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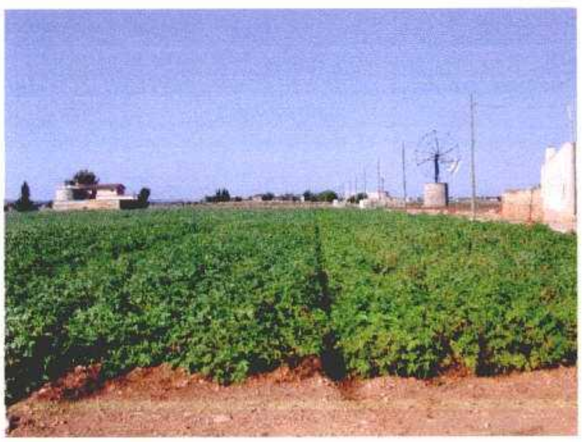
GOVERN BALEAR
Direcció General de Recursos Hídrics

MINISTERIO DE CIENCIA Y TECNOLOGÍA

Nitrate ion investigation in the vadose zone using experimental plots in Sa Pobla, Majorca.



This study forms part of the work planned by the agreement between the Dirección General de Recursos Hídrics del Govern Balear and the Instituto Geológico y Minero de España with the participation of the Universidad Politécnica de Cataluña.

By Kelly-Jane Wallis

Contents

Introduction

In 1996, the Instituto Geológico y Minero de España (IGME) and the Dirección General de Recursos Hídrics del Govern Balear (DGRH) realised a study which concluded that the northern half of the hydrogeologic unit 18.11, the Inca-Sa Pobla plain, should be declared as a nitrate vulnerable zone, originating from agricultural practises. By the order 4484 on the 24th of February 2000, the northern portion of the Sa Pobla sub basin was officially declared as a "*Nitrate Vulnerable Zone*" in accordance with the European Council published in BOCAIB No. 31 (11th of March, 2000). The current situation found in Sa Pobla is alarming. Over the past 30 years there has been a gradual increase in nitrate concentrations found in groundwater. In 2003, nitrate concentrations in bore water samples collected in this vulnerable zone ranged from 10 to 950 mg/L with an average of 180 mg/L.

Study Objectives

The objectives of this study are to contribute to the requirements established in the Art.6 of the Decreto Real 261/1996 "*of the protection of water against contamination produced by nitrates from agricultural sources*", and to complete the requirements ordered by the Consellería de Medio Ambiente on the 24th of February 2000, by realising a program of control. The study incorporates the investigation of the nature and evolution of nitrogen components in the vadose zone and groundwater, the realisation of soil nitrogen balances and the estimation of nitrates leached to the aquifer.

Setting

Geographical Location

The study area is located to the north-east of Majorca Island within the Inca-Sa Pobla plain. The topography of this zone is characterised by a smooth relief declining towards the sea, this flat plain provides favourable conditions for agricultural production.

The Inca-Sa Pobla plain is the main agricultural area of the island. The cultivated area zone covers a total area of 37 070 ha, where potatoes, legumes, cereals and vegetables are the most common produce for local, national and international markets. The majority of plots found in Sa Pobla depend on irrigation for high produce throughout the year.

The 2 current experimental plots are located between Sa Pobla and the natural wetlands Park S'Albufera of Majorca, close by the stream Torrente de Muro (Figure 1). The elevation is 5 m.a.s.l and the ground water depth generally varies between 1.5m and 3.5 m.

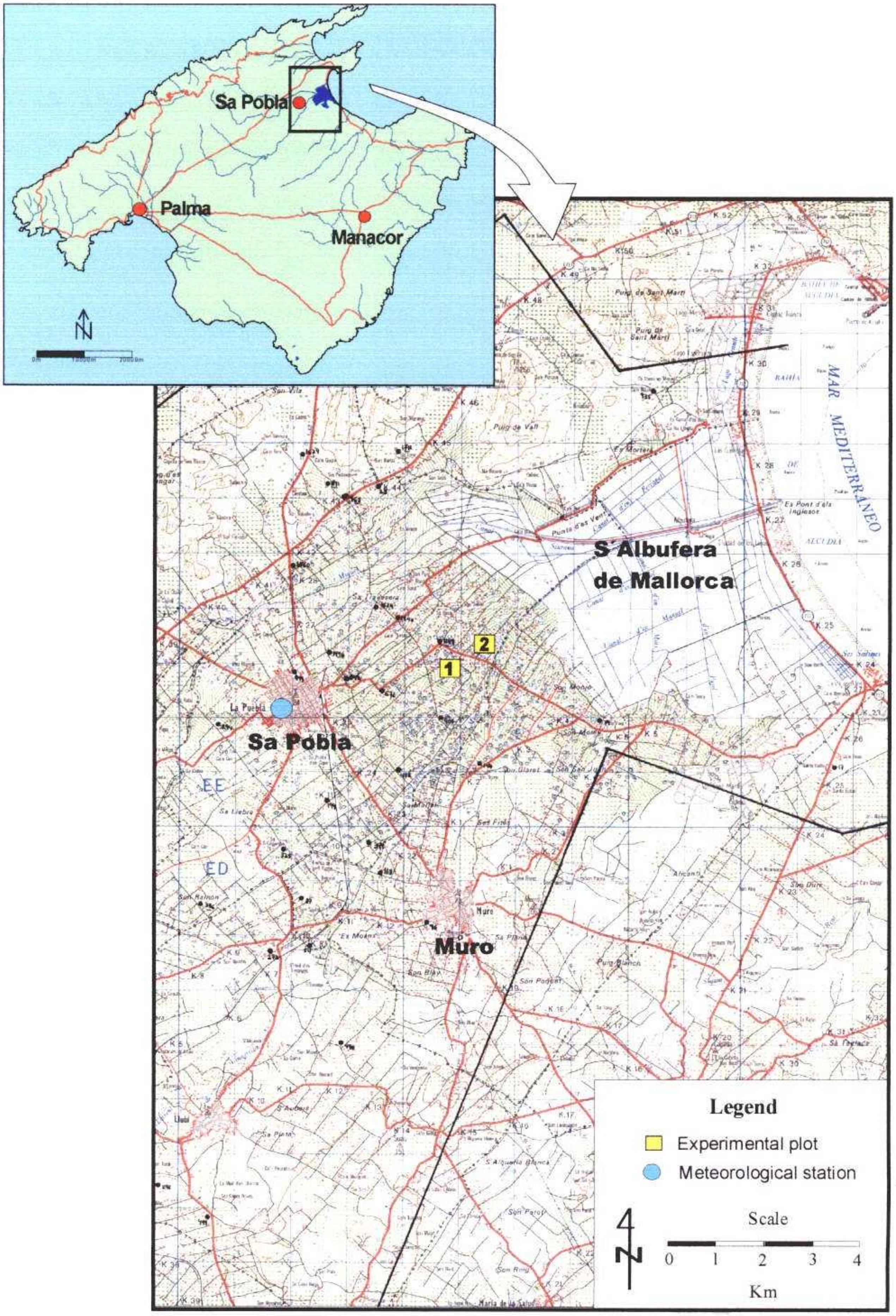


Figure 1: Location of experimental plots.

Geological Context

The Inca-Sa Pobla alluvial plain, located within the central plains of Majorca, is characterised by a NE-SW trending subsiding basin filled with post orogenic Miocene and Quaternary materials. These materials show gentle slopes of less than 20º and generally present a progressive angular unconformity due to different stages of subsidence in the basin. The basin can reach up to 1800 m depth and is subdivided into the Inca and Sa Pobla sub basins. They are separated by the Puig of Santa Magdalena which originated during the sedimentation of the Upper Miocene-Quaternary. The bedrock is composed of impervious Serravalian (Marls from Pina), however locally, structures of an older age can appear (Figures 2 a and 2 b).

The following are the lithologies of the materials which from the Inca-Sa Pobla Unit and its boundaries (After Barón, 2003):

Quaternary (Q): in the central zone, red silts, clays and gravels are found. In the upper 5 m of the profile there is a significant clay portion and abundant pebbles tending to be rounded to well rounded and have been found to reach up to 15 cm in diameter in the study zone. Eolianites are found in the coastal zone. The thickness of this unit can reach up to 70 m.

Pliocene (PL2-PL1): the upper part is composed of yellow calcarenites and eolianites with a thickness of 75 m which outcrop mainly in the Muro sector and the southern edge between Santa Eugenia and Sencelles. The lower portion of the Pliocene is constituted of grey marls which reach a thickness up to 240 m.

Messinian (M52): the upper part outcrops in the southern edge between Marratxí and Muro, and Puig de Santa Magdalena and Costix. It is composed by oolitic shelly limestone, with a lateral change to whitish marls facies towards the centre of the Sa Pobla sub basin. This formation is known as "Pont d'Inca Limestones" and varies in thickness from a few meters up to more than 100 m. The lower part of the Messinian (M51) can reach a thickness of 150 m and is constituted of grey marls with organic matter layers and fauna (osteroids, ceritds). This sector does not outcrop in the study area.

Tortonian and Upper-Messinian (M4-5): is mainly composed by the "Reef Unit"made up of: the shelf limestone and the reef complex, a lagoon facies (calcarenite sediments and oolitic bars with some marl levels), reef facies (bioconstructed dolomitized coral limestones) and slope facies (white limestone). They appear only in the southern edge of the study area and are especially important in Costix-Llubí-Muro. Thickness may range from a few meters up to more than 250 m.

