To link to this article: DOI:10.1016/S0048-9697(03)00262-6
http://dx.doi.org/10.1016/S0048-9697(03)00262-6

To cite this version: Sanchez-Pérez, José-Miguel and Antiguedad, I. and Arrate, I. and Linares, C. and Morell, Ignacio *The influence of nitrate leaching through unsaturated soil on groundwater pollution in an agricultural area of the Basque country: a case study*. (2003) Science of the Total Environment, vol. 317 (n°1-3). pp. 173-187. ISSN 0048-9697

The influence of nitrate leaching through unsaturated soil on groundwater pollution in an agricultural area of the Basque country: a case study

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Abstract

The average nitrate concentration in the groundwater of the Vitoria-Gasteiz (Basque Country) quaternary aquifer rose from 50 mg NO_3^-/l during 1986 to over 200 mg/l in 1995, which represents an increase of some 20 mg NO_3^-/l per year. From 1995 to 2002, the nitrate concentration of the groundwater slightly decreased. Nitrate groundwater pollution during the period 1986–1993 was the result of the abusive use of fertilizers and of the modification in the recharge patterns of the aquifer from surface water sources. From 1993 onwards, apart from a possible rationalization in fertilizer use, the change in the origin of water for irrigation and wetland restoration (water is taken now from artificial pools outside the quaternary aquifer) must be explained in order to account for the observed decrease in nitrate concentration in the groundwater. The water of the aquifer and of the unsaturated zone were studied in two experimental plots (one of them cultivated and the other uncultivated) for 18 months (January 1993–June 1994), during the period of maximum contamination, to evaluate the effect of fertilizers on soil water and on the water in the saturated zone. The soil water was sampled using soil lysimeters at various depths. The volumetric water content of the soil was measured at the same depths using time domain reflectrometry (TDR) probes. Samples of groundwater were taken from a network of wells on the aquifer scale, two located close to the two experimental plots. The temporal evolution of nitrate concentrations in soil solutions depends on the addition of fertilizers and on soil nitrate leaching by rain. During episodes of intense rain ($>$50 mm in a day), the groundwater deposits are recharged with water coming from the leaching of interstitial soil solutions, causing an increase in the groundwater nitrate concentrations. The mass of nitrate leached from the cultivated zone is five times higher than that of the nitrate leached from the uncultivated zone (1147 kg NO_3^-/ha in the cultivated sector as against 211 kg NO_3^-/ha in the uncultivated sector), although part of the nitrate leached into the soil had been previously deposited

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by the rise of the water table. If we consider that the level of groundwater input is similar in both plots, we may conclude that 964 kg NO_3^-/ha circulated towards the groundwater in the cultivated zone during the period under study, representing 87% of the nitrate applied to the soil in the form of fertilizer during that period.

Keywords: Unsaturated zone; Nitrate leaching; Groundwater pollution; Quaternary aquifer

1. Introduction

The pollution of groundwater in areas of high agricultural activity is a consequence of farming practices using large quantities of fertilizers and pesticides. The impact of these practices on the pollution of groundwater in Europe has been demonstrated by Gustafson (1983), Andersen and Kristiansen (1984), Strebel et al. (1989), Bernhard et al. (1992) and Bijay-Singh et al. (1995) among others. In Spain, studies of the contamination of aquifers by nitrates originating from farming practices have been carried out in coastal zones (Guimera, 1993; Ramos and Varela, 1993). In the specific case of the Vitoria-Gasteiz quaternary aquifer in the Basque Country (North Spain), the effects of the abusive addition of fertilizers and the recirculation of groundwater for irrigation have been shown by Arrate et al. (1997).

In regions with high rainfall, such as the Basque Country (average precipitation 700 mm/year for Vitoria-Gasteiz), nitrogen-based fertilizer residues left unused by plants may be leached away, contaminating groundwater. This contamination may occur several days or even months after the fertilizers have been spread. The speed at which the contamination occurs depends on the nitrogenous compound concentration in the unsaturated zone of the soil, on atmospheric input and on the hydrological behavior of the aquifer. The leaching of soil nitrate has been made evident in areas with heavy precipitation (Guillard et al., 1995b) and in areas with a dryer climate where intensive irrigation is used (Cabrera et al., 1995; Guimera et al., 1995).

In some of this research, measures were proposed to reduce the effects of the excessive use of nitrogen fertilizers on the basis of monitoring soil water reserves once a year (Durieux et al., 1995), managing water resources (water table management, as suggested by Kalita and Kanwar (1993)), reducing dosages of fertilizer (Guillard et al., 1995a; Prunty and Greenland, 1997; Ritter et al., 1990) and/or reducing irrigation (Schepers et al., 1995).

The purpose of the present research was to demonstrate the importance of the unsaturated zone of the soil in regulating the contamination of groundwater with nitrogen-based fertilizers. A simultaneous comparative study (1993–1994) was made of two areas in the Vitoria-Gasteiz quaternary aquifer: one cultivated (Arkaute) and the other uncultivated (Jungitu). Nitrate input in these areas and the influence of their hydrological behavior on the circulation of nitrate between the saturated and unsaturated zones were quantified. The results are compared with the nitrate levels in groundwater from the period 1990 to 2002, in relation to agricultural practices and water use modifications.

2. Materials and methods

2.1. Description of the study area

The Vitoria-Gasteiz quaternary aquifer occupies an area of 90 km^2 with an average thickness of 5 m. The deposits are made up of fluvial and alluvial material, which form an unconfined aquifer of intergranular porosity. The substrate is composed of a practically impermeable marl formation. The aquifer's storage coefficient is 0.2 and its average transmissivity varies between 40 and 150 m^2/d (Arrate, 1994). Its water table stands between 0 and 1.5 m from the soil surface. The quaternary aquifer can be subdivided into two hydrogeological sectors, both of which use intensive irrigation (Fig. 1):

- An eastern sector, with a surface area of 50 km^2 and a thickness between 2 and 11 m. This

