especially high in summer (Figure 42) the input value for 2008 was definitely underestimated.

Table 28 illustrates the number of missing values (concentrations and water fluxes) for throughfall and discharge.

Table 28: Missing values in the throughfall and discharge data

Missing values	Throughfall	Discharge	*Discharge
2000	6 of 26 (23%)	No values	No values
2001	2 of 26 (7,7%)	0 of 26 (0%)	8 of 26 (30,8%)
2002	1 of 26 (3,8%)	1 of 26 (3,8%)	7 of 26 (26,9%)
2003	4 of 26 (15,4%)	2 of 26 (7,7%)	5 of 26 (19,2%)
2004	3 of 26 (11,5%)	2 of 26 (7,7%)	2 of 26 (7,7%)
2005	1 of 26 (3,8%)	4 of 26 (15,4%)	4 of 26 (15,4%)
2006	1 of 26 (3,8%)	10 of 26 (38,5%)	12 of 26 (46,2%)
2007	2 of 26 (7,7%)	12 of 26 (46,2%)	12 of 26 (46,2%)
2008	2 of 26 (7,7%)	14 of 26 (53,8%)	15 of 26 (57,7%)

* Discharge calculated with suction cup concentrations at 50cm

4.6.2.1 Deposition loads

Figure 41 illustrates that N deposition loads decreased after 2000. Especially $\text{NH}_4\text{-N}$ loads were much lower what may be caused by interactions with the needles and leaves because NH_4^+ gets taken up preferentially over NO_3^- (MATZNER ET AL., 2004). Nevertheless it is unlikely that this decrease of deposition loads was responsible for the extreme change in the nitrogen cycle in 2004.

Mg^{2+} and Ca^{2+} loads started in 2005 because of the measurement error before 2005 (chapter 4.1.3).

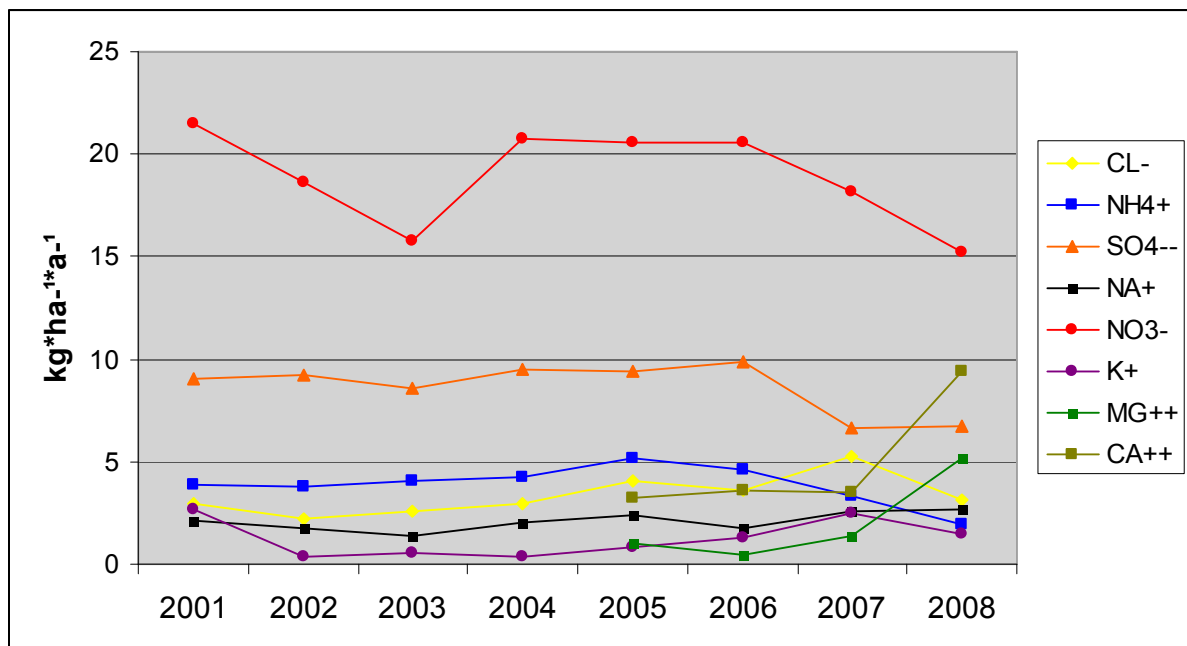


Figure 40: Annual deposition loads of different elements (2001-2008).

The annual deposition loads (Figure 41) in the year 2008 are underestimated due to high precipitation in July 2008 for which no chemical analyses were made. In 1995 two extreme deposition events following each other deposited 3 kg N/ha.

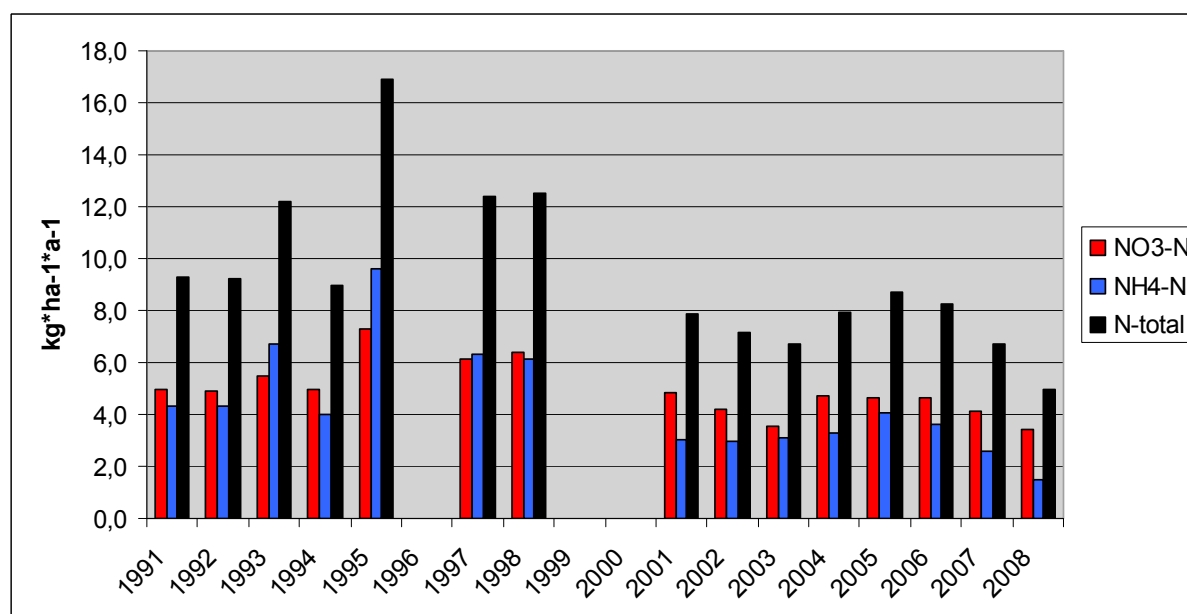


Figure 41: Annual NO₃-N, NH₄-N and N-total deposition loads (1991-2008)

Annual mean values (2001-2008) were calculated by the sum of the arithmetic mean of each week.

Like expected the deposition of nitrogen peaked in summer due to high precipitation and was low in the dormant season (Figure 42).

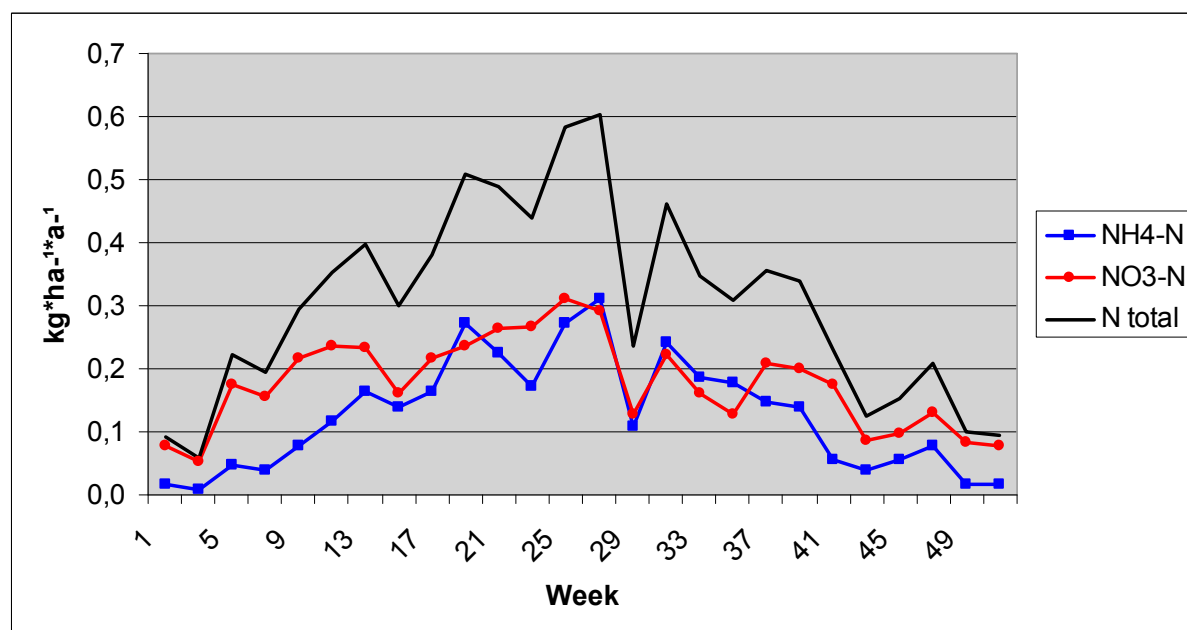


Figure 42: N deposition loads for different weeks (2001-2008)

4.6.2.2 Discharge loads

Like obtained in the concentration data the NO_3^- discharge loads decreased extremely between 2001 and 2008 (Figure 43) from 170 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ in 2001 to 8 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ in 2008. Like the NO_3^- values SO_4^{--} and NH_4^+ declined from 20 and 0,45 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ in 2001 to 4 and 0,04 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$ in 2008. Mg^{++} , Ca^{++} , Cl^- , Na^+ and K^+ loads did not show temporal trends (Table 25).

Table 29: Annual discharge loads of different elements (lysimeter) between 2001 and 2008

Year	Cl^- [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]	NH_4^+ [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]	SO_4^{--} [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]	Na^+ [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]	NO_3^- [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]	K^+ [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]	Mg^{++} [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]	Ca^{++} [$\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$]
2001	4,9	0,45	19,97	1,64	169,59	0,24	193,51	396,2
2002	5,7	0,12	15,55	2,11	162,56	0,59	236,03	458,11
2003	3,83	0,24	19,45	1,26	150,55	0,23	150,74	299,49
2004	5,53	0,13	18,16	1,61	94,92	0,45	199,09	395,87
2005	5,83	0,46	12,26	2,77	100,75	0,41	209,23	377,48
2006	4,43	0,12	10,17	1,67	69,26	0,6	148,46	251,38
2007	5,61	0,06	6,59	1,58	24,65	0,3	171,16	289,98
2008	2,21	0,04	4,15	1,3	8,15	0,46	102,19	186,03

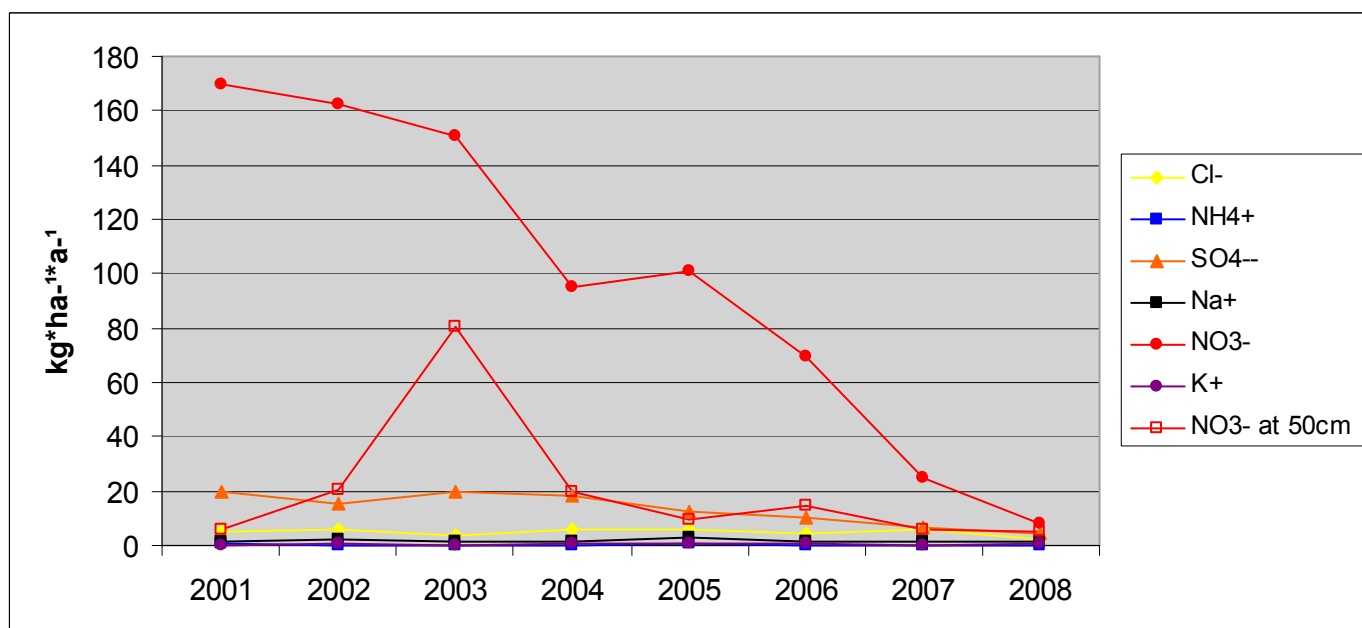


Figure 43: Annual discharge loads of different elements (2001-2008)

If the nitrate discharge was calculated with the arithmetic mean concentration of the suction cups at 50cm much less nitrate leached the system (Figure 43). Only in 2003 really high amounts of nitrogen ($80\text{kg}\cdot\text{ha}^{-1}\cdot\text{a}^{-1}$) leached if the discharge was calculated this way.

Since 2004 high amounts of nitrate leached in the winter and low amounts during summer time (Figure 43 - Figure 45), but there was hardly a decline of leaching nitrate loads in winter after 2003 (Figure 44)

If the nitrate discharge was calculated with the suction cup concentration values at 50cm there was no decline of nitrate leaching between 2001 and 2008 but a peak in 2003. In general the discharge loads were much lower over all years in this case.

Like concentrations, NO_3^- discharge fluxes obtained in the lysimeter data were high all year long between 2001 and 2003. After 2003 much lower amounts of nitrate leached (Figure 45).

Surface run-off values were especially high in summer (Figure 44).

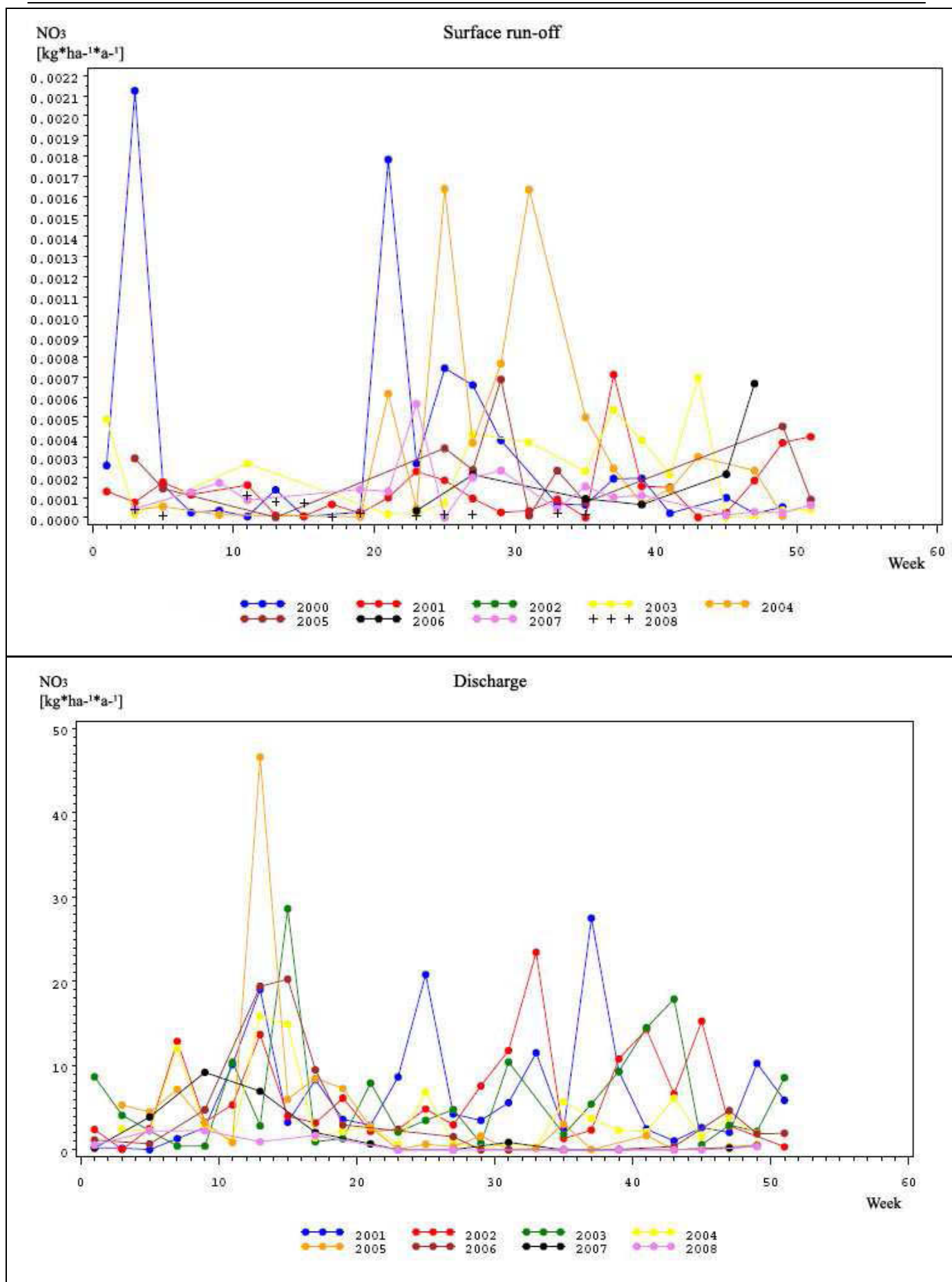


Figure 44: Weekly surface run-off and discharge NO₃⁻ fluxes

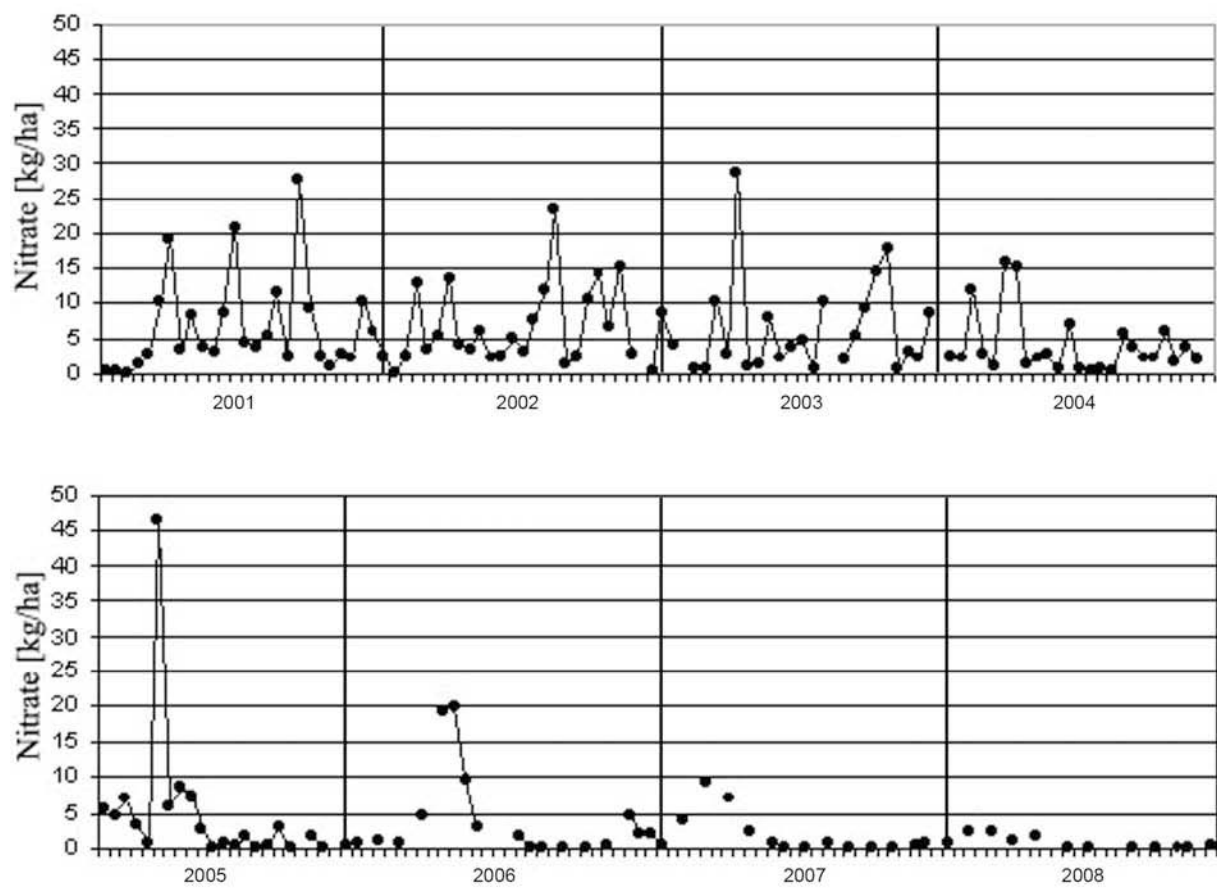


Figure 45: Calculated nitrate fluxes in the discharge (2001-2008)

The analysis of the **influence of water fluxes on nitrate fluxes** showed some interesting pattern, too:

The comparison of annual water and annual nitrate fluxes indicated that since 2006 water leaching wasn't linked to nitrate leaching like the years before (Table 30). After 2005 the water:nitrate ratio increased from 91 to 578 meaning that less NO_3^- leached with the same amount of water. In this case the missing values between 2006 and 2008 are not as relevant due to the fact that a missing measurement sample of a specific date excludes water and nitrate flux information.

Table 30: Comparison of water and nitrate fluxes (2001-2008)

Year	l/ha	Water [m ³ /ha]	NO ₃ ⁻ [kg/ha]	Ratio
2001	11.401.900	11.402	169,59	67
2002	12.053.400	12.053	162,56	74
2003	8.476.900	8.477	150,55	56
2004	9.110.800	9.111	94,92	96
2005	9.120.800	9.121	100,75	91
2006	8.533.100	8.533	69,26	123
2007	7.349.800	7.350	24,65	298
2008	4.710.400	4.710	8,15	578

The calculation of the correlation of water and nitrate fluxes indicated a great difference between 2001-2003 and 2004-2008. While the correlation coefficient between 2001 and 2003 was 0,92, between 2004 and 2008 it was only 0,49.

Figure 46 and Figure 47 illustrate this observation. So therefore uptake or another process must influence the nitrogen cycle since 2004.

If the discharge was calculated with the concentration values of the 50cm suction cups the correlation coefficient was only 0,18 (Figure 48).