Tortonian (M4): grey marls with Heterostegina, which form the base of the post tectonic materials filling the basin. They do not outcrop and reach a thickness up to 100 m.

Terrigenic fringe complex: red silts with pebbles and has a similar facies to the Quaternary. This formation extends from the Tortonian to the Pliocene. The unit outcrops to the north where the thickness reaches over 500 m . In the Campanet sector it changes to a coarser facies with marine influences and constitutes the "conglomerates of Campanet".

Serravalian-Langhian (M3): grey gypsum marls (Marls from Pina, M32) which make up the impermeable bedrock at the base of this unit. In some areas "Son Verdera´s Limestones" a lucustrine limestone overly the grey marls. The marls outcrop to the north of Inca, constituting part of the western impermeable edge. Its thickness is variable.

Burdigalian (M2): is composed of a Turbiditic Unit made up of marls with interlayed sandstone. It outcrops in the Eastern edge of the area and between Sineu and Muro.

Aquitanian (M1): a conglomerate and fluvial sandstone with lucustrine marls. Its thickness may surpass 100 m and outcrops at the edges of the Inca Unit, to the south of Santa Maria and to the north of Campanet.

Eocene-Oligocene: limestones, marls, sandstones and conglomerates outcrop north of Inca and in the Puig de Magdalena.

Cretaceous (C): marls with a whitish marly limestone which outcrop abundantly at the northern border at the Tramuntana Mountain Range. Within the study zone they outcrop between Campanet and Alcudia Port and at Puig de Magdalena.

Lias (L): dolomites, dolomitic limestones and oolitic limestones which outcrop at San Miguel, Es Fangar, Puig de Son Vila and Son Fe, and Puig de Magdalena.

Keuper (K): coloured clays and gypsum which constitute the base materials of the unit. They outcrop at Puig des Fangar.

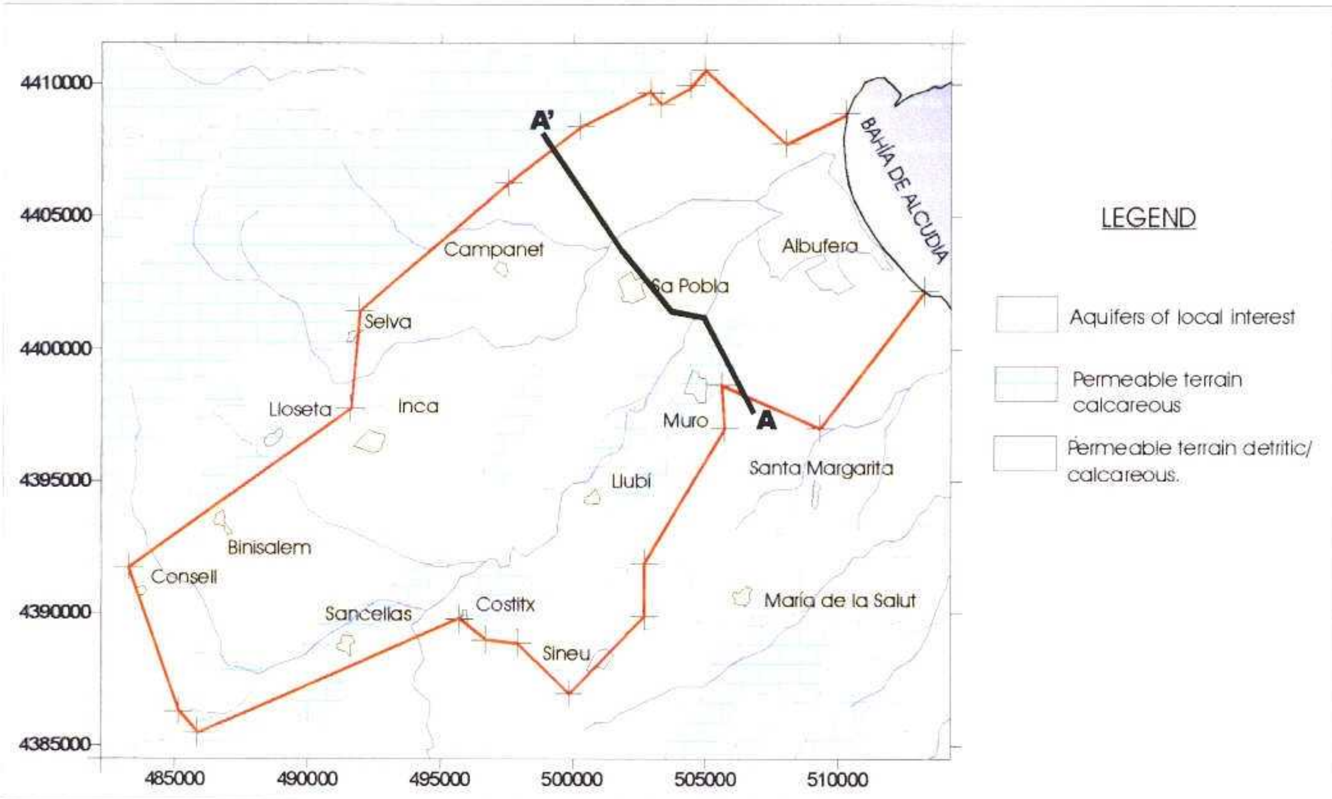


Figure 2 a: Map of Hydrogeologic Unit 18.11, Inca-Sa Pobla plain (Modified from Govern de les Illes Balears. Consellería Medi Ambient, 2002).

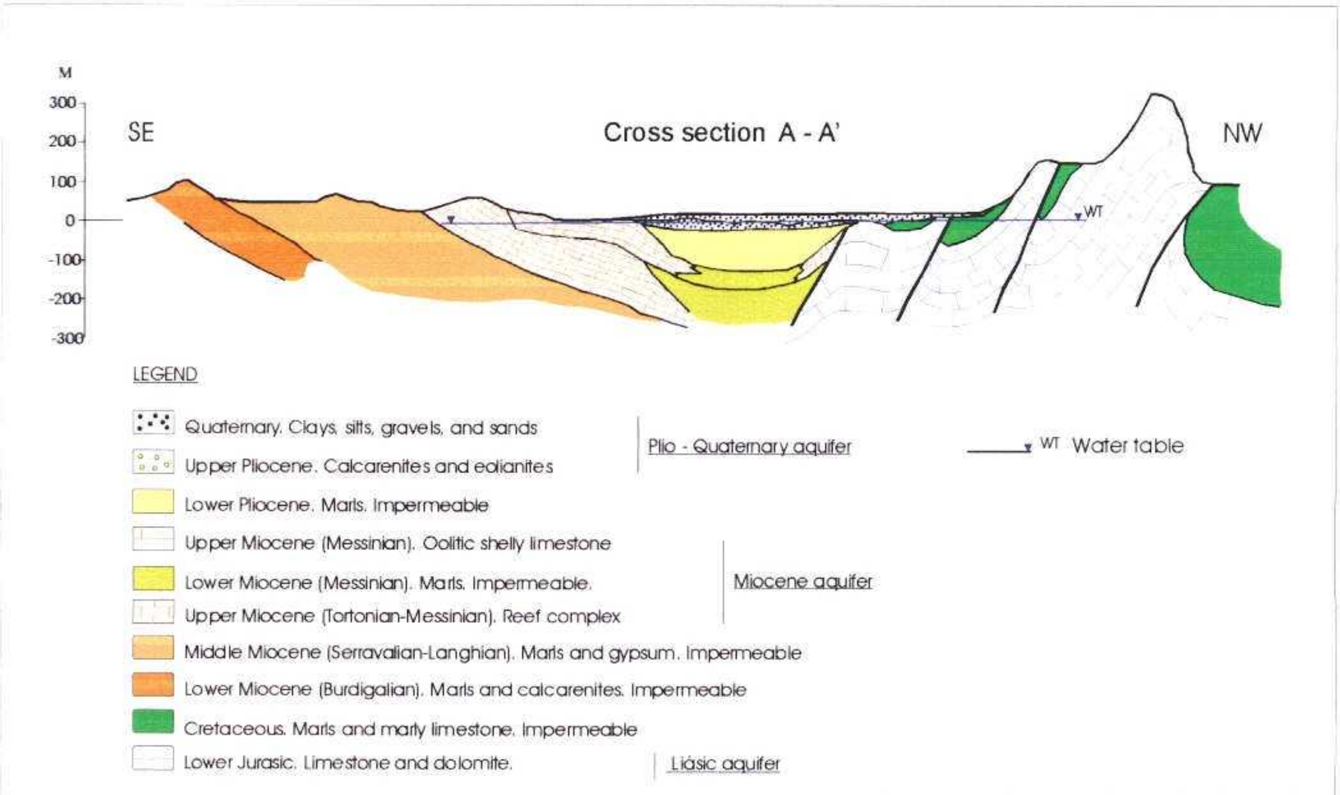


Figure 2 b: Geological cross section of Hydrogeologic Unit 18.11, Inca-Sa Pobla plain (Modified from DGOH, 1987).

Hydrogeological Context

The hydrogeological unit Inca-Sa Pobla has an extension of 415 km^2 elongated NE-SW along 35 km and has the following limits:

- North east - the Mediterranean Sea
- North/north west - the Tramuntana Mountain Range (by the hydrogeologic units Formentor, Almadrava, Ufanes and Alaró)
- South west - the Palma plain, in the area of Marratxí the boundary consists of marls, in the area located between Costix and Biniali the limit is possibly permeable, however the impermeable limit reaches the height of the groundwater table.
- South west – the central mountain range, formed by the hydrogeological units Serres de Llevant and La Marineta.

