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Changes in nutrient leaching and groundwater quality during long-term studies of an arable field on the Swedish south-west coast

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Abstract The aim of this study was to evaluate the long-term (1977-2004) effects of new agricultural practices and reduced acid rain on drainwater and groundwater chemistry for an intensely cultivated arable field with sandy soil in south-west Sweden. Trends in chemical composition of the drainwater were compared with those of atmospheric deposition and groundwater. A modified crop rotation including catch crops significantly decreased the average concentration of nitrate nitrogen (NO_3-N) in drainwater from 13.0 to 7.2 mg l^{-1}. This rotation was also found to be a very effective measure against high NO_3-N concentrations in shallow groundwater (>1.7 m below the soil surface). The degree of phosphorus saturation (DPS) in the subsoil, calculated to be 10% and 9% by two different laboratory methods, corresponded to an average and constant concentration of dissolved reactive phosphate (DRP) in drainwater of 0.006 mg l^{-1}. Generally lower inputs of acid deposition to the soil were confirmed by a decreasing SO_4-S trend (by 3% over 24 years) in drainwater. Changes in cropping had reduced the effect of acid load to the soil, while drainwater alkalinity showed a slow but significant positive trend amounting to 0.4% over 24 years.

Key words: *Drainwater, groundwater, ionic balance, nutrients, trends, water chemistry.*

Introduction

Environmental aspects relating to leaching of nutrients to surrounding surface water and groundwater bodies and countermeasures have become a major issue for agriculture. Thus, since the 1970s there has been a great concern in Sweden about nitrogen (N) and phosphorus (P) losses to surface waters (Gustafson, 1987). In contrast to the situation in Denmark where reduction of groundwater NO_3 by pyrite oxidation is a well-known phenomenon (Postma *et al*., 1991) leaching of nitrate (NO_3) to groundwater is also of great concern in Sweden especially in groundwater intake areas with sandy soils without a protective clay layer (Gustafson, 1983). In both countries a proposed measure to reduce NO_3 leaching both to drain water and groundwater is growing catch crops; fast-growing crops used between seasons of regular planting to reduce the concentration of water-soluble NO_3 and other mineral nitrogen in the soil. Perennial ryegrass (*Lolium perenne* L.) may be undersown in winter crops during spring. Several studies from drained experimental plots have reported that this grass has an appropriate growth pattern for capturing mineral nitrogen in the soil, since it grows fast during autumn (Torstensson, 1998; Torstensson and Aronsson, 2000), and does not compete with the main crop (Kvist, 1992; Andersen and Olsen, 1993; Ohlander *et al.*, 1996; Bergqvist *et al.*, 2002). Repeated cropping with ryegrass for several years may also preserve, or even improve, the soil organic matter content (Aronsson, 2000). In the 1990s, Sweden joined the EU and subsidies for catch crops were introduced in the southern part of the country, but take-up by farmers was low until 2001, when new and improved subsidies became available (Ulén and Fölster, 2007). Estimates of NO_3 leaching based on the database programme SOIL-NDB (Mårtensson and Johansson, 2006) have revealed an essential reduction in NO_3-N in water leaving the root-zone when catch crops are grown compared with ordinary crops. However in agricultural streams with decreasing trends in NO_3-N concentrations theses improvements were not clearly correlated to the acreage of arable land with catch crops in the river basin (Ulén and Fölster, 2007).

Phosphorus losses from single fields in Sweden have primarily been evaluated by a P risk index (Djodjic and Bergström, 2005a) based on results from monitored fields (Djodjic and Bergström, 2005b). Phosphorus in the water may be either bound to particles and colloids, or exist in dissolved forms. Dissolved reactive phosphorus (DRP) may be fixed by soil particles either through anion adsorption or through precipitation of ferric minerals. Consequently one important factor for the P risk index is the P sorption capacity in the soil profile, which is related to the degree of P saturation (DPS). Methods proposed for this characterisation DPS include (i) a laboratory test by which the P sorption of a certain amount of soil (PSI) is deduced from the P concentration remaining in solution after addition of one large dose of P (Börling *et al*., 2001); and (ii) an extraction method based on the molar ration of P to the sum of aluminium (Al) and iron (Fe) in an acid extract (Ulén, 2006). However, no comparison of of these methods has been done. Neither has the spatial variability of DPS been investigated on a single field in order to suggest soil sampling strategies for this soil indicator.

To be an efficient and environmentally-friendly fertiliser, manure should deliver soluble inorganic nutrients at a time when the crop needs them. If nutrients from manure are released too late in the growing season, or after the crop has been harvested, they can potentially leach through the unsaturated zone and cause large leaching loads via tile drains (Bergström and Kirchmann, 1999; Kirchmann *et al*., 2002). In the 1990s, several pieces of Swedish legislation relating to nutrient losses were introduced regarding livestock density and handling of manure (Ulén *et al*., 2004). Through this legislation heavy manure applications are avoided at farm level but for a precision manure application, DPS tests on single fields might be recommended.

The relationships between contamination of agricultural land by mineral fertiliser/manure and nutrient/ionic concentrations in drainwater and groundwater are complex. When groundwater resources are evaluated on the basis of nutrient loads from agriculture, simultaneous changes in acid and ionic load to the soil should be taken into account. Drained agricultural land tends to have high hydraulic permeability in the subsurface horizon, which may cause enhanced downward chemical transport from the topsoil. High concentrations of chloride (Cl^-) may be linked to high intensity of cattle production (Hornish et al., 2002). In addition, agricultural application of potassium (K^+) as a plant nutrient may results in Cl^- contamination of recharging groundwater, since K is commonly applied in the form of KCl. In clay soils K may exchange with the clay mineral, so that K/Cl ratios in agricultural recharge are generally less than 1 (Böhlke, 2001). Several cations such as ammonium (NH_4^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) from agricultural activities have been shown to be capable to displace other cations from exchange sites in soils (Parkhurst and Plummer, 1993). Furthermore sulphate, (SO_4^{2-}) added with NH_4^+ and Ca^{2+} may be retarded by anion sorption.