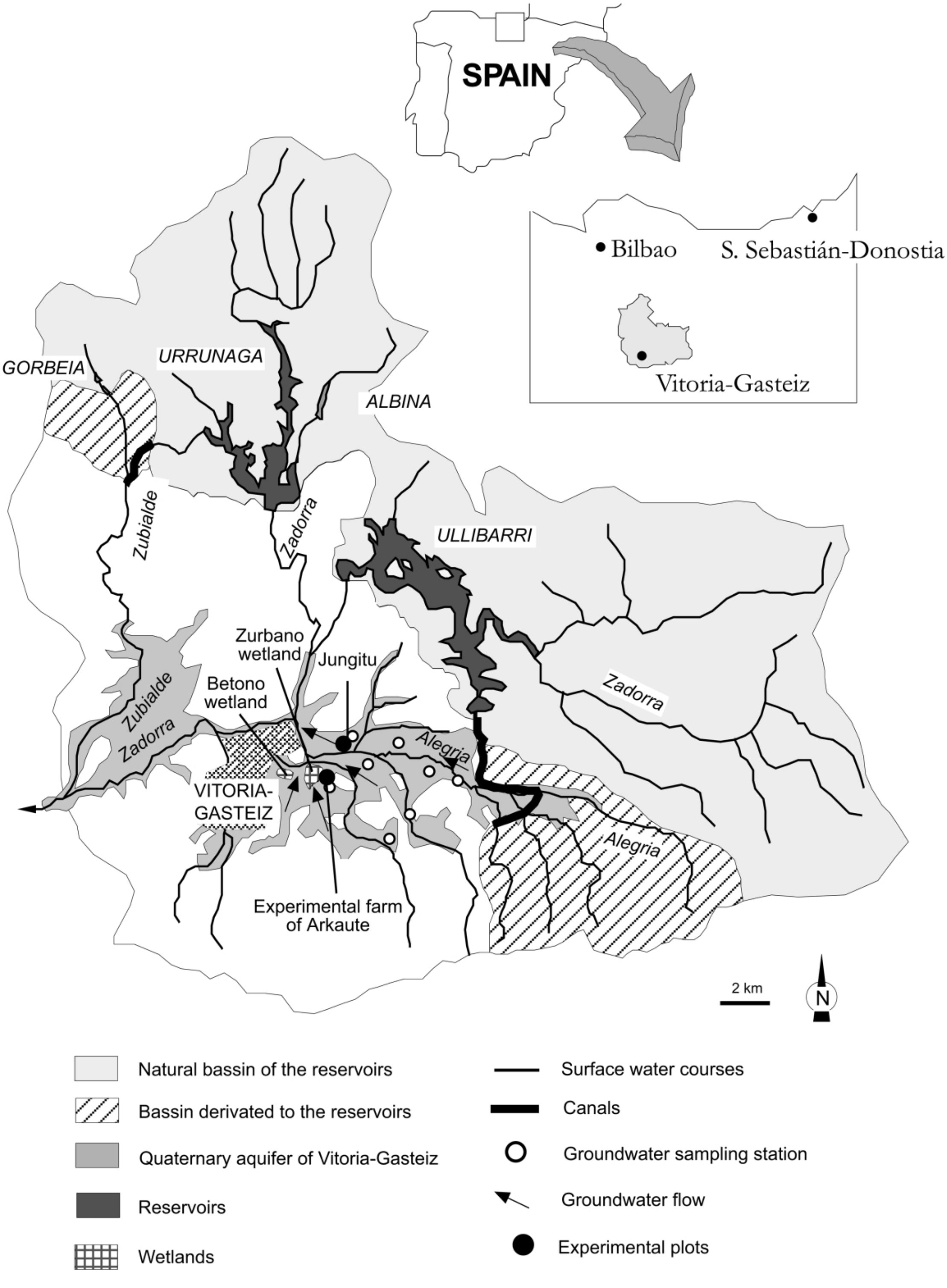


Fig. 1. Location of the Vitoria-Gasteiz quaternary aquifer.

sector is traversed by the Alegria river. This part of the aquifer is made up of heterometric gravel in a sandy argillaceous matrix. In the thicker areas of this sector, transmissivity is higher than 125 m^2/d.

- A western sector, with a surface area of 40 km^2 and a thickness of 1–4 m. This sector is traversed by the Zubialde and Zadorra river. The aquifer is composed of sand and silt. Transmissivity is in the region of 70 m^2/d.

Recharge of the aquifer is from infiltration of precipitation, infiltration from streams during high-water periods and the return of irrigation water. The system outlets (pumping from the aquifer and drainage) flow towards the fluvial network. The main river in the eastern sector (Alegría River) has been completely diverted towards the reservoirs to supply Bilbao and Vitoria-Gasteiz with drinking water (Fig. 1).

2.2. Farming practices and the contamination of groundwater by nitrates

Up until the 1950s, the majority of the land was devoted to non-irrigated agriculture, particularly grains (wheat, oats and barley). The increase in irrigated agriculture during the following years led to both a greater area under cultivation and to a notable increase in the demand for water and fertilizer. The irrigation water was extracted from the aquifer. The water table lay close to the surface (0–1.5 m), which led to frequent flooding in some zones favored by the overflowing of streams during the high water season. Then, in order to avoid the flooding, the network of drainage ditches was increased disproportionately, reaching a density of 8 km/km^2 in this sector (Arrate et al., 1997). The rise in the demand for water was met by pumping from the aquifer. Additionally, at the beginning of the 1970s, the River Alegría was diverted 'at the entrance of the eastern sector' towards the Ullibarri reservoir (Fig. 1) in such a way that the water table was considerably lowered.

The area occupied by irrigated crops grew from less than 1 km^2 in 1954 to a current 60 km^2, in detriment to the dry zones, which decreased substantially from 70 km^2 in 1954 to only 10 km^2 in the late 1990s (Arrate et al., 1997).

2.3. Experimental design

Two experimental plots were set up at the beginning of 1993 in the eastern sector of the quaternary aquifer. One was set up on a field used for the cultivation of potatoes in the experimental farm of Arkaute. The other plot was set up on land which had not been cultivated for several years (Jungitu), and for which no treatment had been planned.

The agricultural plot (Arkaute) had been used in previous years for oats (*Avena sativa* L.). The last applications of fertilizer were carried out in October 1991 (1000 kg/ha) and in March 1992 (1000 kg/ha), using an $N-P_2O_5-K_2O$ compound containing 15% of each component, equivalent to 150 kg/ha of N per application. During 1993, 1200 kg/ha of an N–P–K compound containing 12% N, and 24% P and K were spread in May (144 kg/ha of N), before the plot was planted with potatoes (*Solamun tuberosum* L.) and 83 kg/ha of N in the form of $CaNO_3$ in November, prior to the planting of the plot with oats. After crop harvest of potatoes (end of September), the plants are left in the place in order that they decompose. The uncultivated plot (Jungitu) had not received any fertilizing additives in the course of the previous 3 years and was not planted with any crops during the study period.

The soil on the Arkaute farming plot had a sandy argillaceous texture in its surface levels (0–0.3 m), becoming increasingly sandy at depth (0.3–0.9 m). On the uncultivated plot of Jungitu the soil had an argillaceous texture in its surface levels (0–0.3 m), with more silt and clay components at depth (0.3–1 m) (Table 1).

Soil solutions from the unsaturated zone were sampled using ceramic samplers installed on both plots at different depths (0.15, 0.35, 0.55, 0.75 and 0.95 m). The sampling systems consisted of a suction lysimeter (a ceramic cup of 50 mm outer diameter and 70 mm length glued to a PVC pipe of the same diameter). The ceramics were tested in the laboratory prior to their placement to study nitrate retention and/or desorption by the ceramic (Morell and Sánchez-Pérez, 2000).

Before their placement in the field, the suction

Table 1
Texture and composition of the soil at the two study plots

	Experimental farm (Arkaute)			Uncultivated plot (Jungitu)		
Depth (cm)	0–30	30–40	40–90	0–30	30–50	50–100
Sand (%)	43.5	43.8	74.0	10.5	43.5	11.6
Silt (%)	21.3	17.7	16.2	36.6	21.2	49.4
Clay (%)	35.2	38.5	9.8	52.9	35.3	39.0
pH (1:2.5) in water	8.5	8.3	8.8	8.6	8.4	8.8
P, Olsen (ppm)	32.3	21.4	0.2	10.4	22.4	1.7
$CaCO_3$ (%)	21.3	11.4	60.7	24.5	20.4	67.3
Ca (meq/100 g soil)	33.4	39.3	18.6	42.8	33.9	25.5
Mg (meq/100 g soil)	0.71	1.04	0.21	3.12	0.75	1.69
Na (meq/100 g soil)	0.07	0.13	0.07	0.10	0.06	0.04
K (ppm)	169	205	20	200	150	70
$N–NO_3^-$ (ppm)	13.0	9.5	5.0	18.7	24.5	12.5
$N–NH_4^+$ (ppm)	9.2	18.3	27.0	15.5	11.5	12.0

lysimeters were washed with deionized water under suction. During this phase of the washing, the electrical conductivity of the washing water was measured, as a washing control parameter (Morell and Sánchez-Pérez, 1998). The porous ceramics were stuck to the PVC pipe using an epoxy resin. The soil water samplers were installed vertically in both plots (Arkaute and Jungitu), in a 50-mm bore. In order to facilitate contact with the porous ceramic, a fine paste was made from the fine-grain part of the soil mixed with deionized water, and poured into the bottom of the hole before placing the ceramic.

