

Nitrate source and fate at the catchment scale of the Vibrata River and aquifer (central Italy): an analysis by integrating component approaches and nitrogen isotopes

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Abstract The aim of this study is to apply an integrated approach to determine nitrate sources and fate in the alluvial aquifer of the River Vibrata (Abruzzi, central Italy) by coupling the Isotope and the Component approaches. Collected data include concentration and nitrogen isotope composition of groundwater samples from the alluvial aquifer and nitrogen loads arising from agricultural and non-agricultural sources. The adopted methodology identified synthetic fertilizers as main sources of nitrate in the Vibrata alluvial aquifer. At the catchment scale, two different zones have been identified: the Upper Valley, where infiltration to groundwater is dominant and nitrogen easily migrates into the aquifer; in this area, nitrate content in groundwater is stable and normally higher than EU requirements. Moreover, streamwaters are fed by groundwater with a nitrate content likely lowered by denitrification processes occurring in the hyporheic zone. In the Lower Valley, runoff processes dominate and the nitrate content in surface waters is higher. Nevertheless,

groundwater is locally affected by denitrification that breaks down the nitrate content, which often reaches values consistent with law limits.

Keywords Pollution · Alluvial aquifer · Nitrogen loads · Isotopes · European policy

Introduction

Nitrate contamination has been identified as a major groundwater quality issue in European Community (EC 1991, 2000) and worldwide (USEPA 2001; Choi et al. 2003). Baseline concentrations of nitrate in groundwater beneath natural grassland in temperate regions are typically below 2 mg/L (Foster et al. 1982; Madison and Brunett 1984). Although the chemical composition of soils and the geological feature of the aquifers can determine nitrate content in groundwater even in pristine natural environments (Boyce et al. 1976; Spalding and Exner 1993; Stadler et al. 2008), overloading of nitrogen is predominantly induced by human activities. Nitrate is mobile and can be lost by leaching from the soil profile and the hyporheic zone of streams (Boulton et al. 1998; Grischek et al. 1998; USEPA 2000), while only a small fraction is lost via surface runoff (Jackson et al. 1973; EEA 2005).

Agricultural activities are often indicated as the most significant anthropogenic sources of nitrate contamination in groundwater due to the widespread use of synthetic fertilizers and manure exceeding crops demand (Birkinshaw and Ewen 2000; McLay et al. 2001). Although nitrogen is a vital nutrient to enhance plant growth, when nitrogen-rich fertilizer application exceeds plant demand and soil denitrification capacity, it can usually enter groundwater in the oxidised form of nitrate, which is highly

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mobile with little sorption attitude (Meisinger and Randall 1991). However, the contribution of non-agricultural sources is dramatically increasing, especially in urban areas, where sewage and leaking sewers, septic tanks, industrial spillages and downwelling of nitrate-rich streamwaters can determine significant nitrogen, ammonium or nitrate loads into groundwater (Erickson 1992; MacQuarrie et al. 2001). Due to the mixing of nitrates from diverse sources and the variation in the occurrence and magnitude of the denitrification processes within an aquifer, the discrimination of sources and fate of nitrate in groundwater is a difficult procedure and results are frequently debatable, if not questionable (Spruill et al. 2002; Kellman and Hillaire-Marcel 2003; Stadler et al. 2008; Stigter et al. 2008). According to the European legislation, identification of areas with heavy nitrogen loads and characterisation of nitrogen sources are important tools for land use planners and environmental managers, and of fundamental interest for hydrographic basin management (EC 1991, 2000).

The *components approach* (Barbiero et al. 1990; Wakida and Lerner 2005) is a fast and low-cost tool to gather information of all the potential sources (*components*) of nitrogen occurring into a catchment or at the surface of a hydrogeological basin and estimates the potential nitrogen loads arising from each component. For local authorities in charge of water resources management, the components approach allows a fast identification of high-risk areas in the catchment and is useful for planning remediation alternatives in management policy (CIS 2003). However, it does not allow assessing the fate of nitrogen, since it does not require hydrological or hydrogeological information.

Basic knowledge on the water budget in the hydrological basin under investigation can help to evaluate different components of river and aquifer flow, as runoff and infiltration, taking into account permeability and transmissivity of the aquifers and their relationship with surface waters. The analysis of river discharge in the hydrographic basin and of water table variations in the aquifer can effectively contribute to verify and quantify the water flow and, consequently, the transfer of potential nitrogen loads, estimated by the components approach, to the river and the alluvial aquifer. In this way, a conceptual model of the nitrogen cycle at the catchment scale can be inferred. To provide a validation of this model by a two-way approach, the nitrogen isotope approach has been adopted in this study.