Groundwater contamination of SO_4^{2-} is most likely in areas with preferential flow pathways, high recharge rates and coarse-grained superficial deposits lacking sesquioxides. Recharging groundwater with high acidity or ionic strength may increase the weathering rate and solubility of minerals. Direct acid loads of the soils have been of particular concern for the Swedish south-west coast. For several decades, this region was clearly affected by acid deposition, which carried high amounts of sulphur (S) and N compounds originating from atmospheric reactions with S and N oxides emitted during industrial combustion. In general, atmospheric acid deposition has decreased considerably in recent years and there has also been a slight reduction in N deposition (Lövblad *et al.*, 2002). Presently Sweden is in the early stages of recovery from acidification (Warfvinge and Bertills, 2000). However, in agriculture intensive areas N emission of ammonia from livestock and manure spreading should still be of concern.

In addition to loads of base cations by fertilisers and direct acidification the netto-removal of base cations from arable land by the crop may have an indirect effect on weathering processes and ion exchange. This removal has an acidifying effect unless compensated for by liming (Bergström and Gustafson, 1985; Debreczeni and Kismányoky, 2005) and has been demonstrated to decrease pH in drainage water from a Swedish clay soil in southern Sweden (Ulén *et al.*, 2007).

The aims of the present study were to confirm or reject the following hypotheses: 1) phosphorus retention, proposed to be related to the P sorption ability of the soil, may be indicated by appropriate soil sampling strategy and a well-chosen laboratory method; 2) modified farming practices may reduce nitrogen load to drainwater and surface groundwater;

and 3) crop production and acidification may interact based on drainwater and surface groundwater chemistry.

Materials and methods

An arable field (code 12N) situated seven kilometres from the shore of Laholm Bay in the county of Halland in Sweden (Figure 1) was chosen to test the hypotheses. The agriculture in this area with coarse-textured soil is intense and the livestock density high. The monitored field lies six kilometres from the long-term plot experiments at Mellby, where leaching of nutrients has been studied since 1986. The field and underlying groundwater have been monitored since 1977. It belongs to a monitoring system based on studies of individual Swedish agricultural fields, established in order to systematically evaluate the long-term environmental trends in nutrient leaching in relation to agricultural practices and to determine general quality and trends in drainwater and groundwater chemistry. This programme currently consists of 13 drained fields many of which have been monitored for more than 28 years.

Measuring devices and geochemical description

The field (14.5 ha) is situated 12-15 m above sea level, and has an average slope of 1.4% (Figure 1). The upper 1-2 m layer of the profile contains both fine and coarse water-sorted sand, underlain by deep marine clay. The latter is very dense and especially in the upper part of the field the groundwater is very shallow. Tile drains were installed in a herringbone pattern in 1975 leading the drainwater to a Thomson weir in an underground measuring station. Pairs of groundwater pipes were also installed close to the water monitoring station in 1975. These pipes are at three different depths below the surface (1.7 m, 2.2 m and 5.5 m). The intake of the pipe pair at 1.7 m depth is situated in coarse sand just above the clay layer, while the intakes for the other two pairs of pipes are situated in the clay matrix underlying the drained sandy layers. The infiltrating water forming groundwater mainly streams in the sandy overlayer to a valley south of the field. Groundwater in the sandy layer has been indicated to be young (Gustafson *et al*., 1984) and nearly all has its origin in precipitation that infiltrates the field. The clay layer clearly prevents the shallow groundwater from percolating down into the deeper glacial deposits. Since this water does not percolate down through the clay layer, there is always much water flowing through the drainpipe system. Annual average discharge is 420 mm equal to 58% of the mean annual precipitation. The bedrock contains some pyrite in addition to the main components quartz, K-feldspar and plagioclase (Sjöström, 1993).

Soil quality parameters and field management

Intensive soil sampling took place in 1993 and was extensively followed up in 2005. The topsoil, classified as loamy sand, has a texture of 13% clay, 10% silt and 77% sand. It has an organic carbon (C) content of 3.7% and a C/N ratio of 18. The soil is slightly acid; the pH is 6.0 in topsoil and 6.3 in the subsoil. The soil cannot be defined as calcareous since it does not visibly react with acid and since the CaO concentration is low (0.2%). Effective base saturation is high; 94% in the topsoil and 86% in the upper subsoil, calculated from exchangeable base cations extracted in 0.1 M barium chloride and divided by effective cation exchange capacity (CEC, the sum of exchangeable base cations and exchangeable acidity). In order to evaluate P sorption capacity, 136 soil samples evenly distributed over the field and representing 4 depth layers were investigated. P sorption index (PSI) was determined according to the method of Börling *et al*. (2001), which involves addition of one single dose of P to a soil-water mixture. An acid ammonium lactate solution method according to Egnér *et al*. (1960) was used for extraction of the soil. In addition to the common chemical determination of phosphorus (P-AL) and calcium (Ca-AL) in these extracts, iron (Fe-AL) and aluminium (Al-AL) were also analysed. The results were calculated to the degree of phosphorus saturation (DPS) as the P-AL ratio divided by the sum of Fe-AL and Al-AL on a molar basis according to Ulén (2006). Comparison was made between two independent sets of differently distributed soil samples. One set of soil samples was taken in a regular square grid with 77 m spacings , while the other set was taken at 50 m intervals along three 200-260 m transects that covered the main slopes of the field.

The farmer in charge of the field provided information about fertilisation, harvesting and other agricultural practices. The field is included in regular farm operations. The farm had a pig production unit until 2002 and during the period 1976-1990, pig slurry was relatively frequently applied. When Sweden joined the EU, the field was under green fallow (1991-1992). Thereafter it has been managed as a modified crop rotation with frequent sowing of catch crops of perennial ryegrass (*Lolium perenne* L.). However, the field still receives much fertiliser since potatoes and sugarbeet are intensively cropped (Table 1). In 2002 the field changed ownership and became part of a dairy farm, with application of solid cattle manure in recent years.