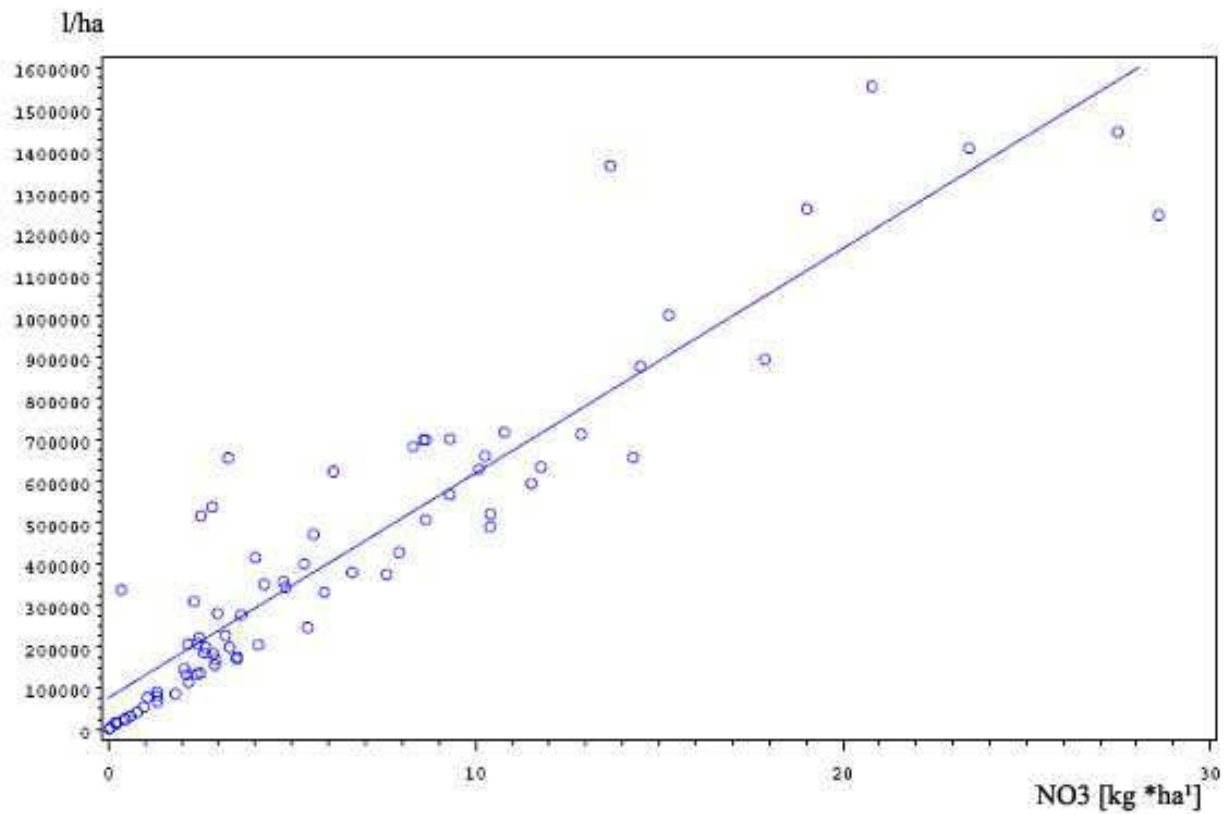


Figure 46: Increasing nitrate fluxes with increasing water fluxes between 2001 and 2003

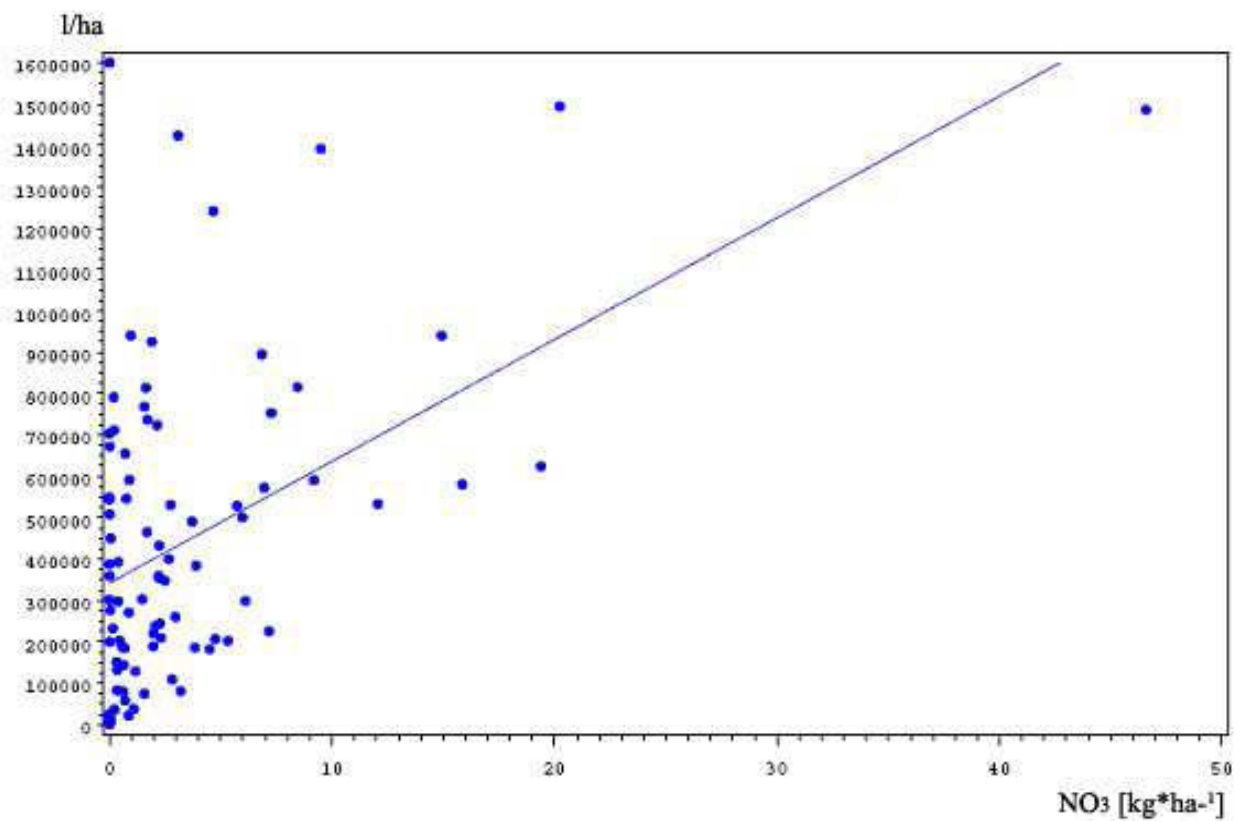


Figure 47: Nitrate fluxes relatively unaffected by water fluxes between 2004 and 2008

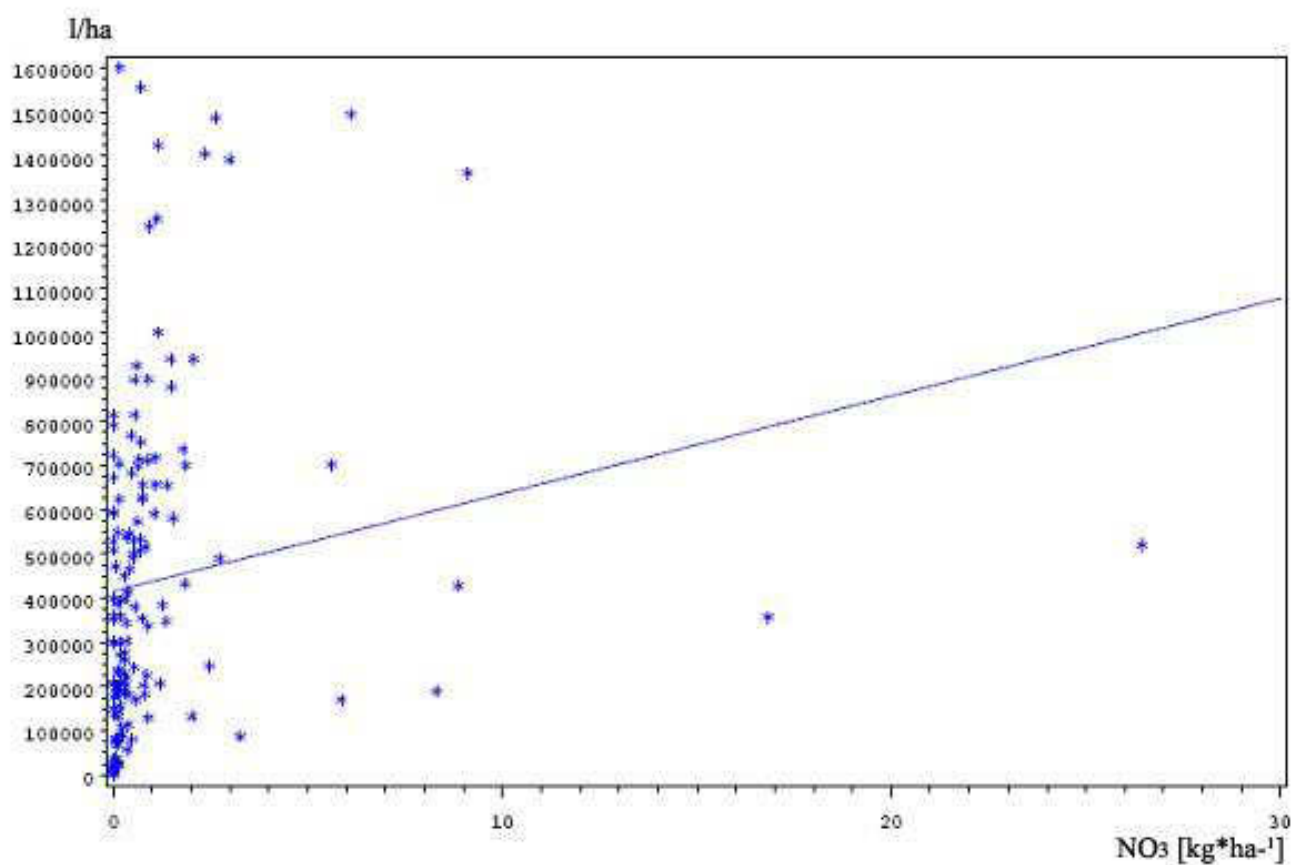


Figure 48: Nitrate fluxes unaffected by water fluxes (2001-2008) if discharge was calculated with 50cm suction cups concentration values.

4.6.3 Determination of the saturation status by comparisons of input and output fluxes

The results indicated extreme high N releases in all years except 2007 and 2008 (Table 32). According to the classification of the BML (2000) only 2008 was classified as non-saturated (Table 31). Therefore it must be kept in mind that 2006-2008 output data was biased by missing data because of which the output is underestimated.

To get this bias into perspective the N release index was calculated a second time including the missing values in throughfall and discharge (chapter 4.6.2). In this case the N release index increased for the years 2006 to 2008 while hardly any change occurred in the other years (Table 32). Based on this calculation only 2008 was classified as non-saturated.

Table 31: Classification of the ecosystem's nitrogen balance based on the N-release Index.

Output [kg*ha ⁻¹ *a ⁻¹]	Input [kg*ha ⁻¹ *a ⁻¹]	Output/Input	Nitrogen status
<5	<25	≤1	non-saturated
5-15	5-35	≤1	saturation at a low level
>15	>15	≤1	saturation at a high level
		>1	N-release (disturbance)

Source: BML, 2000

Table 32: N Release Index calculated with discharge concentrations

*Year	Output [kg*ha ⁻¹ *a ⁻¹]	Missing values	Input [kg*ha ⁻¹ *a ⁻¹]	Missing values	N release Index [output/input]	Nitrogen status
2001	38,65	0,0%	7,88	7,7%	4,91	N-release
2002	36,80	3,8%	7,16	3,8%	5,14	N-release
2003	34,18	7,7%	6,70	15,4%	5,10	N-release
2004	21,54	7,7%	7,90	11,5%	2,73	N-release
2005	23,11	15,4%	8,68	3,8%	2,66	N-release
2006	15,73	38,5%	8,25	3,8%	1,91	N-release
2007	5,61	46,2%	6,68	7,7%	0,84	saturation at low level
2008	1,87	53,8%	4,96	7,7%	0,38	non-saturated
**Year	Output [kg*ha ⁻¹ *a ⁻¹]	Missing values	Input [kg*ha ⁻¹ *a ⁻¹]	Missing values	N release Index [output/input]	Nitrogen status
2001	38,64	0,0%	8,48	7,7%	4,56	N-release
2002	38,20	3,8%	7,43	3,8%	5,14	N-release
2003	36,81	7,7%	7,73	15,4%	4,76	N-release
2004	23,19	7,7%	8,88	11,5%	2,61	N-release
2005	26,67	15,4%	9,01	3,8%	2,96	N-release
2006	21,79	38,5%	8,57	3,8%	2,54	N-release
2007	8,21	46,2%	7,19	7,7%	1,14	N-release
2008	2,88	53,8%	6,51	7,7%	0,44	non-saturated

* Results excluding the influence of missing values

** Results including the influence of missing values

These results indicated that the system was saturated at extreme high level until 2007. For example VAN MIEGROET ET AL. (2001) found N-release indexes <1 in a spruce forest ecosystem in the smoky mountains with N-Input values around $32 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$.

Accordingly, the system was 100% oversaturated with N release Index values which are in common only found in disturbed ecosystems. Since the investigation area was not disturbed, these Index values are unrealistic. Especially the fact that nitrogen concentrations were much lower in the suction cup samples and that there was no evidence for further nitrogen sources (chapter 2.5) like lateral fluxes at a depth below 50cm, makes these high amounts of leaching nitrogen unlikely. Nevertheless it may be possible that there was some unknown process.

To get an idea of relations, the discharge loads were calculated based on 50cm suction cup concentrations, too (Table 33).

Table 33: N-release Index calculated with the combination of suction cup concentrations at 50cm depth and lysimeter water fluxes.

*Year	Output [kg*ha¹*a⁻¹]	Missing values	Input [kg*ha¹*a⁻¹]	Missing values	N release Index [output/input]	Nitrogen status
2001	1,280	30,8%	7,880	7,7%	0,16	non-saturated
2002	6,260	26,9%	7,160	3,8%	0,87	saturation at a low level
2003	19,600	19,2%	6,700	15,4%	2,93	N-release
2004	4,770	7,7%	7,960	11,5%	0,60	non-saturated
2005	3,100	15,4%	8,680	3,8%	0,36	non-saturated
2006	3,450	46,2%	8,250	3,8%	0,42	non-saturated
2007	1,660	46,2%	6,680	7,7%	0,25	non-saturated
2008	1,140	57,7%	4,960	7,7%	0,23	non-saturated
**Year	Output [kg*ha¹*a⁻¹]	Missing values	Input [kg*ha¹*a⁻¹]	Missing values	N release Index [output/input]	Nitrogen status
2001	1,67	30,8%	8,49	7,7%	0,20	non-saturated
2002	7,94	26,9%	7,43	3,8%	1,07	N-release
2003	23,36	19,2%	7,73	15,4%	3,02	N-release
2004	5,14	7,7%	8,88	11,5%	0,58	saturation at a low level
2005	3,58	15,4%	9,01	3,8%	0,40	non-saturated
2006	5,04	46,2%	8,56	3,8%	0,59	saturation at a low level
2007	2,43	46,2%	7,19	7,7%	0,34	non-saturated
2008	1,80	57,7%	6,52	7,7%	0,28	non-saturated

* Results excluding the influence of missing values

** Results including the influence of missing values

Like the lysimeter discharge values, these were calculated in two ways, including and excluding missing water fluxes which were not measured by the lysimeter.

In 2001, 2004 and 2005 missing water flux values appeared especially in fall and winter which are in general determined by high amounts of leaching nitrogen. The output results for the calculations which take the missing water fluxes into account were definitely underestimated in these years due to this fact. The missing water fluxes of the other years were distributed over the whole year. Like in the N release Index calculation based on the lysimeter discharge loads the input in 2008 was underestimated.

The N release index results of this calculation indicated that the system was retaining nitrogen. Only in 2003 there was a net release of nitrogen. If missing samples were included, also 2002 was an N releasing year. These results showed that the ecosystem was able to retain nitrogen in general but that only little changes in the biogeochemical cycle can cause leaching of high nitrogen amounts like in 2003. So the investigation area may be going to reach saturation and stays at a very labile equilibrium of retaining and releasing nitrogen. The high loads in 2003 were assumed to be caused by little disturbances due to the harvesting of the bark beetle infected trees in 2003.

The N release Index, which was calculated with the suction cup concentrations, fitted with the Output/Input ratios obtained in other literature like REICHLE 1998 who analyzed 32 different sites in different forest regions and with different species.

Compared to the lysimeter concentrations based results these suction cups based results indicated low amounts of nitrogen leaching and low N release Indexes. While the suction cup based results were within a region which fit with numbers in the literature.

5 Conclusion

The suction cup (at 50cm depth) and the lysimeter (Discharge) solutions are installed below the main rooting zone. But their composition differed remarkable.

Main characteristics of the discharge samples:

- ➔ The discharge concentrations and loads decreased between 2001 and 2008 significantly from 18 to around 1,5 mg nitrate/l respectively from 170 to around 15 kg nitrate *ha⁻¹a⁻¹. Mean nitrate concentrations and loads (2001-2008) in winter (17,2 mg/l) were about twice as high as in summer (8,8 mg/l).
- ➔ The nitrogen cycle changed extremely in 2004. While there were rather high concentrations (~20mg/l) all year long between 2001 and 2003 with a little peak in winter the amount of leaching nitrate started to decrease in 2004. Since 2004 hardly any nitrate leached in summer and only little in winter. So according to ABER ET AL. (1998) and PETERJOHN ET AL. (1996) the system changed from an N-saturated system to a system in transition which will reach N-limitation status soon.
- ➔ The N release Index indicated that the system was extremely oversaturated between 2001 and 2006. Between 2001 and 2003 about 500% of the nitrogenous input leached. These are values which usually occur only if a system was disturbed, but this system was not. So there must have been another process causing this decrease from enormously high to low values.
- ➔ The analysis of deposition loads showed that there was less nitrogen deposition between 2001 and 2008 than in the decade before. But it is unlikely that this was the reason.
- ➔ An alternative explanation is that the harvesting of mature trees due to the bark beetle diseases in 2003 and 2004 caused a shift in stand maturity and a shift from spruce to deciduous species which changed the nutrient cycle at the site.
- ➔ Possibly, the vegetation has not rooted into the lysimeter soil sample (installed in 1998) until 2004. With the thinning of the stand herbaceous and understory vegetation could have started to root intensively.

-
- ➔ The theory of increasing uptake causing less nitrogenous output was supported by the observation that since 2004 water fluxes did not correlate with nitrate fluxes like they did before.
 - ➔ It is also possible that the soil was disturbed by the installation of the lysimeter what caused high concentrations in the discharge of the following years. Since 2004 these concentrations would be declining due to the systems recovery.

Main characteristics of the suction cup samples:

- ➔ Concentrations and loads at a depth of 50cm did not decrease between 2001 and 2008. In general they were much lower than the ones obtained in the lysimeter samples.
- ➔ In the soil solution samples of all depths concentrations and loads were extremely high in 2003 with a peak in summer (average in summer was 45mg/l at 50cm). If 2003 was excluded mean nitrate concentrations and loads (2001-2008) in winter (2,9 mg/l) were high compared to the ones in summer (0,4 mg/l). If the data from 2003 was included, mean nitrate concentrations and loads (2001-2008) in winter (2,9 mg/l) were low compared to the ones in summer (4,0 mg/l). So excluding the year of 2003 the system would be classified as non-saturated.
- ➔ The high N-loads in 2003 are assumed to be caused by little disturbances of the forest floor in the framework of the forest operations due to the bark beetle diseases.
- ➔ Additionally, the N-release Index indicated that the system was non-saturated most of the years, but that little disturbances or changes of the nutrient cycle can cause leaching of high nitrogen amounts like in 2003. In 2004 and 2006 the system was classified as saturated at a low level. So according to this data the investigation area might be going to reach saturation status in the future and stays in labile nitrogen equilibrium right now.

So there were big differences between the suction cup and the lysimeter data which were becoming similar in recent years. Besides the comparison of concentrations and fluxes, the analysis with MineQL+ indicated differences. For example no precipitation of Mg^{2+} and Ca^{2+} took place in the discharge data, although their concentrations were higher than the ones in the soil solution samples.

While the lysimeter data indicated N saturation, the values at 50cm indicated N retention. Based on the comparison with other literature the 50cm data seems to be more appropriate to describe the ecosystem's status.

It is necessary to continue monitoring N concentrations for some more years and look if the lysimeter data continues to become similar to the suction cup results. This fore it will be absolutely necessary to find out why there are so many missing discharge values in the recent years.

Additionally, it would be useful to investigate the rooting activities and the growth of the vegetation to verify the theories about the high nitrate concentrations in the discharge.

To calculate fluxes more precisely soil physics have to be analyzed in detail. A water balance based on water content and tension would certainly improve their quality.

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9 Appendix

9.1 Appendix A

The data within Appendix A illustrate throughfall, surface run-off, soil solution and lysimeter (discharge) data.

The values of the 15 bulk samplers (throughfall) and the 16 suction cups at depths of 5, 15, 25 and 50cm) are arithmetic mean concentrations.

Throughfall and soil solution data of specific bulk samplers and suction cups are stored at the BFW Achenkirch database.

Table 34: Complete throughfall data

Week	Year	Depth	mm	pH	Cl ⁻ [mg/l]	NH ₄ ⁺ [mg/l]	SO ₄ ²⁻ [mg/l]	Na ⁺ [mg/l]	NO ₃ ⁻ [mg/l]	K ⁺ [mg/l]	Mg ⁺⁺ [mg/l]	Ca ⁺⁺ [mg/l]
1	2000	Throughfall	60,80	5,00	0,10	0,00	0,70	0,10	1,20	0,10	0,00	0,30
3	2000	Throughfall	5,50	5,50	0,20	0,00	0,40	0,20	0,90	0,50	0,10	0,40
5	2000	Throughfall	69,10	4,50	0,50	0,20	0,70	0,30	2,00	0,10	0,20	1,70
7	2000	Throughfall	56,40	6,30	0,70	0,00	0,50	0,60	0,90	0,00	0,30	3,20
9	2000	Throughfall	76,10	6,50	0,30	0,00	0,40	0,10	1,10	0,00	0,40	3,30
11	2000	Throughfall	89,40	5,20	0,20	0,40	0,90	0,20	1,80	0,10	0,10	1,40
13	2000	Throughfall	143,90	5,20	0,10	0,20	1,10	0,10	1,10	0,00	0,00	0,50
15	2000	Throughfall	36,20	4,80	0,10	0,50	0,70	0,00	2,90	0,00	0,10	0,80
17	2000	Throughfall	21,10	5,60	0,20	0,40	0,70	0,10	1,60	0,10	0,10	2,10
19	2000	Throughfall	25,20	5,50	0,30	0,40	1,00	0,30	1,60	0,50	0,20	2,90
21	2000	Throughfall	127,30	5,90	0,20	0,60	0,80	0,20	1,50	0,40	0,10	1,90
23	2000	Throughfall	60,30									
25	2000	Throughfall	49,40									
27	2000	Throughfall	85,00									
29	2000	Throughfall	193,40									
31	2000	Throughfall	107,00									
33	2000	Throughfall	120,90									
35	2000	Throughfall	20,50	5,30	0,20	0,40	1,00	0,10	1,10	0,00	0,10	1,00
37	2000	Throughfall	122,10	4,60	0,10	0,20	0,60	0,10	1,20	0,00	0,10	0,60
39	2000	Throughfall	119,50	4,60	0,20	0,00	0,60	0,10	0,10	0,10	0,10	1,10
41	2000	Throughfall	80,00	4,60	0,20	0,00	0,60	0,00	0,10	0,00	0,10	0,40
43	2000	Throughfall	9,80	4,20	0,20	0,10	0,60	0,10	1,70	0,10	0,10	0,80
45	2000	Throughfall	44,10	5,10	0,10	0,00	0,30	0,10	0,50	0,30	0,30	1,20
47	2000	Throughfall	30,30	4,70	0,20	0,30	0,30	0,10	1,60	0,30	0,20	0,80
49	2000	Throughfall	24,90	4,60	0,10	0,00	0,20	0,10	1,10	0,00	0,10	0,40
51	2000	Throughfall	14,40	4,20	0,20	0,10	0,40	0,10	1,50	0,00	0,10	0,50
1	2001	Throughfall	41,40	4,30	0,12	0,03	0,49	0,08	0,94	0,04	0,11	0,47
3	2001	Throughfall	28,50	4,35	0,12	0,00	0,11	0,05	0,82	0,00	0,07	0,53
5	2001	Throughfall	22,60	4,40	0,13	0,00	0,27	0,09	1,37	0,08	0,08	0,55
7	2001	Throughfall	54,10	4,30	0,07	0,05	0,20	0,05	1,45	0,00	0,00	0,24
9	2001	Throughfall	109,10	4,40	0,18	0,46	0,98	0,09	2,40	0,03	0,04	0,32
11	2001	Throughfall	42,60	4,30	0,08	0,03	0,09	0,07	0,64	0,02	0,06	0,53
13	2001	Throughfall	99,50	4,10	0,09	0,20	0,32	0,11	0,80	0,00	0,10	1,03
15	2001	Throughfall	83,90	4,15	0,08	0,31	0,09	0,33	0,64	0,07	0,11	0,64
17	2001	Throughfall	93,80	4,10	0,21	0,56	0,73	0,23	2,66	0,03	0,06	0,44
19	2001	Throughfall	24,70	4,05	0,14	0,47	1,19	0,09	1,29	0,05	0,12	1,30
21	2001	Throughfall	28,80	4,15	0,03	0,40	0,38	0,04	0,77	0,08	0,37	1,89
23	2001	Throughfall	96,40	4,25	0,36	0,56	1,22	0,20	3,69	1,35	0,44	1,97
25	2001	Throughfall	148,80	4,20	0,06	0,34	0,58	0,04	0,85	0,00	0,10	1,14
27	2001	Throughfall	120,30	4,30	0,13	0,40	0,65	0,07	1,76	0,57	0,34	2,13
29	2001	Throughfall	12,10	4,10	0,17	0,23	0,70	0,19	0,82	0,41	0,14	3,45
31	2001	Throughfall	62,40	4,10	0,10	0,30	0,86	0,09	1,69	0,00	0,20	6,13
33	2001	Throughfall	0,00									
35	2001	Throughfall	0,00									
37	2001	Throughfall	208,20	4,50	0,11	0,00	0,34	0,07	0,00	0,00	0,07	2,73
39	2001	Throughfall	76,80	4,30	0,24	0,17	0,74	0,21	1,47	0,34	0,16	4,25
41	2001	Throughfall	33,00	4,25	0,04	0,18	0,60	0,07	1,83	0,00	0,25	1,28
43	2001	Throughfall	24,20	4,20	0,07	0,00	0,67	0,07	0,29	0,05	0,15	3,87
45	2001	Throughfall	27,60	4,30	0,47	0,26	0,81	0,29	1,08	0,11	0,17	3,41
47	2001	Throughfall	34,50	4,70	0,16	0,11	0,05	0,18	1,16	0,04	0,22	1,81
49	2001	Throughfall	126,50	4,80	0,54	0,00	0,26	0,19	0,80	0,07	0,15	1,08
51	2001	Throughfall	51,40	4,25	0,31	0,12	0,73	0,25	1,86	0,00	0,07	0,96