Sampling was carried out by applying a vacuum of 60 kPa to the suction lysimeter. Samples were taken every 2 weeks, and once a week during periods of intense rainfall. The soil moisture was measured at the same intervals using a TDR system (TRIME System Imko) equipped with a two-rod probe (6 mm in diameter and 140 mm in length, with 40 mm of separation between the rods) at the same depths as the suction lysimeter.

Precipitation was measured continuously on both plots (Arkaute and Jungitu) using meteorological stations located 100 m from the Arkaute plot, and 5 m from the Jungitu plot. At the same time, rainwater samples were taken for chemical analysis in the laboratory.

A system of drip irrigation was installed on 29th June 1993 in the Arkaute experimental plot. On the same plot, three tensiometers were installed at depths of 0.15, 0.35 and 0.50 m. The irrigation system began to function when the soil matrix tension at the tensiometer located 0.35 m below the surface reached 50 kPa. Between 9th July and 19th September, 40.9 l/m^2 were added through this system. During this same period, rains brought in 86.6 l/m^2.

2.4. Groundwater sampling

To investigate water movement between the saturated and unsaturated zones, the fluctuations of groundwater level were monitored continuously by a paper chart recorder attached to a float in various wells located close to the plots. Samples of the groundwater were taken at the same time as the samples from the suction lysimeter. The nitrate concentration of the groundwater in these wells is the result of farming practices over a large area of the quaternary aquifer located upgradient from the study plots. Groundwater samples were taken monthly from a network of eight piezometers covering the aquifer (Fig. 1).

Nitrate concentration was analyzed using colorimetric methods. The mass of nitrate in the soil was calculated by multiplying the nitrate concentration at each sampling depth by the corresponding volumetric content of water measured by TDR.

3. Results

The nitrate concentrations in the groundwater sampled in the wells by the two plots (Arkaute

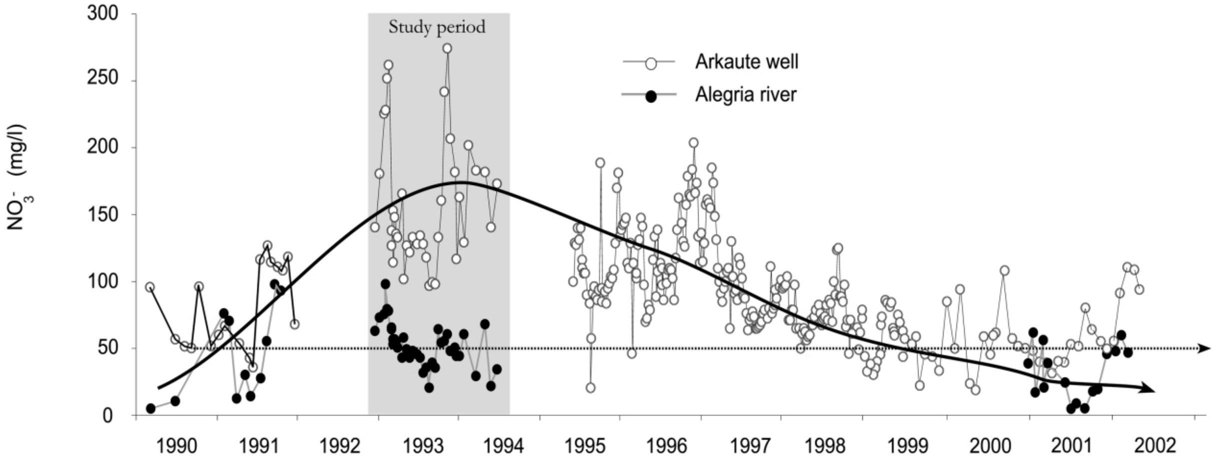


Fig. 2. Trend of nitrate concentration in a well on the Arkaute plot and in the Alegría River at the outlet of the quaternary aquifer.

and Jungitu) presented similar average values, of the order of 150 mg NO_3^-/l. The nitrate concentrations in the surface waters of the Alegría River at the outlet of the quaternary aquifer were approximately 50 mg NO_3^-/l, in no case reaching the values presented by the groundwater. Fig. 2 reports nitrate concentration in the groundwater of the Arkaute well and in the surface waters of the Alegría River from the period 1990 to 2002. It may be observed that the study period (1993–1994) coincided with the period of greatest nitrate contamination in the groundwater.

In April 1986, the average groundwater NO_3^- concentration was higher than 50 mg NO_3^-/l (data not represented in Fig. 2). By February 1990, these concentrations had doubled with average values exceeding 100 mg NO_3^-/l. In November 1991, nitrate concentrations rose to an average of 170 mg NO_3^-/l. This trend continued in January 1993, with nitrate generally in excess of 200 mg /l. From 1993 onwards, the values showed a tendency to decrease.

Rains of an intensity over 50 l/m^2/d occurred in April and December 1993 (Fig. 3). The monthly precipitation recorded during the period under study in the Arkaute plot is shown in Table 2. The nitrate levels in soil solutions were very different in the two zones. At Arkaute, concentrations exceeded 50 mg NO_3^-/l, reaching almost 300 mg NO_3^-/l in some samples taken after fertilization (Fig. 3). Before the first application of fertilizer (February–May), nitrate concentrations in soil solutions (25–120 mg NO_3^-/l) were less than the concentrations found in groundwater (114–260 mg NO_3^-/l). After a rainy interval of 70 l/m^2 over 4 days at the end of April, groundwater concentrations decreased significantly to 1.5–7.2 mg NO_3^-/l. In Jungitu, these concentrations did not generally exceed 20 mg NO_3^-/l, whereas maximum concentrations reached 114 mg NO_3^-/l at the surface.

During the periods of heavy rain, the nitrate retained in the soil was leached into the groundwater, although at times the effect of this leaching was not evident in the saturated zone due to the high concentration of nitrate already in the groundwater (Fig. 3). The maximum nitrate concentrations in soil solutions were observed during the summer–autumn months, after the application of fertilizers. The maximum concentrations were found in the part of the soil that was closest to the surface (0–0.20 m); in this zone, concentrations increased from 58 mg before fertilization to 314 mg NO_3^-/l afterwards.

The mass of leached nitrate in the uncultivated zone was small in comparison to that in the cultivated zone. The nitrate reserves in the cultivated zones varied between 30 kg NO_3^-/ha in June 1993, during a period of heavy rain without the use of fertilizer, and 904 kg NO_3^-/ha at the end of December, after the application of fertilizer at the end of autumn. In the uncultivated zone, the reserves varied between 8 kg NO_3^-/ha in June 1993 and 77 kg NO_3^-/ha in January 1994 (Fig. 4).