Changes in sampling and analytical programme

Water level over a Thomson weir has been recorded continuously with a water stage recorder since installation. The chart has been digitalised on an hourly basis and the water flow has been calculated. During recent years, the chart has been complemented with a datalogger (Thalimedes). Drainwater has been sampled twice a month throughout all years. Groundwater sampling has been monthly in the first years (1977-1982), four times per year in the period 1983-1986 and six times per year from 1987. Water samples have immediately been sent to the Water Laboratory at the Division of Water Quality Management, Swedish University of Agricultural Sciences, where they have been analysed according to the European Committee for Standardisation. The laboratory is accredited for analysis of nutrients, as well as many other water analyses according to SWEDAC (Swedish Board for Accreditation and Conformity Assessment). Total nitrogen was analysed until 2002 after oxidation with persulphate ($K_2S_2O_8$) and thereafter together with organic carbon with a CN analyser (Schimadzu). Nitrate nitrogen and nitrite nitrogen have been analysed together and referred to as nitrate-nitrogen (NO_3-N). Organic nitrogen (ON) is calculated as the difference between Total N and NO_3-N. Ammonium-nitrogen (NH_4-N) was found to be a minor component in both the drainwater and groundwater according to analyses carried out in the first years. Phosphorus fractions have been analysed in the drainwater, but not in the groundwater, since the concentrations were low. Total P has been analysed as soluble molybdate-reactive P after acid oxidation with $K_2S_2O_8$. Dissolved reactive phosphorus (DRP) was analysed after pre-centrifugation until 2001, and subsequently after pre-filtration. For clay soils in Sweden, these different pre-treatments have been found to be of major importance for DRP determination, since the colloidal clay particles are retained more efficiently by filtration (filters from Schleicher and Schüll, Germany, with pore diameter 0.2 μm) than by centrifugation (3000 rpm during 20 minutes). However, in this non-clay soil area differences in pre-treatments were of minor importance and on average less than 0.002 mg P l^{-1}. Nevertheless older RP results were recalculated as if filtration had been performed before analysis using regression equation from analyses with the two pretreatments. Non-reactive phosphorus (NRP) was calculated as the difference between Total P and RP and may consist of both organically- and inorganically-bound P.

Total ionic composition was analysed from 1980 in both drainwater and groundwater and the alkalinity was determined by titration. Analytical procedures for calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) were changed in 2002 from AAS (atomic adsorption spectrophotometry) to ion chromatography (IC). At the same time determination of sulphur in sulphate (SO_4-S) changed from a colorimetric determination by autoanalyser to analysis with IC, and determination of chloride (Cl) from flow injection analysis to IC. Tests indicate that these changes in analytical procedures are of minor importance, in quantitative terms less than the general uncertainty of laboratory handling and analytical determination (10%).

Average water concentrations and ionic composition

The amount of precipitation was measured at a local station close to the field but data on the ion components were obtained from a monitoring station for air and precipitation (Lövblad *et al.*, 2002) 62 kilometres north of the field (Figure 1). The average concentrations are values weighted to the amount of precipitation. Similarly all concentrations in drainwater were weighted to the amount of water, i.e. the total element transport was divided by the total drainage amount. Concentrations in groundwater were calculated as straight average values. Flow-weighted average concentrations in drainwater were compared with management factors in a simple way by testing for significance (T-test). The annual flow-weighted concentrations for periods characterised by one factor were added and compared with annual concentrations for periods characterised by another factor. Similar comparisons have been made based on results from the long-term experimental plots at Mellby (Torstensson *et al.*, 1992; Torstensson *et al.*, 2001; Torstensson and Ekre, 2003; Torstensson, 2003).

Data on ionic composition of the mineral fertilisers were obtained from the manufacturers and the concentrations in manure and crop were calculated based on standard composition data (Eriksson *et al.*, 1997; Steineck *et al.*, 1999). However, the sodium concentration is not reported in the present paper since this concentration varied widely. All major ions were expressed in millimoles of charge in order to check the ionic balance of the drainwater and groundwater. Concentrations from three drainwater samples taken during snowmelt were excluded based on a large ionic imbalance under these conditions. For the rest of the time, the error in ionic balance was generally low, 1-3%, which indicates no analytical problems. Precipitation water was checked for negative alkalinity (-Alk) as the difference in the equivalent sum of base cations (Ca, Mg, Na, K, NH_4-N) and acid anions (Cl, SO_4 and NO_3). The neutralising capacity of calculated alkalinity was also roughly estimated in the fertilisers and in harvested products but without taking into consideration any sodium or nitrogen ions.

Trend analysis

All concentrations in the drainwater and the three levels of groundwater were examined for seasonality according to the Kruskal-Wallis test. All concentrations in the drainwater were flow-normalised with the non-linear method LOWESS (Locally Weighted Scatter-plot Smoothing) before trend analysis (Cleveland, 1979). The recommended factor 0.5 was used for adjustment. Flow-normalised values were the residuals from the curve adjusted to LOWESS. The significance of the trend was tested according to Hirch and Slack (1984) using a non-parametric method (Mann Kendall) in the Visual-Basic program MiniTab®. The 'Theil's slope' (Helsel and Hirch, 1992) was used for calculating the magnitude of the trend. The method assumes no change in the relationship between concentration and discharge over time and no trends in the amount of precipitation or drainwater discharge during the period of investigation, conditions that were completely fulfilled. The concentrations in the groundwater were normalised against the level of the groundwater, which usually involved significant seasonality. Only the directions of the trends in the groundwater, if any, are reported here.

Theoretical estimations of nitrate concentrations leaving the root-zone

Beside actual measurement of NO_3 in tile drain water and groundwater, annual theoretically leaching NO_3 concentrations for water leaving the root-zone have also been estimated for a loamy sand in the actual production area (Mårtensson and Johnsson, 2006). These concentrations have been normalised according to the climate at the actual site. In addition, these annual leaching coefficients estimated with a combined leaching and database programme (SOIL-NDB) have been generalised for normal crops and for possible crop combinations in the production area (Mårtensson and Johnsson, 2006).

Results

Degree of P saturation in the soil

The topsoil of the field had a P-AL number (9 mg 100 g soil^{-1}) that is typical for Sweden. In contrast, both the Fe-AL number and the AL-Al number (13 and 55 respectively) were four times higher than average values based on more than 200 soils in the south of Sweden (Ulén, 2006). The Fe-AL value varied in different parts of the field and the variation was high throughout the entire soil profile (Table 2). This may be a result of the tendency of Fe and iron hydroxide to occur as discrete mineral particles in the soil. DPS calculated with the PSI method was higher than that calculated from the Fe-AL and Al-AL concentrations in the topsoil layer and the layer below plough mixing depth (23-35 cm). The abundant Ca ions in the topsoil may have bound some P in the neutral solution used for the PSI test, resulting in relatively low PSI values. The two methods for calculating DPS gave very similar results in the subsoil and were also well correlated with each other, with a Pearson's correlation coefficient of 0.92 ($p = 0.00$). The low values in the 35-65 cm layer (5.0 and 5.5%) and the 35-100 cm layer (10 and 9%) corresponded well with the low RP concentration in the drainwater (average 0.006 mg l^{-1}).