Stable isotopes of nitrogen can be used to discriminate between sources of nitrate in groundwater, as nitrate originating from different sources has characteristic isotopic ratios (Clark and Fritz 1997; Kreitler and Browning 1983; Strebel et al. 1989; Wells and Krothe 1989; Cole et al. 2006). The nitrogen isotope composition has been used for almost three decades to trace nitrate origin and fate (e.g. Kreitler

1979; Kreitler and Browning 1983; Mariotti et al. 1988; Koba et al. 1997; Green et al. 1998; Kendall and Aravena 1999; Karr et al. 2001). This method allows the discrimination of synthetic fertilizers source from organic sources (i.e. manure and sewage sludge), but is not sensitive in assessing diverse organic sources. More recently, the oxygen isotope composition has also been used in a dual isotopic approach (Bottcher et al. 1990; Aravena et al. 1993; Wasenaar 1995; Aravena and Robertson 1998; Mengis et al. 1999; Panno et al. 2001; Fukada et al. 2004; Katz et al. 2004; Chen and MacQuarrie 2005). This relatively new approach, which relies on the nitrate isotope composition of both oxygen and nitrogen, turned out to be useful in discriminating the atmospheric origin of nitrates from other sources and identifying denitrification processes.

The integration of data at the catchment scale (nitrogen loads, river discharge and solute flux) with local information about nitrogen concentration and isotope composition in groundwater from sampling wells may offer the potential of building conceptual and numerical models about nitrogen cycle (Clilverd et al. 2008; Petitta et al. 2009; Wexler et al. 2011), highlighting the role of denitrification areas corresponding to hyporheic and/or riparian zones (Cey et al. 1999; De Vito et al. 2000; Seitzinger et al. 2006; Curie et al. 2009).

This study is aimed at: (1) analysing nitrate concentration in groundwater of the Vibrata Plain (central Italy), which has been designated *Nitrate Vulnerable Zone* according to the European legislation (EC 2000; Regione Abruzzo 2005); (2) adopting the component approach to calculate nitrogen load possibly transferred to groundwater by infiltration and groundwater/river interactions; (3) using the isotopic approach in order to achieve a rational estimate of different nitrate sources contributions to aquifer contamination, and (4) suggesting management practices for nitrate pollution remediation.

Study site

The hydrographic basin (116 km²) of the River Vibrata (37 km long) is located in the northern part of the Abruzzi Region (central Italy), extended eastward and upright to the Adriatic shoreline. Eighty percent of the catchment surface is cultivated (65 % cereals), 8 % is urbanised and 2 % industrialised. Wheat fertilization takes place from November to April in three different phases: before seeding in November, after tillering in February–March and 15 days after tillering. Corn fertilization occurs before seeding in April–May and after tilling in June. According to farmer information, synthetic fertilizers, mainly ammonium salts, are preferentially used. Wooded areas occur in only 5 % of the catchment, corresponding to the uppermost