1	2002	Througfall	50,90	4,75	0,19	0,02	0,30	0,26	1,28	0,04	0,12	0,92
3	2002	Througfall	0,00									
5	2002	Througfall	39,20	5,20	0,12	0,01	0,13	0,20	0,29	0,02	0,21	1,22
7	2002	Througfall	20,30	4,85	0,14	0,11	0,27	0,07	1,33	0,00	0,12	0,70
9	2002	Througfall	59,20	4,75	0,08	0,20	0,34	0,11	0,86	0,00	0,12	0,60
11	2002	Througfall	18,30	4,50	0,37	0,72	1,06	0,23	3,13	0,07	0,13	0,73
13	2002	Througfall	189,70	5,80	0,07	0,32	0,47	0,09	0,98	0,00	0,14	0,85
15	2002	Througfall	2,10	5,30	0,31	0,93	1,85	0,20	4,13	0,33	0,19	2,04
17	2002	Througfall	36,20	5,30	0,19	0,55	0,79	0,06	2,47	0,00	0,02	0,85
19	2002	Througfall	84,40	4,35	0,12	0,45	0,69	0,03	1,78	0,00	0,10	1,18
21	2002	Througfall	46,50	4,55	0,10	0,77	1,01	0,28	1,61	0,08	0,27	2,81
23	2002	Througfall	42,60	4,65	0,06	0,19	0,24	0,08	0,98	0,06	0,12	1,58
25	2002	Througfall	73,30	4,80	0,16	0,40	0,70	0,08	1,33	0,06	0,33	2,93
27	2002	Througfall	70,90	4,70	0,44	0,55	1,15	0,22	1,70	0,07	0,19	2,80
29	2002	Througfall	76,20	5,20	0,14	0,30	0,87	0,15	1,27	0,02	0,07	1,53
31	2002	Througfall	109,80	4,85	0,07	0,44	1,04	0,06	1,68	0,04	0,03	1,15
33	2002	Througfall	104,60	4,95	0,06	0,00	0,80	0,10	0,43	0,07	0,01	1,02
35	2002	Througfall	22,90	4,60	0,05	0,37	0,51	0,04	1,56	0,05	0,14	1,88
37	2002	Througfall	50,90	4,75	0,19	0,02	0,30	0,26	1,28	0,04	0,12	0,92
39	2002	Througfall	95,50	4,90	0,10	0,31	0,54	0,10	1,37	0,00	0,15	1,77
41	2002	Througfall	88,00	5,30	0,18	0,12	0,53	0,06	1,15	0,00	0,56	2,56
43	2002	Througfall	54,40	5,10	0,07	0,00	0,25	0,00	0,90	0,00	0,21	1,39
45	2002	Througfall	126,00	4,90	0,18	0,00	0,32	0,12	0,65	0,06	0,23	1,55
47	2002	Througfall	82,70	4,90	0,12	0,00	0,29	0,07	0,63	0,00	0,24	1,71
49	2002	Througfall	47,70	4,50	0,19	0,00	0,31	0,07	0,68	0,00	0,18	2,11
51	2002	Througfall	19,80	4,85	0,15	0,00	0,32	0,04	0,60	0,00	0,22	2,61
1	2003	Througfall	74,10	5,10	0,38	0,00	0,19	0,04	0,00	0,00	0,15	1,61
3	2003	Througfall	50,00	4,85	0,36	0,00	0,15	0,06	0,00	0,01	0,27	2,00
5	2003	Througfall	44,70	3,90	0,37	0,00	0,26	0,06	1,67	0,00	0,07	0,81
7	2003	Througfall	63,90	4,20	0,34	0,04	0,22	0,07	1,36	0,00	0,09	0,95
9	2003	Througfall	0,00									
11	2003	Througfall	42,40	4,30	0,17	0,62	0,81	0,10	0,52	0,02	0,07	0,47
13	2003	Througfall	0,00									
15	2003	Througfall	0,00									
17	2003	Througfall	50,90	4,75	0,19	0,02	0,30	0,26	1,28	0,04	0,12	0,92
19	2003	Througfall	31,50	5,00	0,22	0,56	1,45	0,16	1,81	0,18	0,27	4,54
21	2003	Througfall	90,00	5,50	0,25	0,46	0,91	0,15	1,64	0,21	0,34	4,03
23	2003	Througfall	43,00	5,80	0,29	0,75	1,20	0,13	2,20	0,13	0,37	3,13
25	2003	Througfall	53,90	4,50	0,19	0,89	1,09	0,13	1,56	0,08	0,47	3,86
27	2003	Througfall	55,30	5,30	0,20	1,05	1,55	0,17	2,29	0,06	0,40	3,92
29	2003	Througfall	33,30	4,35	0,09	0,17	0,55	0,10	1,16	0,00	0,35	3,55
31	2003	Througfall	100,00	4,30	0,16	0,40	0,78	0,09	1,25	0,07	0,25	3,40
33	2003	Througfall	0,00									
35	2003	Througfall	52,00	4,65	0,18	0,57	1,28	0,12	1,53	0,05	0,28	3,83
37	2003	Througfall	63,90	4,45	0,09	0,33	0,56	0,11	1,04	0,00	0,53	4,01
39	2003	Througfall	123,50	4,30	0,19	0,53	1,20	0,13	2,36	0,00	0,08	1,33
41	2003	Througfall	63,90	4,45	0,09	0,00	0,36	0,09	0,76	0,00	0,29	1,80
43	2003	Througfall	86,80	4,90	0,21	0,00	0,55	0,15	0,83	0,00	0,16	1,26
45	2003	Througfall	20,80	5,10	0,15	0,28	0,57	0,07	1,67	0,13	0,54	2,66
47	2003	Througfall	28,50	4,90	0,17	0,31	0,10	0,07	1,15	0,12	0,53	2,54
49	2003	Througfall	18,80	4,90	0,10	0,00	0,06	0,06	1,19	0,00	0,04	0,82
51	2003	Througfall	22,30	5,10	0,27	0,00	0,48	0,11	0,68	0,05	0,06	1,07

1	2004	Throughfall	0,00									
3	2004	Throughfall	56,50	4,90	0,32	0,00	0,53	0,15	1,19	0,02	0,15	1,18
5	2004	Throughfall	77,40	5,10	0,34	0,02	0,97	0,10	2,04	0,01	0,12	1,49
7	2004	Throughfall	0,00									
9	2004	Throughfall	51,70	4,30	0,30	0,17	0,49	0,20	2,18	0,15	0,16	1,92
11	2004	Throughfall	26,70	4,45	0,33	0,37	0,77	0,02	6,31	0,12	0,12	1,64
13	2004	Throughfall	2,70	4,65	1,11	1,06	0,53	0,36	2,18	0,15	0,60	3,81
15	2004	Throughfall	66,10	4,95	0,16	0,26	1,14	0,14	1,05	0,00	0,65	3,37
17	2004	Throughfall	32,20	5,20	0,12	0,56	1,10	0,13	2,49	0,03	0,16	2,16
19	2004	Throughfall	55,00	5,00	0,45	0,62	0,97	0,22	2,12	0,06	1,13	6,72
21	2004	Throughfall	79,40	4,95	0,17	0,40	0,80	0,09	1,98	0,02	0,12	2,33
23	2004	Throughfall	50,50	5,00	0,14	0,29	0,45	0,12	1,55	0,00	0,55	6,79
25	2004	Throughfall	155,90	4,80	0,08	0,34	0,64	0,13	1,14	0,03	0,16	3,28
27	2004	Throughfall	73,20	6,00	0,14	0,59	1,05	0,18	1,73	0,02	0,23	3,40
29	2004	Throughfall	61,80	4,70	0,04	0,53	0,36	0,14	0,87	0,02	0,28	4,76
31	2004	Throughfall	22,10	4,80	0,05	0,55	0,61	0,13	1,08	0,03	0,28	6,86
33	2004	Throughfall	22,10	4,53	0,03	0,02	0,57	0,08	1,50	0,02	0,12	1,88
35	2004	Throughfall	99,50	4,70	0,08	0,35	0,53	0,12	0,97	0,00	0,36	5,17
37	2004	Throughfall	95,00	4,73	0,09	0,55	0,56	0,16	1,16	0,00	0,31	4,70
39	2004	Throughfall	43,60	4,70	0,21	0,31	0,77	0,16	1,27	0,03	0,27	4,34
41	2004	Throughfall	120,00	4,70	0,29	0,01	0,71	0,13	1,79	0,02	0,17	3,31
43	2004	Throughfall	50,90	4,90	0,11	0,16	0,65	0,12	1,25	0,09	0,64	1,55
45	2004	Throughfall	18,00	4,80	0,11	0,02	0,17	0,20	0,53	0,06	1,62	8,61
47	2004	Throughfall	47,60	4,80	0,46	0,45	0,87	0,35	1,87	0,07	0,31	3,23
49	2004	Throughfall	36,20	4,50	1,37	0,29	0,75	0,34	0,31	0,04	0,35	1,68
51	2004	Throughfall	0,00									
1	2005	Throughfall										
3	2005	Throughfall	23,20	4,80	0,51	0,19	0,79	0,38	0,87	0,06	0,07	0,11
5	2005	Throughfall	59,80	4,45	0,37	0,11	0,84	0,26	1,75	0,07	0,05	0,12
7	2005	Throughfall	139,80	4,60	0,35	0,15	0,44	0,28	1,25	0,06	0,03	0,17
9	2005	Throughfall	11,80	4,05	0,33	0,10	0,58	0,25	4,92	0,10	0,07	0,15
11	2005	Throughfall	40,90	4,10	0,34	0,08	0,53	0,18	4,91	0,19	0,07	0,36
13	2005	Throughfall	29,40	4,90	0,23	0,61	0,81	0,17	2,55	0,05	0,02	0,17
15	2005	Throughfall	33,60	5,00	0,05	0,06	0,07	0,03	0,46	0,01	0,00	0,13
17	2005	Throughfall	98,90	5,05	0,05	0,06	0,21	0,15	0,62	0,03		
19	2005	Throughfall	85,90	5,00	0,20	0,51	0,89	0,16	1,48	0,03	0,05	0,18
21	2005	Throughfall	75,80	5,20	0,06	0,74	1,03	0,09	1,64	0,06	0,06	0,21
23	2005	Throughfall	34,80	5,20	0,15	0,58	0,56	0,17	0,96	0,05	0,04	0,17
25	2005	Throughfall	49,50	4,90	0,34	0,59	1,18	0,31	2,65	0,05	0,08	0,36
27	2005	Throughfall	63,90	5,80	0,24	0,50	0,49	0,12	0,93	0,05	0,04	0,20
29	2005	Throughfall	136,10	4,70	0,11	0,18	0,70	0,06	0,90	0,04	0,03	0,19
31	2005	Throughfall	85,90	5,35	0,08	0,74	0,89	0,10	1,53	0,03	0,03	0,28
33	2005	Throughfall	125,20	4,90	0,09	0,47	0,76	0,08	1,31	0,02	0,02	0,19
35	2005	Throughfall	76,80	4,55	0,91	1,28	0,64	0,03	1,11	0,16	0,01	0,19
37	2005	Throughfall	3,90	4,50	0,22	0,40	0,71	0,07	0,46	0,06	0,02	0,13
39	2005	Throughfall	18,80	4,50	0,03	0,06	0,25	1,21	0,68	0,11	0,56	0,96
41	2005	Throughfall	82,40	4,75	0,54	0,01	0,44	0,19	1,91	0,03	0,56	0,87
43	2005	Throughfall	7,60	4,20	1,04	0,01	0,18	0,12	0,63	0,06	0,00	0,21
45	2005	Throughfall	12,70	4,35	0,02	0,01	0,57	0,07	0,85	0,14	0,03	0,10
47	2005	Throughfall	48,20	4,45	0,56	0,30	0,78	0,11	2,11	0,13	0,06	0,02
49	2005	Throughfall	27,30	4,60	0,12	0,13	0,49	0,11	1,70	0,06	0,07	0,22
51	2005	Throughfall	76,70	4,55	0,55	0,11	0,69	0,18	0,42	0,02	0,03	0,08

1	2006	Througfall	30,80	4,65	0,16	0,02	0,03	0,06	0,94	0,03	0,01	0,11
3	2006	Througfall	15,00	5,00	0,17	0,18	0,47	0,12	1,89	0,07	0,01	0,08
5	2006	Througfall	62,30	4,95	0,56	0,03	0,64	0,19	1,66	0,21	0,02	0,10
7	2006	Througfall	37,50	5,20	0,12	0,17	0,58	0,06	1,89	0,02	0,01	0,09
9	2006	Througfall	36,80	4,90	0,06	0,13	0,32	0,06	2,95	0,02	0,00	0,10
11	2006	Througfall	88,20	5,20	0,18	0,18	0,69	0,10	1,95	0,02	0,01	0,10
13	2006	Througfall	12,70	4,20	0,21	0,15	0,62	0,07	1,75	0,03	0,00	0,09
15	2006	Througfall	65,90	4,85	0,26	0,30	0,51	0,10	1,31	0,03	0,01	0,09
17	2006	Througfall	72,70	4,85	0,03	0,81	0,49	0,07	1,61	0,03	0,01	0,11
19	2006	Througfall	67,70	4,65	0,05	1,04	1,38	0,05	3,12	0,10	0,05	0,25
21	2006	Througfall	71,10	4,50	0,09	0,01	0,47	0,13	1,12	0,19	0,03	0,18
23	2006	Througfall	154,10	4,95	0,16	0,28	0,94	0,06	1,85	0,05	0,00	0,12
25	2006	Througfall		5,60	0,11	0,74	0,95	0,07	1,13	0,06	0,04	0,69
27	2006	Througfall	126,10	5,05	0,25	0,46	1,38	0,13	1,69	0,08	0,09	1,11
29	2006	Througfall	22,10	5,20	0,00	0,20	0,91	0,07	0,98	0,04	0,06	0,39
31	2006	Througfall	22,10	4,55	0,60	0,55	1,41	0,08	3,51	0,10	0,08	0,51
33	2006	Througfall	202,00	4,90	0,18	0,25	0,33	0,00	0,25	0,00	0,00	0,10
35	2006	Througfall	26,80	4,25	0,12	0,04	0,24	0,08	0,65	0,04	0,01	0,10
37	2006	Througfall	26,80	4,90	0,14	0,09	0,52	0,20	1,33	0,08	0,02	0,15
39	2006	Througfall	32,10	5,90	0,01	0,38	0,48	0,09	1,25	1,34	0,30	0,82
41	2006	Througfall	88,00	4,65	0,09	0,44	0,21	0,11	0,05	0,04	0,05	0,53
43	2006	Througfall	1,20	4,85	0,36	0,09	0,22	0,26	1,39	0,05	0,04	0,17
45	2006	Througfall	85,00	4,50	1,00	0,46	1,12	0,52	1,81	0,18	0,07	
47	2006	Througfall	82,60	4,65	0,44	0,18	0,44	0,21	0,96	0,03	0,04	0,12
49	2006	Througfall	10,60	5,25	0,81	0,10	0,22	0,08	0,69	0,03	0,02	0,08
51	2006	Througfall	40,30	5,65	0,35	0,08	0,37	0,12	0,90	0,03	0,02	0,09
1	2007	Througfall	8,80	4,55	0,49	0,01	0,45	0,18	0,44	0,05	0,02	0,06
3	2007	Througfall	34,80	4,90	0,86	0,03	0,44	0,26	1,02	0,03	0,02	0,04
5	2007	Througfall	27,90	4,60	0,59	0,06	0,48	0,74	1,57	0,36	0,05	0,11
7	2007	Througfall	13,20	4,80	0,27	0,20	0,44	0,10	1,82	0,03	0,02	0,06
9	2007	Througfall	59,20	4,35	0,08	0,01	0,25	0,09	1,46	0,06	0,01	0,05
11	2007	Througfall	63,90	4,60	0,21	0,27	0,54	0,33	1,35	0,11	0,06	0,24
13	2007	Througfall	38,80	4,50	0,46	0,86	0,76	0,29	1,95	0,05	0,03	0,10
15	2007	Througfall	14,80	4,70	0,15	0,84	0,57	0,06	3,97	0,03	0,03	0,17
17	2007	Througfall										
19	2007	Througfall	47,30	5,30	0,22	0,73	1,36	0,06	1,54	0,07	0,14	0,82
21	2007	Througfall	108,60	5,10	0,05	0,10	0,29	0,08	1,94	0,05	0,02	0,09
23	2007	Througfall	99,40	4,70	0,21	0,00	0,09	0,09	0,22	0,03	0,00	0,05
25	2007	Througfall										
27	2007	Througfall	110,50	4,55	0,11	0,35	0,72	0,08	1,13	0,03	0,02	0,17
29	2007	Througfall	99,90	5,00	0,04	0,03	0,09	0,11	0,49	0,04	0,08	0,07
31	2007	Througfall	58,30	4,85	1,70	0,36	0,49	0,07	0,69	0,03	0,02	0,15
33	2007	Througfall	68,20	5,20	0,06	0,13	0,44	0,06	1,15	0,02	0,00	0,14
35	2007	Througfall	40,20	4,80	0,06	0,13	0,32	0,22	0,69	0,10	0,21	0,36
37	2007	Througfall	226,20	5,30	0,43	0,28	0,44	0,16	1,67	0,59	0,12	0,39
39	2007	Througfall	86,50	5,55	0,08	0,20	0,48	0,15	1,07	0,03	0,02	0,09
41	2007	Througfall	39,20	4,35	0,70	0,04	0,34	0,20	1,25	0,58	0,01	0,10
43	2007	Througfall	51,50	4,60	0,37	0,64	0,93	0,40	2,20	0,10	0,01	0,09
45	2007	Througfall	14,80	4,95	0,09	0,42	0,56	0,13	1,77	0,22	0,03	0,04
47	2007	Througfall	151,70	4,85	0,39	0,08	0,20	0,21	0,30	0,16	0,48	0,63
49	2007	Througfall	51,40	4,75	0,93	0,10	0,49	0,18	1,20	0,03	0,04	0,04
51	2007	Througfall	57,40	4,85	0,21	0,00	0,09	0,09	0,22	0,03	0,00	0,05

1	2008	Throughfall	12,90	5,10	0,47	0,74	0,89	0,11	2,17	0,85	0,15	0,26
3	2008	Throughfall	21,80	5,00	0,74	0,00	0,13	0,11	0,37	0,22	0,10	0,27
5	2008	Throughfall	32,90	5,30	0,31	0,72	0,27	0,11	1,13	0,25	0,28	0,38
7	2008	Throughfall	23,90	4,80	0,26	0,26	0,44	0,19	1,79	0,43	0,25	0,56
9	2008	Throughfall	2,90	5,20	0,24	0,41	0,36	0,13	2,08	0,94	1,89	0,61
11	2008	Throughfall	33,60	4,72	0,62	0,25	0,59	0,16	1,51	0,28	0,30	0,89
13	2008	Throughfall	118,20	4,80	0,52	0,00	0,70	0,98	1,86	0,15	0,42	0,42
15	2008	Throughfall	82,60	4,60	0,65	0,58	1,32	0,00	2,02	0,00	0,50	0,66
17	2008	Throughfall	25,90	4,50	0,16	0,00	0,48	0,12	2,74	0,00	0,13	0,24
19	2008	Throughfall	120,00	5,10	0,18	0,45	0,31	0,43	1,07	0,07	0,33	0,25
21	2008	Throughfall	32,30	5,55	0,29	0,03	0,81	0,17	1,45	0,00	0,28	0,91
23	2008	Throughfall	18,50	5,15	0,16	0,02	0,72	0,54	1,75	0,37	0,24	0,74
25	2008	Throughfall	92,70	4,80	0,05	0,00	0,74	0,19	2,30	0,01	0,19	0,68
27	2008	Throughfall	43,30	4,70	0,31	0,05	1,01	0,17	1,13	0,02	0,23	0,40
29	2008	Throughfall										
31	2008	Throughfall										
33	2008	Throughfall	61,20	5,20	0,04	0,40	0,50	0,05	0,89	0,05	0,03	0,24
35	2008	Throughfall	77,10	4,90	0,00	0,00	0,64	0,18	1,19	0,49	3,65	6,52
37	2008	Throughfall	27,60	4,50	0,07	0,08	0,59	0,11	0,90	0,09	0,55	0,86
39	2008	Throughfall	38,80	5,60	0,31	0,14	0,72	0,02	1,20	0,03	0,06	0,85
41	2008	Throughfall	42,30	4,90	0,31	0,08	0,59	0,15	1,42	0,06	0,05	0,24
43	2008	Throughfall	19,20	5,40	0,34	0,12	1,49	0,12	0,78	0,21	0,06	0,47
45	2008	Throughfall	10,90	4,95	0,40	0,00	0,31	0,00	1,94	1,61	0,09	0,39
47	2008	Throughfall	35,30	4,90	0,25	0,08	0,29	0,00	0,83	0,05	0,03	0,14
49	2008	Throughfall	39,20	5,00	0,57	0,00	0,42	0,15	0,64	0,02	0,04	0,13
51	2008	Throughfall	27,60	5,20	0,25	0,00	0,56	0,00	2,00	0,00	0,04	0,14

Table 35: Complete surface run-off data

Week	Year	Depth	ml	pH	Cl ⁻ [mg/l]	NH ₄ ⁺ [mg/l]	SO ₄ ⁻ [mg/l]	Na ⁺ [mg/l]	NO ₃ ⁻ [mg/l]	K ⁺ [mg/l]	Mg ⁺⁺ [mg/l]	Ca ⁺⁺ [mg/l]
1	2000	Surface run-off	2600	7,21	1,10	0,00	1,23	0,33	10,96	1,49	4,76	7,06
3	2000	Surface run-off	6867,5	7,96	1,37	0,43	1,69	0,40	17,00	1,54	8,58	14,12
5	2000	Surface run-off	630	7,75	1,63	0,09	3,22	0,51	28,37	1,82	12,55	20,49
7	2000	Surface run-off	310	7,68	2,10	0,79	1,59	0,39	8,76	1,94	12,27	21,59
9	2000	Surface run-off	700	7,96	3,51	0,43	1,18	0,60	5,54	1,15	5,42	10,86
11	2000	Surface run-off	115	7,76	1,25	0,00	0,96	0,80	4,55	1,55	13,23	24,94
13	2000	Surface run-off	2450	6,30	0,25	0,48	1,14	0,26	3,10	0,53	2,37	5,64
15	2000	Surface run-off	195	7,40	1,20	3,06	0,57	0,81	3,10	1,32	8,47	14,90
17	2000	Surface run-off										
19	2000	Surface run-off	82	8,45	2,25	3,04	1,29	0,63	35,96	1,84	16,18	28,10
21	2000	Surface run-off	1825	7,48	3,69	0,57	3,82	0,29	53,66	2,38	10,12	18,75
23	2000	Surface run-off	600	8,25	1,55	1,13	3,55	0,49	24,67	2,87	7,72	13,27
25	2000	Surface run-off	1980	6,53	1,89	0,46	2,30	0,11	41,24	1,36	0,62	3,57
27	2000	Surface run-off	2150	6,90	2,89	0,10	2,72	0,36	33,69	3,16	10,56	20,00
29	2000	Surface run-off	1975	7,20	1,37	0,00	1,64	0,31	10,69	1,88	6,91	13,73
31	2000	Surface run-off										
33	2000	Surface run-off	1345	7,73	0,83	0,11	0,95	0,22	2,75	1,36	5,24	10,73
35	2000	Surface run-off	500	7,33	2,59	0,00	2,06	0,32	13,94	2,35	10,76	20,19
37	2000	Surface run-off	2500	7,58	1,23	0,15	1,04	0,20	8,53	1,74	8,47	16,40
39	2000	Surface run-off	1387,5	7,08	1,13	0,19	1,11	0,22	7,71	1,77	9,07	17,44
41	2000	Surface run-off	600	7,90	0,90	0,34	1,07	0,21	3,96	2,03	11,56	21,86
43	2000	Surface run-off										
45	2000	Surface run-off	470	8,04	1,94	0,09	1,88	0,25	23,11	2,13	14,15	24,87
47	2000	Surface run-off	70	8,19	3,45	0,07	2,68	1,03	32,35	5,33	22,30	36,43
49	2000	Surface run-off	180	7,60	1,74	0,79	1,90	0,33	32,03	2,29	17,01	29,15
51	2000	Surface run-off										
1	2001	Surface run-off	1462,5	7,38	0,59	0,57	1,41	0,28	4,88	1,07	4,34	8,34
3	2001	Surface run-off	110	7,35	2,24	0,12	4,77	0,64	76,02	3,71	23,76	36,87
5	2001	Surface run-off	305	7,35	1,53	0,17	3,60	0,40	63,45	2,09	16,95	27,76
7	2001	Surface run-off	250	7,25	1,46	0,33	3,24	0,53	49,84	2,36	16,73	27,37
9	2001	Surface run-off										
11	2001	Surface run-off	1407,5	7,30	0,54	0,39	1,66	0,42	6,32	1,10	4,88	9,37
13	2001	Surface run-off	310	7,10	0,41	0,30	0,63	0,28	3,99	1,32	8,13	14,63
15	2001	Surface run-off	90	7,20	0,43	0,16	1,48	0,32	8,75	1,68	13,01	22,03
17	2001	Surface run-off	430	7,15	0,61	0,50	1,51	0,28	16,75	1,70	12,52	21,67
19	2001	Surface run-off	185	7,25	0,54	1,11	1,50	0,38	12,72	1,69	11,70	20,78
21	2001	Surface run-off	365	7,20	0,73	0,18	1,81	0,40	29,87	1,76	11,26	20,66
23	2001	Surface run-off	1100	7,30	0,53	0,06	1,95	0,29	11,47	1,05	6,04	12,81
25	2001	Surface run-off	2110	7,30	0,36	0,39	1,24	0,23	9,64	1,48	9,22	17,74
27	2001	Surface run-off	1740	7,30	0,56	0,07	1,04	0,18	3,00	1,13	7,47	15,16
29	2001	Surface run-off	540	7,50	1,06	0,27	1,50	0,23	5,20	1,32	8,84	17,59
31	2001	Surface run-off	1460	7,40	0,64	0,23	1,19	0,19	2,52	1,03	8,67	17,63
33	2001	Surface run-off	2580	7,35	0,75	0,07	0,97	0,15	3,85	1,23	8,05	16,04
35	2001	Surface run-off	850	6,90	0,08	0,00	0,04	0,47	0,07	1,36	6,55	13,92
37	2001	Surface run-off	5560	7,73	0,61	0,00	1,08	0,20	7,03	1,01	5,21	9,81
39	2001	Surface run-off	1285	7,25	0,63	0,19	1,31	0,24	6,67	1,03	6,38	12,64
41	2001	Surface run-off	700	7,15	1,52	0,00	1,73	0,33	23,58	0,99	7,80	14,87
43	2001	Surface run-off	930	6,95	0,25	0,26	14,09	0,28	0,17	1,64	8,21	15,32
45	2001	Surface run-off	205	7,30	2,45	0,11	1,75	0,66	13,08	2,11	11,69	19,89
47	2001	Surface run-off	1680	7,35	1,32	0,09	3,51	0,39	12,02	0,96	6,73	11,21
49	2001	Surface run-off	5960	7,25	0,44	0,00	0,48	0,44	3,43	0,77	5,79	10,16
51	2001	Surface run-off	2450	7,35	2,26	0,06	4,49	1,47	18,05	2,51	21,50	26,23