Soil sampling in transects along the slopes of the field gave slightly higher DPS values in the topsoil compared to sampling an evenly distributed net of squares (+3 and +7% for the extraction method and the PSI method respectively. This was the result of higher P-AL numbers at the lower end of the slope in the south-east part of the field compared with the rest of the field. The general variation in the ability of the field topsoil to sorb P was quite moderate; it varied between 22-44% for the two sampling strategies combined with the two laboratory methods.

Characterisation of precipitation, drainwater and groundwater

Average Na concentration in the precipitation was high in this coastal area (0.10 $\text{mmol}_c\ \text{l}^{-1}$). Precipitation water had a similar large proportion of sulphate and nitrate as the drainwater and the shallow groundwater at the monitored field (24-28%). The precipitation water can be described as a water of Na-SO_4-Cl type, while the drainwater and shallow groundwater represent Ca-NO_3 water types. There was a weak indication of impact from pig slurry since the K:Na ratio in the drainwater was slightly higher than 0.4 (based on weight) and since the average chloride value was relatively high (18 mg l^{-1}). However, pig manure was applied less often during later years and the two indications became even weaker with time. Similarly a low K:Cl ratio in drainwater (0.2 based on weight) tended to become even lower during recent times.

Chemical data for deep groundwater (5.5 m) revealed a water of sodium (Na-Cl) type, reflecting the marine origin of the clay. This saline groundwater is most probably relict water often found at depth in this low-lying area. After the last ice age, the sea covered a large proportion of this landscape. As the land rose out of the sea, groundwater was displaced by precipitation at different rates depending on local conditions.

Nutrient trends in drainwater and groundwater

A substantial reduction in N leaching with catch crops was clearly demonstrated, as was an effect of modified land use of the field (Tables 3 and 4). Comparing rotations with catch crops to rotations without and to applying less pig slurry revealed a reduction in the NO_3-N concentration in the drainwater. Trend analysis also revealed this reduction mainly to take place in September-November, when catch crops are most effective. Similarly, potatoes seemed to be a risk crop compared to cereals, a finding which was confirmed in the experimental plots (Table 3). In addition, organic nitrogen (ON) showed a tendency for lower leaching from the field when catch crops were grown, but this was not evident from the experimental plots. A trend for decreasing NO_3-N in the drainwater equivalent to 5.3 mg l^{-1} over the study period was also apparent, together with the more conservative parameter Na (Figure 2a). Corresponding time-series indicated an even faster NO_3-N-reduction for the groundwater at 1.7 m depth (Figure 2b). The latter was also evident when mean annual concentrations were compared with estimates based on generalising leaching coefficients for the actual soil in this agricultural production area (Figure 3). Measured NO_3-N concentrations in both drainwater and surface groundwater were also comparatively lower than theoretically estimated concentrations in root-zone leaching water.

Different cropping had no impact on the P concentrations in the drainwater, of the field which is not surprising based on the demonstrated good sorption capacity of the subsoil. In addition, Fe in groundwater transported from longer distances in the experimental plots at Mellby may bind P. Based on the results from the experimental plots, catch crops may reduce the NRP concentration in the drainwater. However, there was no such indication in the arable field studied, nor was any trend in P recorded in the drainwater during the entire period.

Soil nutrient and ionic accumulation

Fertilisation generated P accumulation in the soil at a rate of 0.4 kg $ha^{-1}yr^{-1}$, which is a low value for a Swedish farm with livestock. The P-AL index of the topsoil was found to have remained unchanged during the twelve-year modified cropping period 1993-2005. Potassium was removed slightly faster by the crops than applied by the fertiliser during the first production specialisation (1977-1990) but not during the second (Table 5). This may be a result of more potassium-demanding leys being grown during earlier years (Table 1). The composition of the used mineral fertilisers changed. During the first period, with the initial crop rotation, addition of base cations took place in the form of Ca, while there was more net gain of Mg during later years. During both original and modified crop rotation substantial underbalances of Ca^{2+} and alkalinity were estimated based on inputs and removals from the soil (Table 5).

Ionic composition and trends in precipitation, drainwater and groundwater

The ionic composition in precipitation may have differed slightly between the measured site and the observation field. The latter is situated closer to the shore but is on the other hand more protected from western winds by a large spit of land (Figure 1). The ions Na^+ and Cl^- in the precipitation were indicated to be influenced by sea-salt laden storm episodes over a number of years. Such temporary and frequent storms were obvious during the earlier part of this study, namely 1984 and during the period 1989-1992. The episodes were also followed by short-term increases in Cl^- concentration of the drainwater. Lack of such episodes in recent years was probably the main reason for the apparent decrease in Cl^- concentration in drainwater (Table 4). In contrast concentrations of Na^+ did not decreased significantly in the drainwater. These concentrations were positively related to concentrations of Na in the shallow groundwater were the concentrations were relatively high and even increased (Figure 2b). The relationship between NO_3-N and Na concentrations in the shallow groundwater was negative and had a Pearson's correlation coefficient of -0.77 ($p = 0.00$). During late summer (July-September), when there was a generally low groundwater level, this relationship was even stronger (Pearson's correlation coefficient of -0.87).

Decreasing trends in S and increasing trends in alkalinity in the precipitation were quite clear. The composition of the used mineral fertilisers changed so that more S was applied during the modified cropping system in later years (Table 5). Some commercial mineral fertilisers are now enriched in S as compensation for a generally smaller deposition of S from the air. However, the SO_4^{2-} concentration in the drainwater decreased in the period studied (Table 4) along with reduced load by precipitation. In contrast, the complementary studies in deeper groundwater showed that SO_4-S concentrations remained constant in these waters (Table 4).

Deeper groundwater had different chemistry and ionic trends than the shallow groundwater (Table 4). Deeper groundwater mainly provides information about the older long-term translocations. Moderate and decreasing concentrations of Ca indicate relatively old water without contact with Ca-rich layers.