Nitrate input from rain was small compared to the concentrations found in the soil of the farmed zone (Fig. 4). Over the study period, 14.6 kg NO_3^-/ha fell with the rain, against more than 500 kg NO_3^-/ha present in the soil at the beginning and at the end of this period. On the other hand, in the uncultivated area, nitrate inputs due to rain was similar to soil reserve nitrate. These represented 28.3 kg NO_3^-/ha during the same period, against the 32 kg NO_3^-/ha found in the soil at the beginning and end of the period.

In Arkaute, the mass of nitrate retained in the topmost meter of soil decreased from 502 kg NO_3^-/ha in March 1993 to 130 kg NO_3^-/ha in mid-May, falling progressively to 30 kg NO_3^-/ha at the end of May, just before fertilizer was spread, implying the leaching of 472 kg NO_3^-/ha (Fig. 5). This decrease in the soil reserves is explained by the leaching of the soil solutions due to precipitation, in the form of snow at the beginning of March and in the form of heavy rains in April.

In the Jungitu sector, soil nitrate levels (Fig. 5) showed a similar steady decrease. The nitrate reserves accumulated in the soil fell from 125 kg NO_3^-/ha in March 1993 to 29 kg NO_3^-/ha in May, to reach a level of 8 kg NO_3^-/ha in June. The mass of nitrate leached in this area for this period represents 117 kg NO_3^-/ha.

Soil nitrate in Arkaute during the period May 1993–March 1994, which includes the application of fertilizers at the end of May 1993 and at the end of November is shown in Fig. 6. In this plot, the possible effect of the rise in the water table is negligible in comparison to the input of nitrates from fertilizers. Fertilizing in May 1993 gave rise to a steady increase in soil nitrate reserves, which reached a maximum value at the end of October 1993 (772 kg NO_3^-/ha), just before the second application of fertilizer (November). This second application of fertilizer produced an increase in nitrate reserves (904 kg NO_3^-/ha). Heavy December rains produced a rapid leaching of the soil nitrate (498 kg NO_3^-/ha) between 16th December and 22nd March.

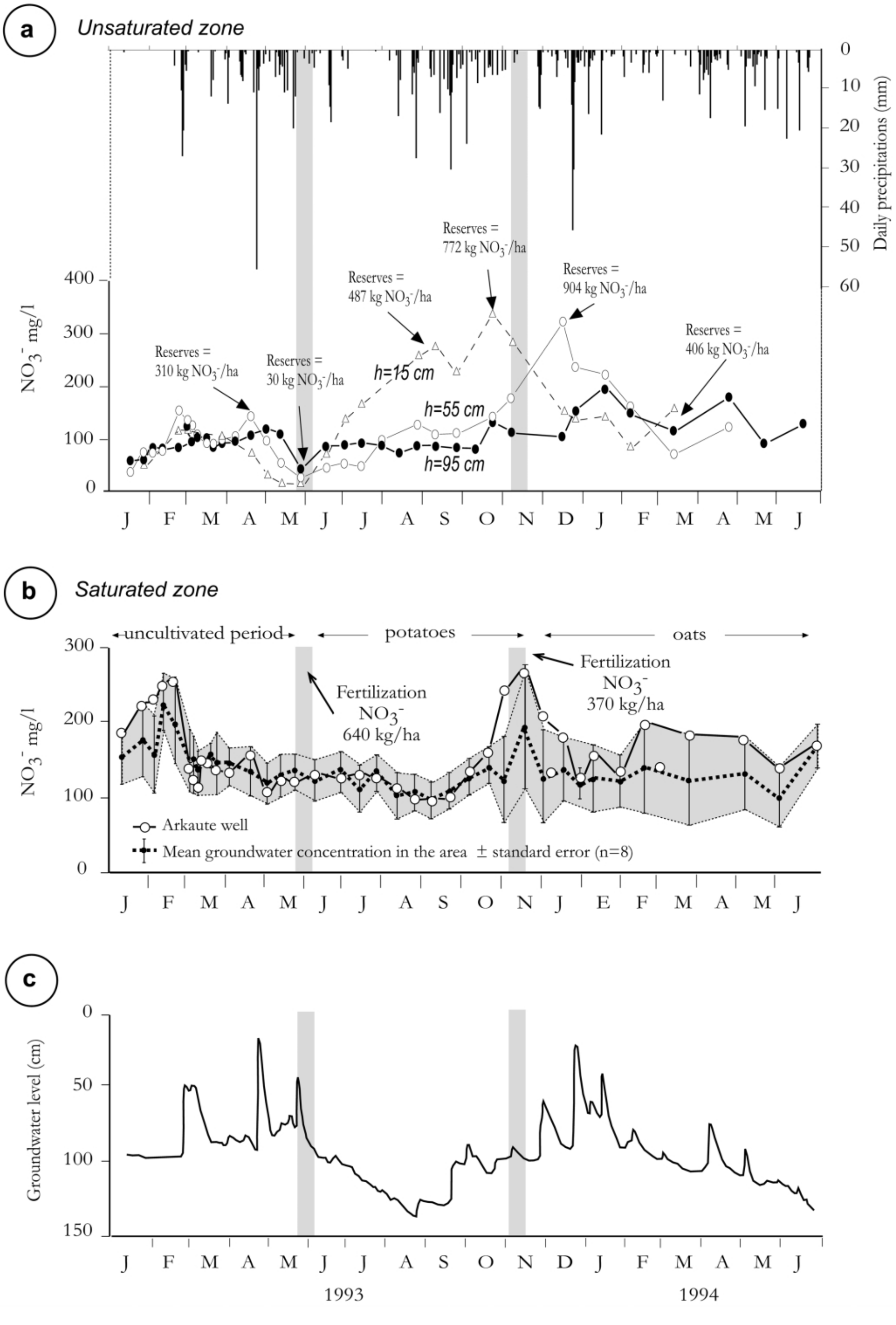
The mass of nitrate leached in the cultivated zone (1147 kg NO_3^-/ha) was five times greater than that in the uncultivated zone: 211 kg NO_3^-/ha, even though part of the leached nitrate had been previously deposited in the soil by an increase in the groundwater level. If the groundwater fluctuations were similar in both plots, and in the uncultivated plot the variation of soil reserves exclusively originated from atmospheric input and the rise of groundwater levels, the increases would represent 183 kg NO_3^-/ha. In the cultivated plot, nitrate input is the sum of addition due to fertilization, rain and variations in overall reserves in the soil between the first and last samples (Table 3). The total net balance represents 1147 kg NO_3^-/ha, of which 964 kg NO_3^-/ha circulated towards the groundwater during the period under study, representing 87% of the added nitrate.

4. Discussion

4.1. Hydrogeological behavior and the contamination of the unsaturated zone

A comparison of the variations of nitrate concentrations in the soil waters of the Arkaute plot with the nitrate concentrations in the saturated zone of the aquifer (Fig. 3) indicates that the cause–effect relationship between the leaching of the soil and the pollution of the aquifer is not always clear-cut. It must be kept in mind that the nitrate levels in groundwater are indicative of land use practices in the aquifer on the regional scale (horizontal flow component), whereas the levels in soil waters have a local explanation (vertical flow component).