1	2002	Surface run-off										
3	2002	Surface run-off										
5	2002	Surface run-off										
7	2002	Surface run-off										
9	2002	Surface run-off										
11	2002	Surface run-off										
13	2002	Surface run-off										
15	2002	Surface run-off										
17	2002	Surface run-off										
19	2002	Surface run-off										
21	2002	Surface run-off										
23	2002	Surface run-off										
25	2002	Surface run-off										
27	2002	Surface run-off										
29	2002	Surface run-off										
31	2002	Surface run-off										
33	2002	Surface run-off										
35	2002	Surface run-off										
37	2002	Surface run-off										
39	2002	Surface run-off										
41	2002	Surface run-off										
43	2002	Surface run-off										
45	2002	Surface run-off										
47	2002	Surface run-off										
49	2002	Surface run-off										
51	2002	Surface run-off										
1	2003	Surface run-off	12075	6,95	0,16	0,01	0,40	0,10	2,23	0,49	5,10	11,38
3	2003	Surface run-off	1505	7,18	0,21	0,00	0,28	0,11	0,66	0,68	5,51	11,51
5	2003	Surface run-off										
7	2003	Surface run-off										
9	2003	Surface run-off										
11	2003	Surface run-off	2465	7,00	0,56	0,00	1,34	0,17	6,00	0,55	4,39	9,50
13	2003	Surface run-off										
15	2003	Surface run-off										
17	2003	Surface run-off										
19	2003	Surface run-off	40	6,80								
21	2003	Surface run-off	170	6,90	2,42	0,00	4,03	0,83	10,87	1,23	13,40	25,67
23	2003	Surface run-off	67,5	6,60	1,14	0,05	1,21	0,44	14,65	1,07	13,76	25,76
25	2003	Surface run-off	175,5	7,10	1,55	0,98	2,04	0,76	22,55	1,72	10,47	21,24
27	2003	Surface run-off	605	7,00	1,01	0,00	2,98	0,33	37,80	1,12	12,41	25,19
29	2003	Surface run-off										
31	2003	Surface run-off	900	6,95	1,23	0,00	2,17	0,36	22,88	0,87	10,06	23,16
33	2003	Surface run-off	0									
35	2003	Surface run-off	730	6,95	2,12	0,11	3,07	0,22	17,38	1,14	8,74	20,25
37	2003	Surface run-off	1275	6,85	1,63	0,87	5,36	0,37	23,14	0,46	12,77	30,57
39	2003	Surface run-off	1482,5	6,55	1,40	0,00	2,15	0,45	14,30	2,95	7,05	15,20
41	2003	Surface run-off	1605	7,50	0,85	0,00	1,35	0,45	7,35	0,80	6,95	15,00
43	2003	Surface run-off	10645	7,05	0,44	0,01	0,99	0,26	3,59	0,35	3,78	9,19
45	2003	Surface run-off	32,5	6,65	1,64	0,26	0,00	0,56	2,45	1,66	7,51	16,07
47	2003	Surface run-off	127,5	6,65	0,39	0,20	0,53	0,56	3,90	1,61	7,61	16,11
49	2003	Surface run-off	500	6,55	0,36	0,00	0,38	0,11	3,79	0,00	2,94	9,58
51	2003	Surface run-off	82,5	6,30	3,19	0,08	2,48	0,41	28,51	0,66	10,21	22,92

1	2004	Surface run-off	0									
3	2004	Surface run-off	1312,5	6,50	1,04	0,04	1,00	0,55	1,58	0,78	3,05	8,72
5	2004	Surface run-off	1150	7,15	2,06	0,12	1,13	0,27	2,61	0,49	3,15	9,92
7	2004	Surface run-off	0									
9	2004	Surface run-off	152,5	5,96	0,96	0,00	1,26	0,63	4,99	0,31	10,13	19,26
11	2004	Surface run-off	0									
13	2004	Surface run-off	0									
15	2004	Surface run-off	0									
17	2004	Surface run-off	226,5									
19	2004	Surface run-off	13,5		3,32	1,22	1,76	0,20	17,82	0,86	1,75	12,91
21	2004	Surface run-off	442,5	6,10	1,34	0,00	4,02	0,48	76,56	0,83	13,75	32,44
23	2004	Surface run-off	16,5		2,85	0,00	6,65	1,05	152,81	1,84	23,91	53,33
25	2004	Surface run-off	450	7,40	2,86	0,00	1,66	0,46	199,69	1,77	26,08	48,37
27	2004	Surface run-off	67,5	7,85	4,93	0,00	10,17	0,82	302,80	3,15	34,49	62,08
29	2004	Surface run-off	115	7,20	6,03	0,00	9,61	0,52	366,19	4,11	41,51	74,42
31	2004	Surface run-off	1127,5	7,90	1,29	0,00	3,45	0,28	79,55	2,95	13,93	31,77
33	2004	Surface run-off	0									
35	2004	Surface run-off	182,5	7,90	3,68	0,00	6,08	0,65	150,08	4,35	27,51	53,05
37	2004	Surface run-off	105	8,30	3,54	0,00	4,97	0,59	127,79	3,99	31,35	59,55
39	2004	Surface run-off	54	8,35	4,17	0,00	5,36	0,56	70,59	3,57	26,65	52,13
41	2004	Surface run-off	107,5	8,30	3,07	0,00	4,62	0,67	72,42	3,63	29,96	57,77
43	2004	Surface run-off	170	8,00	3,46	0,01	5,47	0,58	97,86	3,04	23,78	48,85
45	2004	Surface run-off	0									
47	2004	Surface run-off	80	7,55	5,17	0,02	8,43	0,56	160,87	2,92	36,33	65,33
49	2004	Surface run-off	210	8,25	1,17	0,80	0,95	0,44	1,97	0,90	3,56	15,82
51	2004	Surface run-off	0									
1	2005	Surface run-off										
3	2005	Surface run-off	240	7,70	6,21	1,15	6,46	1,84	134,87	3,35	20,37	35,56
5	2005	Surface run-off	1240	7,54	1,37	0,20	1,45	0,46	12,77	1,13	5,75	8,84
7	2005	Surface run-off										
9	2005	Surface run-off										
11	2005	Surface run-off										
13	2005	Surface run-off	60	7,80	2,08	0,10	0,92	0,98	2,73	1,90	7,53	12,21
15	2005	Surface run-off										
17	2005	Surface run-off										
19	2005	Surface run-off	0									
21	2005	Surface run-off	0									
23	2005	Surface run-off	0									
25	2005	Surface run-off	160	8,25	4,69	0,06	6,13	1,40	236,76	5,20	33,34	46,48
27	2005	Surface run-off	180	8,30	3,90	0,05	3,65	0,87	144,70	3,94	27,01	39,57
29	2005	Surface run-off	3155	6,00	1,19	1,48	2,95	0,98	11,98	4,62	5,98	10,64
31	2005	Surface run-off	2470	6,70	0,28	0,01	1,86	0,30	0,44	1,66	11,06	34,12
33	2005	Surface run-off	1300	7,50	0,59	0,12	1,54	0,16	9,87	1,13	5,93	10,11
35	2005	Surface run-off	2470	7,50	0,17	1,33	0,58	0,03	3,41	1,87	0,58	12,86
37	2005	Surface run-off										
39	2005	Surface run-off										
41	2005	Surface run-off	1120	7,50								
43	2005	Surface run-off										
45	2005	Surface run-off										
47	2005	Surface run-off										
49	2005	Surface run-off	790	7,10	3,18	0,00	3,67	0,24	63,09	1,27	16,34	24,95
51	2005	Surface run-off	510	7,15	1,97	0,33	1,90	0,32	19,13	1,22	11,15	17,14

1	2006	Surface run-off										
3	2006	Surface run-off										
5	2006	Surface run-off										
7	2006	Surface run-off										
9	2006	Surface run-off										
11	2006	Surface run-off										
13	2006	Surface run-off										
15	2006	Surface run-off										
17	2006	Surface run-off										
19	2006	Surface run-off										
21	2006	Surface run-off										
23	2006	Surface run-off	53	7,50	4,51	0,09	2,77	0,74	69,59	3,59	39,04	0,00
25	2006	Surface run-off										
27	2006	Surface run-off	705	8,30	1,15	0,00	1,86	0,68	33,21	1,54	10,42	16,93
29	2006	Surface run-off										
31	2006	Surface run-off										
33	2006	Surface run-off		7,95	3,91	0,00	3,90	0,70	194,96	2,80	33,28	54,39
35	2006	Surface run-off	130	8,25	2,75	0,84	2,90	0,61	79,03	0,09	21,58	37,82
37	2006	Surface run-off										
39	2006	Surface run-off	43	8,35	4,31	0,03	3,30	0,77	163,77	6,14	29,70	48,02
41	2006	Surface run-off										
43	2006	Surface run-off										
45	2006	Surface run-off	127	8,20	5,45	1,04	8,52	1,02	186,99	2,49	36,83	
47	2006	Surface run-off	600	7,95	3,63	0,96	4,98	0,44	122,14	1,44	18,95	31,46
49	2006	Surface run-off										
51	2006	Surface run-off										
1	2007	Surface run-off										
3	2007	Surface run-off	51	8,10	4,84	0,09	3,62	1,05	94,14	2,93	31,55	49,20
5	2007	Surface run-off										
7	2007	Surface run-off	72	7,50	6,19	0,39	9,76	0,73	194,21	2,48	32,96	42,97
9	2007	Surface run-off	1440	6,90	1,07	0,04	1,39	0,51	13,17	1,29	6,73	10,45
11	2007	Surface run-off	850	7,90	0,65	0,33	0,99	0,28	11,25	0,95	5,51	8,79
13	2007	Surface run-off										
15	2007	Surface run-off										
17	2007	Surface run-off										
19	2007	Surface run-off	370	7,10	1,25	0,02	2,51	0,44	41,61	2,01	13,77	29,01
21	2007	Surface run-off	260	7,65	1,66	0,02	3,24	0,52	55,23	2,72	18,52	29,99
23	2007	Surface run-off	470	7,95	2,23	0,73	5,08	0,33	132,32	2,73	21,10	34,16
25	2007	Surface run-off	117,5	8,25	0,08	0,01	1,42	0,10	0,21	0,02	7,95	12,77
27	2007	Surface run-off	155	7,15	3,28	0,00	3,57	0,91	141,16	4,54	28,40	46,38
29	2007	Surface run-off	104	7,80	3,62	0,00	6,90	1,18	246,78	6,34	26,81	43,33
31	2007	Surface run-off										
33	2007	Surface run-off	61	7,95	3,86	0,05	2,39	0,80	77,45	4,37	22,36	37,92
35	2007	Surface run-off	195	7,90	1,84	0,05	1,81	0,54	87,34	3,40	20,18	33,52
37	2007	Surface run-off	620	8,50	1,18	4,84	2,55	0,35	17,78	7,40	17,79	29,74
39	2007	Surface run-off	335	8,15	1,14	0,41	2,77	0,34	36,36	0,92	15,72	26,29
41	2007	Surface run-off										
43	2007	Surface run-off										
45	2007	Surface run-off	38		5,98	3,52	3,74	0,69	34,45	2,48	47,18	69,33
47	2007	Surface run-off	57		8,06	0,00	7,58	1,26	54,55	6,86	73,12	74,06
49	2007	Surface run-off	82	8,45	3,37	0,00	4,46	0,53	31,75	4,63	37,72	47,82
51	2007	Surface run-off	52		2,47	0,28	5,66	0,40	130,70	2,33	22,70	41,19

1	2008	Surface run-off										
3	2008	Surface run-off	167	8,50	2,11	0,09	2,57	0,24	26,30	1,58	23,24	36,62
5	2008	Surface run-off	30		3,14	0,00	2,10	0,75	40,12	2,62	29,18	46,42
7	2008	Surface run-off										
9	2008	Surface run-off										
11	2008	Surface run-off	670	8,20	2,29	0,52	2,08	0,41	18,51	1,12	14,27	23,15
13	2008	Surface run-off	685	8,30	1,31	0,00	1,57	0,18	12,47	0,25	15,25	21,92
15	2008	Surface run-off	2525	8,40	1,22	0,00	1,22	0,35	3,10	0,24	4,24	6,28
17	2008	Surface run-off	123	8,30	1,00	0,83	1,04	0,30	3,94	0,69	16,93	28,10
19	2008	Surface run-off	180	8,50	1,35	0,18	3,73	1,04	11,40	3,36	16,03	23,73
21	2008	Surface run-off										
23	2008	Surface run-off	53	8,80	1,11	0,91	0,82	0,25	16,61	1,87		
25	2008	Surface run-off	187	8,50	0,86	0,46	1,37	0,87	8,07	1,19		
27	2008	Surface run-off	137	8,40	1,04	1,86	1,07	0,10	14,54	1,34	14,52	29,33
29	2008	Surface run-off										
31	2008	Surface run-off										
33	2008	Surface run-off	125	8,60	2,96	4,12	1,41	0,75	19,17	1,81	14,56	25,28
35	2008	Surface run-off	39		4,25	0,05	1,43	0,96	37,99	2,39	17,52	31,98
37	2008	Surface run-off										
39	2008	Surface run-off										
41	2008	Surface run-off										
43	2008	Surface run-off										
45	2008	Surface run-off										
47	2008	Surface run-off										
49	2008	Surface run-off										
51	2008	Surface run-off										

Table 36: Complete 05cm data

Week	Year	Depth	pH	Cl- [mg/l]	NH ₄ ⁺ [mg/l]	SO ₄ ⁻ [mg/l]	Na ⁺ [mg/l]	NO ₃ ⁻ [mg/l]	K ⁺ [mg/l]	Mg ⁺⁺ [mg/l]	Ca ⁺⁺ [mg/l]
1	2000	05cm	8,19	0,59	0,01	3,73	0,18	14,74	0,03	20,52	35,06
3	2000	05cm	8,28	0,50	0,01	3,77	0,21	16,41	0,13	19,25	37,08
5	2000	05cm	8,07	0,30	0,00	3,75	0,18	18,06	0,04	17,38	31,58
7	2000	05cm	8,09	0,45	0,34	2,11	0,20	9,85	0,11	14,31	26,60
9	2000	05cm	8,04	2,24	0,00	1,63	0,28	7,13	0,16	14,67	28,36
11	2000	05cm	8,05	1,61	0,00	1,21	0,18	5,23	0,11	13,95	24,67
13	2000	05cm	7,80	0,18	0,00	0,85	0,19	3,58	0,02	12,92	22,29
15	2000	05cm	8,04	0,30	0,00	0,71	0,18	3,23	0,01	14,38	23,75
17	2000	05cm	7,63	0,41	0,00	0,36	0,20	1,44	0,22	11,93	20,53
19	2000	05cm	8,42	0,46	0,01	0,67	0,26	2,91	0,04	14,27	24,66
21	2000	05cm	8,22	0,57	0,00	0,85	0,34	3,79	0,09	16,70	29,11
23	2000	05cm	8,44	1,00	0,01	0,80	0,53	2,60	1,08	18,30	31,80
25	2000	05cm	8,14	0,35	0,00	0,57	0,42	2,29	0,06	19,49	32,92
27	2000	05cm	8,01	0,36	0,00	0,62	0,47	1,81	0,06	20,11	33,15
29	2000	05cm	8,11	0,43	0,00	0,59	0,44	1,59	0,05	21,71	38,01
31	2000	05cm									
33	2000	05cm	8,53	0,37	0,00	0,42	0,37	0,91	0,05	21,95	38,58
35	2000	05cm	8,50	0,38	0,01	0,36	0,49	0,65	0,09	20,56	36,08
37	2000	05cm	8,12	0,62	0,01	0,45	0,18	0,20	0,02	17,86	32,43
39	2000	05cm	7,87	0,66	0,00	0,62	0,33	0,00	0,04	17,17	30,47
41	2000	05cm	8,23	0,92	0,00	0,67	0,34	0,58	0,06	17,32	30,59
43	2000	05cm	8,28	0,68	0,00	0,76	0,17	3,59	0,04	19,12	33,15
45	2000	05cm	8,22	1,36	0,00	0,88	0,17	3,55	0,03	17,29	30,07
47	2000	05cm	8,24	1,47	0,01	1,01	0,15	4,22	0,04	17,61	30,25
49	2000	05cm	8,04	0,87	0,00	1,11	0,17	8,77	0,06	21,66	37,06
51	2000	05cm	7,16	0,41	0,45	1,70	0,18	1,99	0,06	6,33	13,40
1	2001	05cm	8,30	0,90	0,15	4,38	0,33	10,46	0,04	18,67	32,00
3	2001	05cm	8,28	0,70	0,00	2,16	0,24	12,87	0,02	20,24	34,27
5	2001	05cm	8,23	0,84	0,00	2,26	0,36	14,82	0,41	20,28	34,18
7	2001	05cm	8,23	0,62	0,01	2,37	0,21	16,25	0,03	20,91	35,23
9	2001	05cm	8,18	0,54	0,00	2,11	0,15	13,00	0,04	19,62	33,15
11	2001	05cm	8,25	0,32	0,00	1,54	0,22	8,90	0,02	19,83	33,83
13	2001	05cm	8,18	0,26	0,00	0,83	0,16	3,08	0,01	15,47	26,99
15	2001	05cm	8,05	0,28	0,00	0,68	0,20	2,16	0,02	16,54	28,90
17	2001	05cm	8,18	0,32	0,00	0,57	0,23	1,96	0,03	17,63	30,60
19	2001	05cm	8,25	0,30	0,00	0,64	0,29	2,83	0,04	18,00	31,02
21	2001	05cm	8,20	0,48	0,00	0,97	0,22	2,53	0,04	15,71	27,90
23	2001	05cm	8,25	0,34	0,00	0,74	0,24	0,27	0,03	17,89	31,81
25	2001	05cm	8,10	0,37	0,00	0,68	0,34	0,00	0,35	19,91	35,31
27	2001	05cm	8,00	0,31	0,00	0,43	0,22	0,00	0,04	20,97	37,46
29	2001	05cm	8,10	0,31	0,00	0,39	0,19	0,00	0,03	19,59	35,30
31	2001	05cm	7,90	0,38	0,00	0,42	0,35	0,10	0,04	20,40	36,77
33	2001	05cm	7,90	1,19	0,00	0,49	0,22	0,05	0,05	18,90	34,27
35	2001	05cm	8,08	0,21	0,32	1,16	0,23	0,06	0,05	10,24	22,28
37	2001	05cm	8,06	0,48	0,00	1,30	0,31	0,15	0,03	18,31	34,68
39	2001	05cm	8,05	0,89	0,01	1,26	0,26	0,07	0,03	19,22	36,29
41	2001	05cm	8,00	1,24	0,02	0,69	0,44	0,14	0,05	22,30	41,64
43	2001	05cm	8,03	2,47	0,00	0,85	0,25	0,06	0,05	18,56	34,11
45	2001	05cm	8,02	3,55	0,00	1,15	0,30	0,23	0,04	17,82	32,29
47	2001	05cm	7,83	2,12	0,00	1,31	0,24	0,70	0,02	18,91	35,17
49	2001	05cm	8,10	1,53	0,02	1,74	0,23	2,06	0,05	19,59	34,59
51	2001	05cm	8,10	0,97	0,00	0,91	0,33	1,32	0,03	13,84	24,70

1	2002	05cm	8,35	0,56	0,00	3,81	0,28	1,16	0,02	15,91	28,17
3	2002	05cm	8,32	0,52	0,00	5,85	0,27	1,40	0,01	16,85	29,46
5	2002	05cm	8,40	0,44	0,00	7,09	0,27	1,55	0,02	17,75	30,32
7	2002	05cm	8,33	0,36	0,00	4,77	0,15	1,19	0,00	15,39	27,47
9	2002	05cm	8,40	0,53	0,00	3,32	0,20	1,13	0,33	15,50	27,89
11	2002	05cm	8,38	0,30	0,00	6,37	0,09	1,27	0,03	16,78	29,78
13	2002	05cm	8,37	0,14	0,23	1,88	0,38	1,38	0,04	9,26	32,60
15	2002	05cm	8,28	0,36	0,00	0,96	0,12	0,70	0,00	14,14	25,92
17	2002	05cm	8,38	0,23	0,00	0,53	0,12	0,90	0,05	14,75	27,15
19	2002	05cm	8,35	0,35	0,00	1,13	0,14	0,98	0,05	14,98	27,94
21	2002	05cm	8,28	0,37	0,00	0,00	0,26	0,93	0,97	17,75	32,40
23	2002	05cm	8,38	0,24	0,00	0,62	0,21	0,96	0,10	18,45	33,92
25	2002	05cm	8,25	0,19	0,00	0,50	0,24	0,47	0,08	19,24	35,83
27	2002	05cm	8,40	0,43	0,00	10,96	0,37	1,61	0,02	19,35	35,85
29	2002	05cm	8,35	0,25	0,00	0,00	0,27	0,71	0,04	18,30	35,07
31	2002	05cm									
33	2002	05cm	8,28	0,42	0,00	0,00	0,18	0,76	0,10	16,36	31,94
35	2002	05cm	8,28	0,37	0,00	0,00	0,15	0,75	0,03	16,69	32,29
37	2002	05cm	8,35	0,56	0,00	3,81	0,28	1,16	0,02	15,91	28,17
39	2002	05cm	8,23	0,79	0,00	0,34	0,17	1,08	0,01	18,18	34,41
41	2002	05cm	8,25	1,51	0,00	0,93	0,15	1,14	0,00	17,44	32,62
43	2002	05cm	8,18	2,33	0,00	1,77	0,18	1,76	0,02	18,32	34,95
45	2002	05cm	8,23	3,24	0,02	0,81	0,17	1,79	0,02	18,12	34,34
47	2002	05cm	8,18	1,41	0,00	0,32	0,14	1,17	0,00	14,82	28,50
49	2002	05cm	8,20	2,42	0,00	0,79	0,12	2,01	0,00	17,69	34,24
51	2002	05cm	8,15	2,18	0,00	0,67	0,15	2,35	0,00	20,20	37,54
1	2003	05cm	8,00	0,09	0,10	1,26	0,18	1,41	0,06	20,12	35,42
3	2003	05cm	7,58	1,04	0,62	6,89	0,56	4,50	0,35	11,04	41,01
5	2003	05cm	7,85	2,56	0,45	7,51	0,19	9,14	0,03	19,59	36,05
7	2003	05cm	7,85	0,82	0,07	3,98	0,26	10,77	0,53	19,81	35,41
9	2003	05cm	7,85	0,29	0,04	2,70	0,18	13,66	0,03	22,99	40,23
11	2003	05cm	8,23	0,59	0,00	2,53	0,15	11,78	0,04	19,99	36,58
13	2003	05cm	7,83	0,48	0,00	1,92	0,11	2,35	0,00	18,51	34,29
15	2003	05cm									
17	2003	05cm	8,35	0,62	0,00	1,20	0,30	3,82	0,02	15,87	28,19
19	2003	05cm	6,68	25,49	2,43	14,42	0,53	1,19	0,17	3,03	24,60
21	2003	05cm	7,40	1,92	0,00	4,29	0,31	9,01	0,20	16,81	32,98
23	2003	05cm	7,70	1,15	0,06	2,55	0,24	15,53	0,05	19,24	36,47
25	2003	05cm	7,85	1,25	0,00	2,87	0,34	24,34	0,04	21,50	40,87
27	2003	05cm	8,00	1,70	0,00	3,51	0,25	40,26	0,04	22,79	42,85
29	2003	05cm	7,93	2,16	0,00	4,05	0,45	45,15	0,45	22,65	46,85
31	2003	05cm	8,05	1,77	0,00	4,15	0,36	40,21	0,02	21,09	44,47
33	2003	05cm									
35	2003	05cm	8,25	1,20	0,00	3,55	0,41	29,57	0,06	21,52	45,01
37	2003	05cm	8,35	1,63	0,00	3,98	0,46	27,95	0,05	20,68	44,05
39	2003	05cm	7,90	1,10	0,00	2,50	0,30	6,60	0,00	18,40	35,80
41	2003	05cm	8,10	1,00	0,00	2,30	0,30	3,30	0,00	18,10	36,10
43	2003	05cm	7,29	0,54	0,36	4,23	0,28	0,54	0,05	6,13	15,02
45	2003	05cm	7,82	1,01	0,18	3,96	0,31	2,99	0,06	17,89	35,81
47	2003	05cm	7,93	0,87	0,10	3,94	0,34	10,92	0,17	18,01	35,82
49	2003	05cm	7,85	1,03	0,01	3,91	0,13	12,16	0,00	15,89	38,48
51	2003	05cm	7,88	1,43	0,00	4,33	0,15	16,51	0,04	17,64	41,59