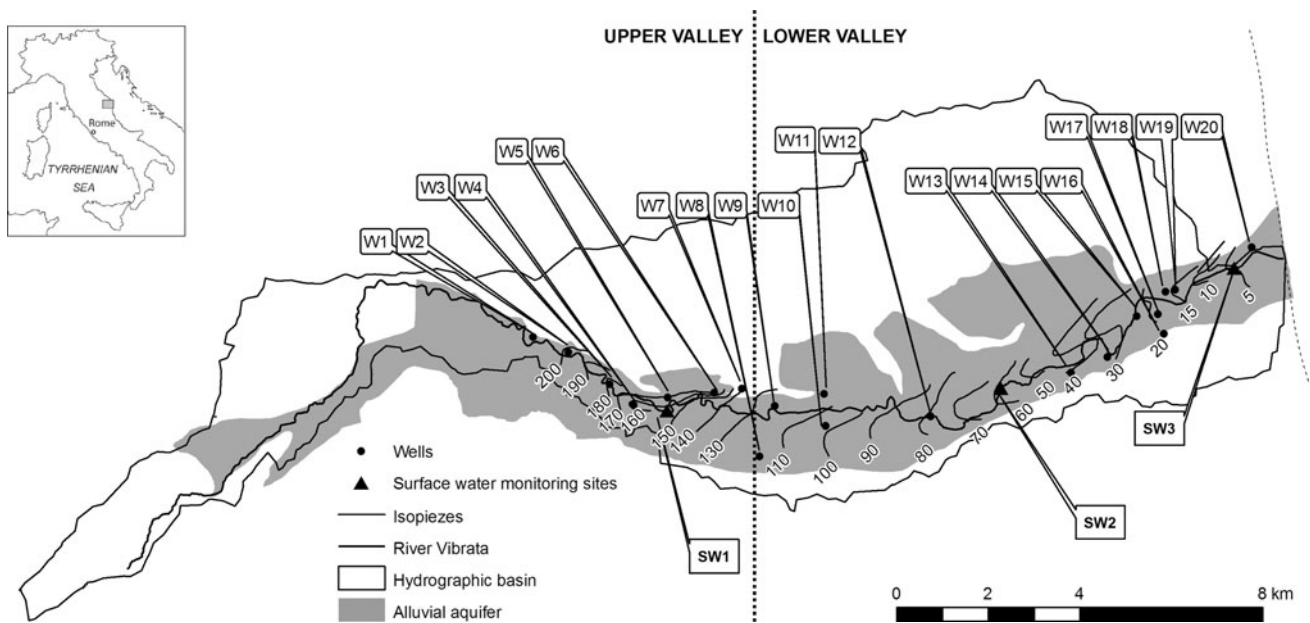


Fig. 1 Limits of the hydrographic basin of the River Vibrata and of the alluvial aquifer (Abruzzi, central Italy)

part of the basin. With the exception of the first 4 km of the river, riparian strips are discontinuous, thin and mainly formed by shrub vegetation.

The hydrogeological basin is part of the hydrographic basin (48 km² corresponding to 41 % of the catchment), occupying the strip of the valley closest to the River Vibrata and it coincides with the alluvial aquifer of the Vibrata Plain (Fig. 1). Only 13 % of the hydrogeological basin is external to the hydrographic one, on the southwestern boundary and close to the Adriatic shorelines. The alluvial aquifer consists of Quaternary terraced alluvial sediments mainly represented by gravel and sand with silty lenses and levels with variable thickness (Desiderio et al. 2007). The gravel bodies dominate the terraced part of the valley, while sand and silt components increase in the bottomland. The aquifer is unconfined and supported by an aquiclude of Plio-Pleistocene clay deposits: it reaches the maximum thickness of 40 m. The lateral limits of the hydrogeological basin are represented by the outcrop of the marine clays constituting the low-permeability bedrock of the aquifer. The valley can be divided (Fig. 1) in an upper western portion (Upper Valley), where the aquifer largely outcrops and the infiltration process is predominant, and a lower eastern part (Lower Valley), where the runoff becomes prevalent due to the wide clay outcrop. As represented in Fig. 1, the Upper Valley shows a limited extent of the clay outcrop and more than 50 % of the hydrographic basin coincides with the alluvial aquifer; in this area the River Vibrata clearly receives contribution from groundwater (Fig. 2). Conversely, in the Lower Valley, the bedrock outcrop becomes predominant, with a large extent of low-permeability sediments mainly located on the left northern

part of the hydrographic basin, and the alluvial aquifer occupies only a minority portion of the basin. Groundwater/river interactions become variable in space and time (Fig. 2).

Although sediment heterogeneity determines a highly variable permeability both vertically and horizontally (Desiderio et al. 2007), the alluvial aquifer can be considered as a monolayer groundwater body. The transmissivity is about $2 \times 10^{-3} \text{ m}^2/\text{s}$ and the mean hydraulic conductivity is roughly about $1 \times 10^{-4} \text{ m/s}$ (Celico 1983; Desiderio et al. 2007). Gravel and sand are of predominantly siliciclastic origin, and in the subordinate finest sediments, alkalis represent a significant fraction. The aquifer recharge is largely due to rainfall, which has a mean value of 800 mm/year. By considering the mean evapotranspiration value of about 600 mm/year, the effective available water is about 200 mm/year, which corresponds for the aquifer outcrop to 10 million of m³/year.

Infiltration can be estimated at 100 mm/year, taking into account both the permeability of outcropping deposits and river discharge, whose regime indicates a long-term runoff of about 500 L/s at the catchment scale, compared to a baseflow close to 150 L/s by seepage from the alluvial aquifer.