During the first months of the study (January–February 1993), groundwater nitrate concentrations presented a significant increase, reaching 260 mg NO_3^-/l. At the end of February, a period of snowfall produced a strong decrease in the concentrations of the saturated zone as a result of dilution. Nonetheless, the nitrate concentration in the interstitial solution of the soil presented a slight increase (with values close to 100 mg NO_3^-/l) as a consequence of the contamination caused by the rise in the groundwater level (see hydrograph in Fig. 3).



a
Unsaturated zone
Daily precipitations (mm)
0
10
20
30
40
50
60
NO$_3^-$ mg/l
400
300
200
100
0
Reserves = 310 kg NO$_3^-$/ha
Reserves = 30 kg NO$_3^-$/ha
Reserves = 487 kg NO$_3^-$/ha
Reserves = 772 kg NO$_3^-$/ha
Reserves = 904 kg NO$_3^-$/ha
Reserves = 406 kg NO$_3^-$/ha
h=15 cm
h=55 cm
h=95 cm
J F M A M J J A S O N D J F M A M J
b
Saturated zone
uncultivated period
potatoes
oats
Fertilization NO$_3^-$ 640 kg/ha
Fertilization NO$_3^-$ 370 kg/ha
NO$_3^-$ mg/l
300
200
100
0
Arkaute well
Mean groundwater concentration in the area ± standard error (n=8)
J F M A M J J A S O N J E F M A M J
c
Groundwater level (cm)
0
50
100
150
J F M A M J J A S O N D J F M A M J
1993
1994

Fig. 3.

Heavy rain at the end of April caused significant leaching of soil nitrate during the month of May (Fig. 3); this leaching occurred first in the topmost layer (15 cm) subsequently repeating itself at depth (55 and 95 cm). The effect of the leaching was not clearly observed in the nitrate concentrations of the groundwater, which presented higher values. The increase in soil solution nitrate levels starting in June was the result of the application of fertilizer prior to the planting of potatoes.

In the cultivated plot, heavy rainfall at the end of April (153.6 mm between 20th April and 25th May) caused leaching of nitrate into the groundwater in Arkaute (310–30 kg NO_3^-/ha). These results are similar to the findings of Delin and Landon (2002) for a region of Minnesota. These authors estimated a mean mass flux of 46 kg NO_3^-/ha to the water table during a runoff recharge of 165 mm of water. In Jungitu, nonetheless, with its relatively smaller nitrate reserves in the soil, nitrate addition to the deepest part of the soil was found at the end of May 1993, which should be interpreted as a consequence of a rise in the water table, high at that time (Fig. 5).

Although rises in the water table can contaminate interstitial soil solutions with nitrate, especially in the deepest parts of the unsaturated zone, the input is small compared to that of nitrate addition originating from farming. Average nitrate concentrations in the groundwater of the saturated zone (from December 1992 to June 1993) presented very similar values in both plots: 165 mg NO_3^-/l at Jungitu and 160 mg NO_3^-/l at Arkaute. On the other hand, the piezometric level in both zones was located at a very similar average depth (100–120 cm from the ground), with similar fluctuations in height.

Nonetheless, the nitrate concentrations of the unsaturated zone were much greater in the farmed area (Arkaute). The contamination of the soil solutions by the rise in the water table cannot thus be the sole reason for the contamination of the unsaturated zone at Arkaute. In the uncultivated area (Jungitu), unsaturated zone nitrate concentrations may be due to contamination resulting predominantly from the rise in groundwater, and from the atmospheric input of nitrate.

Table 2
Monthly rainfall at the meteorological station of Arkaute

Month	Rainfall (mm)	Month	Rainfall (mm)
January 1993	0.3	October	71.4
February	60.3	November	46.5
March	28.6	December	131.8
April	125.6	January 1994	58.5
May	81.7	February	30.2
June	53.2	March	19.2
July	26.5	April	78.4
August	62.5	May	67.5
September	101.5	June	73.0

4.2. Hydrological management and agricultural practices

Because of the change from dry to irrigated farming and the need to enlarge the area of arable land, a series of land transformations, involving a dense drainage network, took place 40 years ago. This led to a notable loss of water input to the aquifer, evaluated to 40%, and strong contamination by nitrogenous compounds. Thus, concentrations of nitrate in the groundwater of the eastern sector steadily increased by 20 mg NO_3^-/l per year in the early 1990s due to the recirculation of irrigation water.

Groundwater pollution by nitrate has been demonstrated in other works concerning potato farming in Quebec (Levallois et al., 1998). The estimated mass fluxes of nitrate obtained in the present work (964 kg NO_3^-/ha) were similar to the fluxes reported by Costa et al. (2002) for potatoes plot in Argentina (862 kg NO_3^-/ha) over the annual cycle.

Fig. 3. (a) Nitrate concentrations in the soil solution of the unsaturated zone at 15 (△), 55 (○) and 95 (●) cm depth. Daily precipitation for the same period is indicated by the bar graph in the upper part of the figure. Total calculated soil nitrate reserves to a depth of 1 m are given for key periods (kg NO_3^-/ha). (b) Nitrate concentrations in the groundwater in the Arkaute well (○) alongside the mean values (±S.E.) for the eight sampling stations over the aquifer (●). (c) Depth of the water table in the Arkaute well over the study period. The broad grey vertical lines indicate the addition of fertilizer.

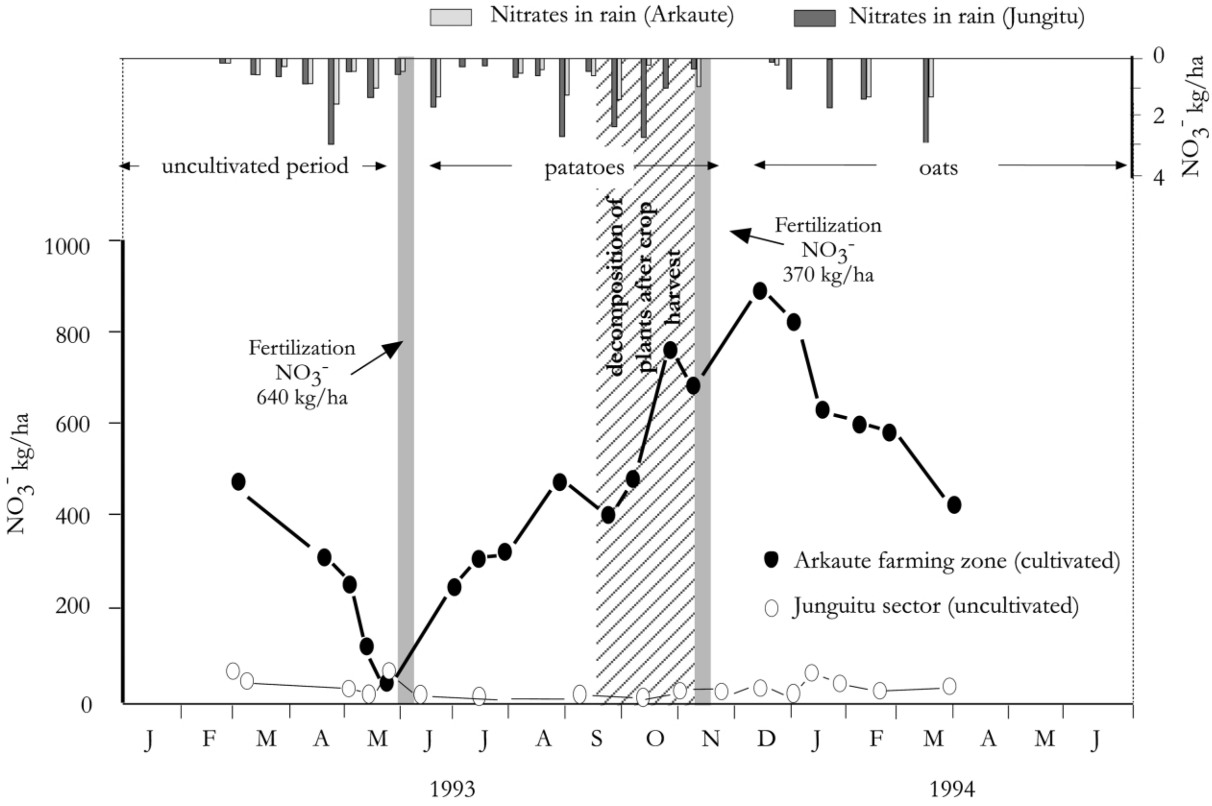
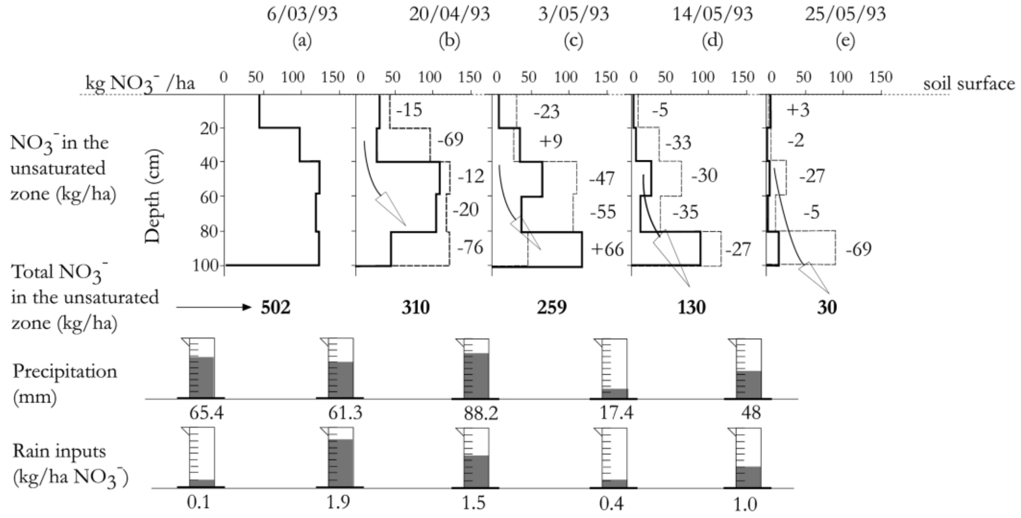