1	2004	05cm									
3	2004	05cm	7,93	1,88	0,00	4,91	0,28	19,18	0,28	22,00	41,40
5	2004	05cm	8,00	1,87	0,02	4,77	0,23	19,23	0,06	19,55	37,70
7	2004	05cm	7,98	1,21	0,00	5,53	0,05	8,77	0,03	20,80	38,27
9	2004	05cm	8,03	1,07	0,00	5,48	0,19	10,58	0,11	21,45	41,12
11	2004	05cm	8,22	0,98	0,00	4,17	0,09	9,73	0,10	21,35	40,59
13	2004	05cm	8,10	0,72	0,00	2,96	0,04	8,65	0,09	20,79	39,93
15	2004	05cm	7,82	0,53	0,00	2,54	0,03	4,44	0,09	18,29	36,21
17	2004	05cm	7,98	0,32	0,00	1,29	0,25	2,86	0,00	20,61	38,67
19	2004	05cm	7,93	0,40	0,00	1,52	0,23	3,02	0,05	13,96	32,88
21	2004	05cm	8,00	0,51	0,00	2,09	0,29	4,15	0,01	15,20	37,16
23	2004	05cm	8,03	0,56	0,00	1,48	0,45	1,55	0,09	16,78	42,78
25	2004	05cm	8,10	0,30	0,00	1,99	0,35	1,15	0,00	20,41	42,66
27	2004	05cm	8,10	0,36	0,00	2,37	0,49	0,28	0,03	22,59	46,90
29	2004	05cm	8,08	0,22	0,00	1,79	0,40	1,26	0,00	23,09	47,88
31	2004	05cm	8,45	0,27	0,00	2,05	0,46	1,27	0,00	24,38	50,65
33	2004	05cm	8,50	0,24	0,02	1,95	0,46	0,85	0,00	25,42	52,49
35	2004	05cm	8,45	0,63	0,05	2,92	0,44	1,43	0,12	24,37	50,80
37	2004	05cm	8,47	0,59	0,10	2,59	0,38	1,31	0,05	24,86	51,93
39	2004	05cm	8,35	0,59	0,03	3,04	0,43	1,18	0,13	23,68	50,53
41	2004	05cm	8,42	0,80	0,09	3,50	0,39	2,04	0,11	23,95	50,93
43	2004	05cm	8,47	0,80	0,00	2,66	0,39	3,75	0,08	23,21	49,62
45	2004	05cm	8,23	0,96	0,01	2,30	0,37	3,92	0,15	23,68	49,73
47	2004	05cm	8,25	1,19	0,02	2,74	0,48	5,48	0,20	24,04	50,80
49	2004	05cm	8,15	0,38	0,03	4,09	0,30	5,67	0,05	21,83	47,53
51	2004	05cm	8,30	0,83	0,07	4,55	0,58	1,33	0,17	25,03	51,88
1	2005	05cm									
3	2005	05cm	8,43	2,24	0,04	1,42	0,37	10,61	0,06	16,98	28,04
5	2005	05cm	8,30	1,75	0,04	2,00	0,22	7,22	0,06	13,35	20,80
7	2005	05cm	8,38	1,10	0,05	4,52	0,27	7,78	0,06	16,56	28,75
9	2005	05cm	8,45	0,87	0,03	4,13	0,24	6,17	0,05	17,98	31,61
11	2005	05cm	8,50	0,98	0,08	5,34	0,23	8,34	0,04	18,76	32,39
13	2005	05cm	8,53	0,93	0,10	3,12	0,22	2,17	0,05	15,54	25,93
15	2005	05cm	8,45	0,53	0,11	1,30	0,23	0,51	0,04	11,90	19,93
17	2005	05cm	8,23	0,42	1,29	1,56	0,41	1,28	1,48	13,08	21,75
19	2005	05cm	8,53	0,47	0,11	1,25	0,36	1,02	0,12	14,19	23,95
21	2005	05cm	8,60	0,50	0,11	1,32	0,35	0,24	0,05	14,83	25,09
23	2005	05cm	8,57	0,30	0,05	1,19	0,32	0,71	0,05	15,38	26,06
25	2005	05cm	8,68	0,27	0,04	2,23	0,43	0,01	0,11	17,18	28,76
27	2005	05cm	8,70	0,54	0,04	3,55	0,49	0,25	0,11	18,67	31,91
29	2005	05cm	8,70	0,50	0,04	2,80	0,39	0,66	0,11	19,90	34,57
31	2005	05cm	8,40	0,31	0,02	1,66	0,48	0,00	0,09	22,24	44,71
33	2005	05cm	8,50	0,44	0,02	2,49	0,33	0,94	0,09	23,42	46,19
35	2005	05cm	8,30	0,42	0,67	2,09	0,10	0,76	0,21	13,21	27,68
37	2005	05cm	8,35	0,28	0,05	1,90	0,20	0,02	0,18	15,39	27,50
39	2005	05cm	8,25	0,18	0,53	3,23	0,14	0,06	0,01	10,74	17,64
41	2005	05cm	8,18	0,65	0,03	2,90	0,26	1,25	0,07	17,41	29,89
43	2005	05cm	8,32	0,65	0,04	2,80	0,23	1,97	0,03	18,50	30,65
45	2005	05cm	8,28	0,65	0,00	3,86	0,25	3,38	0,01	20,17	33,55
47	2005	05cm	8,30	0,41	0,01	3,42	0,23	3,24	0,04	21,03	39,64
49	2005	05cm	8,28	1,80	0,00	6,98	0,20	7,12	0,02	19,73	31,93
51	2005	05cm	8,28	3,02	0,04	5,60	0,16	10,96	0,00	17,64	28,22

1	2006	05cm	8,32	2,29	0,02	4,82	0,21	4,95	0,10	19,23	30,80
3	2006	05cm	8,32	2,34	0,05	5,71	0,50	9,09	1,12	19,37	30,91
5	2006	05cm	8,35	1,67	0,02	5,92	0,26	9,36	0,10	18,99	30,11
7	2006	05cm	8,27	2,39	0,02	6,06	0,18	10,30	0,05	18,89	29,87
9	2006	05cm	8,32	1,16	0,02	5,87	0,18	10,04	0,05	19,26	30,50
11	2006	05cm	8,37	0,68	0,04	5,32	0,07	8,67	0,03	19,19	30,31
13	2006	05cm	8,37	0,45	0,03	4,40	0,17	4,92	0,06	18,31	29,03
15	2006	05cm	8,13	0,40	0,01	2,77	0,16	2,29	0,06	15,76	25,18
17	2006	05cm	8,27	0,25	0,01	1,53	0,15	0,50	0,03	13,28	21,38
19	2006	05cm	8,27	0,30	0,01	0,88	0,12	0,76	0,02	12,06	19,59
21	2006	05cm	8,30	0,35	0,02	1,36	0,20	0,17	0,06	15,90	30,94
23	2006	05cm	8,07	0,25	0,01	1,18	0,17	0,04	0,03	16,05	26,34
25	2006	05cm	8,27	0,24	0,00	1,69	0,16	0,03	0,03	17,04	27,87
27	2006	05cm	8,17	0,44	0,10	0,84	0,12	0,00	0,00	18,21	30,62
29	2006	05cm	8,33	0,38	0,02	1,95	0,25	0,19	0,02	20,11	34,10
31	2006	05cm									
33	2006	05cm									
35	2006	05cm	8,30	0,34	0,04	1,77	0,23	0,00	0,07	15,26	26,10
37	2006	05cm	8,28	0,45	0,01	1,75	0,08	0,23	0,01	18,73	31,58
39	2006	05cm	8,35	0,41	0,04	1,53	0,29	0,31	0,16	15,74	27,08
41	2006	05cm	8,30	0,37	0,01	2,16	0,13	0,26	0,02	18,87	32,41
43	2006	05cm	7,90	0,53	0,79	4,99	0,15	0,50	0,04	8,57	15,42
45	2006	05cm	8,37	0,76	0,00	3,35	0,23	0,68	0,00	16,94	
47	2006	05cm	8,32	1,60	0,00	3,59	0,12	1,37	0,02	15,58	25,67
49	2006	05cm	8,33	1,32	0,00	2,40	0,07	2,44	0,01	15,12	24,98
51	2006	05cm	8,23	1,12	0,00	2,92	0,07	4,09	0,00	16,69	27,42
1	2007	05cm	8,37	1,27	0,00	2,97	0,15	6,08	0,01	17,61	28,30
3	2007	05cm	8,37	1,41	0,01	3,12	0,20	6,37	0,07	17,13	27,51
5	2007	05cm	8,32	0,99	0,01	3,03	0,15	8,23	0,03	15,87	25,32
7	2007	05cm	8,38	1,08	0,02	2,02	0,23	6,05	0,07	14,34	22,24
9	2007	05cm	8,33	0,77	0,01	3,51	0,20	7,62	0,07	16,19	26,07
11	2007	05cm	8,32	0,65	0,01	2,29	0,19	3,90	0,03	13,75	22,54
13	2007	05cm	8,30	0,32	0,01	1,75	0,15	2,44	0,03	13,82	22,34
15	2007	05cm	8,35	0,34	0,03	2,88	0,32	2,29	0,04	17,54	26,96
17	2007	05cm	8,30	0,25	0,00	0,67	0,17	0,20	0,04	14,34	22,45
19	2007	05cm		0,10	0,01	4,74	0,19	8,30	0,06	19,13	40,32
21	2007	05cm	8,30	0,55	0,01	2,21	0,23	0,09	0,05	16,15	26,42
23	2007	05cm	8,07	0,14	0,06	1,40	0,17	0,16	0,10	8,37	13,87
25	2007	05cm	8,37	1,27	0,00	2,97	0,15	6,08	0,01	17,61	28,30
27	2007	05cm	8,08	0,08	0,02	1,75	0,25	0,31	0,04	18,46	31,06
29	2007	05cm	7,92	0,03	0,00	1,28	0,23	0,00	0,12	19,23	32,33
31	2007	05cm		0,17	0,00	1,78	0,18	0,00	0,02	18,86	31,55
33	2007	05cm	8,00	0,43	0,01	1,94	0,19	0,35	0,04	19,40	32,56
35	2007	05cm	8,12	0,48	0,17	0,86	0,21	0,13	0,05	14,45	23,92
37	2007	05cm	8,03	0,64	0,04	0,43	0,25	0,02	0,04	20,38	34,52
39	2007	05cm	8,03	0,62	0,00	1,23	0,30	0,10	0,03	17,51	29,14
41	2007	05cm	8,18	0,65	0,01	1,42	0,20	0,46	0,00	17,78	29,44
43	2007	05cm	8,20	0,22	0,00	0,00	0,29	0,16	0,03	19,65	31,47
45	2007	05cm	8,07	0,61	0,03	0,92	0,22	2,22	0,03	19,74	30,64
47	2007	05cm	8,13	1,16	0,01	3,24	0,14	3,61	0,01	20,28	28,71
49	2007	05cm	8,23	1,08	0,01	2,88	0,36	3,45	0,18	18,92	24,89
51	2007	05cm	8,13	0,15	0,06	2,65	0,09	0,28	0,18	14,57	27,33

1	2008	05cm		0,90	0,00	5,65	0,17	18,89	0,00	15,03	27,57
3	2008	05cm		0,67	0,00	10,41	0,87	29,11	0,28	19,48	30,39
5	2008	05cm	8,33	0,70	0,00	6,75	0,17	16,56	0,00	18,59	28,99
7	2008	05cm	8,23	0,25	0,00	5,81	0,18	11,74	0,00	22,02	35,55
9	2008	05cm		0,24	0,00	7,12	0,17	10,76	0,00	20,03	31,58
11	2008	05cm	8,50	0,36	0,00	9,63	0,21	10,75	0,00	18,55	27,09
13	2008	05cm	8,40	0,60	0,00	1,11	0,00	7,27	0,44	20,56	34,48
15	2008	05cm	8,45	1,34	0,00	5,11	0,19	5,24	0,06	14,98	23,40
17	2008	05cm	8,43	0,37	0,00	3,23	0,22	3,44	0,00	15,50	24,21
19	2008	05cm	8,28	0,28	0,00	2,67	0,62	2,13	0,45	14,84	23,91
21	2008	05cm		0,69	0,05	2,89	0,20	1,94	0,01	14,58	23,30
23	2008	05cm		1,04	0,02	0,53	0,20	0,93	0,00	16,39	27,68
25	2008	05cm	8,40	0,38	0,01	3,74	0,32	1,10	0,09	17,55	29,91
27	2008	05cm	8,38	0,43	0,07	3,22	0,26	2,63	0,23	18,87	31,94
29	2008	05cm									
31	2008	05cm									
33	2008	05cm	8,57	0,49	0,02	1,92	0,33	2,15	0,12	19,72	33,66
35	2008	05cm	8,48	0,61	0,02	3,23	0,37	0,69	0,12	22,48	38,27
37	2008	05cm	8,27	0,42	0,00	1,77	0,01	1,79	0,04	12,51	26,85
39	2008	05cm	8,52	0,70	0,00	1,93	0,36	2,75	0,03	21,71	36,48
41	2008	05cm	8,32	0,38	0,00	2,02	0,37	6,88	0,12	23,33	38,05
43	2008	05cm	8,20	0,63	0,00	2,45	0,28	6,55	0,04	22,84	37,56
45	2008	05cm	8,30	0,57	0,12	3,24	0,34	8,78	0,16	22,22	36,56
47	2008	05cm	8,43	0,50	0,00	2,84	0,14	10,50	0,00	21,92	35,73
49	2008	05cm	8,27	1,30	0,00	3,28	0,12	8,28	0,00	22,51	36,41
51	2008	05cm	7,95	0,85	0,00	4,57	0,09	9,65	0,00	22,35	36,21

Table 37: Complete 15cm data

Week	Year	Depth	pH	Cl ⁻ [mg/l]	NH ₄ ⁺ [mg/l]	SO ₄ ²⁻ [mg/l]	Na ⁺ [mg/l]	NO ₃ ⁻ [mg/l]	K ⁺ [mg/l]	Mg ⁺⁺ [mg/l]	Ca ⁺⁺ [mg/l]
1	2000	15cm	8,03	1,08	0,00	1,53	0,18	12,18	0,06	18,19	32,63
3	2000	15cm	8,17	0,67	0,08	1,95	0,16	17,15	0,06	17,41	35,78
5	2000	15cm	7,96	0,19	0,00	1,50	0,15	14,90	0,05	16,45	31,93
7	2000	15cm	7,77	0,31	0,00	1,20	0,12	6,24	0,04	13,62	26,78
9	2000	15cm	7,88	0,24	0,00	1,12	0,13	6,31	0,06	14,18	32,31
11	2000	15cm	7,79	0,31	0,00	0,82	0,14	4,33	0,00	12,50	23,18
13	2000	15cm	7,63	0,18	0,00	0,70	0,32	2,52	0,08	15,15	27,46
15	2000	15cm	8,04	0,27	0,00	0,85	0,16	5,62	0,00	16,33	29,03
17	2000	15cm	8,02	0,26	0,00	0,46	0,24	3,35	0,27	14,40	25,99
19	2000	15cm	8,46	0,46	0,02	0,73	0,26	3,99	0,04	16,67	30,69
21	2000	15cm	8,16	0,38	0,00	0,98	0,24	4,23	0,00	17,71	32,92
23	2000	15cm	8,51	0,31	0,01	0,71	0,26	2,37	0,04	18,62	33,86
25	2000	15cm									
27	2000	15cm									
29	2000	15cm									
31	2000	15cm									
33	2000	15cm									
35	2000	15cm									
37	2000	15cm									
39	2000	15cm									
41	2000	15cm									
43	2000	15cm									
45	2000	15cm	8,20	0,78	0,77	18,24	0,38	5,97	0,91	21,64	55,97
47	2000	15cm	8,39	0,66	0,02	10,59	0,23	6,99	0,73	21,33	54,13
49	2000	15cm	7,89	0,54	0,00	1,76	0,88	5,88	0,10	22,73	43,12
51	2000	15cm	7,80	1,31	0,02	5,37	1,13	7,11	0,38	20,60	46,04
1	2001	15cm	8,37	0,33	0,00	13,48	0,17	10,15	0,91	19,36	52,45
3	2001	15cm	8,28	1,45	0,00	6,43	1,02	9,38	0,39	15,31	35,48
5	2001	15cm	8,42	0,86	0,00	1,96	0,27	11,35	0,05	17,71	33,03
7	2001	15cm	8,38	0,43	0,01	1,77	0,32	11,74	0,28	19,24	35,13
9	2001	15cm	8,45	0,36	0,00	1,52	0,20	8,72	0,17	12,94	22,55
11	2001	15cm	8,18	0,30	0,01	1,32	0,24	8,01	0,04	18,52	34,10
13	2001	15cm	8,08	0,40	0,00	1,10	0,39	5,37	0,88	15,85	29,63
15	2001	15cm	8,15	0,37	0,00	1,16	0,25	4,24	0,04	16,78	31,12
17	2001	15cm	8,20	0,23	0,03	0,78	0,21	2,89	0,03	16,11	29,92
19	2001	15cm	8,20	0,27	0,01	1,07	0,21	3,05	0,01	15,31	28,65
21	2001	15cm	8,20	0,37	0,03	1,17	0,24	2,47	0,02	16,84	31,85
23	2001	15cm	8,23	0,39	0,00	1,54	0,18	2,03	0,04	18,22	34,52
25	2001	15cm	7,95	0,28	0,01	0,94	0,11	1,24	0,00	17,47	33,41
27	2001	15cm	8,07	0,30	0,03	0,85	0,26	1,36	0,04	17,74	34,05
29	2001	15cm	8,03	0,34	0,05	1,19	0,40	1,54	0,05	20,29	38,68
31	2001	15cm	8,10	0,34	0,03	1,40	0,34	0,87	0,08	20,07	38,48
33	2001	15cm	8,20	0,41	0,32	3,93	0,23	0,05	0,04	19,37	37,27
35	2001	15cm	7,98	0,17	2,42	10,68	0,29	0,11	0,24	21,57	41,87
37	2001	15cm	7,87	0,14	0,52	4,74	0,17	0,02	0,02	12,94	31,01
39	2001	15cm	8,05	0,11	0,02	0,69	0,28	0,30	0,01	17,12	33,98
41	2001	15cm	8,18	0,19	0,03	1,26	0,40	0,66	0,04	21,49	41,77
43	2001	15cm	8,20	0,10	0,04	1,56	0,41	0,06	0,11	21,41	40,82
45	2001	15cm	7,95	0,34	0,04	2,08	0,36	0,47	0,38	21,08	40,55
47	2001	15cm	8,25	0,23	0,04	2,56	0,38	1,10	0,37	21,77	41,56
49	2001	15cm		0,19	0,05	0,83	0,66	0,67	0,06	21,62	41,30
51	2001	15cm	8,08	0,27	0,00	1,35	0,27	2,25	0,04	14,72	27,89

1	2002	15cm									
3	2002	15cm									
5	2002	15cm	7,49	19,44	0,03	1,56	1,79	1,63	0,31	4,99	65,97
7	2002	15cm									
9	2002	15cm									
11	2002	15cm		0,53	0,36	8,31	0,81	3,64	0,07	12,83	55,64
13	2002	15cm	7,88		1,35	2,08	1,73	10,50	0,14	5,57	94,00
15	2002	15cm	7,90	0,00	0,38	0,37	1,68	2,36	0,08	3,87	90,75
17	2002	15cm	8,25		0,24	0,07	1,98	0,90	0,07	0,66	99,14
19	2002	15cm	8,30		0,00	2,52	0,69	1,16	0,10	12,77	51,00
21	2002	15cm	8,30	4,74	0,07	1,69	0,30	1,03	0,00	15,85	34,16
23	2002	15cm		4,37	0,07	1,55	0,28	1,01	0,03	12,70	19,70
25	2002	15cm		4,28	0,08	1,59	0,22	0,97	0,08	12,23	24,33
27	2002	15cm									
29	2002	15cm		0,54	0,20	1,43	0,47	2,40	0,03	21,24	41,85
31	2002	15cm									
33	2002	15cm	8,27	2,03	0,37	0,06	0,80	2,83	0,02	13,24	57,56
35	2002	15cm	8,40	0,27	2,42	0,63	0,95	17,51	0,01	12,08	63,14
37	2002	15cm									
39	2002	15cm	7,95	5,70	0,47	0,53	0,47	4,02	0,03	21,51	45,09
41	2002	15cm	8,25	1,77	0,25	0,86	0,45	1,80	0,03	21,55	43,09
43	2002	15cm	8,25	6,87	0,53	1,23	0,52	3,91	0,00	20,78	45,16
45	2002	15cm	8,25	6,64	0,55	1,25	0,45	4,43	0,00	20,48	44,44
47	2002	15cm	7,95	0,41	1,89	1,76	0,06	14,56	0,00	15,10	29,73
49	2002	15cm	7,90	8,23	0,51	0,84	0,84	2,68	0,04	15,05	57,81
51	2002	15cm									
1	2003	15cm									
3	2003	15cm									
5	2003	15cm									
7	2003	15cm									
9	2003	15cm	7,00	0,00	0,34	2,90	0,85	0,41	0,05	0,46	44,04
11	2003	15cm									
13	2003	15cm									
15	2003	15cm									
17	2003	15cm									
19	2003	15cm	6,98	13,11	2,74	18,30	0,38	1,71	0,21	9,17	28,48
21	2003	15cm	7,25	4,78	1,43	11,99	0,30	9,91	0,06	15,63	35,04
23	2003	15cm	7,73	1,25	1,80	12,44	0,27	12,17	0,05	20,79	41,49
25	2003	15cm	7,83	1,37	1,43	10,66	0,29	16,88	0,04	22,50	44,77
27	2003	15cm	7,90	1,40	3,14	22,79	0,25	17,36	0,17	22,29	44,23
29	2003	15cm	8,13	1,49	1,10	10,97	0,31	26,28	0,08	23,00	50,16
31	2003	15cm	8,04	1,59	0,86	8,84	0,32	20,85	0,04	21,36	47,41
33	2003	15cm									
35	2003	15cm	8,03	2,90	1,39	12,40	0,39	22,34	0,10	21,61	48,78
37	2003	15cm	7,97	1,72	0,25	4,65	0,43	12,70	0,07	20,63	45,15
39	2003	15cm	7,75	1,90	0,58	6,18	0,40	16,83	0,03	18,93	39,15
41	2003	15cm	8,05	1,05	0,45	5,85	0,38	7,18	0,00	18,75	38,68
43	2003	15cm	7,98	0,73	0,40	4,35	0,32	3,11	0,02	16,20	33,86
45	2003	15cm	7,98	0,49	0,76	9,85	0,23	2,55	0,17	12,23	27,50
47	2003	15cm	8,00	0,41	0,78	7,74	0,25	8,56	0,18	12,28	27,61
49	2003	15cm	8,04	0,42	0,63	7,71	0,10	8,50	0,00	14,05	36,17
51	2003	15cm	8,08	0,59	0,42	5,19	0,24	8,48	0,08	15,05	37,97

1	2004	15cm									
3	2004	15cm	8,07	0,66	2,08	21,84	0,29	13,73	0,43	19,20	38,23
5	2004	15cm	8,07	0,69	0,16	14,29	0,20	14,92	0,04	18,99	38,00
7	2004	15cm	8,13	0,65	0,12	4,81	0,14	11,07	0,23	19,60	39,25
9	2004	15cm	7,95	0,54	0,09	2,47	0,08	13,63	0,14	19,42	38,93
11	2004	15cm	8,07	0,57	0,19	2,78	0,11	11,76	0,34	19,49	39,13
13	2004	15cm	8,02	0,54	0,29	2,64	0,07	9,34	0,14	18,37	37,19
15	2004	15cm	8,03	0,58	0,14	2,99	0,06	5,94	0,12	17,60	36,35
17	2004	15cm	7,95	0,45	0,72	5,60	0,41	4,02	0,09	20,35	39,91
19	2004	15cm	7,83	1,21	0,22	6,78	0,33	4,40	0,13	13,16	32,87
21	2004	15cm	7,85	0,48	0,19	2,91	0,27	3,10	0,02	15,00	37,93
23	2004	15cm	7,95	0,38	0,45	5,42	0,30	2,40	0,05	15,36	42,15
25	2004	15cm	8,02	0,36	0,14	2,12	0,30	2,27	0,00	18,14	40,02
27	2004	15cm	8,05	0,31	0,29	2,91	0,30	2,30	0,00	19,98	44,02
29	2004	15cm	8,05	0,30	0,30	2,28	0,30	2,19	0,00	20,99	45,94
31	2004	15cm	8,25	0,65	0,36	3,31	0,40	1,36	0,00	21,74	47,59
33	2004	15cm	8,33	0,52	0,31	2,93	0,36	1,82	0,00	22,76	49,71
35	2004	15cm	8,40	0,74	0,32	3,95	0,39	2,14	0,04	22,43	48,85
37	2004	15cm	8,23	0,66	0,26	2,18	0,42	2,97	0,00	22,30	48,84
39	2004	15cm	8,42	0,86	0,45	3,40	0,41	2,48	0,05	22,26	49,39
41	2004	15cm	8,40	0,91	0,45	3,33	0,35	2,12	0,06	21,92	48,31
43	2004	15cm	8,00	0,38	0,34	2,11	0,30	1,20	0,08	16,42	39,69
45	2004	15cm	8,24	0,51	0,38	2,86	0,31	1,84	0,07	20,44	45,70
47	2004	15cm	8,13	0,74	0,16	2,28	0,39	2,01	0,09	21,51	47,39
49	2004	15cm	8,16	0,71	0,15	1,83	0,27	3,83	0,14	21,24	46,04
51	2004	15cm	8,22	0,60	0,74	4,39	0,47	3,00	0,04	23,26	49,38
1	2005	15cm									
3	2005	15cm	8,38	0,32	0,05	2,31	0,21	14,11	0,05	14,52	24,53
5	2005	15cm	7,36	0,44	0,24	4,21	0,22	15,65	0,07	15,04	27,40
7	2005	15cm	8,33	0,54	0,38	4,93	0,26	15,93	0,06	15,81	28,22
9	2005	15cm	8,38	0,50	0,20	3,37	0,24	14,25	0,05	17,38	30,26
11	2005	15cm									
13	2005	15cm	8,40	0,49	0,59	6,61	0,28	10,70	0,09	15,33	26,17
15	2005	15cm	8,41	0,42	0,16	2,07	0,22	5,50	0,07	13,11	22,38
17	2005	15cm	8,23	0,41	3,45	3,87	0,36	3,51	1,68	12,81	22,04
19	2005	15cm	8,55	0,31	0,20	1,30	0,32	2,44	0,08	13,37	23,40
21	2005	15cm	8,48	0,26	0,16	1,27	0,27	1,27	0,04	13,91	24,37
23	2005	15cm	8,48	0,80	0,43	3,13	0,35	0,71	0,06	14,69	25,84
25	2005	15cm	8,53	0,44	0,98	10,19	0,26	0,41	0,13	15,63	27,02
27	2005	15cm	8,60	0,58	0,40	3,25	0,29	0,39	0,06	16,18	28,36
29	2005	15cm	8,58	0,38	0,12	1,58	0,25	0,58	0,05	16,25	28,68
31	2005	15cm	8,16	0,54	1,00	1,65	0,38	10,47	0,08	17,98	32,93
33	2005	15cm	8,43	0,40	0,12	1,98	0,26	0,84	0,05	18,00	33,56
35	2005	15cm	8,31	0,51	1,07	6,72	0,10	0,70	0,32	12,90	27,74
37	2005	15cm	8,30	0,37	0,34	2,44	0,15	0,76	0,05	16,97	31,23
39	2005	15cm	8,15	0,68	0,28	1,61	0,45	0,94	0,04	15,06	26,56
41	2005	15cm	8,25	1,05	1,63	13,51	0,32	1,26	0,31	16,43	28,49
43	2005	15cm	8,32	0,73	0,18	1,62	0,24	2,70	0,04	16,65	28,45
45	2005	15cm	8,32	0,63	2,25	20,09	0,23	4,24	0,05	16,52	27,99
47	2005	15cm	8,28	1,21	1,23	12,43	0,25	8,08	0,13	16,84	28,33
49	2005	15cm	8,33	1,18	0,08	1,95	0,22	10,70	0,01	18,04	29,91
51	2005	15cm	8,30	1,39	0,08	2,18	0,16	11,64	0,02	18,40	30,32