Water table depth was measured in 20 wells in July 2007 and in 19 wells in November 2007. Water table depth attained its maximum values in the western part of the aquifer and progressively decreases eastward, reaching its lowest values in the proximity of the Adriatic shorelines (Fig. 1; Table 1). Phreatic level ranged between 2.9–35.2 m b.g.s. in July 2007 and 2.4–34.0 m b.g.s. in

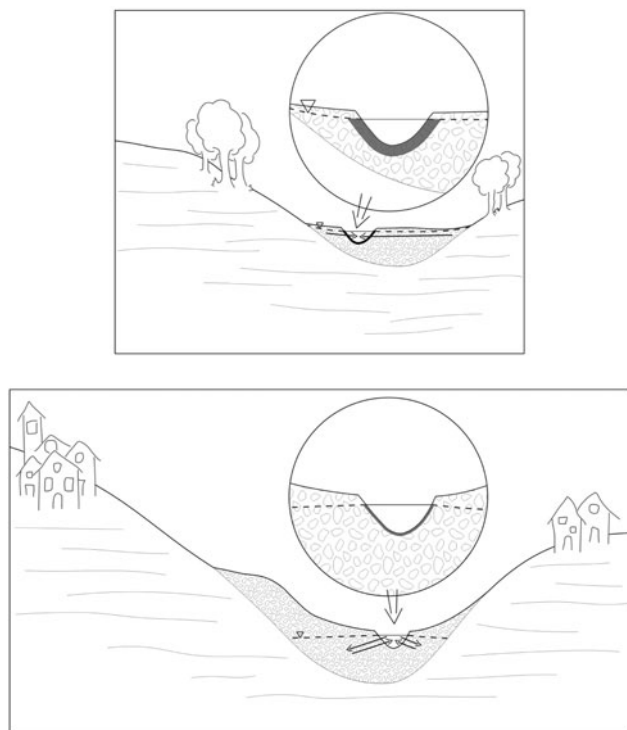


Fig. 2 Comparison between the hydrogeological sections located in the Upper (*up*) and Lower Valley (*down*) of the River Vibrata. In the Upper Valley, aquifer largely outcrops and the river is mainly fed by groundwater; in the Lower Valley runoff becomes prevalent and groundwater/river interactions are variable in space and time

November 2007; seasonal variations of the water table ranged between a minimum value of 0.4 m and a maximum value of 5.1 m, with reference to sites W20 and W6, respectively (Table 1).

Groundwater is mostly exploited for farming supplies and, to a lesser extent, for industrial and domestic uses.

Since 2004, nitrate concentrations in groundwater are quite over 50 mg/L, exceeding the international standard for drinking water and the European standard for *good groundwater quality*. Due to the high nitrate concentrations, the Vibrata Plain has been designated as *Nitrate Vulnerable Zone*, according to Directive 91/676/CE (EC 1991).

Groundwater nitrate content was measured in 20 wells in July 2007 and in 16 wells in November 2007, respectively (Table 2). The groundwater nitrate content ranged between 0.1 to 148 mg/L in summer and between 2 to 151 mg/L in fall. In July 2007, groundwater nitrate content exceeded the European standard of groundwater quality (50 mg/L) in 15 out of 20 monitoring wells, while in November 2007 in 9 out of 16 monitoring wells.

At the same time, the River Vibrata showed a relatively high nitrate content in three gauging stations (SW), with a sharp increase at SW2 (Fig. 3).

Methods

Groundwater samples for chemical and isotopic analyses were taken from 20 wells in July 2007 and 16 wells in November 2007 (Table 1; Fig. 1), because four wells were found sealed.

All monitoring wells belong to private owners; 14 wells out of 20 are exploited for crop irrigation during the summer period, 5 wells are used for multiple purposes and are always active and 1 well is permanently inactive. Wells are all spread through the River Vibrata alluvial plain; wells depth ranges from 5 to 52 m, their altitude decreasing eastward, from 221 to 14 m a.s.l. The River Vibrata distance from monitoring wells ranges between 10 and 820 m (Table 1).

Samples were collected and stored in polyethylene bottles and kept refrigerated until analysed by chromatography technique for nitrate, sulphate and chloride concentrations. Dissolved oxygen and electrical conductivity were measured in the field with a multiparametric probe (ECM MultiTM; Dr. Lange GmbH, Düsseldorf, Germany). Information on well depths was derived from the Regione Abruzzo *Water Quality Database*. Spearman's rank correlation coefficient (r) was used to assess relationships among the measured chemical parameters. The statistical significance of r was tested using a t test.