Recharge sources to the Inca-Sa Pobla unit are rainfall (with an average annual rainfall of 670 mm), irrigation water return, infiltration of streamwater, infiltration of waste water, domestic supply losses and seawater intrusion. The main points of discharge is directly to the sea, bore water extraction for irrigation and domestic supply. As part of the MEDIS European project, data loggers are to be installed in S'Albufera of Majorca to monitor water outflow in order to have greater precision in quantifying the water balance.

The prominent groundwater flow direction is from the west to the east. Table 1 represents these gains and losses of groundwater to this unit.

Input	**hm^3/year**
Infiltration of rainwater	50
Infiltration of stream water	10
Returns of irrigation water	4.6
Waste water infiltration	3.7
Domestic supply losses	1.7
Seawater intrusion	1.6
TOTAL	**71.6**
Output	
Discharge via S'Albufera	30
Irrigation	30
Domestic supply	11.6
TOTAL	**71.6**

Table 1: Groundwater balance for hydrogeological unit Inca-Sa Pobla (Modified from Barón, 2003).

The following six geological formations previously mentioned constitute aquifer materials:

- Quaternary deposists (Q)
- Pliocene limestones and sandy limestones (PL2)
- Messinian carbonated upper complex (M52)
- Messinian-Tortonian facies and reef complex sandy limestones (M4-5)
- Lias dolomites and limestones (L)
- Gravels and conglomerates of the marginal Terrigenic complex.

The differing geological materials can be grouped into 2 different aquifers, the upper aquifer and the lower aquifer.

The upper aquifer, that of the study area, is an unconfined detritic aquifer consisting of Quaternary deposits varying in thickness between a few meters up to 70 m found in the central part of the Sa Pobla sub basin. This aquifer is hydraulically connected with the other neighbouring aquifers. Transmissivity rates are between 50 and 100 m^2/day and permeability rates between 8 and 15 m/day (Barón, 2003).

The lower aquifer consists of Messinian aged materials (M52, M4-5) and of Lias limestones and dolomites. The M52 can also form an independent aquifer of varying thickness with a maximum of 100 m. Messinian aquifers can act as unconfined or semiconfined. The transmissisity is 500-5 000 m^2/day and sometimes higher than 10000-15 000 m^2/day. Lias limestone and dolomites always constitute an unconfined aquifer which rest on the Keuper clays and gypsum. It is laterally connected with the Plio-Quaternary and Miocene formations with a transmissivity varying between 200 and 10 000 m^2/day.

Values of the storage coefficient for the different aquifers are (Barón, 2003)

- Unconfined detritic aquifers: 0.01 – 0.02
- Limestone: 0.02 – 0.04
- Confined aquifers: 0.0001 – 0.001

Methodology

Following a meeting with the participation of Alfredo Barón (DGRH), Concha Gonzalez (DGRH), Rosa María Mateos (IGME), Lucila Candela (UPC), and Kelly-Jane Wallis (UPC/IGME), on the 24th of April 2003, the characteristics of this project were set out. It was decided that 4 experimental plots would be studied, selected by the following criteria:

- That each plot is located within the zone vulnerable in Sa Pobla
- That each of the 4 plots cultivate different crops.
- That the farmer is a trustworthy person and forwards all information of treatments applied on the plot (ploughing, fertilisers, pesticides and irrigation applied).
- That the water table is at a depth between 1 and 5 m in order to control with greater precision the time taken for nitrates to be leached to the aquifer.
- That a meteorological station is located close by permitting precise precipitation data.

Field Work

With collaboration from the co-operative Illacamp S.A., Plot 1 was selected, belonging to Tolo Payeras a member of Illacamp, who sowed potatoes on the 28th of August 2003 and harvested 4 tons of potatoes on the 20th of January 2004. This plot is of particular interest to the study as potatoes are one of the most widely spread crops cultivated in the zone, also for the combination of organic and inorganic fertilisers used. The study of this plot is currently being repeated for a second potato cycle, taking advantage of the already installed instruments to be able to compare between distinct time periods of wet and dry seasons. In this report, the first cycle is discussed.

Plot 2 is a private plot owned by Gabriel Serra who sowed onions on the 1st of December 2003 and plans to harvest in May 2004.

Instrumentation for in-situ observation in the vadose zone

In each plot the following was installed in order to monitor the vadose zone (see Figure 3):

- 3 Time Domain Reflectometry (TDR) tubes to 2 m depth. The TDR probe used is a TRIME-FM model, a geophysical method used to determine the in-situ moisture content in the soil.
- Tensiometers to 30, 60, 90 and 120 cm depth with duplicates where instruments are available. Tensiometers are used to determine the in-situ suction capacity of the soil and an indirect method of determining soil moisture content. Tensiometers are revised weekly.
- Suction capsules (or suction lysimeters) to 30, 60, 90 and 120 cm depth with duplicates where available. The suction capsules were sampled approximately once a month with a vacuum of 65 cb applied weekly. The amount of water sample recovered in each capsule varied from 0.2 litres to more than 1.0 litre. In the case of scarce water sample recovery, the rubber stopper was revised, replaced with new tubing and sealed airtight with silicon.
- One piezometer made of PVC tube with slits along 3 meters (1 to 4 meters depth) to allow for water table fluctuation.

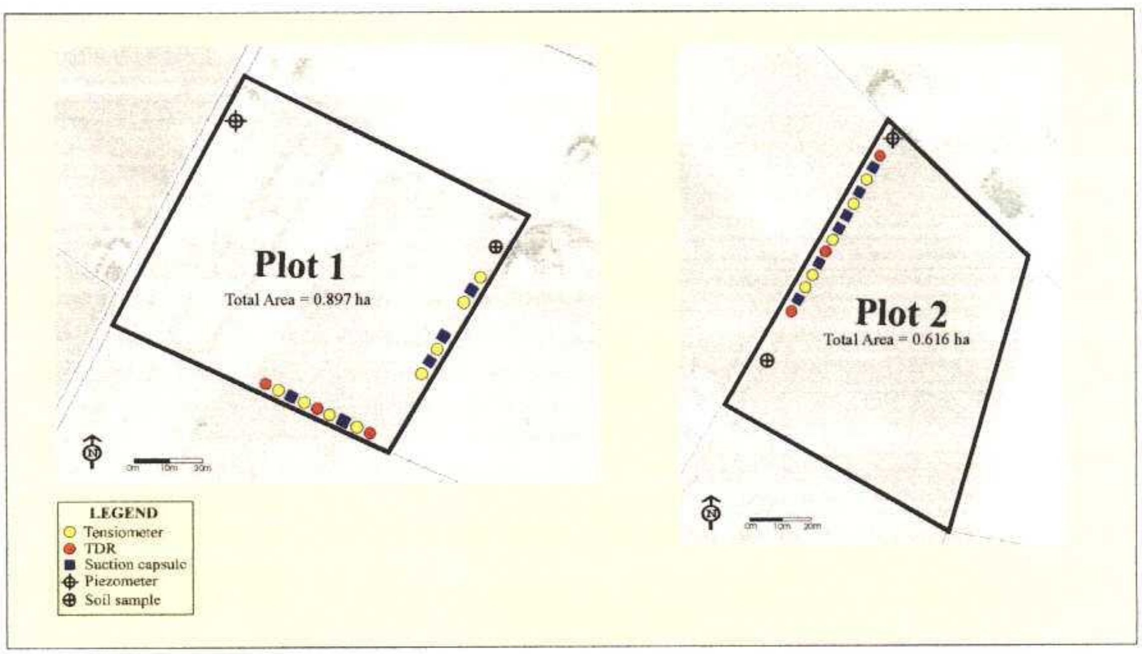


Figure 3: Design of plots 1 and 2.

Drilling and Installation of Instruments

A manual helicoidal T-bar perforated the soil for the installation of suction capsules and tensiometers. Each of the 30 cm and 60cm lengthed instruments were installed using this technique, however, with those of greater length it was not physically possible to lower the T-bar past 60 cm depth due to the presence of eolianites and gravels with up to 15 cm diameter. The use of machinery was necessary.

From the 23rd of September until the 2nd of October 2003, a total of 46.1 meters were drilled in the 2 experimental plots distributed in the following manner:

- 2 x 5m depth for soil sampling and piezometer installation
- 3 x 2m depth for the installation of TDR tubes.
- Sections of 90cm and 120cm for the installation of suction capsules and tensiometers.

In Plot 1, the instrumentation was installed 6 weeks after the start of the crop cultivation. In Plot 2 the instrumentation was installed prior to start of the cultivation.

Soil Sampling

From the 2 profiles drilled to 5 m depth, the continuous soil sample was recovered and stored in sections of 1m glass fibre tubes. Exact depths were marked on the tubes at each drilling interval. The tubes were closed with fitting lids and masking tape to prevent moisture loss and were later transported to the Universidad Politécnica de Cataluña (UPC) Soils Laboratory for analysis.

Laboratory Work

All laboratory work has been carried out in the UPC Soils Laboratory, except for water analyses, which have been completed in the IGME Water Analysis Laboratory. Physical properties have been determined for 3 of the 4 soil profiles obtained during the drilling, as shown in Table 1. The 4th soil profile, from Plot 2, remains in the laboratory waiting for its examination.

	Recovered Soil Profiles		
	T1 Plot 1	**T2 Plot 1**	**G2 Plot 2**
Granulometry	✓	✓	✓
Density test		✓	
Moisture content test	✓	✓	✓
Suction-Tension Curve Test	✓		

Table 2: Laboratory tests completed for each soil profile.