Fig. 4. Quantity of nitrates in the first meter of soil in both experimental plots. Nitrate inputs from rain is indicated in the bar graph at the top. The broad grey vertical lines indicate the addition of fertilizer. The hatch vertical area indicated the decomposition of plant after crop harvest.

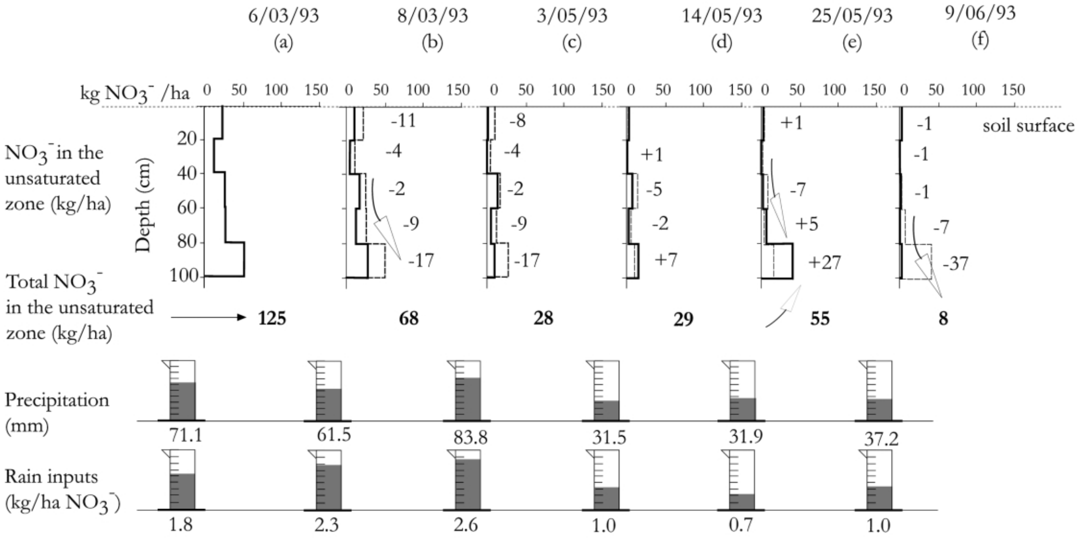
The groundwater pollution by nitrate decreased and seems to have stabilized during recent years as a result of some changes in the use of agricultural fertilizers and in the origin of the water used for irrigation. Nevertheless, nitrate levels in groundwater continue to be higher than reasonable (60–80 mg NO_3^-/l). As a result of the intensification of agriculture, both forests and wetlands have disappeared along with the biogeochemical role that they played.

4.3. Wetland management and groundwater pollution

In the present case, the criterion for groundwater contamination is its use for domestic purposes. In most of the European countries (EEC, 1980), the maximum nitrate concentration permitted in drinking water is now 50 mg NO_3^-/l. Several types of action have been carried out recently to diminish nitrate contamination in the study area. In 1999, the eastern sector of the quaternary aquifer was designated by the Basque Government as a Nitrate Vulnerable Zone according to the European Directive (EEC, 1991) and, consequently, a Code of Good Practices and an Actuation Plan were approved. At the end of 1998, wetlands close to Vitoria-Gasteiz (Zurbano and Betoño wetlands; Fig. 1) were restored by the city council, by closing the main drainage ditches which led to an elevation in the water table, so the wetlands have recovered their biogeochemical role. Nitrate levels



Arkaute farming zone (uncultivated period)



Jungitu sector (uncultivated period)

Fig. 5. Nitrate reserve in the soil of both experimental plots illustrating the effects of a rainy period before fertilizer spreading. The measuring cylinders indicate the rainfall (mm) and the NO_3^- (kg NO_3^-/ha) contained in the rain between the two sample dates in the upper graph. The upper graph represents the amount of NO_3^- at different depths at the various sampling dates. The histogram in dotted lines shows the values of the previous sampling date. The positive and negative figures report the change in NO_3^- between the two dates for each depth. Total calculated soil nitrate reserves to a depth of 1 m are given in bold.