Isotope analysis

Groundwater samples were also collected for nitrogen and oxygen isotope analyses of NO_3^- . Dissolved NO_3^- was precipitated as AgNO_3 following the procedure described by Silva et al. (2000). Nitrogen isotopes ratios ($^{15}\text{N}/^{14}\text{N}$) were measured using a Carlo Erba CHNS 1110 elemental analyser coupled in continuous flow to a Finnigan Delta Plus mass spectrometer. A small amount of AgNO_3 was transferred into tin capsules and combusted with the standard configuration for nitrogen isotope analysis. For the oxygen isotope analysis, the NO_3^- -N samples, inserted into silver capsules, were pyrolysed with the Finnigan TC EA at 1,450 °C. Carbon monoxide produced was transferred into the mass spectrometer for oxygen isotope ratio ($^{18}\text{O}/^{16}\text{O}$) measurements. The nitrogen and oxygen isotope ratios (R) are reported as per mil deviation ($\delta^{15}\text{N}$ or $\delta^{18}\text{O}$) from the $^{15}\text{N}/^{14}\text{N}$ or $^{18}\text{O}/^{16}\text{O}$ ratios relative to AIR and V-SMOW standards, according to the following equation:

$$\delta = 1,000 \times (R_{\text{sample}}/R_{\text{standard}} - 1)$$

Data from all samples were normalised against internationally accepted reference materials (IAEA-N1, IAEA-N2 and USGS25 for nitrogen and IAEA-N3 and USGS-34 for oxygen). To check the precision of the method, 10 replicate measurements were made on solution

Table 1 Sampling points (wells) characteristics

Well code	Municipal district	Well depth (m)	Well altitude (m a.s.l.)	Distance from River Vibrata (m)	River Vibrata altitude (m a.s.l.)	Phreatic level July 2007 (m u.g.l.)	Phreatic level November 2007 (m u.g.l.)	Piezometric level July 2007 (m a.s.l.)	Piezometric level November 2007 (m a.s.l.)
W1	SE	30	221	223	204	27.6	25.3	193.4	195.7
W2	SE	5	197	93	192	3.2	2.9	193.8	194.1
W3	TO	5	197	11	196	2.9	2.8	194.1	194.2
W4	SO	30	194	198	172	24.7	22.3	169.3	171.7
W5	TO	15	192	103	152	7.7	7.7	184.3	184.3
W6	TO	20	181	211	138	12.7	7.6	168.3	173.4
W7	TO	52	169	531	129	35.2	34.2	133.8	134.8
W8	SO	22	141	820	125	14.9	14.9	126.1	126.1
W9	SO	7	137	80	123	6.3	6.9	130.7	130.1
W10	SO	25	129	370	112	17.3	15.6	111.7	113.4
W11	NE	32	130	317	112	10.8	10.2	119.2	119.8
W12	CO	7	87	10	80	3.4	2.4	83.6	84.6
W13	CO	30	70	145	44	12.7	11.8	57.3	58.2
W14	AA	30	55	98	30	15.4	14.6	39.6	40.4
W15	AA	23	32	60	25	12.7	11.8	19.3	20.2
W16	AA	30	44	710	17	22.0	n.m.	22.0	n.m.
W17	TR	50	33	340	18	17.3	15.6	15.7	17.4
W18	CL	12	24	180	17	5.6	4.1	18.4	19.9
W19	CL	21	22	285	17	5.0	4.2	17.0	17.7
W20	MA	18	14	108	2	2.9	2.5	11.1	11.5

Location is in Figs. 1 and 4

n.m. not measured, AA Alba Adriatica, AN Ancarano, CL Colonnella, CO Corropoli, CN Controguerra, CV Civitella, MA Martinsicuro, NE Nereto, SE Sant’Egidio alla Vibrata, SO Sant’Omero, TO Torano Nuovo, TR Tortoreto

containing 25 mg/L of NO₃⁻ of a laboratory KNO₃ standard. The 1σ analytical precisions for δ¹⁵N and δ¹⁸O analyses were ±0.3 and ±0.6, respectively, for the water samples of the laboratory standard processed through the entire analytical procedure.

Components approach

Boundaries of municipal districts pertaining to Abruzzi Region (central Italy) were overlapped to both catchment and hydrogeologic basin surface by ESRI® ArcMap™ 9.2 (Fig. 4). Anthropogenic sources of nitrogen, concerning agricultural (synthetic fertilizers and manure) and non-agricultural pressures (municipal wastewater plants, minor wastewater plants and industrial sewages), were identified in the municipal districts areas occurring, respectively, into the catchment and at the hydrogeological basin surface. Nitrogen loads potentially produced by anthropic sources were computed per each municipal district. Moreover, the nitrogen loads at the catchment scale were separately calculated for the outcrop of the alluvial aquifer, corresponding to the hydrogeological basin. This last

contribution was assumed directly affecting the aquifer zone corresponding to the source location.