Granulometries

The particle size classification used to determine the percentages of grain size was modified from the United States Department of Agriculture standard. The following particle diameter fractions were used (all measurements are given in mm):

> 2.00	Gravel
0.25 – 2.00	Coarse sand
0.05 – 0.25	Fine sand
0.00 – 0.05	Clay and silt

Clay and silt fractions were determined by the difference of the original weighed sample and the remaining fractions, and by taking into account the original soil moisture at corresponding depths. Figure 4 illustrates the vertical distributions of grain size. In profile T1 the major component, gravel, reaches its maximum percentage at a depth of 120 cm and slowly declines with depth as the proportion of the finer fraction clay and silt increases. The second profile from Plot 1, T2, has a higher proportion of clay and silt in the first 30 cm, which then changes to a gravel dominant soil until a depth of 220 cm, where clay and silt once again predominates the composition until the end at 5.25 m. The grain size distribution for the second plot demonstrated by profile G2 is more uniform along its depth with gravels dominating the majority of the profile except for its lower extreme where clay and silt compose over 80% of its composition.

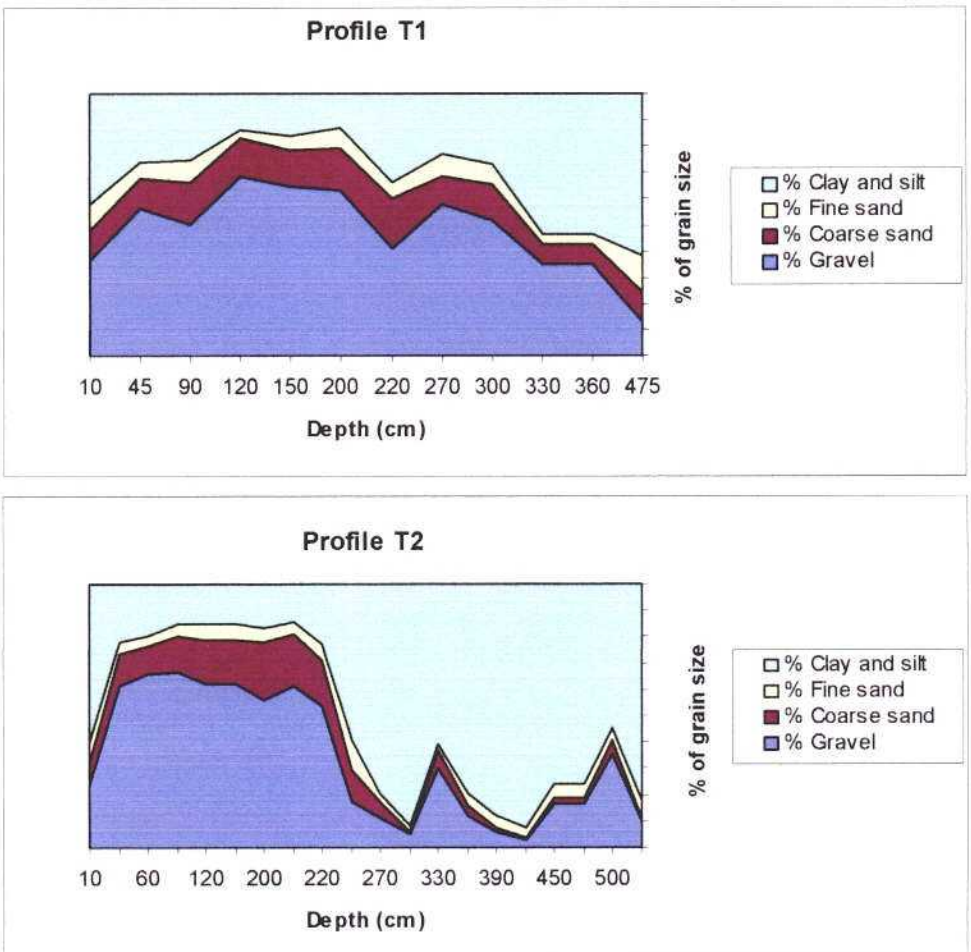


Figure 4: Grain size vertical profiles for soil profiles T1, T2 (Plot 1)and G2 (Plot 2), where each shaded area corresponds to the percentage of that grain size at each depth.

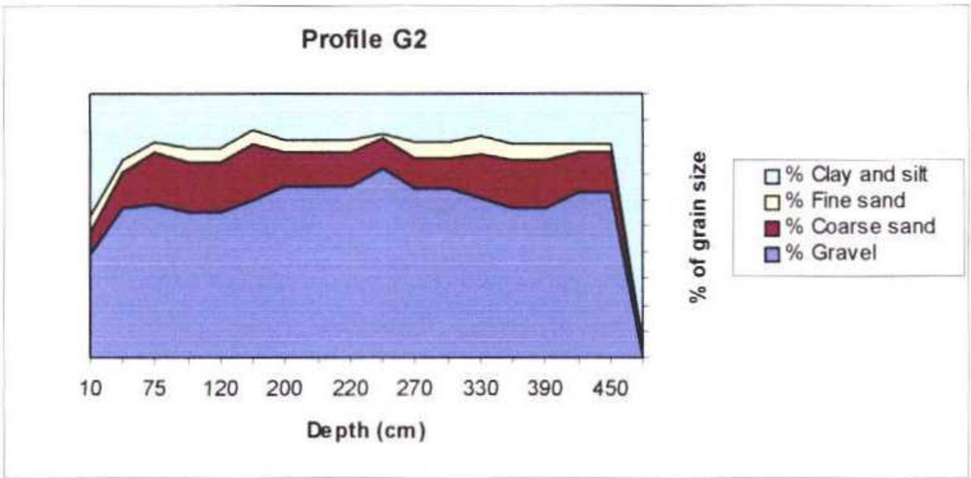


Figure 4 (continued).

Soil Density

Apparent densities were calculated for the soil profile T2 by using rings with 2 cm and 5 cm diameters, with known internal areas. Density tests will be performed on the remaining soil profile G2, in order to have density profiles data from both plots. Figure 5 illustrates that the majority of apparent density values lay between 1.9 and 2.1 g/cm^3. The density obtained by the smaller ring shows an outlier at a depth of 2.85 m, and corresponds to a particle grain size less than 0.05 mm diameter.

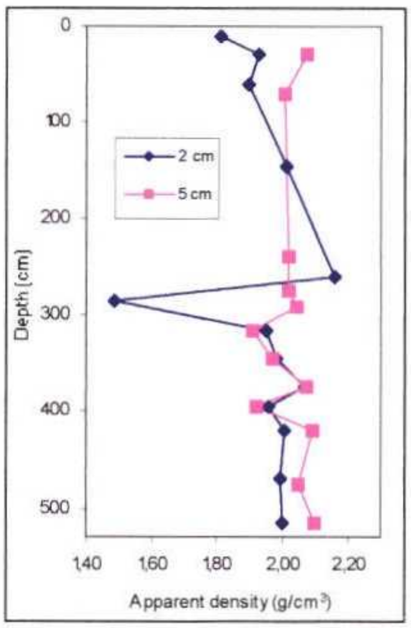


Figure 5: Apparent density profile for Plot 1.

Soil Moisture Content

Figure 6 demonstrates the gravimetric water content as found in the 3 soil profiles. Results were obtained by dividing the water content by the dry soil, dried in an oven for 24 hours at 105° C. Generally the water content is elevated at the beginning of the profile, at depth of 2.5 m and at the bottom of the profile where capillary water is present.

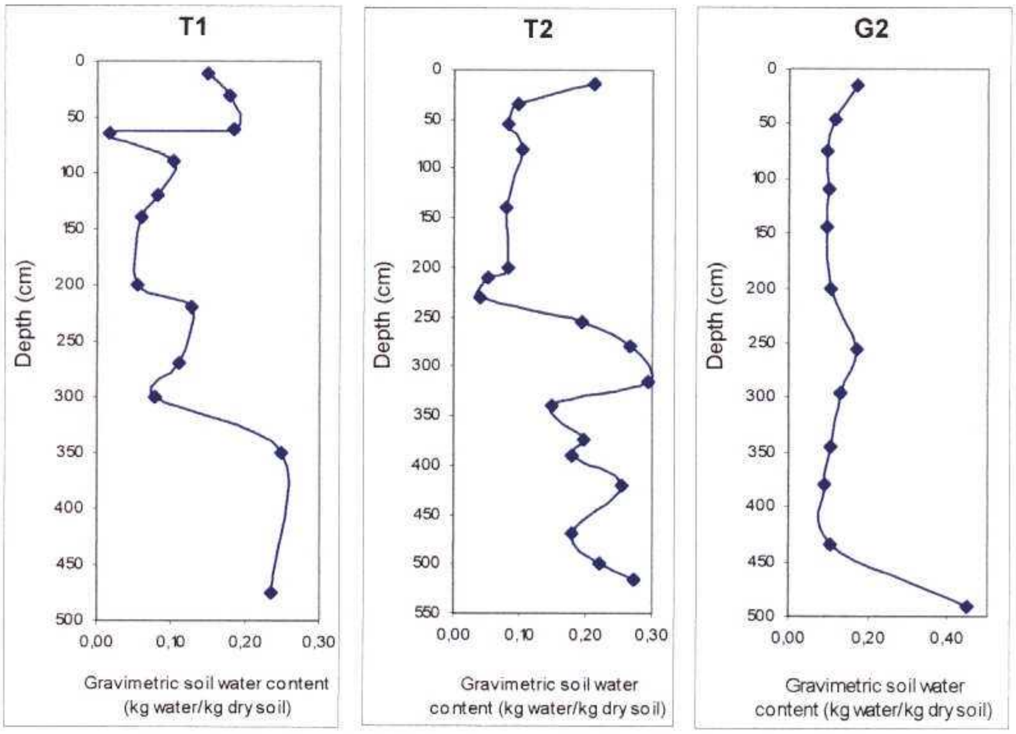


Figure 6: Gravimetric soil water content for profiles T1, T2 and G2.6

Suction-Tension Curve

Water in the vadose zone is subjected to negative pressures defined as suction or capillary tension. This tension is very low under close to saturation conditions and increases as water content decreases. Tensiometers are an instrument designed to measure the water tension in soil. Manipulation of suction value data make an estimation of the water content in the soil and in this way an estimation of the vertical flow can be made (Varela, 1991).