1	2006	15cm	8,32	1,04	0,81	7,69	0,25	13,81	0,22	16,88	27,66
3	2006	15cm	8,38	1,22	0,14	3,80	0,16	16,47	0,05	17,50	28,12
5	2006	15cm	8,37	0,53	0,01	4,00	0,12	14,92	0,07	18,11	28,96
7	2006	15cm	8,40	0,48	0,14	2,86	0,19	13,25	0,07	18,54	30,55
9	2006	15cm	8,28	0,28	0,09	2,53	0,20	16,89	0,03	18,50	30,05
11	2006	15cm	8,35	0,37	0,07	2,78	0,10	16,03	0,05	17,89	29,05
13	2006	15cm	8,28	0,57	0,50	5,24	0,20	12,33	0,14	17,26	28,20
15	2006	15cm	8,28	0,31	0,10	1,76	0,16	7,23	0,03	15,66	25,57
17	2006	15cm	8,32	0,57	0,08	2,29	0,14	6,68	0,05	14,22	23,28
19	2006	15cm	8,27	0,37	0,05	1,42	0,15	4,45	0,03	13,07	21,78
21	2006	15cm	8,37	0,52	0,11	1,79	0,17	3,58	0,05	13,27	22,44
23	2006	15cm	8,28	0,15	0,12	1,26	0,16	3,18	0,03	14,20	24,03
25	2006	15cm	8,25	0,20	0,04	1,19	0,11	1,98	0,02	14,96	25,51
27	2006	15cm	8,18	0,51	0,19	1,90	0,12	1,06	0,00	17,77	31,15
29	2006	15cm	8,31	0,29	0,13	1,31	0,20	0,60	0,00	19,15	33,76
31	2006	15cm	8,27	0,60	0,47	3,58	0,17	0,68	0,00	19,56	34,22
33	2006	15cm									
35	2006	15cm	8,33	0,34	0,03	1,73	0,25	0,21	0,25	19,68	33,76
37	2006	15cm	8,35	0,36	0,12	0,99	0,13	0,10	0,02	16,94	29,57
39	2006	15cm	8,26	0,77	0,14	1,07	0,22	0,13	0,05	19,47	33,92
41	2006	15cm	8,35	0,85	0,03	0,61	0,22	0,68	0,08	17,66	30,87
43	2006	15cm	8,04	0,44	0,14	1,42	0,13	0,93	0,04	12,98	22,64
45	2006	15cm	8,28	0,45	0,06	0,96	0,09	3,14	0,01	13,31	
47	2006	15cm	8,33	0,56	0,66	5,90	0,14	2,37	0,03	15,82	26,91
49	2006	15cm	8,35	0,41	0,05	1,34	0,14	4,03	0,01	15,23	25,71
51	2006	15cm	8,31	0,51	0,48	6,38	0,16	7,74	0,02	15,84	26,67
1	2007	15cm	8,36	0,47	0,03	1,92	0,16	8,01	0,05	16,15	26,57
3	2007	15cm	8,33	0,49	0,13	2,76	0,32	8,81	0,12	15,19	25,03
5	2007	15cm	8,27	0,32	0,23	3,11	0,24	8,20	0,07	14,80	24,29
7	2007	15cm	8,35	0,21	0,02	2,23	0,19	9,17	0,05	14,76	23,60
9	2007	15cm	8,28	0,20	0,08	2,08	0,17	7,66	0,04	14,44	23,76
11	2007	15cm	8,35	1,70	0,94	6,53	0,18	6,17	0,05	13,28	22,78
13	2007	15cm	8,35	0,36	0,07	1,79	0,17	7,00	0,03	15,11	25,11
15	2007	15cm	8,30	1,10	0,07	2,03	0,15	1,87	0,07	15,60	25,29
17	2007	15cm	8,40	0,16	0,63	5,84	0,21	7,28	0,05	15,93	26,64
19	2007	15cm	8,30	0,34	0,11	2,74	0,20	2,51	0,03	13,49	25,63
21	2007	15cm	8,35	0,34	0,16	5,43	0,25	2,11	0,07	16,16	27,55
23	2007	15cm	8,33	0,07	0,15	2,29	0,12	0,19	0,02	9,76	16,36
25	2007	15cm	8,36	0,47	0,03	1,92	0,16	8,01	0,05	16,15	26,57
27	2007	15cm	8,08	0,07	1,54	14,95	0,76	0,34	0,08	17,87	31,07
29	2007	15cm	8,17	0,03	0,12	1,86	0,11	0,17	0,02	17,44	30,19
31	2007	15cm	8,08	0,03	0,02	5,02	0,11	0,27	0,00	18,86	32,67
33	2007	15cm	8,24	0,43	0,07	3,60	0,07	0,07	0,03	19,13	33,26
35	2007	15cm	8,20	0,43	1,16	8,36	0,16	0,39	0,07	19,27	33,51
37	2007	15cm	8,00	0,69	0,02	2,52	0,03	0,57	0,02	18,96	32,76
39	2007	15cm	8,12	0,41	0,42	3,43	0,16	0,24	0,00	17,50	30,12
41	2007	15cm	8,03	0,42	0,15	1,50	0,13	0,32	0,00	18,87	32,23
43	2007	15cm	8,00	0,15	0,49	2,79	0,18	0,32	0,00	20,35	33,75
45	2007	15cm	8,07	0,30	0,47	4,26	0,22	1,43	0,01	21,60	35,36
47	2007	15cm	7,95	0,25	0,43	4,52	0,15	1,66	0,01	18,39	26,71
49	2007	15cm	8,13	0,33	0,70	8,95	0,19	2,38	0,23	19,09	26,30
51	2007	15cm	8,22	0,09	0,15	2,26	0,19	0,19	0,02	14,36	29,56

1	2008	15cm	8,35	0,30	0,00	1,57	0,50	4,16	0,00	12,61	19,35
3	2008	15cm	8,40	0,45	0,44	5,17	0,43	4,01	0,00	14,34	22,21
5	2008	15cm	8,42	0,51	0,16	1,49	0,29	3,25	0,00	12,70	19,57
7	2008	15cm	8,32	0,33	0,63	5,66	0,72	3,09	0,00	16,39	25,87
9	2008	15cm	8,30	0,24	0,04	2,02	0,35	4,23	0,00	16,54	26,07
11	2008	15cm	8,32	0,08	0,27	3,22	0,20	4,39	0,10	10,28	22,82
13	2008	15cm	8,35	0,47	0,32	2,17	0,16	3,71	0,02	14,30	22,39
15	2008	15cm	8,37	0,35	0,63	5,17	0,11	5,46	0,06	15,41	24,76
17	2008	15cm	8,35	0,37	0,13	1,10	0,44	3,44	0,00	15,06	24,33
19	2008	15cm	8,22	0,22	0,00	0,76	0,19	1,86	0,00	13,02	21,29
21	2008	15cm	8,41	0,26	0,11	2,05	0,21	2,28	0,01	15,92	26,39
23	2008	15cm	8,50	0,27	0,13	2,23	0,23	1,23	0,06	15,22	25,28
25	2008	15cm	8,50	0,08	0,10	1,77	0,25	1,22	0,03	14,71	24,25
27	2008	15cm	8,35	0,23	0,20	2,83	0,17	0,46	0,01	16,23	27,24
29	2008	15cm									
31	2008	15cm									
33	2008	15cm	8,57	0,55	0,25	1,48	0,20	0,20	0,02	19,75	34,81
35	2008	15cm	8,40	0,55	0,23	1,50	0,19	0,25	0,02	20,66	36,37
37	2008	15cm	8,25	0,29	0,03	7,81	0,54	0,40	1,32	14,64	27,84
39	2008	15cm	8,30	0,10	0,18	1,16	0,22	0,12	0,03	23,99	50,92
41	2008	15cm	8,30	0,28	0,72	6,45	0,24	0,12	0,04	21,23	36,41
43	2008	15cm	8,13	0,38	0,04	1,59	0,16	0,02	0,00	19,15	32,84
45	2008	15cm	8,18	0,51	0,13	5,82	0,11	1,93	0,06	19,32	32,62
47	2008	15cm	8,33	1,25	0,11	2,32	0,07	0,05	0,00	19,21	32,37
49	2008	15cm	8,28	1,00	0,01	1,52	0,06	0,09	0,02	17,92	30,10
51	2008	15cm	8,15	0,67	0,34	3,02	0,11	0,95	0,02	18,66	31,06

Table 38: Complete 25cm data

Week	Year	Depth	pH	Cl ⁻ [mg/l]	NH ₄ ⁺ [mg/l]	SO ₄ ⁻⁻ [mg/l]	Na ⁺ [mg/l]	NO ₃ ⁻ [mg/l]	K ⁺ [mg/l]	Mg ⁺⁺ [mg/l]	Ca ⁺⁺ [mg/l]
1	2000	25cm	8,21	0,67	0,00	1,51	0,24	5,95	0,06	18,89	31,49
3	2000	25cm	8,21	0,66	0,00	1,77	0,17	5,77	0,03	18,53	36,37
5	2000	25cm	8,16	0,25	0,00	1,73	0,25	5,45	0,06	16,62	30,50
7	2000	25cm	8,16	0,28	0,00	1,70	0,20	4,68	0,04	15,73	30,26
9	2000	25cm	8,17	0,54	0,06	1,38	0,52	3,24	0,40	14,71	30,41
11	2000	25cm	8,13	0,32	0,00	0,96	0,17	1,82	0,02	15,96	28,74
13	2000	25cm	7,79	0,13	0,00	0,73	0,16	1,23	0,11	12,76	22,18
15	2000	25cm	8,04	0,40	0,00	1,06	0,16	1,59	0,12	16,11	26,77
17	2000	25cm	8,03	0,27	0,00	0,36	0,19	1,25	0,04	14,56	24,86
19	2000	25cm	8,47	0,30	0,00	0,33	0,23	1,04	0,04	13,51	23,39
21	2000	25cm	8,22	0,39	0,00	0,40	0,22	0,75	0,02	15,91	27,80
23	2000	25cm	8,55	0,33	0,00	0,49	0,27	0,13	0,00	17,91	23,71
25	2000	25cm	8,19	0,35	0,00	0,60	0,59	0,15	0,06	23,85	41,90
27	2000	25cm	8,08	0,42	0,00	0,68	0,39	0,00	0,00	25,36	43,75
29	2000	25cm									
31	2000	25cm									
33	2000	25cm	8,30	0,60	0,00	0,93	0,38	0,27	0,00	27,40	47,18
35	2000	25cm	8,47	0,44	0,00	0,73	0,30	0,00	0,03	25,91	44,88
37	2000	25cm	8,05	1,19	0,00	0,93	0,31	0,00	0,00	25,71	45,61
39	2000	25cm	8,45	0,95	0,00	1,04	0,39	0,00	0,03	26,45	45,99
41	2000	25cm	8,50	0,60	0,00	0,96	0,22	0,00	0,00	25,51	44,31
43	2000	25cm	8,44	0,55	0,00	0,79	0,24	0,00	0,03	26,10	44,95
45	2000	25cm	8,48	0,55	0,00	1,00	0,26	0,00	0,08	25,65	44,09
47	2000	25cm	8,53	0,60	0,00	0,76	0,22	0,24	0,00	24,39	41,96
49	2000	25cm	7,90	0,65	0,00	0,70	0,22	0,37	0,03	23,91	41,18
51	2000	25cm	7,51	0,37	0,43	3,76	0,21	1,02	0,07	9,91	18,96
1	2001	25cm	8,27	0,38	0,03	1,44	0,39	1,24	0,59	16,42	28,64
3	2001	25cm	8,37	0,37	0,00	1,22	0,32	0,91	0,40	16,32	28,21
5	2001	25cm	8,28	0,42	0,00	1,22	0,41	1,18	0,80	16,70	28,82
7	2001	25cm	8,33	0,31	0,01	1,49	0,28	2,08	0,17	17,00	29,29
9	2001	25cm	8,32	0,26	0,15	1,07	0,19	1,32	0,06	19,15	33,22
11	2001	25cm	8,08	0,25	0,00	0,83	0,24	0,59	0,03	16,60	28,83
13	2001	25cm	8,10	0,18	0,04	0,82	0,37	0,43	0,15	13,11	23,31
15	2001	25cm	8,03	0,25	0,00	0,83	0,25	0,59	0,03	13,66	24,40
17	2001	25cm	8,18	0,19	0,00	0,44	0,22	0,41	0,05	13,83	24,61
19	2001	25cm	8,22	0,46	0,00	0,64	0,55	0,44	1,04	14,48	25,49
21	2001	25cm	8,28	0,24	0,00	0,53	0,19	0,42	0,03	14,76	26,17
23	2001	25cm	8,20	0,31	0,00	0,64	0,17	0,37	0,02	16,37	29,23
25	2001	25cm	8,00	0,42	0,00	1,18	0,17	0,29	0,04	23,47	40,77
27	2001	25cm	7,90	0,49	0,00	1,00	0,40	0,00	0,69	23,96	41,62
29	2001	25cm	8,20	0,42	0,00	0,84	0,26	0,00	0,07	24,79	42,89
31	2001	25cm									
33	2001	25cm									
35	2001	25cm		0,09	0,07	0,07	0,13	0,05	0,03	1,70	6,60
37	2001	25cm	8,20	0,08	0,05		0,12	0,00	0,05		
39	2001	25cm	8,20	0,25	0,00	2,30	0,33	0,00	0,00	17,71	35,70
41	2001	25cm	8,00	0,19	0,00	1,39	0,35	0,00	0,00	18,38	34,49
43	2001	25cm									
45	2001	25cm	8,00	0,46	0,00	0,80	0,46	0,65	0,09	16,67	31,14
47	2001	25cm	8,30	0,12	0,00	0,76	0,35	0,84	0,03	16,94	31,33
49	2001	25cm	8,30	0,18	0,00	0,75	0,23	2,05	0,00	16,38	29,87
51	2001	25cm	7,95	0,19	0,03	0,89	0,97	0,51	0,06	21,49	40,79

1	2002	25cm	8,45	0,25	0,00	1,39	0,32	0,57	0,00	13,23	24,69
3	2002	25cm									
5	2002	25cm	8,18	0,26	0,05	1,20	1,00	0,79	0,02	9,72	37,95
7	2002	25cm	8,13	1,18	0,00	0,96	0,23	0,83	0,00	11,22	21,72
9	2002	25cm	8,28	0,55	0,00	0,87	0,16	0,57	0,00	11,58	21,87
11	2002	25cm	8,23	0,57	0,00	1,05	0,11	0,59	0,02	12,10	22,63
13	2002	25cm	8,40	0,29	0,00	0,53	0,12	0,64	0,00	8,23	16,49
15	2002	25cm	8,35	0,40	0,00	0,64	0,13	0,68	0,00	11,21	21,32
17	2002	25cm	8,28	0,19	0,00	1,67	0,13	1,04	0,00	11,62	22,13
19	2002	25cm	8,38	0,26	0,00	2,01	0,15	0,90	0,00	11,42	22,05
21	2002	25cm	8,38	0,16	0,03	0,97	0,17	0,59	0,05	12,54	24,23
23	2002	25cm	8,33	0,18	0,04	0,76	0,26	0,66	0,10	14,00	27,22
25	2002	25cm	8,35	0,22	0,06	0,75	0,33	0,68	0,06	17,37	36,08
27	2002	25cm									
29	2002	25cm			0,00		0,15		0,60	8,17	16,42
31	2002	25cm									
33	2002	25cm	8,25	1,73	0,00	0,15	0,19	1,26	0,00	12,25	26,20
35	2002	25cm	8,30	0,25	0,00	0,15	0,19	1,22	0,00	14,97	29,78
37	2002	25cm	8,45	0,25	0,00	1,39	0,32	0,57	0,00	13,23	24,69
39	2002	25cm	8,10	0,18	0,07	0,00	0,04	2,48	0,04	19,28	37,18
41	2002	25cm	8,15	0,10	0,00	0,29	0,21	1,03	0,00	19,79	37,56
43	2002	25cm	8,30	0,23	0,00	1,72	0,18	1,62	0,06	17,63	34,23
45	2002	25cm	8,15	0,45	0,00	0,11	0,20	1,05	0,03	16,61	32,21
47	2002	25cm	8,10	0,57	0,00	0,00	0,14	1,00	0,00	14,03	27,71
49	2002	25cm									
51	2002	25cm									
1	2003	25cm									
3	2003	25cm	7,00	0,00	3,41	12,81	0,81	0,67	0,23	2,53	42,41
5	2003	25cm	7,55	1,29	0,03	1,85	0,17	1,94	0,01	12,87	26,14
7	2003	25cm	7,75	0,64	0,00	1,71	0,16	5,16	0,07	14,02	27,16
9	2003	25cm									
11	2003	25cm	8,00	0,62	0,00	1,91	0,12	8,52	0,00	14,26	26,79
13	2003	25cm	7,90	0,68	0,00	1,48	0,10	5,97	0,00	14,14	26,61
15	2003	25cm									
17	2003	25cm	8,45	0,29	0,00	0,59	0,36	1,42	0,00	13,17	24,65
19	2003	25cm	7,15	32,01	6,85	36,92	0,64	1,42	0,41	6,39	35,14
21	2003	25cm	7,47	1,54	0,55	8,09	0,29	3,12	0,06	15,64	31,04
23	2003	25cm	7,45	0,68	0,29	3,59	0,29	2,68	0,06	17,63	33,69
25	2003	25cm	8,30	0,71	0,19	4,14	0,33	3,65	0,10	19,26	36,22
27	2003	25cm	8,00	0,84	0,36	5,74	0,36	2,76	0,42	21,89	40,47
29	2003	25cm									
31	2003	25cm									
33	2003	25cm									
35	2003	25cm									
37	2003	25cm									
39	2003	25cm									
41	2003	25cm									
43	2003	25cm	7,83	0,47	0,34	3,83	0,17	0,28	0,03	3,47	11,18
45	2003	25cm	7,99	0,28	0,13	1,92	0,14	0,93	0,03	7,38	16,14
47	2003	25cm	8,05	0,47	0,22	2,43	0,13	1,56	0,01	7,40	16,14
49	2003	25cm	8,08	0,45	0,00	2,42	0,10	1,52	0,00	11,36	28,56
51	2003	25cm		0,55	0,01	2,46	0,13	2,64	0,04	12,33	29,91

1	2004	25cm									
3	2004	25cm	7,93	0,73	0,15	2,60	0,44	3,98	1,12	15,77	30,67
5	2004	25cm	7,95	0,89	0,01	2,74	0,17	3,95	0,03	16,67	30,65
7	2004	25cm		0,60	0,03	1,57	0,06	2,53	0,09	17,29	33,04
9	2004	25cm	8,15	0,52	0,00	1,72	0,05	1,72	0,06	18,07	34,20
11	2004	25cm	8,10	0,49	0,00	1,70	0,06	2,47	0,10	18,17	34,42
13	2004	25cm	7,93	0,51	0,05	1,69	0,08	2,24	0,09	18,07	34,18
15	2004	25cm	7,85	0,47	0,00	0,99	0,02	1,33	0,15	17,54	33,77
17	2004	25cm	8,02	0,23	0,04	0,95	0,23	0,95	0,03	21,53	39,02
19	2004	25cm	8,10	0,39	0,00	1,11	0,22	0,00	0,10	12,65	29,79
21	2004	25cm	8,08	0,28	0,00	1,16	0,21	1,85	0,04	13,70	33,83
23	2004	25cm	8,00	0,58	0,00	1,31	0,35	1,19	0,11	12,85	34,98
25	2004	25cm	8,08	0,32	0,00	1,53	0,33	0,90	0,28	16,21	34,68
27	2004	25cm	8,00	0,25	0,00	2,51	0,32	0,28	0,09	17,85	38,12
29	2004	25cm	8,20	0,19	0,00	1,65	0,30	0,70	0,00	18,95	39,74
31	2004	25cm	8,33	0,30	0,00	1,66	0,32	0,27	0,00	19,87	41,63
33	2004	25cm	8,20	0,24	0,00	0,81	0,32	0,00	0,00	14,67	33,83
35	2004	25cm	8,40	0,84	0,45	2,97	0,44	0,55	0,10	24,47	49,33
37	2004	25cm	8,30	0,65	0,07	1,69	0,34	0,31	0,08	25,88	52,01
39	2004	25cm	8,50	0,48	0,02	2,99	0,37	0,06	0,10	25,39	51,91
41	2004	25cm	8,40	0,72	0,01	1,44	0,28	0,31	0,06	23,60	49,04
43	2004	25cm	8,07	0,38	0,20	1,90	0,29	2,98	0,04	15,34	34,44
45	2004	25cm	8,25	0,49	0,01	2,11	0,38	3,53	0,26	18,99	40,59
47	2004	25cm	8,15	0,66	0,01	1,95	0,31	3,77	0,08	19,28	41,74
49	2004	25cm	8,08	0,95	0,10	2,81	0,33	2,41	0,04	19,72	39,47
51	2004	25cm	8,18	0,39	0,62	1,94	0,72	1,25	0,05	21,60	42,93
1	2005	25cm									
3	2005	25cm	8,27	0,46	0,03	2,29	0,23	9,17	0,05	13,78	22,42
5	2005	25cm	8,32	0,46	0,04	2,76	0,20	9,95	0,12	12,88	23,09
7	2005	25cm	8,30	0,71	0,06	2,59	0,21	9,05	0,04	15,11	24,15
9	2005	25cm	8,25	1,26	0,03	1,97	0,20	6,17	0,03	14,08	22,83
11	2005	25cm	8,30	0,57	0,12	1,34	0,31	3,54	0,28	12,80	19,73
13	2005	25cm	8,43	0,53	0,10	1,42	0,53	3,23	0,06	14,29	23,04
15	2005	25cm	8,48	0,14	0,11	0,98	0,20	1,50	0,05	12,61	20,19
17	2005	25cm	7,85	0,31	0,71	0,73	0,31	0,70	0,74	9,73	14,76
19	2005	25cm	8,33	0,22	0,13	0,92	0,32	1,15	0,08	11,26	18,68
21	2005	25cm	8,40	0,17	0,12	0,90	0,30	0,07	0,05	11,60	19,04
23	2005	25cm	8,20	0,54	0,11	2,17	0,33	1,00	0,24	15,47	25,46
25	2005	25cm	8,50	0,33	0,04	1,17	0,36	0,00	0,29	13,50	22,09
27	2005	25cm	8,57	0,39	0,06	1,09	0,39	0,76	0,05	14,24	23,42
29	2005	25cm	8,65	0,43	0,04	1,58	0,35	0,00	0,06	17,78	29,75
31	2005	25cm	8,43	0,32	0,02	2,46	0,46	0,62	0,06	19,25	33,68
33	2005	25cm	8,57	0,44	0,01	1,52	0,32	0,00	0,06	22,99	41,86
35	2005	25cm	8,28	0,47	0,67	1,20	0,14	0,12	0,19	15,40	31,81
37	2005	25cm	8,28	0,15	0,42	0,70	0,08	0,05	0,02	15,70	32,47
39	2005	25cm	8,30	0,10	0,32	0,51	0,23	0,10	0,05	8,69	14,92
41	2005	25cm	8,20	0,37	0,05	3,74	0,21	0,18	0,14	13,71	23,81
43	2005	25cm	8,33	0,92	0,00	4,19	0,33	0,25	0,12	17,74	29,01
45	2005	25cm	8,38	0,64	0,12	3,88	0,29	1,76	0,01	17,68	28,57
47	2005	25cm	8,28	0,86	0,17	3,82	0,29	0,55	0,08	17,71	28,54
49	2005	25cm	8,28	0,58	0,04	4,62	0,29	2,85	0,05	17,42	27,66
51	2005	25cm	8,33	0,78	0,00	2,51	0,20	3,47	0,01	15,62	24,33

1	2006	25cm	8,35	0,74	0,02	2,10	0,21	1,70	0,14	16,39	25,58
3	2006	25cm	8,38	1,22	0,03	2,08	0,33	5,02	0,11	16,88	26,39
5	2006	25cm									
9	2006	25cm	8,35	0,42	0,02	2,72	0,21	4,24	0,04	17,34	26,84
11	2006	25cm	8,35	0,47	0,07	2,03	0,23	5,11	0,04	19,05	29,08
13	2006	25cm	8,25	1,21	0,02	1,72	0,20	2,32	0,10	18,96	29,42
15	2006	25cm	8,30	0,58	0,02	1,14	0,16	1,88	0,03	16,03	25,07
17	2006	25cm	8,28	0,27	0,06	0,74	0,15	1,85	0,02	13,93	21,86
19	2006	25cm	8,33	0,19	0,01	0,71	0,16	1,99	0,03	11,96	19,02
21	2006	25cm	8,28	0,33	0,01	0,99	0,17	0,55	0,05	13,98	22,51
23	2006	25cm	8,28	0,27	0,00	1,09	0,15	0,17	0,02	14,87	24,22
25	2006	25cm	8,17	0,18	0,06	1,03	0,12	0,16	0,03	11,02	17,85
27	2006	25cm	8,20	0,31	0,06	1,68	0,12	0,80	0,00	16,08	26,81
29	2006	25cm	8,32	0,25	0,07	1,76	0,29	2,02	0,00	19,44	32,48
31	2006	25cm									
33	2006	25cm									
35	2006	25cm	8,35	0,50	0,04	3,96	0,74	0,69	2,13	20,09	33,41
37	2006	25cm	8,25	0,69	0,02	2,25	0,35	0,00	0,07	20,68	33,94
39	2006	25cm	8,15	0,22	0,03	2,63	0,29	0,42	0,04	21,30	34,82
41	2006	25cm	8,25	0,65	0,00	2,03	0,00	0,31	0,00	21,41	35,00
43	2006	25cm	7,27	0,24	0,31	1,97	0,22	0,17	0,13	3,12	5,70
45	2006	25cm	8,35	0,62	0,02	1,52	0,10	2,25	0,00	13,72	
47	2006	25cm	8,30	0,91	0,02	1,48	0,11	0,35	0,01	12,22	19,63
49	2006	25cm	8,25	0,84	0,00	1,30	0,11	1,84	0,00	12,16	19,45
51	2006	25cm	8,30	0,96	0,02	1,48	0,19	3,72	0,04	13,01	20,72
1	2007	25cm	8,37	1,10	0,01	1,55	0,18	3,74	0,03	12,90	20,37
3	2007	25cm	8,37	0,69	0,01	1,56	0,20	3,94	0,06	12,81	19,86
5	2007	25cm	8,38	0,40	0,01	0,83	0,15	2,10	0,02	11,67	18,12
7	2007	25cm	8,27	0,44	0,01	2,02	0,20	2,03	0,55	12,47	21,58
9	2007	25cm	8,27	0,67	0,02	1,29	0,19	1,54	0,05	12,33	19,35
11	2007	25cm	8,28	0,39	0,01	0,65	0,16	0,26	0,04	10,26	16,23
13	2007	25cm	8,33	0,26	0,02	0,69	0,18	0,98	0,04	11,16	17,59
15	2007	25cm	8,33	0,48	0,00	0,77	0,12	0,51	0,02	13,80	21,60
17	2007	25cm	8,25	0,70	0,02	1,98	0,20	0,47	0,06	14,02	22,28
19	2007	25cm	8,33	0,53	0,02	1,17	0,25	1,78	0,04	13,90	25,16
21	2007	25cm	8,38	0,32	0,01	1,22	0,21	0,02	0,03	13,91	22,44
23	2007	25cm	8,26	0,23	0,03	0,83	0,16	0,02	0,03	13,87	22,83
25	2007	25cm	8,32	0,66	0,00	0,81	0,16	2,21	0,07	13,57	24,69
27	2007	25cm	8,28	0,16	0,01	2,38	0,24	0,37	0,03	16,10	26,68
29	2007	25cm	8,10	0,02	0,00	2,21	0,21	0,00	0,03	16,85	27,84
31	2007	25cm		0,06	0,10	2,18	0,19	0,00	0,00	16,50	26,80
33	2007	25cm									
35	2007	25cm	8,22	0,09	0,46	2,86	0,20	0,13	0,05	8,07	13,57
37	2007	25cm	8,13	0,68	0,00	2,76	0,00	6,29	0,00	16,56	26,98
39	2007	25cm	8,15	0,33	0,01	0,97	0,18	0,16	0,01	14,04	22,82
41	2007	25cm	8,18	0,33	0,00	1,11	0,17	0,27	0,00	15,10	24,51
43	2007	25cm	8,05	0,52	0,00	1,15	0,23	0,17	0,06	15,57	24,40
45	2007	25cm	8,05	0,87	0,00	1,16	0,15	1,43	0,00	16,25	24,84
47	2007	25cm	8,18	0,66	0,00	1,44	0,18	1,35	0,02	12,95	16,80
49	2007	25cm	8,15	0,35	0,01	0,93	0,14	1,97	0,00	13,19	15,89
51	2007	25cm	8,12	0,28	0,00	1,00	0,21	0,02	0,02	14,70	24,16