The nitrogen load in t/year deriving from municipal wastewater treatment plants was obtained from the Regione Abruzzo *Water Quality Database*.

The nitrogen load in t/year deriving from minor wastewater treatment plants, as septic tanks or imhoff, was computed as follows:

$$NWTP = TC \times 12 \times 365$$

where NWTP is the nitrogen load in t/year deriving from a wastewater plant; TC is the treatment capacity of the plant, i.e. the plant purifying power, measured in population equivalent (p.e.¹); 12 is the nitrogen load coefficient for urban wastewater effluent (Barbiero et al. 1990) per population equivalent and per day (as gr/p.e. days) and 365 is the number of days in a year (days/year).

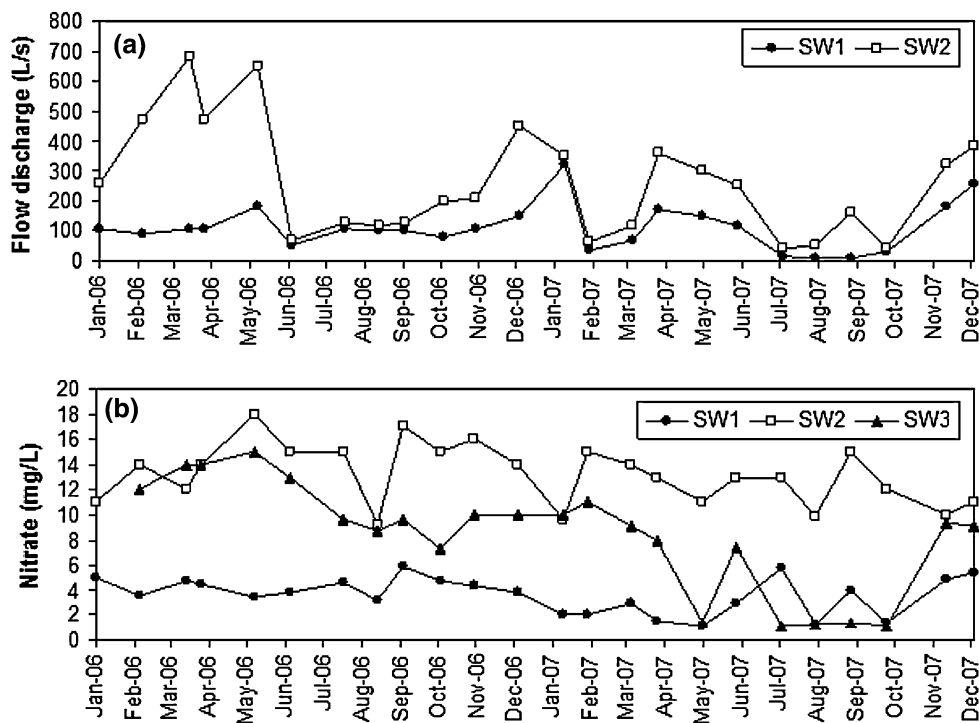
¹ One population equivalent is defined as the organic biodegradable load having a 5-day biochemical oxygen demand (BOD₅) of 60 g of oxygen per day (EC 1991).

Table 2 Groundwater chemical parameters

Well code	July 2007				November 2007				
	EC ($\mu\text{S/cm}$)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	EC ($\mu\text{S/cm}$)	O_2 (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)
W1	1,092	77	66	47	1,006	1.9	6	21	2
W2	1,076	45	85	116	1,043	6.6	37	78	140
W3	838	45	32	26	883	1.1	32	42	38
W4	912	35	53	68	991	7.6	65	64	66
W5	876	47	107	2	n.m.	n.m.	n.m.	n.m.	n.m.
W6	993	57	71	148	n.m.	n.m.	42	121	129
W7	869	351	75	82	855	2.7	36	64	18
W8	862	36	42	68	862	5.5	35	41	66
W9	1,515	137	81	141	1,497	3.7	149	91	151
W10	1,021	72	195	107	1,038	6.1	66	68	85
W11	1,043	45	34	15	992	3.5	43	33	22
W12	1,192	97	98	86	1,170	1.6	175	145	34
W13	1,560	149	171	121	1,444	5.3	120	149	125
W14	1,357	140	121	91	n.m.	n.m.	n.m.	n.m.	n.m.
W15	1,370	134	131	91	381	1.5	17	11	15
W16	1,344	122	127	127	n.m.	n.m.	n.m.	n.m.	n.m.
W17	1,380	147	121	77	1,376	4.2	160	127	70
W18	1,390	172	121	56	1271	5.2	116	109	73
W19	1,361	145	114	74	n.m.	n.m.	n.m.	n.m.	n.m.
W20	1,452	138	171	0.1	1551	0.9	130	230	27