Hydraulic conductivity increases in a non-lineal form with increasing soil water content and suction. The suction-tension curve test represents the established relationship between the soil water content and its energy status.

Currently in the UPC Soils Laboratory, a soil suction test in function, using the vapour pressure method as described by Lloret (2003). These results together with tensiometer data from fieldwork will be analysed using the suction-tension curve in order to have a further understanding of soil water content, hydraulic conductivity and leaching rate.

Results

The analytical results for 3 sampling rounds are analysed here, results from the most recent water samples taken on the 9th of February and the 8th of March 2004 are yet to be returned from the laboratory.

Plot 1 - Potato

Background

The previous crop cultivated on this plot before the start of this study was maize sowed in May 2003. In June 2003, 55 000 kg/ha of manure (a mixture of hen and cow manure) was spread evenly over the plot. According to Illacamp, each ton of manure corresponded to 50 kg N, meaning a total input of 275 kg N/ha (Guimerá, 1992). Further historical land use data beyond May 2003 is not readily available, however it is understood that the plot has been habitually sowed with potato and maize crops, with up to 3 cycles annually.

Vadose Zone Water Samples

Peak nitrate concentrations are found at 90cm depth reaching 3800 mg/L in the water sample taken on the 30th of October , 2003 (Table 3). This depth maintains the highest in concentration for each of the sampled periods. Nitrate evolution graphs for water samples taken in the vadose zone for Plot 1 show the vertical distribution of nitrate concentrations and a gradual decrease in the concentration over time (Figure 7).

The sampling points to 90 cm and 120 cm depth are located along the southern extreme of the experimental plot (Figure 3). This border is connected to that of the neighbour, who most likely influences nitrate concentrations in these 2 sampling points, however to what extent is unknown.

Depth	Date	O_2	pH	Conductivity	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	NO_3^-	NO_2^-	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	K^+	NH_4^+	SiO_2
30cm	30/10/03	15,5	7,6	6305	536	980	228	0	1700	0,38	3,40	156	200	812	34	0,09	41,3
60cm (a)	30/10/03	6,4	7,2	4685	464	388	69	0	1600	0,00	0,24	147	65	680	12	0,30	72,4
60cm (b)	30/10/03	8,9	7,2	5715	744	420	67	0	1800	0,00	0,00	127	103	870	11	0,40	62,4
90cm	30/10/03	10,5	7,2	11085	1125	1005	106	0	3800	0,76	0,09	369	215	1530	30	0,13	34,4
120cm	30/10/03	7,3	7,3	7945	860	930	144	0	2300	0,40	0,18	230	160	1130	29	0,00	37,5
30cm	14/11/03	11,4	7,3	4163	230	830	175	0	1100	0,25	2,00	155	99	554	25	0,07	41,6
60cm (a)	14/11/03	3,7	7,1	5103	393	669	92	0	1515	0,06	0,26	157	70	730	8	0,90	72,6
60cm (b)	14/11/03	N/a*	7,0	5843	487	682	26	0	1795	0,20	0,07	148	86	851	13	0,23	41,8
90cm	14/11/03	5,8	7,0	10523	1160	1050	100	0	3400	0,00	0,12	354	160	1540	26	0,00	36,8
120cm	14/11/03	4,0	7,1	6813	580	920	163	0	2100	0,16	0,16	273	120	953	21	0,00	38,1
60cm (a)	02/12/03	5,6	7,3	4064	288	800	117	0	1000	0,00	0,20	134	53	602	11	0,10	55,6
90cm	02/12/03	6,0	7,3	10154	1120	1220	102	0	3100	0,00	0,00	325	140	1560	21	0,00	33,7
120cm	02/12/03	4,2	7,5	5694	416	990	183	0	1600	0,11	0,00	206	95	824	15	0,00	38,4

N/a* Not available due to lack of sample

Table 3: Analytical results for vadose zone water samples. (All results are given in mg/L except for conductivity, given in uS/cm).

Vadose zone water samples show a higher electrical conductivity compared with irrigation water samples with maximum values of 11 165 uS/cm and 4335 uS/cm respectively. These values are due to high concentrations of Cl^-, SO_4^{2-}, NO_3^-, Na^+, Ca^{+2+} and to a lesser extent Mg^{2+} in vadose zone water samples. Elevated values of SO_4^{2-},

NO_3^- and Ca^{2+} can be explained by the addition of fertilisers while elevated values of Cl^- represents the occurrence of marine water intrusion.

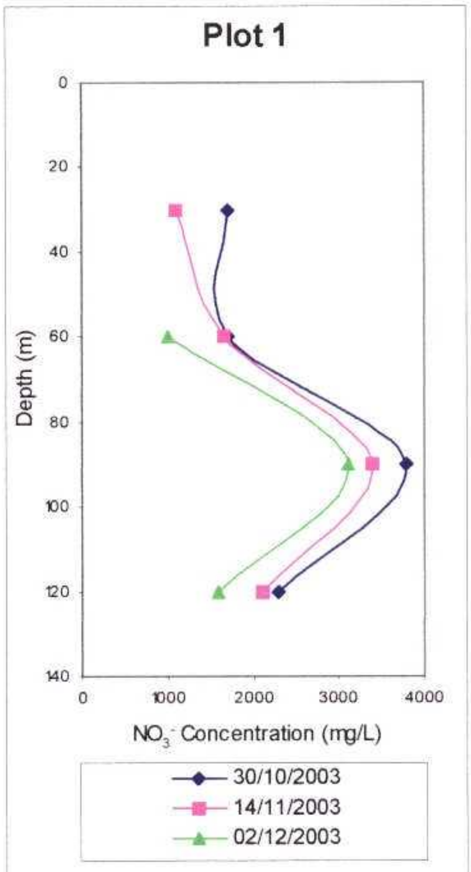


Figure 7: Evolution of NO_3^- vertical profile concentrations for Plots 1.

Figure 8 demonstrates the nitrate concentration trend for water samples over the 3 sampling rounds where is a distinct decline in concentrations is observed.

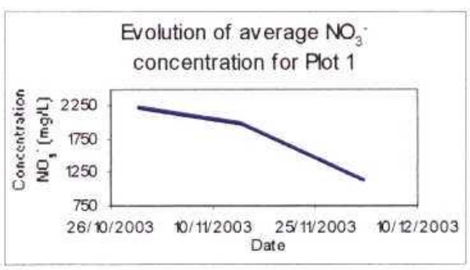


Figure 8: Trend of vadose zone NO3- concentrations over time for Plots 1.

Rainfall

Daily precipitation values were collected from Sa Pobla meteorology station, the closest station corresponding to the study site and represent data for both Plots 1 and 2. Meteorological data is available up until December 2003. The total registered rainfall for 2003 was 659 mm with the highest monthly value 157 mm recorded in February. During the months September, October, November and December the monthly rainfall totals were 94.5, 94.0, 47.5, and 82.0 mm respectively, representing 48% of the registered annual rainfall for 2003 and an important increment after August, which registered a total of 2 mm.

Nitrogen input due to rainfall for the period of August until December 2003, corresponds to 2.18 kg N/ha (Guimerá, 1992). One rainwater sample was collected by means of pluviometers, the analytical results are shown in Table 4.

Date	O_2	pH	Conductivity	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	NO_3^-	NO_2^-	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	K^+	NH_4^+	SiO_2
24/11/03	0,8	8,1	66	5	4	35	0	3	0,35	0,23	2	2	11	0	0,00	0,9

Table 4: Analytical results for rain water sample
(Results are given in mg/L except for conductivity, given in uS/cm).

Irrigation

Irrigation amounts were calculated by taking into account irrigation time spans, pump flow and area of the plot. Currently, five pluviometers have been installed strategically between 4 sprinklers in each plot in order to collect irrigation water during irrigation periods. Their aim is to measure the exact water applied during irrigation in order to compare observed measurements with calculated values. Water analyses results are shown in Table 5 and irrigation amounts for Plot 1 are shown in Figure 9.

Date	O_2	pH	Conductivity	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	NO_3^-	NO_2^-	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	K^+	NH_4^+	SiO_2
18/09/03	2,0	7,1	4265	340	852	204	0	880	0,00	0,00	174	58	599	10	0,00	11,3
28/09/03	1,9	7,1	4125	320	808	204	0	840	0,00	0,00	172	58	587	11	0,00	11,6
20/10/03	5,8	6,9	4335	328	900	146	0	950	53,00	3,00	175	58	622	22	0,00	11,7
19/11/03	1,7	7,1	3953	324	560	166	0	880	0,23	0,09	176	52	490	12	0,00	14,3

Table 5: Analytical results for irrigation and bore water samples
(All results are given in mg/L except for conductivity, given in uS/cm).