Soil acid load

The high leaching of Ca removed by drainwater (Table 5) might enhance soil acidification. However, the documented high effective base saturation of the soil, topsoil as well as subsoil, indicates a good ability to buffer acidity loads and average pH was satisfactorily high, namely 6.6 in the drainwater and 6.5 in the surface groundwater. Plant uptake of base cations and their removal in harvested products might also involve substantial soil acidification but were approximately counteracted by the added fertilisers, as indicated by the rough estimates of calculated alkalinity (Table 5). Removal of excess base cations by drainwater and by harvested products was in both cases similar to an approximately ten times higher acid load than the negative alkalinity via precipitation (Table 5). The latter was calculated to be reduced by 6.3 $kmol_c\ ha^{-1}$ during the modified cropping system compared to the original, equal to a reduction of more than 50%, while acidification by plant uptake of base-cations remained constantly high. A slow but significant increase in HCO_3^- ions was indicated to occur in the drainwater, as well as a faster increase in the groundwater (Figure 4). The increase in the drainwater was equal to 0.4% as calculated for the entire period 1977-2004. Meanwhile the catch crops had efficiently taken up NO_3^- ions but the soil had delivered more HCO_3^- ions instead. Intensive catch cropping during the modified period reduced the NO_3-N leaching from 44-to 32 $kmol_c$ ha^{-1} in comparison with the original period. The reduction in NO_3^- ions (equal to 12 $kmol_c$ ha^{-1}) loaded the soil, while leached alkalinity increased from 35 to 42 $kmol_c$ ha^{-1}. Based on these estimates, changes in cropping were indicated to be a more important mitigation of water acidification than the reduction in acid rain. This is also indicated by the negative correlation between HCO_3^- and $NO3^-$ ions in the drainwater during the periods with catch crops (Pearson's correlation coefficient = -0.60, p = 0.00).

Discussion

Even for this sandy soil some minor lateral long-transport of P may have taken place since higher P-AL numbers were found at the topsoil lower end of the slope in the south-east part of the field compared with the rest of the field. Since the two sampling strategies gave similar results, sampling along slopes is of less importance for this loamy and sandy soil. In contrast sorption capacity in the subsoil is more important since P probably sorbs to the soil matrix when water is moving slowly down through the profile. Subsoil values have also proposed for use in calculating the risk of P leaching in sandy soils in general (Ulén, 2006). Furthermore, since the ability to retain P in the subsoil based on chemical analysis was indicated to be similar by the two laboratory methods the most appropriate method may be chosen.

Similar sorption abilities are often found in this region. In contrast the degree of P saturation (DPS) of 5% in the soil extract of the subsoil was low for the condition of other counties of southern Sweden, where median values for sandy soil are more than twice as high

(Ulén, 2006). For clay soils significantly lower sorption ability of the topsoil were often found. In addition, for clay soils susceptible to erosion less Ca addition might influence the future capacity of the topsoil to bind P, since formation of Ca-P complexes has been found to be important for retention of colloidal P even on non-calcareous soils (Ulén and Snäll, 2007). For the present field, with documented very low losses of colloidal particles, this change should be of minor importance. Consequently this soil seems to have a very good ability to sorb P in drainwater, and agricultural practices such as changes in manure application based on in-field variations in DPS values seem to be of minor importance for P leaching via field drains at this part of the region. However, sampling along slopes should be recommended for more fine-textured soils (Heckrath *et al*., 2005; McDowell *et al*., 2001), and P manuring application rate should be adapted to site conditions based on the ability to retain P determined from chemical analysis of the soil.

The findings from the present site demonstrate the general differences between P and N retention mechanisms in agricultural water from a sandy soil. Even after storm- or snowmelting events no abrupt changes in P concentration took place, no general macropore flow might have occur but adsorption may take place of P during water percolating through the soil profile. In contrast, reduced N mass transport is an essential part of reduced NO_3^- concentration from the root zone. In certain areas groundwater may constitute an important N store for receiving streams (Ruiz *et al*., 2002).

The magnitude of NO_3-N reduction in the present study was faster than indicated by recent (1993-2004) trends in agricultural rivers in SW Sweden, where catch crops have been cropped on 13-17% of the arable land for five years (Ulén and Fölster, 2007). This is not surprising since the present field represent more than ten years of modified crop rotation and, in addition, more frequent cultivation of catch crop, equal to 41% of the area. Theoretically and generalised relative reduction in NO_3-N leaving the root-zone as a result of the corresponding crop rotation including catch crops was also slower, only 13% during the entire period, based on estimates from model calculations. The apparent reductions in drainage and shallow groundwater were even faster (Figure 3). Generally sandy soils with good water drainage are relatively unlikely to promote fast microbial denitrification and this process has also been estimated to be of minor importance at the Mellby experimental field (Aronsson and Torstensson, 1998). Since NO_3 generally follows advective forces of the water, a main reason for fast reduction in concentrations may be a generally short transit time in the present surface groundwater moving just above a clay layer. In this shallow groundwater K decreased in a similar way as in the drainwater, as did NO_3 - N. These similarities in observed concentration changes supports the general finding that the transit time for the surface groundwater is short at the present site, in contrast to several other Swedish sites (Gustafson, 1983). Chemical reduction of NO_3-N by pyrite may also have taken place in the groundwater near the clay layer in the field studied here. This cannot be clearly verified since no significant increase in the pyrite oxidation product SO_4^{2-} could be estimated in the shallow groundwater. The concentration of this ion that decreased in the drainwater showed no trends in the shallow groundwater. These results were most probably the result of negative S load to the soil together with retardation by sorption.

The direct impact from fertilisers on ionic composition of the groundwater was small in the present study but. Furthermore indirect changes in weathering rates and ion-exchange equilibrium of most constituents in groundwater as a result of agricultural impacts on the recharge fluxes of NO_3^- and H^+ were apparently small except for HCO_3^-. Based on the poor correlation no exchange of Na^+ ion apparently occurs between drainwater and surface water. In contrast, the relatively high and increasing concentrations of Na in the shallow groundwater may indicate a net accumulation of this ion.

The clay layer in the subsoil of the agricultural field bottom mainly seems to form a hydraulic and transport barrier since more constant concentrations occurred in the deep groundwater. However the Na^+ ion may be an exception and increasing concentration of Na in the shallow groundwater at the present site might have been a result of mass transfer from deeper to more shallow groundwater, the former being quite rich in Na. Alternatively ionic exchange may occur between the lower layer of shallow groundwater and the clay matrix layer. The latter suggestion may explain the fact that the apparent relationship between NO_3^- and Na^+ concentrations in the shallow groundwater was negative and was even stronger when groundwater level was generally low. At the deepest sampling depth (5.5 m), the Na concentration probably increases as more water is pumped out from the groundwater pipes by sampling. The very sampling may be a significant water movement in this rather stagnant water with slow lateral transport.