n.m. not measured, *EC* electrical conductivity, *Cl⁻* chloride, *SO₄²⁻* sulphate, *NO₃⁻* (mg/L) nitrate, *O₂* dissolved oxygen

Fig. 3 Flow discharge (a) and nitrate content (b) measured at three gauging stations in the River Vibrata (location of the stations as shown in Fig. 1)



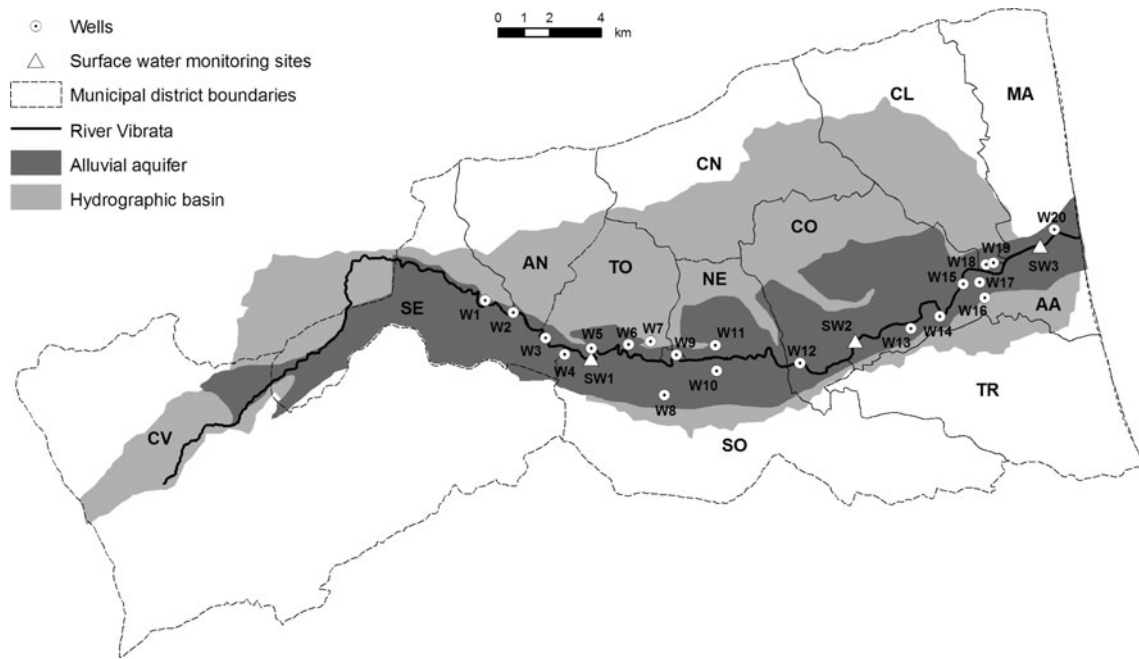


Fig. 4 Location of sampling sites (wells and gauging stations) and municipal districts (acronyms in capital fonts). Codes as in Table 1

The industrial nitrogen load in t/year was computed as follows for each industry:

$$NI = W \times C \times 10 \times 365$$

where NI is the industrial nitrogen load in t/year; W is the number of industry workers; C is an industrial coefficient (p.e./W), which varies according to the industry typology (Barbiero et al. 1990); 10 is the nitrogen load coefficient (as gr/p.e. days) for industrial sewages (Barbiero et al. 1990) and 365 is the number of days in a year (days/year).

The nitrogen load due to synthetic fertilizers was computed as follows:

$$NSF = (NU \times Ha) \times A$$

where NSF is the nitrogen load in t/year from mineral synthetic fertilizers; NU is the nitrogen uptake (as kg/ha year) of the crop species (e.g. wheat, corn, etc.) occurring in the municipal district (Barbiero et al. 1990; Trevisan et al. 1998), Ha is the area (as hectares) used for the crop species in the municipal district derived from ISTAT database (ISTAT 2001) and A is the percentage of the municipal district area falling into the catchment or the hydrogeological basin.