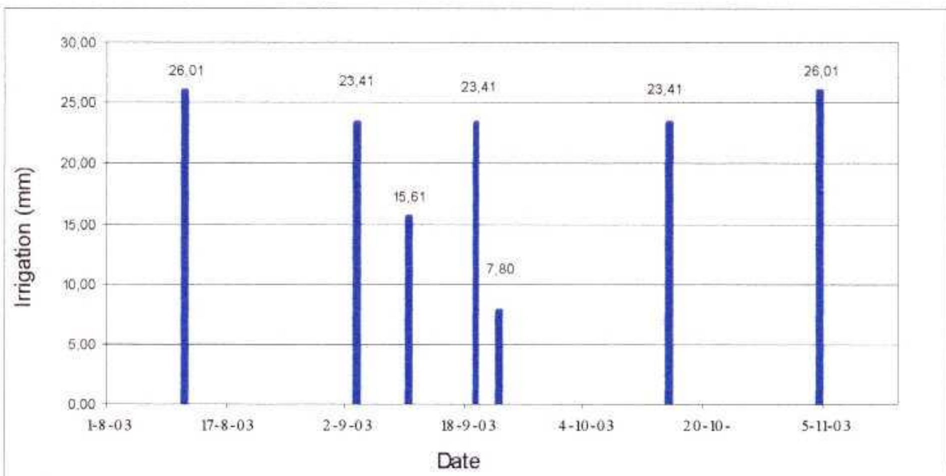


Figure 9: Irrigation amounts for Plot 1.

Nitrate concentrations reach a maximum of 950 mg/L in the irrigation water sample taken on the 20th of October 2003. In this water sample, elevated concentrations of O_2 and oxidised species such as SO_4^{2-} and PO_4^{3-} coexist with the reduced nitrate species NO_2^-. This is an indication of an external contamination source as reduction is unlikely to occur in this oxidised environment.

Figure 10 illustrates daily water available for infiltration for Plot 1 in relation to the time of the crop being sown. Figure 11 shows the monthly total water available for infiltration during 2003.

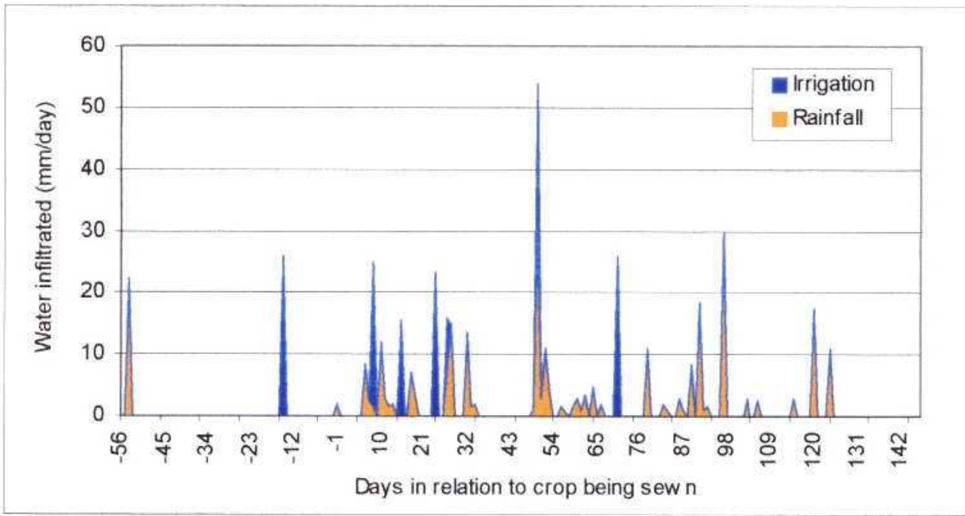


Figure 10: Daily evolution of rainfall and irrigation during crop cultivation for Plot 1.

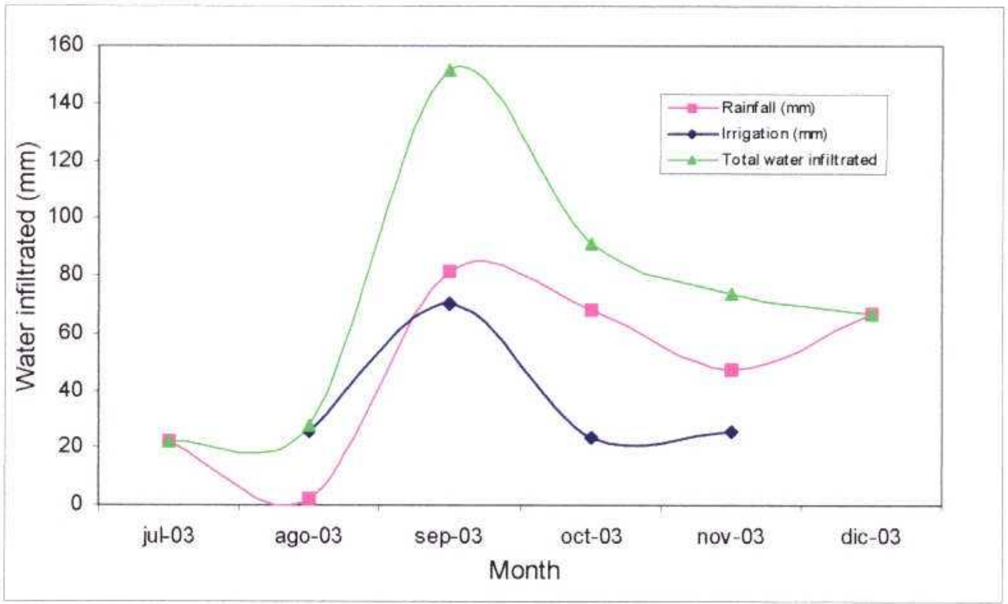


Figure 11: Total monthly water infiltrated for Plot 1 during 2003

Elevated nitrate values found in September are the direct result of leaching. The first and most elevated value corresponds to the flush of rainwater received in September which is further exaggerated by irrigation where the water moistens the soil after the dry summer season (Figure 12).

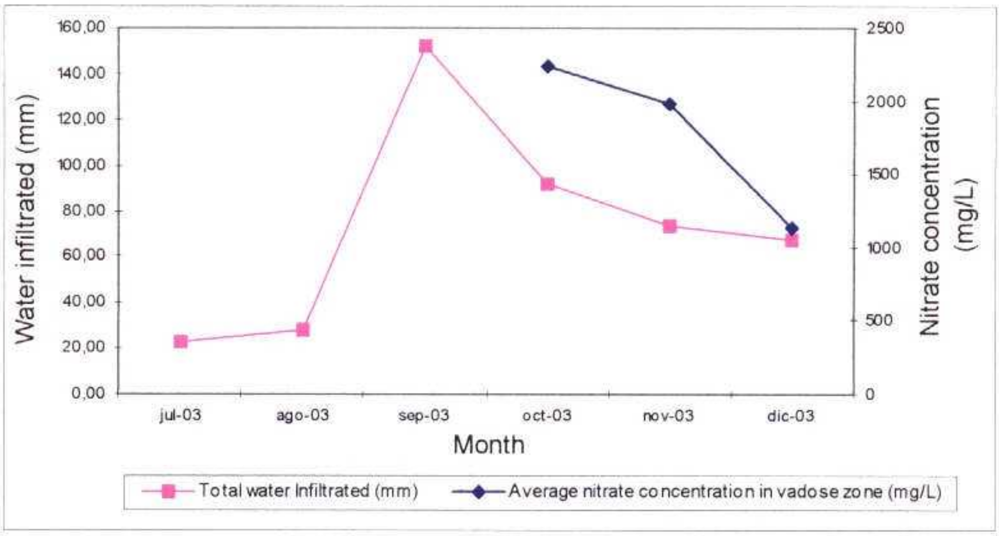


Figure 12: Average nitrate concentration in the vadose zone compared with total water infiltrated for Plot 1.

Irrigation water accounts for a fair proportion of the nitrogen components introduced to the plot. Through knowing the applied irrigation amounts (Figure 9) and nitrate concentrations of each irrigation period (Table 5), the total input of nitrogen to the system by irrigation water was calculated as 290 kg N/ha (Guimerá, 1992).

Fertiliser Application

In Plot 1, fertilisers are applied by fertirrigation. The fertiliser is mixed with bore water in a bath, which is later pumped out as normal irrigation water. On the 19th of September 2003, 400 kg of Urea (46%N) was applied; corresponding to 205 kg N/ha. Later on the 15th of October, 130 kg of fertiliser with a composition of 30-5-30 NPK was applied, corresponding to 16.9 kg N/ha (Guimerá, 1992).
The relationship between the total water infiltrated and total N input for the crop duration of 2003 is illustrated in Figure 13.