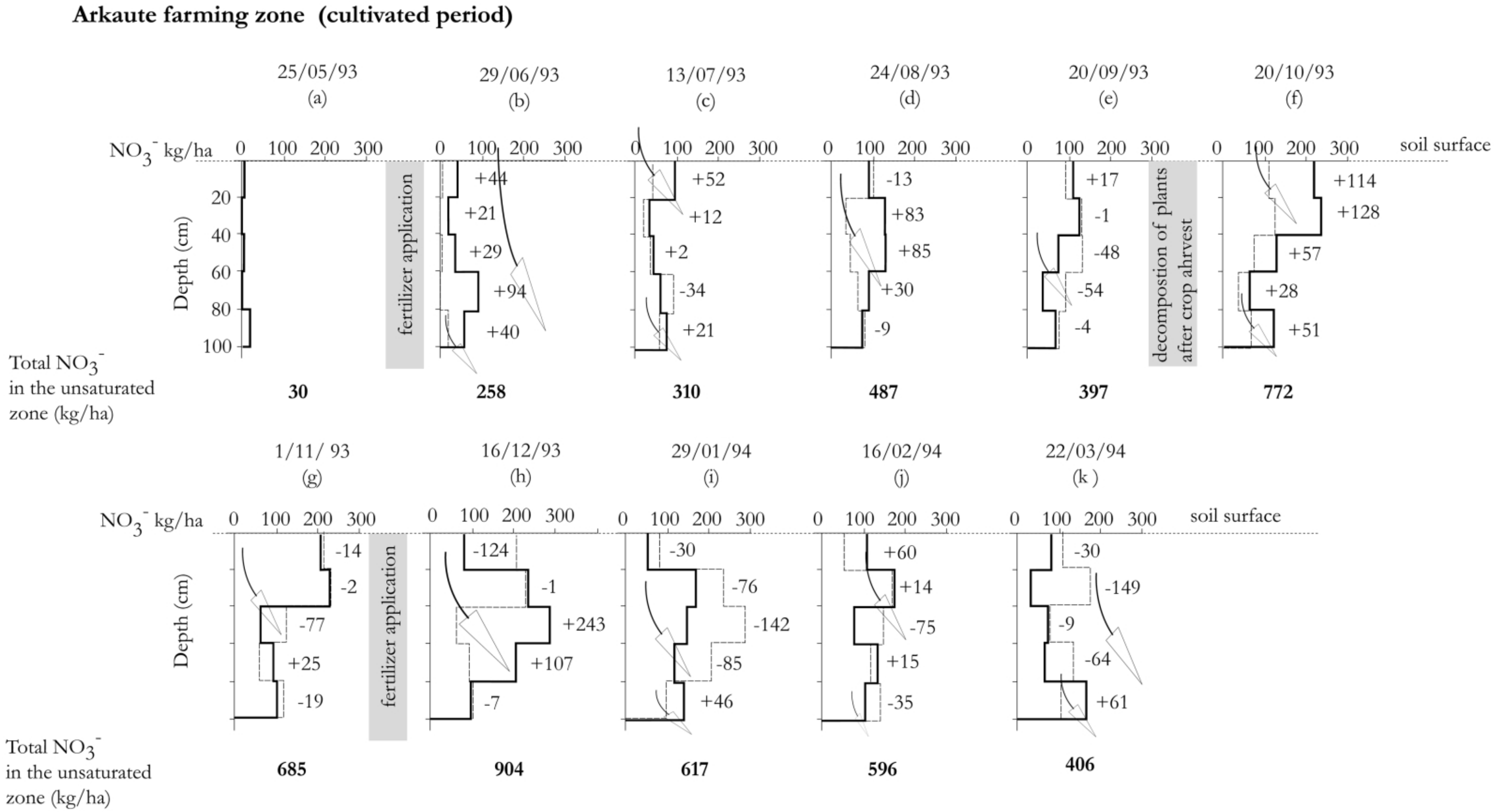


Fig. 6. Nitrate reserve in the Arkaute plot vs. time, shows the effect of both fertilizations. The histogram in dotted lines shows the values of the previous sampling date. The positive and negative figures report the change in NO_3^- between the two dates for each depth. Total calculated soil nitrate reserves to a depth of 1 m are given in bold. The broad grey vertical lines indicate the addition of fertilizer and crop harvest.

Table 3
Budget of exportation of nitrates in both studied plots

	Arkaute (kg NO_3^-/ha)	Jungitu (kg NO_3^-/ha)
Input of nitrate by the fertilizers (FI)	1007	0
Input of nitrate by the rain (R)	15	28
Nitrate leached out of the unsaturated zone (LN)	1147	211
Input by groundwater rising (GR) = LNj − Rj	183	183
Balance budget (BB)	84	79
Net budget (NB) = FI + R + BB	1106	107
Nitrate output (NO) = LN − GR	964	28
NO/NB	87%	26%

LN, leached nitrate, represents the sum of nitrates lost between each of the sampling dates; GR, input by groundwater rising, represents the difference between the leached nitrates and the nitrate contribution by rain; BB, balance budget, represents the difference between the reserves of nitrates on the first date of sampling and the last; NB, net budget, represents the sum of the nitrate inputs by fertilizers + rain + balance budget; NO, nitrate output, represents the difference between the nitrate leached out of the unsaturated zone and the inputs into the unsaturated zone but groundwater rising.

are higher than 50 mg NO_3^-/l in groundwater entering the wetland area and fall to less than 10 mg NO_3^-/l in the water leaving it.

In the early 1960s, the last existing wetland (Zurbano wetland in Fig. 1) was drained by deepening and modifying several watercourses. In order to avoid possible floods, enlargement of the rest of the drainage ditches was carried out as well, adapting them to the geometry of agricultural terrain. The trenches were, on several occasions, more than 2.5 m deep. The drainage density of the study area went from 5.3 km/km^2 in 1954 to 7.7 km/km^2 in 1982, a similar situation to the present one.

Moreover, a crop change from traditional grains (wheat, oats and barley) to the present potato and sugar beet meant a greater demand for water during the summer months. This need was satisfied with aquifer water in most of the eastern sector. As a result, nitrate concentrations increased very rapidly due to groundwater recirculation in an almost closed system. However, in the western sector, groundwater resources were not sufficient to meet the demands so it was necessary to take water from small rivers nearby. The crop change also entailed the use of large quantities of fertilizers and pesticides on the aquifer surface.

The area occupied by irrigated farming went from less than 1% of the study area in 1954 to 11.5% in 1968 and 67.5% in 1982. This increase has occurred at the cost of the dry farming areas which have fallen from 78.9% in 1954 to only 11.4% in 1982—a similar situation to the present one (Arrate et al., 1997).

In order to increase water supplies to Vitoria-Gasteiz city at the beginning of the seventies, complete diversion of the Alegría River and two of its tributaries was carried out at the entrance of the eastern sector of the aquifer (Fig. 1) sending supplies towards the Ullibarri reservoir system. The average annual volume diverted was of the order of 18 hm^3.

Consequences of these changes was the fall of the water table by 1–2.5 m, the disappearance of wetlands, with the resulting loss of their biogeochemical function, and an increase in the nitrate in groundwater (frequently more than 150–200 mg/l). Monitoring the nitrate concentration in groundwater since 1990 in a representative part of the sector and in the outlet of the Alegría River showed that the highest levels appeared in 1993–1994. In recent years, groundwater nitrate is on the decrease due to a possible rationalization in fertilizer use (not easy to prove owing to lack of data) and the change in the origin of the water used for irrigation which now comes from artificial pools (surface water stored outside the quaternary aquifer) avoiding recirculation.

Currently, nitrate concentrations are higher in groundwater than in surface water. After the recent wetland restoration, nitrate loss has become evident near the wetland area, although the processes involved are not well known in detail but the environment favors the conditions for denitrification: soil rich in organic matter and clay allowing a local semi-confined flow (García-Linares et al., 2003). Discharge from the wetland helps to decrease nitrate levels in the Alegría River.

5. Conclusions

The scale of soil nitrate leaching in the unsaturated zone is dependent on atmospheric input, fertilizer application and the existing reserves in the unsaturated zone. Rainy periods lead to leaching of the fertilizers and, as a consequence, of the nitrates in the soil, polluting the groundwater. The results, obtained in this work, may be generalized to cover all the cultivated zones of the alluvial plains in temperate and humid regions.