Generally groundwater reaction rates may be estimated based on tracers and not on conservative ions. Separation of the components derived from groundwater and soilwater is also desirable for a deeper understanding of the processes (Langan and Hirst, 2004), but was outside the scope of the present study.

Conclusions

- Phosphorus losses were related to the ability of the subsoil to retain P at the present site, whereas soil sampling strategy and laboratory method were of minor importance for risk estimates of P losses.
- Modification of the crop rotation can rapidly decrease surface water and shallow groundwater nitrogen loads by leaching, even under intense farming. At the present site this might have been promoted by a short transit time of the shallow groundwater.

- Modification of the crop rotation in the present study, i.g. inclusion of a catch crop, also prevented acidification of the drainwater since the alkalinity increased while the nitrate concentration decreased. Compared with this, reduced load of acid rain was indicated to be of less importance.
- Deeper knowledge of processes resulting in changed ionic composition of the groundwater should be obtained by tracer studies.

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Table 1. Acreage of crops (%) grown during the original cropping period (1977-1990) and in the modified crop rotation (1992-2004), including catch crops

Crop/Year	Original 1977-1990	Modified 1991-2004
Oats	13	14
Barley	3	11
Spring wheat	7	19
Winter wheat	25	7
Spring oilseeds	14	0
Catch crop	*0*	*41*
Peas	10	0
Potatoes	14	21
Sugarbeet	0	13
Ley	13	0
Fallow	0	14

Table 2. Average (Av) and variance (Var) of calcium, phosphorous, iron and aluminium extracted in acid ammonium lactate (Ca-AL, P-AL, Fe-AL and Al-AL) (mg 100 g dry soil^{-1}). Phosphorus saturation index (PSI) and calculated degree of phosphorus saturation (%) based on the extraction (DPS-EXT) and on phosphorus sorption index (DPS-PSI) at different soil depths based on 34 samples

Depth	Ca-AL		P-AL		Fe-AL		Al-AL		PSI		DPS-EXT		DPS-PSI	
	Av	Var	Av	Var	Av	Var	Av	Var	Av	Var	Av	Var	Av	Var
0-23	147	26	8.8	27	12.5	62	54.9	36	9.5	13	13.6	34	30.6	32
23-35	92	73	2.8	57	10.8	120	56.0	57	10.1	33	5.2	89	10.0	75
35-65	36	81	0.9	87	7.4	123	27.0	70	6.6	42	5.0	172	5.5	105
65-100	26	92	1.3	73	3.5	95	11.9	81	4.5	40	15.2	97	12.4	89

Table 3. Average concentrations (mg l^{-1}) of nitrate nitrogen (NO_3-N), organic nitrogen (ON), dissolved reactive phosphorus (RP), non-reactive phosphorus (NRP) and potassium (K) in drainwater during 1976-2005. Comparisons were made between: periods/years of original (1977-90) crop rotation and modified (1992-2004) crop rotation; loadings of pig slurry (Pig slurry); growing cereals with catch crops (Catch crop); growing potatoes and growing cereals/oilseeds without catch crops (Cereals). Concentrations with non-significant differences are given within brackets. The last column shows number of years (Y) and number of fields/plots (No) with the different agricultural managements

	NO_3-N	ON	RP	NRP	K	YxNo
Arable field years 1977-2005						
Pig slurry, original	13.0	1.2	(0.005)	(0.014)	5.4	14x1
Catch crop, dairy, modified	7.2 ^{b}	0.9 ^{b}	(0.006)	(0.015)	4.0 ^{b}	14x1
Pig slurry	11.8	1.1	(0.007)	(0.018)	5.0	8x1
Catch crop	6.2 ^{b}	0.8 ^{b}	(0.005)	(0.016)	3.9 ^{b}	7x1
Potatoes	13.9	(1.2)	(0.007)	(0.014)	(5.3)	6x1
Cereals	10.3 ^{a}	(1.1)	(0.005)	(0.014)	(5.1)	9x1
Experimental plots 1984-1997						
Pig slurry	19.4	(1.7)	(0.032)	0.047	15.0	4x4
Catch crop	3.6 ^{b}	(1.5)	(0.040)	0.028 ^{b}	8.0 ^{b}	7x2
Potatoes	17.6	(1.8)	(0.038)	(0.044)	(6.1)	6x3
Cereals	11.1 ^{a}	(1.8)	(0.032)	(0.053)	(9.4)	10x2

[b] Highly significant ($p \leq 0.01$)

[a] Significant ($0.01 < p \leq 0.05$)

Table 4. Average concentration (Conc.) in precipitation, drainwater *(Drainwater*), and in groundwater at 1.7 m, 2.2 and 5.5 m depth (*Groundwater*) of calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), nitrogen as nitrate (N^-), chloride (Cl^-) sulphate as sulphur (S^{2-}) and alkalinity (Alk) in millimole of charge per litre ($mmol_c\ l^{-1}$) during 1981-2004. Estimated significant ($z > 1.78$) trends in drainwater (non-significant trend within brackets) and the direction of significant trends (Trend direc.) for precipitation and groundwater. Significant seasonality (ssy) according to Kruskal-Wallis test is indicated for the parameters in the groundwater

Period	Ca^{2+}	Mg^{2+}	K^+	Na^+	N^-	Cl^-	S^{2-}	Alk
*Precipitation**								
Conc.	0.008	0.012	0.003	0.050	0.043	0.060	0.052	-0.035
Trend direc.	0	0	0	0	0	0	-	+
Drainwater								
Conc.	1.79	0.28	0.13	0.52	0.55	0.50	0.72	0.88
Trend direc.	-0.025	(-0.001)	-0.001	(-0.001)	-0.38	-0.005	-0.022	+0.004
Groundwater (1.7 m)								
Conc.	1.65	0.40	0.12	0.91	0.42	0.63	1.30	0.73
Trend direc.	-	+	-	+ (ssy)	- (ssy)	(ssy)	(ssy)	0
Groundwater (2.2 m)								
Conc.	2.76	0.77	0.12	2.45	0.054	1.10	1.42	3.41
Trend direc.	-	+	0	+	- (ssy)	+	(ssy)	+
Groundwater (5.5 m)								
Conc.	1.66	1.30	0.31	11.91	0.026	5.85	1.47	7.72
Trend direc.	- (ssy)	+	- (ssy)	+ (ssy)	-	+ (ssy)	0	+