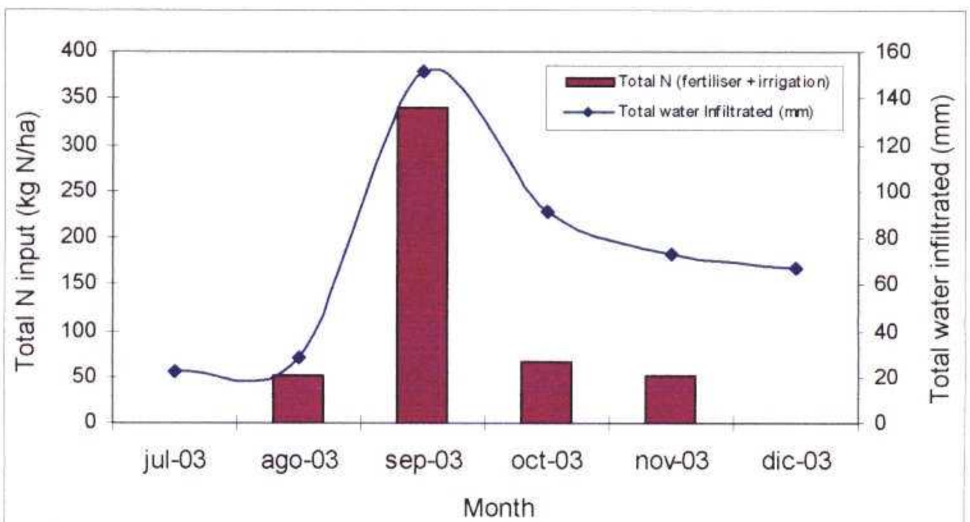


Figure 13: Monthly water infiltrated and total N applied for Plot 1 during 2003.

Piezometric Levels

In Plot 1, piezometric levels were controlled by the installed piezometer (Figure 14). The vadose zone registers an average constant thickness of 2.70 m.

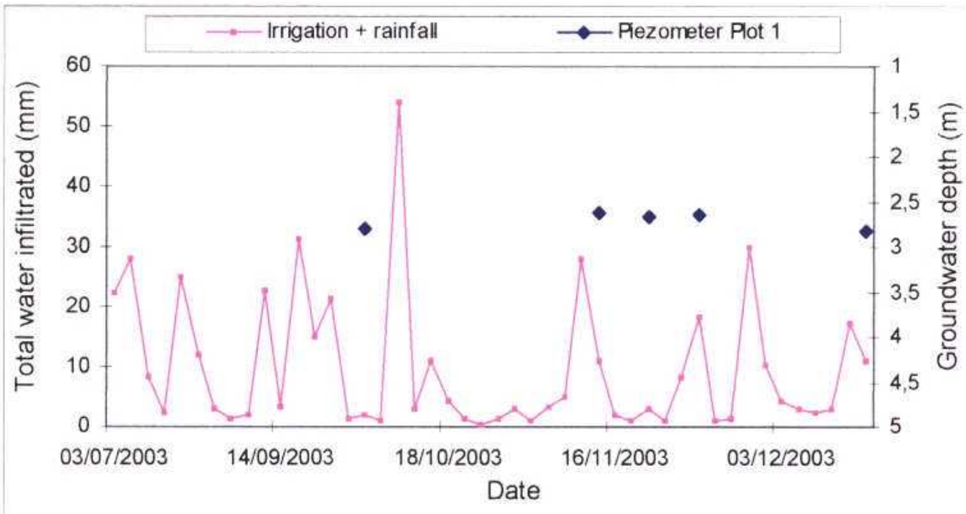


Figure 14: Evolution of groundwater depth versus daily water infiltrated.

Soil Moisture Content

In the vadose zone, hydraulic conductivity depends on the degree of soil saturation or soil moisture. Water movement in the saturated zone depends on the presence of marcopores for groundwater flow, whereas water flow in the vadose zone is more dependant on micropores. Water moves from high to low pressure and is highly dependant on the suction forces which are present. A saturated soil will have low suction values and increase as a soil becomes water deficient. All of which are factors than control the leaching of nitrates. The soil moisture content registered by TDR for Plot 1 is displayed in Figure 15.

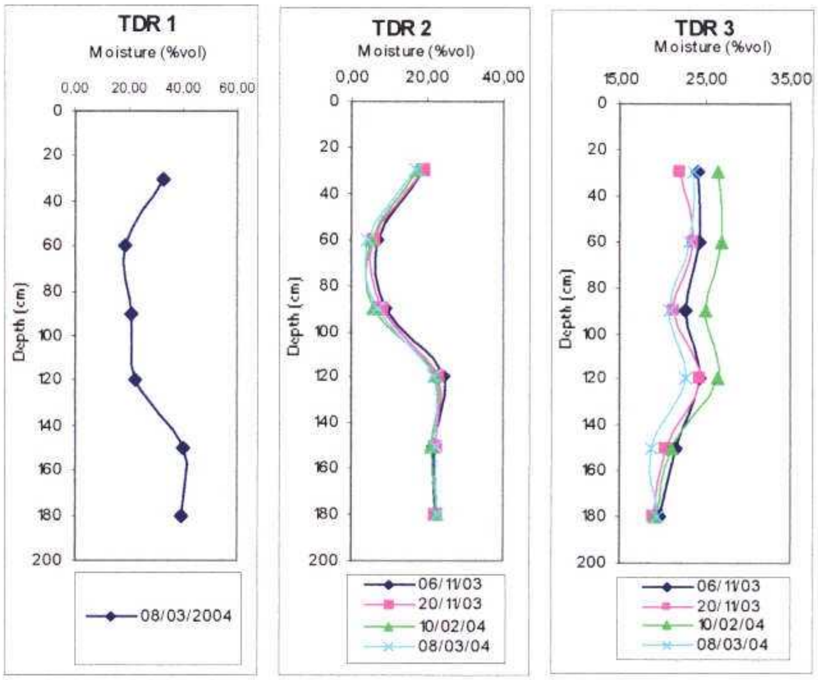


Figure 15: Moisture content profiles for Plot 1.

Soil Nitrogen Balance

The soil nitrogen balance is used to determine the conditions in which nitrates are leached to the aquifer and form one of the main objectives of the study. Table 6 is a provisional soil nitrogen balance for Plot 1. Other inputs such as mineralisation and nitrification are yet to be quantified. It should also be noted in this balance that nitrogen in its solid form available for ion exchange is not considered, nor the quantity of nitrogen components evaporated directly from the grounds surface or by plant transpiration.

Terms of Inputs and Outputs of N		**kg N/ha**
INPUTS	Organic fertilisation Background values	275
	Inorganic fertilisation	222
	Irrigation water	290
	Rain water	2
	TOTAL	789
OUTPUTS	Crop extraction 5kg N / ton potatoes / ha	18
	Recharge/leached (Input-crop extraction)	771

Table 6: Soil nitrogen balance for Plot 1 for first crop cycle.

Plot 2 – Onion

Vadose Zone Water Samples

In Plot 2, elevated nitrate concentrations are found at 90 cm depth reaching a maximum value of 790 mg/L. Nitrate concentrations in intersticial water show an increase of nitrate concentration with depth (Figure 16) and an increase in nitrate concentration during the last 2 sampled months (Figure 17).

Depth	Date	O_2	pH	Conductivity	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	NO_3^-	NO_2^-	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	K^+	NH_4^+	SiO_2
30cm	01/12/2003	6,2	8,1	1523	162	320	131	0	380	0,13	0,50	88	64	224	12	0,00	19,8
60cm (a)	01/12/2003	3,7	10,3	1162	113	120	281	19	240	0,00	0,00	76	89	52	32	0,16	4,1
60cm (b)	01/12/2003	4,6	8,1	1161	114	240	156	0	220	0,00	0,30	52	19	190	9	0,00	18,3
90cm	01/12/2003	5,1	10,9	2854	340	448	1	45	580	0,17	0,00	193	9	342	105	0,25	2,5
120cm	01/12/2003	3,9	10,9	2744	340	240	1	68	640	0,07	0,00	136	9	332	149	0,22	3,4
30cm	18/12/2003	4,1	8,0	689	67	107	93	0	136	0,00	1,10	38	11	95	7	0,00	12,9
60cm (a)	18/12/2003	2,1	11,1	975	103	138	2	62	180	0,00	0,00	57	6	118	58	0,00	6,6
60cm (b)	18/12/2003	3,6	8,0	559	47	78	100	0	88	0,00	0,55	31	9	77	5	0,00	11,4
90cm	18/12/2003	3,3	10,6	1493	189	206	2	31	380	3,70	0,00	109	6	198	39	0,15	3,5
120cm	18/12/2003	N/a*	10,7	1730	219	138	1	32	370	0,15	0,00	160	1	21	328	0,65	2,7
30cm	08/01/2004	N/a	8	1728	217	270	143	0	360	0,2	0,8	77	36	264	10	0	14
60cm (a)	08/01/2004	N/a	9,3	1414	178	197	41	9	290	0	0,09	92	8	132	94	0,08	8,2
60cm (b)	08/01/2004	3,7	7,7	1601	206	250	150	0	340	0	0,47	51	34	280	9	0	12,1
90cm	08/01/2004	3,1	7,7	2874	380	328	10	0	790	0,6	0	142	19	412	47	0	4,1

N/a* Not available due to lack of sample

Table 7: Analytical results for vadose zone water samples.
(All results are given in mg/L except for conductivity, given in uS/cm).