1	2008	25cm	8,38	0,17	0,00	0,91	0,19	3,10	0,00	11,18	15,82
3	2008	25cm	8,30	0,42	0,00	1,10	0,14	4,39	0,00	12,60	18,35
5	2008	25cm	8,28	0,54	0,00	1,19	0,16	3,90	0,30	9,83	13,79
7	2008	25cm	8,28	0,51	0,00	0,89	0,39	2,42	0,00	15,63	23,68
9	2008	25cm	8,27	0,37	0,00	0,93	0,17	3,67	0,19	16,86	24,52
11	2008	25cm	8,22	0,95	0,00	1,35	0,13	2,76	0,05	11,75	17,66
13	2008	25cm	8,22	0,68	0,18	1,06	0,07	2,47	0,21	10,75	15,67
15	2008	25cm	8,20	0,49	0,00	0,72	0,14	3,03	0,05	10,81	16,33
17	2008	25cm	8,18	0,46	0,00	0,70	0,17	2,37	0,00	10,36	15,87
19	2008	25cm	8,32	0,46	0,06	0,47	0,70	1,25	0,03	9,96	15,38
21	2008	25cm	8,32	0,34	0,00	0,80	0,22	0,30	0,00	12,20	19,30
23	2008	25cm	8,43	0,25	0,00	1,11	0,33	0,03	0,07	15,97	24,70
25	2008	25cm	8,42	0,29	0,00	0,84	0,36	0,01	0,02	17,98	28,35
27	2008	25cm	8,38	0,13	0,00	1,74	0,39	0,06	0,05	19,06	29,73
29	2008	25cm									
31	2008	25cm									
33	2008	25cm	8,43	0,43	0,07	4,83	0,24	0,07	0,03	16,27	27,36
35	2008	25cm	8,48	0,19	0,02	0,72	0,31	0,00	0,08	17,12	28,52
37	2008	25cm		0,22	0,00	0,77	0,01	0,74	0,53	12,08	26,16
39	2008	25cm	8,17	0,87	0,00	1,31	0,28	0,27	0,02	17,26	28,86
41	2008	25cm	8,33	0,36	0,00	1,40	0,19	2,26	0,00	17,19	27,98
43	2008	25cm	8,30	0,43	0,00	1,10	0,10	1,12	0,02	14,56	24,15
45	2008	25cm	8,33	0,62	0,01	1,67	0,15	0,07	0,05	16,27	26,37
47	2008	25cm	8,28	0,58	0,00	1,33	0,13	2,83	0,00	15,66	25,13
49	2008	25cm	8,35	0,69	0,00	1,47	0,01	0,35	0,00	14,39	22,91
51	2008	25cm	8,18	0,59	0,00	1,06	0,09	2,66	0,00	14,48	22,82

Table 39: Complete 50cm data

Week	Year	Depth	pH	Cl ⁻ [mg/l]	NH ₄ ⁺ [mg/l]	SO ₄ ⁻ [mg/l]	Na ⁺ [mg/l]	NO ₃ ⁻ [mg/l]	K ⁺ [mg/l]	Mg ⁺⁺ [mg/l]	Ca ⁺⁺ [mg/l]
1	2000	50cm	7,84	0,71	0,00	1,61	0,29	1,98	0,42	17,18	29,58
3	2000	50cm	8,16	0,51	0,00	1,43	0,19	2,40	0,08	16,66	33,03
5	2000	50cm	8,04	0,35	0,00	1,42	0,18	2,82	0,04	14,73	27,09
7	2000	50cm	7,99	0,59	0,00	1,45	0,22	3,29	0,03	13,83	27,32
9	2000	50cm	8,13	1,10	0,00	0,85	0,33	2,82	0,10	13,84	30,65
11	2000	50cm	8,05	0,49	0,00	0,97	0,36	2,01	0,02	17,40	32,06
13	2000	50cm	7,90	0,17	0,00	0,81	0,36	0,00	0,00	15,11	27,32
15	2000	50cm	8,20	0,31	0,00	0,69	0,33	1,52	0,00	18,03	30,80
17	2000	50cm	8,13	0,30	0,00	0,36	0,36	1,23	0,04	16,11	28,32
19	2000	50cm	8,51	0,36	0,00	0,51	0,56	1,37	0,07	18,04	32,23
21	2000	50cm	8,49	0,50	0,00	0,54	0,37	1,41	0,00	20,72	37,22
23	2000	50cm	8,53	0,54	0,00	0,77	0,53	0,00	0,07	22,29	28,48
25	2000	50cm	8,13	1,03	0,30	0,98	0,49	0,56	4,03	9,67	18,62
27	2000	50cm	8,02	0,68	0,00	1,06	0,57	0,00	0,03	24,56	44,08
29	2000	50cm	7,93	0,61	0,03	1,58	0,43	0,41	0,19	24,19	42,82
31	2000	50cm									
33	2000	50cm	8,32	0,57	0,00	0,93	0,30	0,31	0,00	25,45	45,54
35	2000	50cm	8,45	0,62	0,03	0,80	0,36	0,04	0,12	25,35	45,43
37	2000	50cm	8,05	0,74	0,00	1,24	0,41	0,47	0,03	23,77	43,92
39	2000	50cm	7,48	0,80	0,00	1,18	0,38	0,00	0,03	27,19	48,91
41	2000	50cm	8,44	0,81	0,00	1,15	0,42	0,00	0,00	24,73	44,71
43	2000	50cm	8,41	0,70	0,00	0,98	0,26	0,32	0,00	24,31	43,64
45	2000	50cm	8,37	0,82	0,00	1,14	0,46	0,00	0,07	24,89	44,27
47	2000	50cm	8,48	0,73	0,00	1,10	0,25	1,04	0,03	22,30	39,66
49	2000	50cm	8,08	0,70	0,00	1,23	0,23	1,71	0,00	20,97	37,61
51	2000	50cm	6,94	0,35	0,96	6,76	0,20	1,02	0,04	8,45	16,20
1	2001	50cm	8,18	0,45	0,02	1,21	0,27	0,96	0,30	14,17	25,07
3	2001	50cm	8,18	0,39	0,00	1,06	0,22	1,76	0,20	14,09	24,79
5	2001	50cm	8,23	0,51	0,05	2,04	0,38	1,67	0,61	13,71	24,04
7	2001	50cm	8,34	0,45	0,00	1,17	0,26	2,46	0,40	14,53	25,42
9	2001	50cm	8,24	0,37	0,01	0,86	0,26	1,59	0,17	17,24	31,31
11	2001	50cm	8,23	0,30	0,00	1,02	0,22	1,20	0,04	15,26	26,67
13	2001	50cm	8,00	0,24	0,01	0,65	0,17	0,90	0,03	13,06	23,26
15	2001	50cm	8,17	0,32	0,00	1,01	0,21	1,17	0,04	15,32	27,51
17	2001	50cm	8,15	0,28	0,00	0,54	0,25	0,70	0,04	15,04	27,03
19	2001	50cm	8,27	0,23	0,00	0,70	0,24	1,05	0,03	15,13	27,04
21	2001	50cm	8,17	0,33	0,00	0,78	0,21	1,14	0,02	16,69	30,03
23	2001	50cm	8,17	0,41	0,00	0,91	0,29	1,36	0,03	18,03	32,41
25	2001	50cm	8,10	0,46	0,00	1,17	0,23	0,45	0,02	21,46	38,61
27	2001	50cm	8,10	0,37	0,00	0,79	0,31	0,00	0,08	22,00	39,56
29	2001	50cm	8,20	0,31	0,00	0,61	0,28	0,10	0,02	21,64	38,95
31	2001	50cm	8,10	0,44	0,00	0,89	0,41	0,12	0,06	23,81	43,25
33	2001	50cm									
35	2001	50cm		0,17	0,05	3,58	0,28	0,15	0,06	3,28	8,51
37	2001	50cm									
39	2001	50cm									
41	2001	50cm									
43	2001	50cm									
45	2001	50cm									
47	2001	50cm									
49	2001	50cm									
51	2001	50cm									

1	2002	50cm									
3	2002	50cm									
5	2002	50cm	7,48	0,36	0,19	2,32	0,99	1,58	0,19	4,88	40,06
7	2002	50cm	8,33	0,73	0,00	0,29	0,25	0,93	0,10	15,40	28,46
9	2002	50cm	8,28	0,38	0,00	0,31	0,19	0,73	0,07	16,37	29,62
11	2002	50cm	8,38	0,34	0,00	0,79	0,13	0,78	0,03	16,66	29,57
13	2002	50cm	7,31	0,14	0,96	0,42	1,04	6,69	0,14	8,74	81,67
15	2002	50cm	8,35	0,40	0,00	0,79	0,19	0,88	0,02	16,68	30,03
17	2002	50cm	8,23	0,25	0,00	0,57	0,19	1,22	0,05	17,72	32,05
19	2002	50cm	8,30	0,22	0,00	1,61	0,21	1,20	0,00	18,58	33,69
21	2002	50cm	8,30	0,24	0,00	0,51	0,25	0,98	0,10	20,75	37,47
23	2002	50cm	8,33	0,26	0,00	0,25	0,32	0,98	0,07	22,23	40,11
25	2002	50cm	8,38	0,28	0,00	0,14	0,27	0,95	0,08	22,30	40,47
27	2002	50cm									
29	2002	50cm									
31	2002	50cm									
33	2002	50cm	8,20	0,64	0,00	0,39	0,28	1,68	0,03	25,19	46,50
35	2002	50cm	8,28	0,37	0,00	0,28	0,26	1,34	0,02	27,02	49,63
39	2002	50cm	8,10	0,49	0,00	0,00	0,44	1,52	0,03	28,57	51,75
41	2002	50cm	8,30	0,66	0,00	0,00	0,35	1,66	0,07	24,12	44,21
43	2002	50cm	8,25	0,70	0,00	0,00	0,30	1,45	0,40	23,42	43,47
45	2002	50cm	8,30	0,75	0,00	0,00	0,27	1,15	0,00	21,86	40,42
47	2002	50cm	8,30	0,55	0,00	0,00	0,20	0,63	0,11	16,90	32,33
49	2002	50cm	7,95	10,60	4,29	0,46	0,80	1,83	0,24	8,45	58,39
51	2002	50cm	7,85	5,42	1,88	0,55	0,80	2,64	0,40	16,18	43,25
1	2003	50cm	7,85	0,34	0,00	1,75	0,34	0,92	0,31	17,02	31,24
3	2003	50cm	7,88	0,02	0,00	1,28	0,35	0,00	0,43	16,71	30,32
5	2003	50cm	7,73	0,09	0,00	1,79	0,29	1,26	0,12	16,96	30,47
7	2003	50cm	7,80	0,17	0,00	1,61	0,31	4,39	0,28	18,43	32,54
9	2003	50cm	7,95	0,18	0,11	2,22	0,31	6,05	0,14	19,58	34,05
11	2003	50cm	8,15	0,79	0,00	2,24	0,25	5,56	0,08	19,59	35,33
13	2003	50cm	7,80	0,41	0,00	1,93	0,23	2,18	0,07	15,98	29,70
15	2003	50cm									
17	2003	50cm									
19	2003	50cm	7,00	13,51	1,43	8,65	0,37	0,72	0,15	2,78	17,51
21	2003	50cm	7,53	2,41	0,17	6,11	0,53	20,76	0,14	19,46	35,29
23	2003	50cm	7,90	1,01	0,22	4,88	0,43	15,28	0,12	16,06	29,72
25	2003	50cm	8,10	1,56	0,32	6,22	0,58	34,31	0,16	23,21	40,55
27	2003	50cm	7,90	1,97	0,50	9,39	0,51	47,12	0,16	25,55	44,42
29	2003	50cm									
31	2003	50cm	8,00	3,11	0,00	5,35	0,59	50,85	0,12	28,09	56,14
33	2003	50cm									
35	2003	50cm		2,47	0,00	4,76	0,53	37,61	0,14	27,07	53,39
37	2003	50cm	8,25	1,65	0,00	1,36	0,35	10,06	0,80	7,65	18,05
39	2003	50cm	7,90	1,50	0,00	2,30	0,60	8,00	0,10	12,20	42,90
41	2003	50cm	8,20	1,50	0,00	2,00	0,60	1,70	0,10	24,30	44,50
43	2003	50cm	7,33	1,81	1,55	9,57	0,29	0,62	0,11	7,43	17,49
45	2003	50cm	8,12	0,59	0,13	1,86	0,23	1,24	0,05	11,93	24,29
47	2003	50cm	8,05	1,23	0,16	3,26	0,24	3,41	0,04	12,02	24,33
49	2003	50cm	8,15	1,18	0,00	3,18	0,20	3,34	0,00	13,56	29,45
51	2003	50cm	7,95	0,74	0,00	1,91	0,17	2,66	0,05	12,31	28,64

1	2004	50cm									
3	2004	50cm	8,05	0,86	0,00	1,69	0,27	3,93	0,07	17,21	30,72
5	2004	50cm	7,95	1,08	0,03	2,00	0,27	4,28	0,07	16,52	29,71
7	2004	50cm	8,20	0,90	0,00	1,28	0,21	1,31	0,11	18,16	32,19
9	2004	50cm	8,20	0,75	0,00	1,34	0,24	1,98	0,09	18,39	32,42
11	2004	50cm	8,15	0,74	0,00	1,40	0,23	2,00	0,09	18,41	32,69
13	2004	50cm	8,08	0,73	0,00	1,41	0,20	2,64	0,09	18,22	32,29
15	2004	50cm	7,98	0,53	0,00	2,62	0,07	2,19	0,09	16,29	29,91
17	2004	50cm	8,05	0,41	0,00	0,80	0,34	1,16	0,12	18,41	32,80
19	2004	50cm	8,03	0,70	0,00	1,42	0,40	0,52	0,17	13,63	29,91
21	2004	50cm	7,80	0,57	0,02	1,58	0,35	0,94	0,14	15,45	35,59
23	2004	50cm	7,90	0,31	0,00	0,97	0,42	0,85	0,11	14,99	36,83
25	2004	50cm	7,93	0,34	0,00	2,00	0,46	1,01	0,00	18,44	36,21
27	2004	50cm	8,08	0,38	0,00	0,57	0,54	0,68	0,47	18,83	37,06
29	2004	50cm	8,40	0,38	0,00	0,63	0,53	0,49	0,00	26,79	51,18
31	2004	50cm	8,50	0,55	0,00	0,65	0,55	0,74	0,00	29,23	55,50
33	2004	50cm	8,20	0,67	0,00	0,95	0,60	0,00	0,00	30,76	58,25
35	2004	50cm	8,20	0,98	0,00	1,53	0,49	0,00	0,15	29,55	59,32
37	2004	50cm	7,95	0,66	0,00	1,33	0,46	1,03	0,03	22,68	43,78
39	2004	50cm	8,45	1,12	0,00	1,36	0,80	0,05	0,60	31,79	60,02
41	2004	50cm	8,50	0,89	0,00	1,00	0,54	0,01	0,09	28,52	55,31
43	2004	50cm	7,73	0,56	0,53	2,60	0,35	0,57	0,08	15,59	34,13
45	2004	50cm	8,28	0,92	0,35	4,25	0,45	0,81	0,11	21,03	40,22
47	2004	50cm	7,95	1,09	0,28	4,26	0,45	0,91	0,21	21,76	41,16
49	2004	50cm	8,23	2,08	0,67	3,78	0,46	43,99	1,14	24,77	49,00
51	2004	50cm	8,15	0,84	0,20	1,98	0,98	0,97	0,30	24,45	47,71
1	2005	50cm									
3	2005	50cm	8,28	1,19	0,13	2,35	0,34	3,86	0,14	13,17	21,26
5	2005	50cm	8,27	1,12	0,08	3,33	0,34	4,45	0,07	12,88	21,93
7	2005	50cm	8,20	1,42	0,07	3,28	0,34	3,83	0,09	15,36	23,03
9	2005	50cm	8,32	1,81	0,05	2,58	0,35	6,07	0,06	15,66	28,60
11	2005	50cm	8,40	1,41	0,05	2,32	0,34	5,78	0,04	16,97	24,71
13	2005	50cm	8,30	0,92	0,09	1,72	0,48	1,77	0,10	15,44	22,39
15	2005	50cm	8,37	0,38	0,10	0,65	0,33	1,03	0,04	11,77	17,20
17	2005	50cm	8,43	0,41	0,69	0,69	0,38	0,68	0,68	13,88	21,23
19	2005	50cm	8,47	0,51	0,12	0,75	0,47	0,94	0,12	13,32	16,55
21	2005	50cm	8,50	0,46	0,08	0,94	0,45	0,02	0,08	13,40	20,16
23	2005	50cm	8,45	0,26	0,05	1,01	0,41	1,09	0,08	14,08	21,09
25	2005	50cm	8,70	0,49	0,05	1,10	0,47	0,46	0,14	16,86	25,57
27	2005	50cm		0,59	0,06	1,04	1,00	0,95	0,17	21,15	33,01
29	2005	50cm	8,70	0,68	0,04	1,21	0,50	0,00	0,01	22,76	36,19
31	2005	50cm	8,60	0,32	0,01	15,70	0,68	0,63	0,12	29,74	61,18
33	2005	50cm	8,50	0,68	0,01	1,69	0,53	0,00	0,11	29,24	57,23
35	2005	50cm	8,35	0,70	0,00	1,92	0,18	0,81	0,31	9,95	23,04
37	2005	50cm	8,35	10,27	3,55	24,89	0,27	0,16	0,17	7,88	18,55
39	2005	50cm	8,35	0,21	0,74	3,03	0,10	1,46	1,92	15,51	28,74
41	2005	50cm	8,23	0,49	0,18	2,79	0,10	0,91	0,76	17,09	27,45
43	2005	50cm	8,20	1,49	0,00	1,97	0,45	1,29	0,10	22,82	35,77
45	2005	50cm	8,25	1,11	0,00	1,81	0,38	2,72	0,06	21,28	32,60
47	2005	50cm	8,25	0,98	0,00	2,36	0,39	1,05	0,00	21,02	32,17
49	2005	50cm	8,25	1,00	0,00	2,54	0,48	2,02	0,18	18,65	28,19
51	2005	50cm	8,35	1,33	0,00	2,48	0,34	9,78	0,06	19,25	28,97

1	2006	50cm	8,20	1,23	0,03	2,37	0,33	6,97	0,08	18,44	27,74
3	2006	50cm	8,35	1,16	0,02	2,37	0,38	6,60	0,32	18,26	27,20
5	2006	50cm	8,25	1,25	0,05	1,97	0,36	6,14	0,10	19,08	27,50
7	2006	50cm									
9	2006	50cm	8,30	0,79	0,02	2,12	0,31	5,76	0,06	19,74	29,38
11	2006	50cm	8,35	0,73	0,03	2,25	0,34	5,80	0,08	20,71	30,38
13	2006	50cm	8,30	1,53	0,04	1,93	0,39	0,25	0,28	19,30	28,87
15	2006	50cm	8,30	0,87	0,00	1,54	0,30	4,09	0,06	18,30	27,31
17	2006	50cm	8,35	0,46	0,03	0,58	0,23	2,15	0,07	14,48	22,20
19	2006	50cm	8,35	0,51	0,00	0,57	0,19	1,19	0,09	14,61	22,09
21	2006	50cm	8,20	0,71	0,03	0,58	0,24	1,75	0,09	17,72	27,04
23	2006	50cm	8,30	0,55	0,00	0,94	0,23	0,99	0,11	18,89	29,12
25	2006	50cm	8,20	0,18	0,05	0,92	0,16	0,12	0,05	18,55	28,52
27	2006	50cm	8,20	0,59	0,12	2,15	0,26	0,60	0,02	13,79	21,35
29	2006	50cm	8,25	0,36	0,10	2,91	0,41	0,48	0,09	19,24	30,10
31	2006	50cm	8,30	0,74	0,05	1,57	0,56	1,55	0,16	27,24	42,90
33	2006	50cm									
35	2006	50cm									
37	2006	50cm									
39	2006	50cm									
41	2006	50cm									
43	2006	50cm	7,85	0,53	0,08	1,73	0,24	0,52	0,06	8,29	13,50
45	2006	50cm	8,27	1,36	0,01	3,40	0,21	0,82	0,00	14,45	
47	2006	50cm	8,32	1,62	0,00	2,75	0,32	0,75	0,02	15,37	22,73
49	2006	50cm	8,25	1,19	0,00	1,55	0,28	0,66	0,13	13,88	20,61
51	2006	50cm	8,37	1,19	0,01	1,76	0,33	1,52	0,04	14,30	21,03
1	2007	50cm	8,30	0,99	0,22	1,97	0,35	0,41	0,21	12,62	18,80
3	2007	50cm	8,30	0,78	0,02	1,70	0,42	2,49	0,11	14,23	20,45
5	2007	50cm	8,38	0,82	0,01	1,43	0,33	3,28	0,07	14,04	19,99
7	2007	50cm	8,40	0,36	0,03	1,36	0,39	3,17	0,08	16,36	24,45
9	2007	50cm	8,35	0,83	0,03	1,32	0,37	1,77	0,06	13,54	19,66
11	2007	50cm	8,35	0,50	0,02	1,19	0,36	0,66	0,07	12,21	17,66
13	2007	50cm	8,33	0,39	0,04	0,71	0,33	1,09	0,06	12,44	18,08
15	2007	50cm	8,38	0,58	0,00	1,10	0,25	0,09	0,05	15,27	22,04
17	2007	50cm	8,33	0,52	0,01	0,85	0,34	0,55	0,06	14,02	20,55
19	2007	50cm	8,35	0,58	0,02	1,12	0,41	1,72	0,08	17,65	36,53
21	2007	50cm	8,28	0,83	0,01	2,31	0,41	2,11	0,13	17,72	26,74
23	2007	50cm	8,30	0,51	0,01	1,30	0,26	0,01	0,07	13,92	21,24
25	2007	50cm	8,09	0,10	0,05	1,92	0,09	0,12	0,07	14,34	26,91
27	2007	50cm	8,18	0,51	0,00	1,44	0,26	0,02	0,07	18,89	29,08
29	2007	50cm	8,13	0,48	0,02	2,73	0,30	0,76	0,05	22,49	34,67
31	2007	50cm	8,30	0,15	0,19	0,72	0,30	0,00	0,00	24,59	38,42
33	2007	50cm	8,35	0,59	0,00	0,94	0,00	0,00	0,00	27,95	43,85
35	2007	50cm	8,03	0,45	0,58	3,87	0,27	0,23	0,08	15,53	24,01
37	2007	50cm	8,63	0,77	0,00	1,69	0,00	0,62	0,00	21,83	32,35
39	2007	50cm	8,07	0,59	0,00	1,30	0,25	0,10	0,01	17,99	26,46
41	2007	50cm	8,18	0,56	0,00	1,08	0,28	0,52	0,01	18,88	27,89
43	2007	50cm	8,23	0,43	0,00	1,19	0,35	0,30	0,01	20,40	29,21
45	2007	50cm	8,27	0,54	0,01	1,17	0,24	2,02	0,01	9,60	19,49
47	2007	50cm	8,23	0,53	0,00	1,14	0,17	1,22	0,00	13,87	15,91
49	2007	50cm	8,17	0,49	0,00	0,74	0,38	1,55	0,03	15,51	16,93
51	2007	50cm	8,02	0,54	0,01	1,28	0,26	0,01	0,07	16,83	30,70