The pollution of groundwater by nitrogenous compounds from agricultural activity is evident in areas with high fertilizer consumption. In this experiment, we have demonstrated how monitoring nitrate concentrations in soil solutions in the unsaturated zone can be used to establish a budget of nitrate exportation to the saturated zone which is a good indicator of the risks of groundwater contamination.

Nitrate leaching in the unsaturated zone due to rain or irrigation is directly related to the leaching of the soil, although the degree of its impact does depend on the amount of water involved. The rise in piezometric level modifies the reserves of soil nitrate due to contamination of the interstitial solution, although its significance is limited to the area close to the water table. This contamination from the water table was similar in both experimental plots, since the groundwater presented comparable movements in height and comparable levels of contamination. Nonetheless, concentrations in the interstitial solutions were much lower in the uncultivated zone, a fact that cannot be exclusively explained by contamination due to a rise in the water table.

Nitrate concentrations in the groundwater of the Vulnerable Zone of the Vitoria-Gasteiz quaternary aquifer were highest in the early 1990s, when values of 200 mg/l were measured in groundwater. Afterwards, nitrate concentrations decreased and, in recent years, seem to remain stable, between 50 and 70 mg NO_3^-/l. Apart from a possible rationalization of fertilizer use, the drop in nitrate can be attributed to (i) the change in the origin of the water used for irrigation; water now being taken from artificial pools outside the quaternary aquifer and not from the aquifer itself as before, and (ii) nitrate loss owing to the recent restoration of wetlands in the sector.

Acknowledgments

This work was funded by the HID99-0333 Project (CICYT, Spanish Government) and by the Basque Country Government (funding of a post-doctoral fellowship to one of the authors). The authors thank the personnel of the Experimental Farm of Arkaute for their contribution. In the memory of M. Etxeandia (owner of the Jungitu experimental plot).

References

Andersen LJ, Kristiansen H. Nitrate in groundwater and surface water related to land use in the Karup basin, Denmark. Environ Geol 1984;5:207–212.

Arrate I. Estudio hidrogeológico del acuífero cuaternario de Vitoria-Gasteiz (Araba, País Vasco). Ph.D. Univ. País Vasco; 1994. p. 251.

Arrate I, Sánchez-Pérez JM, Antiguedad I, Vallecillo MA, Iribar V, Ruiz M. Groundwater pollution in quaternary aquifer of the Vitoria-Gasteiz (Basque Country, Spain). Environ Geol 1997;30:257–265.

Bernhard C, Carbiener R, Cloots AR, Froehlicher R, Schenk C, Zilliox L. Nitrate pollution of groundwater in the Alsatian plain (France). A multidisciplinary study of an agricultural area: the central ried of the Ill river. Environ Geol Water Sci 1992;20:125–137.

Bijay-Singh , Yadvinder-Singh , Sekhon GS. Fertilizer-N use efficiency and nitrate pollution of groundwater in developing countries. J Contam Hydrol 1995;20:167–184.

Cabrera F, Fernandez-Bohy E, Aparicio MG, Murillo JM, Moreno F. Leaching of nitrate from a sandy loam soil under corn and two N-fertilizations. Fres Environ Bull 1995;4:250–255.

Costa JL, Massone H, Martinez D, Suero EE, Vidal CM, Bedmar F. Nitrate contamination of a rural aquifer and accumulation in the unsaturated zone. Agric Water Manage 2002;1744:1–15.

Delin GN, Landon MK. Effects of surface run-off on the transport of agricultural chemicals to ground water in a sandplain setting. Sci Total Environ 2002;295:143–155.

Durieux RP, Brown HJ, Stewart EJ, Zhao JQ, Jokel WE, Magdoff FR. Implications of nitrogen management strategies for nitrate leaching potential: roles of nitrogen source and fertilizer recommendation system. Agronomy J 1995;87:884–887.

EEC. Council Directive 88/778/EEC of 15 July 1980 relating to the quality of water intended for human consumption. OJL 229; 30.8.1980. p. 11.

EEC. Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. OJL 375; 31.12.1991. p. 1.

García-Linares C, Martínez-Santos M, Martínez-Bilbao V, Sánchez-Pérez JM, Antiguedad I. The functionality of a restored wetland in nitrate elimination. The example of the peri-urban wetland of Victoria-Gasteiz (Basque Country, North Spain). Hydrol. Earth Sci. System 2003;7:109–121.

Guillard K, Griffin GF, Allison DW, Rafey MM, Yamartino WR, Pietrzyk SW. Nitrogen utilization of selected cropping systems in the US northeast: I. Dry matter yield, N uptake, apparent N recovery, and N use efficiency. Agronomy J 1995;87:193–199.

Guillard K, Griffin GF, Allison DW, Yamartino WR, Rafey MM, Pietrzyk SW. Nitrogen utilization of selected cropping systems in the US northeast: II. Soil profile nitrate distribution and accumulation. Agronomy J 1995;87:199–207.

Guimera J. Metodologia de estudio de la contaminacion de acuiferos por nitratos. Aplicacion al acuifero del Maresme. In: Candela L, Varela M, editors. La zona no saturada y la contaminacion de las aguas subterraneas. Barcelona: CIMNE, 1993. p. 197–219.

Guimera J, Marfa O, Candela L, Serrano L. Nitrate leaching and strawberry production under drip irrigation management. Agric Eco Environ 1995;56:121–135.

Gustafson A. Leaching of nitrate from arable land into groundwater in Sweden. Environ Geol 1983;5:65–71.

Kalita PK, Kanwar RS. Effect of water-table management practices on the transport of nitrate-N to shallow groundwater. Trans ASAE 1993;36:413–422.

Levallois P, Theriault M, Rouffignat J, Tessier S, Landry R, Ayotte P, Girard M, Gingras S, Gauvin D, Chiasson C. Groundwater contamination by nitrates associated with intensive potato culture in Quebec. Sci Total Environ 1998;217:91–101.

Morell I, Sánchez-Pérez JM. Evaluation of porous cup soil-water samplers under laboratory conditions: comparison of ceramic and PFTE cups. Toxicol Environ Chem 2000;74:231–244.

Morell I, Sánchez-Pérez JM. Evaluación de tomamuestras de cápsula porosa bajo condiciones de laboratorio: comparacion entre cápsulas en cerámica porosa y PFTE. In: Gonzalez Martinez D, Orihuela Calvo L, Romero Macias E, Garrido Morillo R, editors. Progresos en la Investigación en Zona no saturada. Huelva: Servicio Central de Publicaciones de la Universidad de Huelva, 1998. p. 89–108.

Prunty L, Greenland R. Nitrate leaching using two potato-corn N-fertilizer plans on sandy soil. Agric Eco Environ 1997;65:1–13.

Ramos C, Varela M. Lixiviacion de nitratos en dos parcelas experimentales en regadio de valencia. In: Candela L, Varela M, editors. La zona no saturada y la contaminacion de las aguas subterraneas. Barcelona: CIMNE, 1993. p. 183–197.

Ritter WF, Chirnside AEM, Scarborough RW. Soil nitrate profiles under irrigation on coastal plain soils. J Irrigation Drainage Eng 1990;116:738–752.

Schepers JS, Varvel GE, Watts DG. Nitrogen and water management strategies to reduce nitrate leaching under irrigated maize. J Contam Hydrol 1995;20:227–239.

Strebel O, Duynisveld WHM, Böttcher J. Nitrate pollution of groundwater in western Europe. Agric Eco Environ 1989;26:189–214.