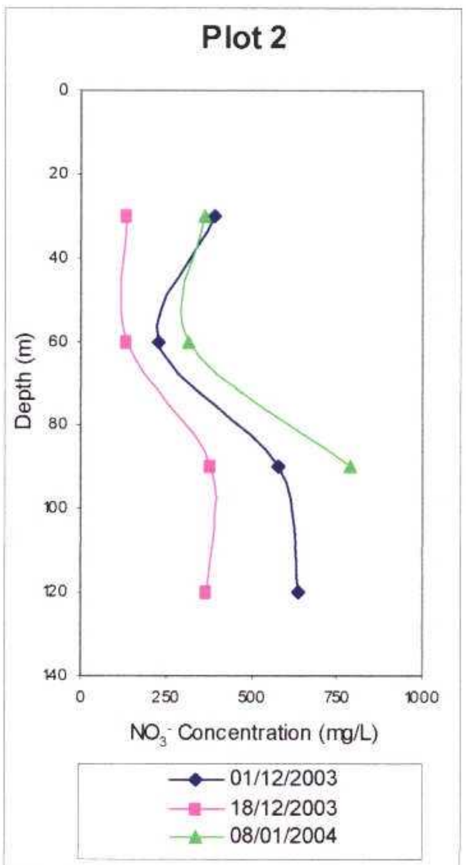


Figure 16: Evolution of NO_3^- vertical profile concentrations for Plot 2.

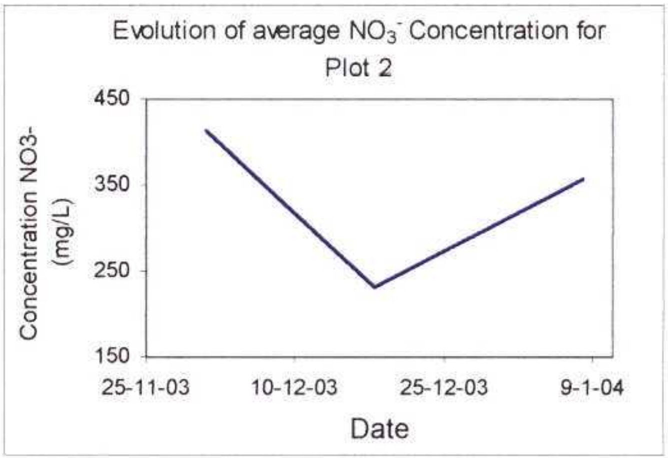


Figure 17: Trend of vadose zone $NO3^-$ concentrations over time for Plot 2.

Water samples taken at depths of 90 cm and 120 cm register elevated concentrations of NO_3^- and minor concentrations of NO_2^- and NH_4^+. Denitrification is unlikely to be occurring, as elevated levels of dissolved oxygen and oxidised species are present. The presence of reduced nitrogen species is therefore an indication of a different source of contamination. The stream Torrente de Muro is located 100 m to the east of Plot 2 and could be the source of organic material which is oxidised to nitrate. A water sample will be taken from this stream for its analysis.

Irrigation

Two water samples were taken previous to sowing, analytical results are shown in Table 8 with maximum nitrate concentrations reaching 480mg/L. This concentration is half of that of Plot 1, however is more than 9 times the European standard of 50 mg/L.

Date	O_2	pH	Conductivity	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	NO_3^-	NO_2^-	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	K^+	NH_4^+	SIO_2
19/09/2003	2,0	7,4	3055	320	528	217	0	450	0,00	0,00	129	51	410	10	0,00	8,3
19/11/2003	1,0	7,1	3153	312	380	192	0	480	0,00	0,00	146	44	319	12	0,00	10,1

Table 8: Analytical results for irrigation and bore water samples
(Results are given in mg/L except for conductivity, given in uS/cm).

Piezometric Levels

In Plot 2 (Figure 18) piezometric levels were controlled by the installed piezometer.
The vadose zone profile has an average thickness of 1.75 m. The vadose zone thickness follows the same pattern as in Plot 1, however the phreatic level is closer to ground surface due to its location being closer to the wetlands.

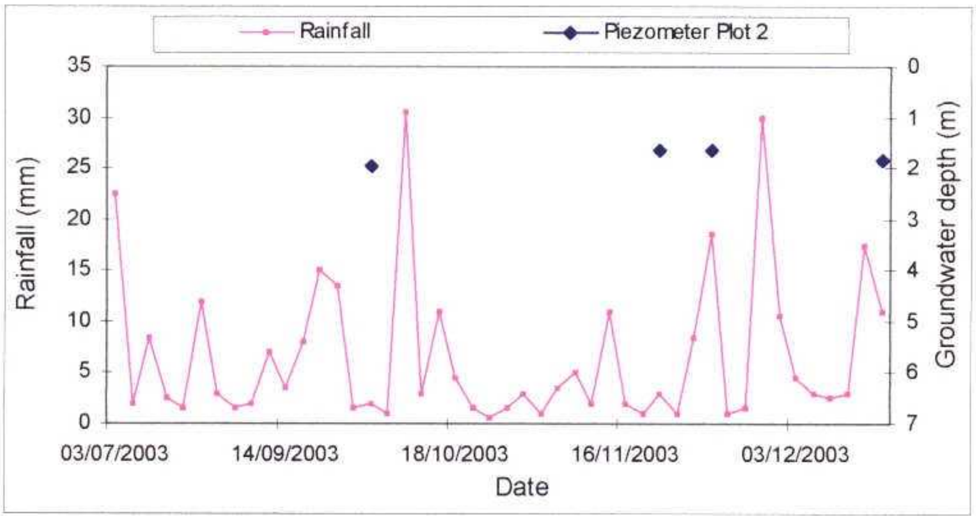


Figure 18: Evolution of groundwater depth versus daily rainfall.

Soil Moisture Content

The soil moisture content profiles taken in Plot 2 are illustrated in Figure 19. In each of profiles, the moisture content increases at 120cm depth where capillary water is present.

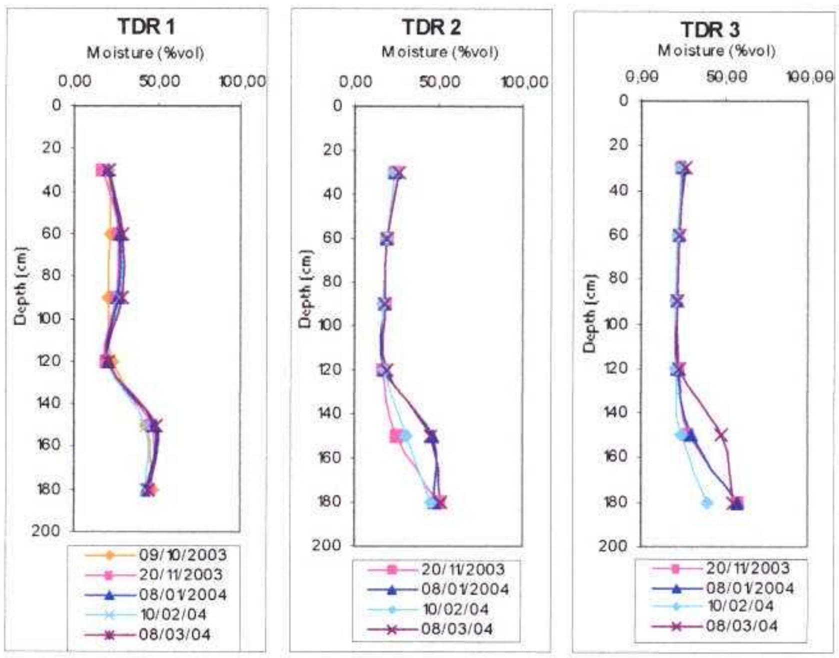


Figure 19: Soil moisture content profiles for Plot 2.

Soil Nitrogen Balance

At this stage there is insufficient data from Plot 2 in order to realise a representable soil nitrogen balance. On the 16th of February 50 kg of ammonium sulphate was distributed over the plot, and to date 4 irrigation periods have taken place. The analytical results from irrigation water samples corresponding to the current cultivation are still to be returned.

Proposed Field and Laboratory Work

The following field and laboratory work is to be realised in both plots.

1. A tracer test is proposed in order to understand infiltration rates. Since Cl^- concentrations are elevated, bromide is likely to be the most cost efficient and readily available tracer that could be used. The water samples taken on the 10th of February are currently being analysed for Br. The results will confirm whether or not Br is an appropriate tracer to be employed.

2. In order to know mineral content composition in the soil profile, to understand the adsorption and ion exchange capacity of the clay portion, and the particle size of that clay portion an x-ray test is proposed.

3. To have a better understanding of the biotic processes and decomposition of N occurring in the vadose zone a soil microbiology test is proposed.

4. A plant analysis is proposed in order to measure the amount of N taken up by the plant.

5. Once the current 2 plots have finished their crop cycle, 2 more plots will be selected and studied. The next experimental plots will follow the same procedure set out by the first 2 plots. A farmer with a plot located approximately 400 m to the west of Plot 1 is willing to co-operate with this project, where maize is planned to be seeded. This plot would be representable of crop rotation, currently potato is being cultivated on this plot.

Conclusions

In Plot 1, elevated nitrate concentrations taken from vadose zone water samples reaching up to 3800 mg/L, are the response of a combination of rainwater and irrigation water washing the soil profile, leaching nitrates held in the soil profile during the dry season. A decreasing nitrate concentration over time is found as the winter months provide fresh water diluting nitrate concentrations.

The calculated quantity of nitrogen leached to the below aquifer corresponds to 771 kg N/ha or a total of 690 kg N for Plot 1. This indicates a clear surplus of fertiliser application. Nitrate concentrations in bore water samples used for irrigation bear the result of this leaching demonstrated by nitrate values surpassing 980 mg/L. Over the past years agricultural practises have improved, less fertilisers are applied, however, as shown by these results further change is required.

Nitrate concentrations in intersticial water samples for Plot 2 demonstrate an increase in concentration over time. Peak nitrate concentrations in vadose zone water samples reach 780 mg/L with irrigation water sample concentration at maximums of 480 mg/L.

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