* in addition H^+ 0.035 and NH_4^+ 0.046 ($mmol_c\ l^{-1}$)

** Negative alkalinity calculated from the ionic composition

Table 5. Inputs by precipitation (*+Precipitation*) and by fertilisers and manure *(+Fertilisation*), removed by crops (*-Crop*) and loss by drainage *(-Drain*) of calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), nitrogen as ammonium, (N^{+}), nitrogen as nitrate (N^{-}), phosphorus as hydrogen phosphate (P^{-}), chloride (Cl^{-}) and sulphate as sulphur (S^{2-}) and alkalinity (Alk) in kilomoles of charge per hectare ($kmol_c$ ha^{-1}) during two (14 year) periods of different crop rotations, original (1977-1990) and modified (1992-2004)

Period	Ca^{2+}	Mg^{2+}	K^{+}	N^{+}	N^{-}	P^{-}	Cl^{-}	S^{2-}	Alk
+Precipitation[a]									
Original	1.2	2.6	0.3	4.9	4.6	-	15.2	8.5	-11.7[b]
Modified	1.0	2.0	0.3	3.8	4.1	-	9.8	5.2	-5.4[b]
+Fertilisation									
Original	33.9	11.6	21.6	48.6	49.9	10.8	7.5	17.6	(31)[b]
Modified	25.6	23.8	31.1	67.8	44.4	11.6	6.6	27.0	(35)[b]
-Crop									
Original	8.6	10.0	23.9	-	-	6.3	2.0	4.2	(43)[b]
Modified	9.5	10.0	22.2	-	-	6.9	2.5	2.1	(41)[b]
*-Drain**									
Original	104.3	14.0	7.4	0.1	43.5	0.1	28.6	43.4	34.5
Modified	89.6	15.1	6.0	0.1	31.5	0.1	24.4	36.8	42.1

[a] Estimates from the period 1980-2002 and 1980-2004 respectively

[b] Calculated from the ionic composition. The calculated alkalinity is negative in precipitation water

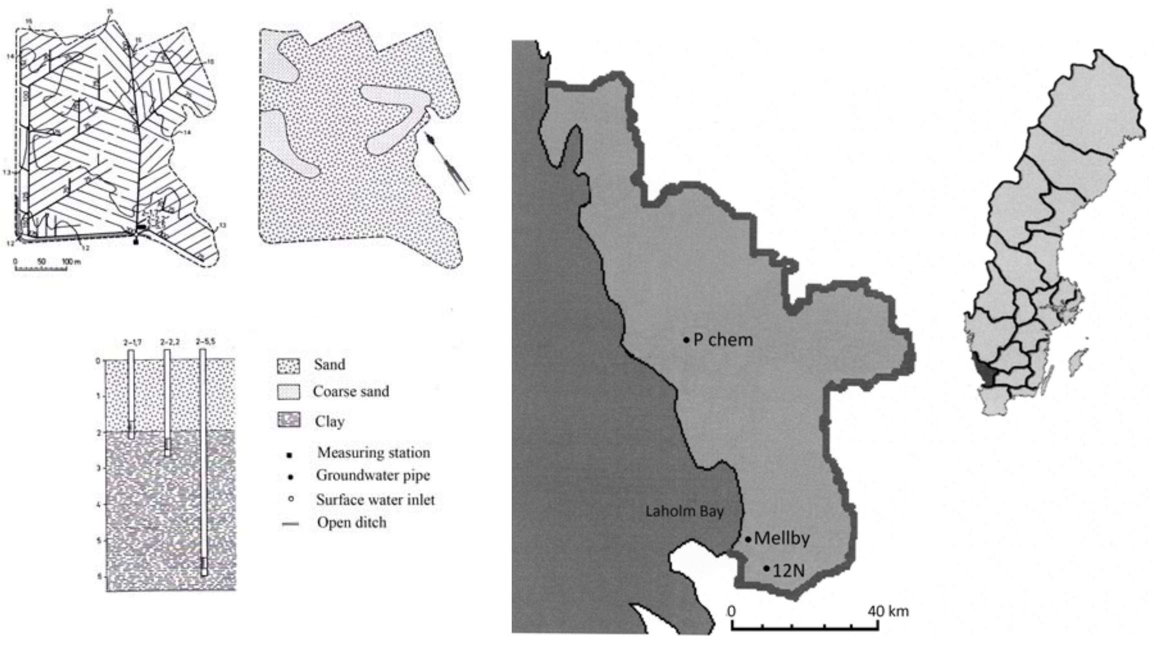
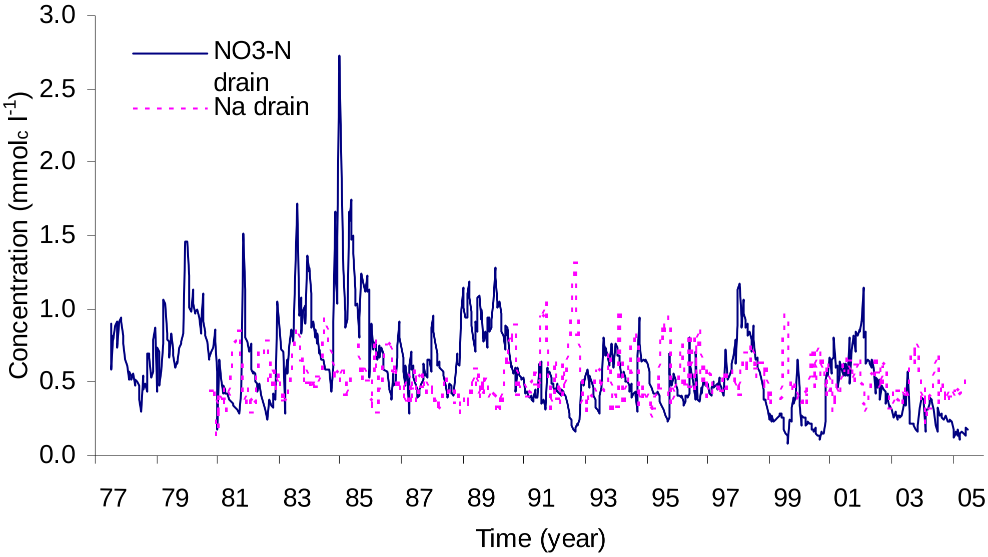


Figure 1. Central county of Halland in SW Sweden with the arable monitored field N12, the experimental site Mellby and precipitation station used for chemical determinations (P chem). To the left tile drainage map, soil map and soil profiles with groundwater

pipes.