1	2008	50cm									
3	2008	50cm	8,33	0,49	0,00	1,37	0,27	3,13	0,00	14,06	18,98
5	2008	50cm	8,42	0,58	0,00	0,99	0,16	2,09	0,00	11,87	15,16
7	2008	50cm	8,23	0,70	0,00	0,89	0,23	1,72	0,32	14,47	19,98
9	2008	50cm	8,30	0,54	0,00	0,97	0,25	2,18	0,00	17,44	25,91
11	2008	50cm	8,25	0,54	0,00	1,29	0,21	2,17	0,34	13,69	18,87
13	2008	50cm	8,27	1,30	0,01	1,00	0,23	1,56	0,13	10,98	16,43
15	2008	50cm	8,30	0,68	0,02	1,03	0,26	1,90	0,02	14,25	18,37
17	2008	50cm	8,30	0,65	0,00	0,61	0,21	2,43	0,26	15,40	26,66
19	2008	50cm	8,22	0,39	0,06	0,50	0,30	0,65	0,45	12,88	17,85
21	2008	50cm	8,43	0,36	0,03	0,60	0,37	0,00	0,02	14,30	20,81
23	2008	50cm	8,55	0,45	0,00	1,16	0,51	0,00	0,42	19,07	29,53
25	2008	50cm	8,50	0,58	0,08	1,19	1,17	0,20	0,73	20,64	32,36
27	2008	50cm	8,25	0,69	0,09	1,45	0,33	0,23	0,61	19,38	30,68
29	2008	50cm									
31	2008	50cm									
33	2008	50cm	8,55	0,47	0,05	1,57	0,47	0,86	0,04	21,44	32,66
35	2008	50cm	8,28	0,43	0,00	2,15	0,49	0,21	0,04	25,93	40,92
37	2008	50cm	8,35	0,63	0,02	0,91	0,25	0,00	0,08	17,63	35,37
39	2008	50cm	8,40	0,36	0,00	0,96	0,38	0,06	0,02	25,43	40,54
41	2008	50cm	8,45	0,73	0,00	1,47	0,42	0,03	0,05	24,73	38,71
43	2008	50cm	8,30	0,54	0,00	1,45	0,07	0,02	0,00	10,63	17,74
45	2008	50cm	8,35	0,77	0,00	1,35	0,25	0,04	0,00	24,25	37,99
47	2008	50cm	8,35	0,76	0,00	1,52	0,27	0,02	0,00	22,54	34,19
49	2008	50cm	8,35	0,88	0,00	1,63	0,15	0,03	0,00	19,09	28,92
51	2008	50cm	8,15	1,06	0,00	1,52	0,27	2,34	0,00	19,10	29,44

Table 40: Complete discharge data

Week	Year	Depth	ml	pH	Cl ⁻ [mg/l]	NH ₄ ⁺ [mg/l]	SO ₄ ⁻ [mg/l]	Na ⁺ [mg/l]	NO ₃ ⁻ [mg/l]	K ⁺ [mg/l]	Mg ⁺⁺ [mg/l]	Ca ⁺⁺ [mg/l]
1	2001	Discharge	660	8,50	0,28	0,00	2,08	0,25	17,44	0,04	15,37	31,50
3	2001	Discharge	800	8,60	0,37	0,00	1,63	0,10	12,37	0,05	21,02	42,20
5	2001	Discharge	75	8,50	0,52	0,01	0,99	0,12	20,63	0,02	17,44	36,08
7	2001	Discharge	4.540	8,50	0,22	0,00	1,48	0,15	14,63	0,10	18,50	36,08
9	2001	Discharge	9.250	8,50	0,47	0,00	2,08	0,12	14,15	0,20	20,45	41,00
11	2001	Discharge	31.460	8,50	0,36	0,00	2,30	0,09	16,04	0,04	19,98	40,11
13	2001	Discharge	62.900	8,50	0,47	0,20	1,86	0,15	15,12	0,00	17,15	35,01
15	2001	Discharge	32.800	8,40	0,64	0,10	3,05	0,14	4,99	0,00	14,29	30,58
17	2001	Discharge	34.140	8,30	0,68	0,03	1,38	0,08	12,16	0,02	16,44	35,02
19	2001	Discharge	13.830	8,25	0,39	0,01	2,09	0,30	13,08	0,00	17,05	35,31
21	2001	Discharge	7.830	8,20	0,70	0,05	1,55	0,24	18,51	0,00	13,36	28,57
23	2001	Discharge	25.350	8,15	0,67	0,00	1,36	0,14	17,04	0,05	17,31	35,01
25	2001	Discharge	77.700	8,00	0,42	0,00	1,69	0,14	13,38	0,04	15,39	32,08
27	2001	Discharge	17.520	8,20	0,25	0,00	0,69	0,15	12,12	0,05	15,48	31,11
29	2001	Discharge	8.760	7,80	0,30	0,00	1,58	0,12	20,01	0,05	20,36	41,07
31	2001	Discharge	23.570	8,10	0,40	0,00	0,96	0,14	11,86	0,01	16,65	33,20
33	2001	Discharge	29.720	8,15	0,41	0,00	3,05	0,11	19,38	0,05	20,15	40,12
35	2001	Discharge	6.820	8,15	0,25	0,01	2,30	0,12	18,35	0,02	18,51	37,18
37	2001	Discharge	72.180	7,95	0,36	0,02	0,98	0,12	19,04	0,00	19,33	40,17
39	2001	Discharge	28.390	7,90	0,53	0,01	2,38	0,25	16,37	0,00	11,36	23,57
41	2001	Discharge	11.090	8,00	0,23	0,04	1,74	0,14	11,14	0,00	15,52	29,96
43	2001	Discharge	3.840	7,90	0,28	0,05	1,39	0,20	13,87	0,00	13,29	27,74
45	2001	Discharge	9.910	7,85	0,16	0,04	1,89	0,14	13,39	0,00	15,63	30,28
47	2001	Discharge	7.320	8,30	0,18	0,01	2,38	0,14	14,14	0,00	20,57	41,06
49	2001	Discharge	33.050	7,65	0,30	0,00	1,36	0,20	15,52	0,00	17,33	35,08
51	2001	Discharge	16.590	8,60	0,36	0,12	1,67	0,12	17,73	0,02	16,62	33,41
1	2002	Discharge	6.680	8,30	0,20	0,00	1,74	0,09	18,05	0,05	17,02	33,08
3	2002	Discharge	220	8,50	0,38	0,00	3,04	0,08	14,15	0,02	18,05	35,38
5	2002	Discharge	25.800	8,40	0,16	0,03	2,16	0,12	4,89	0,05	20,34	41,11
7	2002	Discharge	35.680	8,45	0,15	0,05	1,59	0,17	18,04	0,04	15,44	32,05
9	2002	Discharge	9.920	8,30	0,37	0,00	2,50	0,08	16,65	0,05	15,08	25,85
11	2002	Discharge	20.010	8,40	0,95	0,04	1,16	0,09	13,32	0,12	21,05	40,85
13	2002	Discharge	68.100	8,40	0,59	0,00	0,98	0,13	10,04	0,00	18,18	35,38
15	2002	Discharge	20.760	8,20	0,37	0,00	1,54	0,18	9,65	0,14	17,15	32,07
17	2002	Discharge	11.380	8,15	0,57	0,00	2,07	0,23	14,00	0,05	12,35	22,58
19	2002	Discharge	31.150	8,15	0,63	0,02	1,39	0,14	9,84	0,00	13,52	26,30
21	2002	Discharge	10.330	8,15	0,57	0,02	1,46	0,15	10,52	0,13	18,00	35,08
23	2002	Discharge	10.420	8,35	0,44	0,03	1,75	0,14	11,65	0,05	14,40	30,07
25	2002	Discharge	17.170	8,35	0,48	0,00	0,88	0,20	14,08	0,07	17,05	30,28
27	2002	Discharge	14.040	8,35	0,37	0,05	1,44	0,18	10,60	0,07	14,30	29,29
29	2002	Discharge	18.730	8,30	0,19	0,00	2,13	0,09	20,24	0,05	18,09	39,35
31	2002	Discharge	31.720	8,15	0,38	0,00	1,08	0,32	18,57	0,05	16,52	30,24
33	2002	Discharge	70.230	8,15	0,82	0,00	0,95	0,28	16,69	0,04	12,35	25,28
35	2002	Discharge	3.350	8,30	0,28	0,00	0,57	0,40	20,07	0,05	21,40	42,08
37	2002	Discharge	15.460	8,25	0,23	0,00	1,02	0,14	7,56	0,05	28,44	52,99
39	2002	Discharge	35.900	8,20	0,20	0,00	1,02	0,33	15,02	0,14	23,69	50,02
41	2002	Discharge	32.850	8,05	0,19	0,03	1,27	0,14	21,75	0,03	30,57	55,89
43	2002	Discharge	18.980	8,25	0,37	0,00	1,39	0,13	17,49	0,00	27,96	52,59
45	2002	Discharge	50.050	8,15	0,46	0,00	1,34	0,13	15,24	0,04	26,41	49,99
47	2002	Discharge	26.870	8,35	0,84	0,00	1,21	0,09	5,27	0,07	24,40	46,68
49	2002	Discharge										
51	2002	Discharge	16.870	7,96	0,58	0,00	0,47	0,11	1,06	0,00	26,55	48,75

1	2003	Discharge	35.000	7,80	0,39	0,08	1,36	0,08	12,36	0,02	22,36	48,50
3	2003	Discharge	10.220	7,60	0,58	0,00	1,05	0,20	20,00	0,00	19,35	41,02
5	2003	Discharge										
7	2003	Discharge	1.290	7,85	0,57	0,00	1,25	0,11	17,88	0,03	18,51	39,58
9	2003	Discharge	1.220	7,95	0,25	0,00	1,87	0,20	18,36	0,02	24,20	48,38
11	2003	Discharge	24.510	8,10	0,24	0,00	1,95	0,17	21,21	0,00	20,30	41,08
13	2003	Discharge	9.140	8,10	0,33	0,00	1,96	0,14	15,63	0,06	15,63	32,04
15	2003	Discharge	62.125	8,20	0,58	0,00	2,08	0,25	23,02	0,04	17,04	33,33
17	2003	Discharge	2.730	8,10	0,25	0,00	1,69	0,19	17,74	0,04	14,58	30,09
19	2003	Discharge	4.050	7,40	0,60	0,04	1,38	0,19	16,52	0,00	16,16	33,00
21	2003	Discharge	21.370	7,60	0,26	0,00	2,05	0,24	18,54	0,00	18,07	35,01
23	2003	Discharge	6.610	7,90	0,37	0,00	1,93	0,21	16,09	0,04	20,34	40,04
25	2003	Discharge	8.540	8,00	0,52	0,00	2,13	0,17	20,48	0,02	19,58	40,35
27	2003	Discharge	17.860	8,20	0,64	0,00	2,08	0,11	13,36	0,05	21,52	41,11
29	2003	Discharge	2.060	8,10	0,29	0,00	1,87	0,24	19,07	0,06	18,76	37,52
31	2003	Discharge	26.000	7,90	0,39	0,00	1,58	0,09	20,01	0,01	14,05	30,07
33	2003	Discharge										
35	2003	Discharge	4.330	8,20	0,52	0,00	3,04	0,15	21,16	0,05	17,36	31,31
37	2003	Discharge	12.330	8,15	0,58	0,00	2,65	0,13	22,01	0,05	15,24	28,96
39	2003	Discharge	35.100	7,80	0,60	0,00	3,58	0,08	13,25	0,04	15,85	30,05
41	2003	Discharge	43.870	7,90	0,49	0,20	2,86	0,14	16,51	0,03	20,17	40,24
43	2003	Discharge	44.680	8,10	0,47	0,00	3,01	0,15	20,01	0,05	13,93	26,65
45	2003	Discharge	1.620	7,95	0,35	0,04	2,84	0,14	18,68	0,04	17,98	36,36
47	2003	Discharge	8.490	8,15	0,89	0,00	1,79	0,13	17,24	0,02	15,08	28,21
49	2003	Discharge	5.700	7,95	0,36	0,00	1,38	0,09	19,21	0,00	22,06	41,05
51	2003	Discharge	35.000	8,20	0,15	0,00	2,55	0,08	12,25	0,00	17,52	33,57
1	2004	Discharge										
3	2004	Discharge	17.380	8,15	1,49	0,00	1,76	0,14	7,14	0,02	21,11	41,34
5	2004	Discharge	21.620	8,30	0,67	0,00	3,50	0,28	5,17	0,03	17,25	35,24
7	2004	Discharge	26.630	8,25	0,51	0,08	1,61	0,03	22,64	0,16	23,99	46,61
9	2004	Discharge	5.440	8,35	0,81	0,00	1,90	0,03	25,90	0,13	25,17	48,03
11	2004	Discharge	1.880	8,15	0,65	0,10	2,09	0,03	29,09	0,14	24,82	47,59
13	2004	Discharge	29.040	8,15	0,70	0,00	1,96	0,09	27,29	0,00	24,19	46,22
15	2004	Discharge	47.000	8,10	0,60	0,00	2,08	0,05	15,88	0,18	22,94	44,51
17	2004	Discharge	15.160	8,30	1,35	0,00	2,16	0,20	4,88	0,06	23,14	40,36
19	2004	Discharge	17.980	8,25	0,83	0,05	1,90	0,09	6,14	0,04	18,17	37,50
21	2004	Discharge	26.530	8,00	0,99	0,00	2,22	0,09	5,18	0,05	19,83	40,03
23	2004	Discharge	7.190	7,95	0,53	0,00	1,59	0,08	4,50	0,07	17,50	34,19
25	2004	Discharge	44.730	8,20	0,26	0,00	2,01	0,19	7,66	0,00	25,33	51,56
27	2004	Discharge	13.540	8,00	0,29	0,00	1,18	0,24	3,23	0,00	26,97	54,66
29	2004	Discharge	11.600	7,90	0,19	0,00	0,60	0,19	0,68	0,00	28,90	58,38
31	2004	Discharge	27.300	8,05	0,30	0,00	0,52	0,19	1,38	0,00	29,99	60,08
33	2004	Discharge	7.550	8,25	0,33	0,00	0,40	0,27	2,22	0,00	30,73	61,08
35	2004	Discharge	26.420	8,50	0,88	0,00	2,08	0,29	10,85	0,00	14,30	29,29
37	2004	Discharge	24.530	8,50	0,18	0,05	0,99	0,17	7,58	0,05	19,58	40,00
39	2004	Discharge	10.450	8,50	0,68	0,05	1,58	0,09	11,11	0,04	17,36	34,02
41	2004	Discharge	36.170	8,45	0,39	0,04	4,19	0,37	2,96	0,02	20,11	40,37
43	2004	Discharge	14.940	8,40	0,28	0,00	3,25	0,44	20,45	0,03	14,00	29,04
45	2004	Discharge	3.720	8,45	0,65	0,00	0,83	0,19	21,07	0,03	18,35	36,52
47	2004	Discharge	9.290	8,35	1,07	0,00	1,17	0,20	20,65	0,03	19,51	40,81
49	2004	Discharge	9.450	8,15	0,96	0,00	1,35	0,21	10,42	0,10	18,23	36,89
51	2004	Discharge										

1	2005	Discharge										
3	2005	Discharge	10.100	8,50	0,79	0,03	1,62	0,20	26,31	0,04	26,16	47,30
5	2005	Discharge	9.110	8,40	0,90	0,02	1,79	0,18	24,69	0,04	24,04	42,17
7	2005	Discharge	11.260	8,40	0,74	0,03	1,78	0,16	31,84	0,02	25,67	46,09
9	2005	Discharge	4.040	8,50	0,24	0,04	2,30	0,39	39,63	0,16	28,34	57,53
11	2005	Discharge	1.080	8,47	0,34	0,00	2,06	0,10	40,19	0,20	20,54	40,16
13	2005	Discharge	74.300	8,50	0,88	0,00	2,61	0,19	31,35	0,03	21,88	37,46
15	2005	Discharge	25.040	8,25	0,75	0,08	1,82	0,29	11,95	0,04	16,96	29,10
17	2005	Discharge	40.770	8,12	0,54	0,36	1,45	0,29	10,37	0,22	12,04	19,85
19	2005	Discharge	37.650	8,60	0,69	0,02	1,33	0,20	9,66	0,02	20,32	35,02
21	2005	Discharge	20.000	8,56	0,69	0,03	1,45	1,27	6,66	0,03	20,99	36,30
23	2005	Discharge	415	8,60	0,54	0,00	1,17	0,22	5,98	0,08	19,31	34,04
25	2005	Discharge	9.220	8,74	0,55	0,03	1,17	0,02	3,63	0,03	22,65	38,76
27	2005	Discharge	6.600	8,70	0,77	0,05	1,05	0,25	2,67	0,05	23,66	40,65
29	2005	Discharge	40.700	8,70	0,77	0,03	1,03	0,24	2,02	0,03	25,32	43,90
31	2005	Discharge	22.510	8,30	0,55	0,03	0,75	0,23	0,13	0,03	26,79	47,14
33	2005	Discharge	39.570	8,42	0,51	0,03	0,62	0,23	0,24	0,03	31,89	69,09
35	2005	Discharge	71.200	8,17	0,44	0,00	0,69	0,44	2,16	0,00	25,45	47,03
37	2005	Discharge	980	8,17	0,35	0,03	1,05	0,18	1,88	0,03	21,05	36,43
39	2005	Discharge										
41	2005	Discharge	23.270	8,10	0,35	0,02	0,50	0,19	3,61	0,03	22,38	38,63
43	2005	Discharge	135	8,05	0,70	0,00	0,90	0,22	5,77	0,02	25,15	41,11
45	2005	Discharge										
47	2005	Discharge	4.110	8,17	0,68	0,00	0,84	0,56	4,20	0,18	24,09	40,93
49	2005	Discharge	3.980	8,45	0,69	0,00	1,01	0,22	7,73	0,01	25,70	43,49
51	2005	Discharge										
1	2006	Discharge	6.440	8,50	0,29	0,02	0,63	0,16	9,11	0,02	25,67	42,76
3	2006	Discharge										
5	2006	Discharge	2.890	8,25	0,30	0,01	0,96	0,17	12,22	0,02	25,21	42,03
7	2006	Discharge										
9	2006	Discharge	10.320	8,40	0,51	0,01	1,85	0,15	23,03	0,03	22,84	37,64
11	2006	Discharge										
13	2006	Discharge	31.200	8,20	0,67	0,01	2,32	0,18	31,07	0,03	20,30	33,37
15	2006	Discharge	74.700	8,25	0,42	0,01	1,67	0,12	13,55	0,01	14,55	24,12
17	2006	Discharge	69.580	6,95	0,56	0,01	1,33	0,13	6,82	0,02	13,69	22,71
19	2006	Discharge	12.980	8,30	0,16	0,00	1,55	0,12	11,39	0,02	17,73	29,59
21	2006	Discharge										
23	2006	Discharge		8,30	0,40	0,00	1,69	0,14	7,67	0,02	22,22	37,58
25	2006	Discharge										
27	2006	Discharge	38.410	8,40	0,49	0,00	1,33	0,23	2,04	0,00	25,72	44,27
29	2006	Discharge	100	8,20	1,04	0,00	0,74	0,29	0,87	0,21	19,98	34,68
31	2006	Discharge	105	8,20	0,12	0,00	0,99	0,25	3,45	0,18	17,94	24,62
33	2006	Discharge										
35	2006	Discharge	27.200	8,15	0,54	0,02	0,86	0,24	0,00	0,05	22,56	39,20
37	2006	Discharge										
39	2006	Discharge	13.810	8,20	0,07	0,02	0,11	0,23	0,14	0,04	22,72	39,38
41	2006	Discharge										
43	2006	Discharge	19.640	8,25	0,46	0,01	0,75	0,28	1,00	0,08	21,70	37,53
45	2006	Discharge										
47	2006	Discharge	62.050	8,10	0,46	0,02	0,62	0,24	3,76	0,18	23,33	40,04
49	2006	Discharge	46.250	6,00	0,85	0,02	0,63	0,30	2,06	0,24	0,18	0,45
51	2006	Discharge	10.980	8,35	0,76	0,02	1,29	0,19	9,00	0,03	22,32	38,02

1	2007	Discharge	1.830	8,60	0,62	0,00	1,61	0,33	6,09	0,03	22,97	38,57
3	2007	Discharge										
5	2007	Discharge	19.180	8,60	0,60	0,01	1,51	0,22	10,16	0,18	22,52	37,56
7	2007	Discharge										
9	2007	Discharge	29.530	8,70	0,86	0,00	1,54	0,19	15,56	0,03	21,64	36,59
11	2007	Discharge										
13	2007	Discharge	28.650	8,50	0,79	0,00	1,65	0,18	12,14	0,03	19,42	32,75
15	2007	Discharge										
17	2007	Discharge	11.900	6,10	1,02	0,00	1,90	0,18	8,69	0,03	20,25	33,91
19	2007	Discharge										
21	2007	Discharge	32.750	8,90	1,94	0,01	1,52	0,22	1,08	0,03	20,20	34,25
23	2007	Discharge	33.600	8,60	0,57	0,01	1,25	0,29	0,03	0,06	19,73	33,87
25	2007	Discharge										
27	2007	Discharge	25.400	8,15	0,05	0,00	0,89	0,19	0,02	0,03	22,85	40,70
29	2007	Discharge										
31	2007	Discharge	29.570	8,15	0,00	0,00	0,73	0,00	1,52	0,00	24,63	48,36
33	2007	Discharge										
35	2007	Discharge	19.370	8,35	0,65	0,01	0,76	0,24	0,00	0,04	24,17	41,88
37	2007	Discharge										
39	2007	Discharge	80.000	8,10	1,10	0,02	0,24	0,29	0,00	0,06	24,19	41,82
41	2007	Discharge										
43	2007	Discharge	9.990	8,25	0,28	0,00	0,17	0,22	0,06	0,00	25,80	43,47
45	2007	Discharge										
47	2007	Discharge	35.550	8,55	0,39	0,00	0,20	0,21	0,30	0,00	29,86	43,59
49	2007	Discharge	10.170	8,60	0,62	0,01	0,36	0,22	2,24	0,02	28,69	41,41
51	2007	Discharge										
1	2008	Discharge	9.350	8,55	0,74	0,00	0,67	0,15	3,07	0,00	21,60	35,00
3	2008	Discharge										
5	2008	Discharge	17.680	8,50	0,52	0,00	1,11	0,15	6,34	0,00	20,35	36,70
7	2008	Discharge										
9	2008	Discharge	12.200	8,40	0,42	0,00	0,98	0,21	9,27	0,07	30,50	45,50
11	2008	Discharge										
13	2008	Discharge	47.020	8,60	0,46	0,00	1,84	0,15	1,02	0,10	23,04	48,63
15	2008	Discharge										
17	2008	Discharge	36.840	8,50	0,61	0,00	0,92	0,16	2,32	0,28	19,60	36,90
19	2008	Discharge		8,60	0,47	0,00	1,03	0,23	2,56	0,00	19,04	30,24
21	2008	Discharge										
23	2008	Discharge	670	8,70	0,89	0,01	0,70	0,17	0,24	0,00	14,84	23,32
25	2008	Discharge										
27	2008	Discharge	27.450	8,35	0,34	0,02	0,67	0,15	0,00	0,08	22,01	37,03
29	2008	Discharge										
31	2008	Discharge										
33	2008	Discharge										
35	2008	Discharge	35.160	8,00	0,56	0,04	0,19	0,96	0,00		17,67	32,79
37	2008	Discharge										
39	2008	Discharge	15.050	8,40	0,22	0,00	0,95	0,29	0,00	0,00	25,93	45,06
41	2008	Discharge										
43	2008	Discharge	17.980	8,15	0,32	0,00	0,22	0,16	0,02	0,01	27,19	47,32
45	2008	Discharge	1.260	5,30	0,64	0,00	0,13	0,10	0,02	0,00	27,37	46,95
47	2008	Discharge										
49	2008	Discharge	14.860	8,20	0,37	0,00	0,34	0,03	1,31	0,31	14,90	23,65
51	2008	Discharge										

9.2 Appendix B

Table 41: MineQL+ results for different soil depth

No solids	5cm	%	15cm	%	25cm	%	50cm	%
Cl ⁻	inert		inert		inert		inert	
SO ₄ ²⁻	CaSO ₄ ,MgSO ₄	54,45	CaSO ₄ ,MgSO ₄	58,42	CaSO ₄ ,MgSO ₄	55,44	CaSO ₄ ,MgSO ₄	56,43
NO ₃ ⁻	CaNO ₃	71	CaNO ₃ ⁺	75	CaNO ₃ ⁺	75	CaNO ₃ ⁺	76
NH ₄ ⁺	NH ₃	22	NH ₃	19	NH ₃	25	NH ₃ ,CaNH ₃ ²⁺	21,6
Na ⁺	inert		inert		inert		inert	
K ⁺	inert		inert		inert		inert	
Mg ⁺⁺	Hydromagnesite	1	MgSO ₄	2	MgHCO ₃ ⁺	2	MgHCO ₃ ⁺	1
Ca ⁺⁺	CaNO ₃ ⁺	7	CaNO ₃ ⁺	9	CaNO ₃ ⁺ ,CaHCO ₃ ⁺	2,2	CaNO ₃ ⁺ ,CaHCO ₃ ⁺	2,1

Table 42: MineQL+ results for different soil depth if solids were taken into account (dolomite ordered and disordered)

Solids incl.	Depth	Complexes	%	Solids	%
Cl ⁻	5cm	inert		no	
	15cm	inert		no	
	25cm	inert		no	
	50cm	inert		no	
SO ₄ ²⁻	5cm	CaSO ₄	84	no	
	15cm	CaSO ₄	95	no	
	25cm	CaSO ₄	86	no	
	50cm	CaSO ₄	90	no	
NO ₃ ⁻	5cm	CaNO ₃ ⁺	10	no	
	15cm	CaNO ₃ ⁺	31	no	
	25cm	CaNO ₃ ⁺	12	no	
	50cm	CaNO ₃ ⁺	17	no	
NH ₄ ⁺	5cm	NH ₃	22	no	
	15cm	NH ₃ , NH ₄ SO ₄ ⁻	20,1	no	
	25cm	NH ₃ , NH ₄ SO ₄ ⁻	27,1	no	
	50cm	NH ₃	22	no	
Na ⁺	5cm	inert		no	
	15cm	inert		no	
	25cm	inert		no	
	50cm	inert		no	
K ⁺	5cm	KSO ₄ ⁻	1	no	
	15cm	inert		no	
	25cm	inert		no	
	50cm	inert		no	
Mg ⁺⁺	5cm	no		Dolomite (ordered)	100
	15cm	no		Dolomite (ordered)	100
	25cm	no		Dolomite (ordered)	100
	50cm	no		Dolomite (ordered)	100
Ca ⁺⁺	5cm	CaSO ₄	1	Dolomite (ordered)	94
	15cm	CaSO ₄ , CaNO ₃ ⁺	3,4	Dolomite (ordered)	80
	25cm	CaSO ₄	1	Dolomite (ordered)	94
	50cm	CaSO ₄	1	Dolomite (ordered)	92