3.0
2.5
2.0
1.5
1.0
0.5
0.0
Concentration (mmolc l-1)
NO3-N drain
Na drain
77
79
81
83
85
87
89
91
93
95
97
99
01
03
05
Time (year)

1

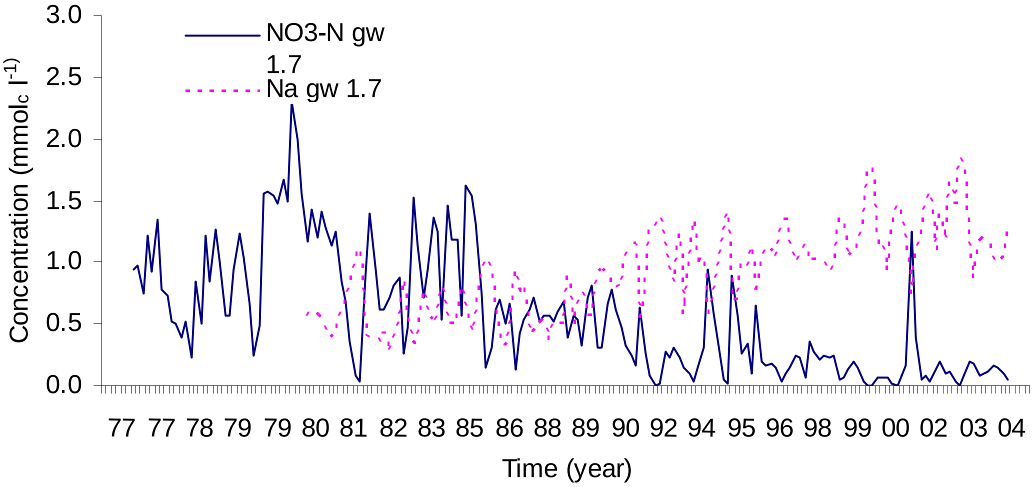


Figure 2. a) Measured concentration (mmol$_c$ l^{-1}) of nitrate nitrogen (NO$_3$-N) and sodium (Na) in drainwater. b) Measured concentration (mmol$_c$ l^{-1}) of nitrate nitrogen (NO$_3$-N) and sodium (Na) in the shallow groundwater pipe with the inlet at 1.7 m depth.

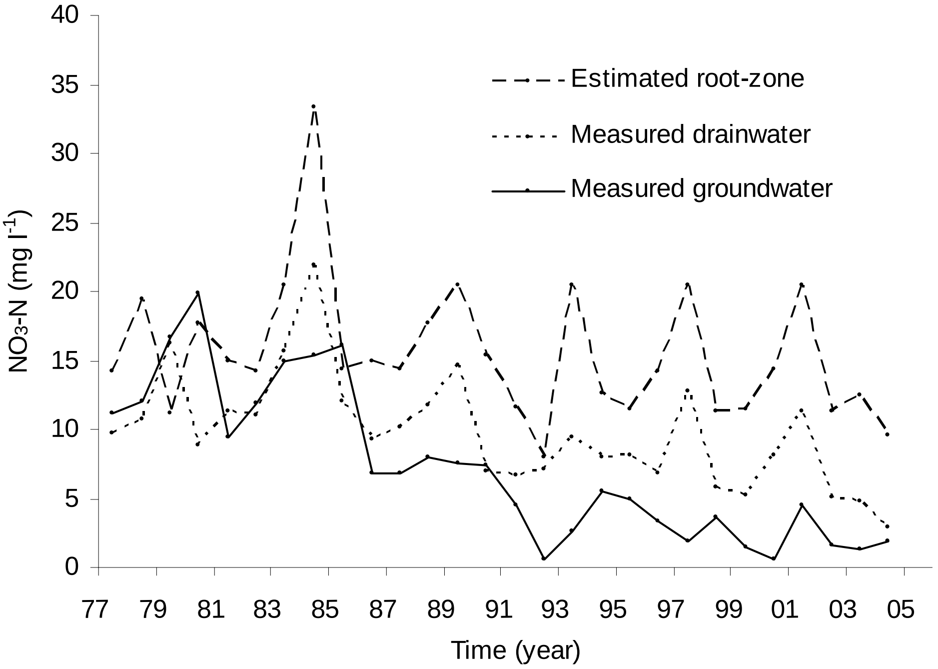


Figure 3. Theoretically estimated yearly concentrations of nitrate nitrogen (NO$_3$-N in mg l^{-1}) leaving the root-zone together with actual measured concentrations in drainwater (flow-weight averaged) and shallow groundwater (right averages).

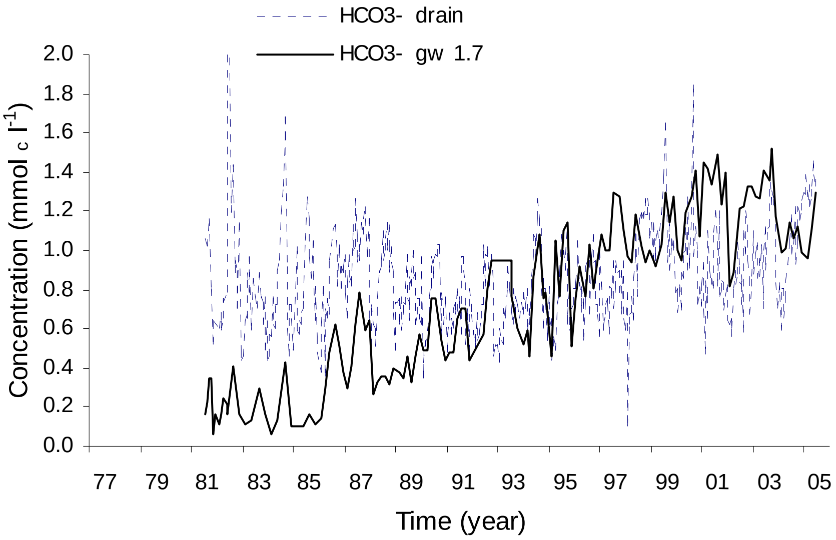


Figure 4. Concentrations (mmol$_c$ l^{-1}) of hydrocarbonate-ions (HCO_3^-) in drainwater and in shallow groundwater.