The nitrogen load due to manure was computed as follows:

$$NM = N \times H$$

where NM is the nitrogen load (t/year) from manure; N is the nitrogen content (kg/head year) of the manure produced by the cattle species (e.g. bovine, ovine-caprine, swine) in the municipal district (ENEA 2001); H is the

number of heads in the livestock of the cattle species obtained from Istituto Zooprofilattico Caporale database.

Results

Hydrochemical analyses

The results of field and laboratory analyses are listed in Table 2 and summarised in Fig. 5, where groundwater has been classified as bicarbonate-alkaline-terrigenous. In both surveys, the electrical conductivity (EC) showed an increasing trend at the sampling sites (wells) close to the coastline, as did chloride concentrations (Table 2). Positive correlations were observed between EC and Cl^- (July 2007: $r = 0.66, p < 0.05$; November 2007: $r = 0.80, p < 0.05$), between EC and SO_4^{2-} (July 2007: $r = 0.67, p < 0.05$; November 2007: $r = 0.84, p < 0.05$) and obviously between Cl^- and SO_4^{2-} (July 2007: $r = 0.57, p < 0.05$; November 2007: $r = 0.75, p < 0.05$). NO_3^- concentration ranged from 0.1 to 148 mg/L (mean value = 77.2 mg/L) in July 2007, and from 2 to 151 mg/L (mean value = 66.3 mg/L) in November 2007. The maximum admissible concentration of NO_3^- for drinking water (50 mg/L), established by the European Commission, was exceeded in 67 % of the samples; 56 % exceeded the limit in both surveys, while only 25 % was below the limits in both sampling surveys. Moreover, NO_3^- concentrations were not significantly correlated to the other parameters; i.e. EC, Cl^- and SO_4^{2-} ($p > 0.05$), while NO_3^- data from both surveys returned a fairly close relationship ($r = 0.76, n = 16; p < 0.05$).

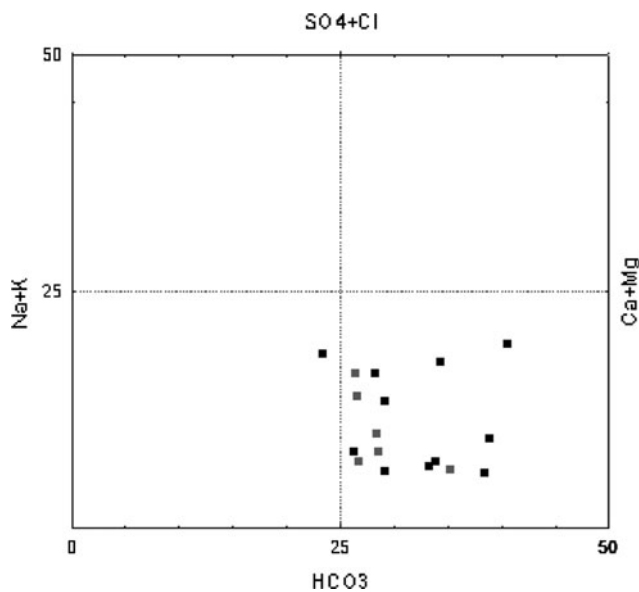


Fig. 5 Hydrogeochemical classification plot: *grey squares* represent sampling sites from the Upper Valley of the Vibrata Plain; *black squares* represent sampling sites from the Lower Valley

NO_3^- concentrations did not show clear spatial or temporal trends, in accordance with non-parametric t test; concentrations higher than 100 mg/L were measured in wells close to others with values lower than 2 mg/L; some wells showed concentrations highly variable between the two sampling times. Correlations were not found even taking into account the well depth and the distance from the River Vibrata, except for the closest samples (W3 and W12).

Components approach

Twelve municipal districts intersect the catchment area, while only ten municipal districts partially intersect the hydrogeological basin outcrop limits (Fig. 4). The largest portion of both the hydrogeological and hydrographic basins (more than 80 %) is covered by agricultural lands, with the dominance of cereals, as wheat and corn (Table 3).

Cumulatively, nitrogen load from synthetic fertilizers at catchment scale was higher than that occurring at the hydrogeological basin scale (812 t/year vs. 324 t/year). At the hydrogeological basin scale, nitrogen load from synthetic fertilizers ranged from a minimum of 1.3 t/year in AN municipal district to a maximum of 121.2 t/year in CO, and from a minimum of 2.6 t/year in MA and a maximum of 203 t/year in CO at the catchment scale (Table 3). In 6 out of 10 municipal districts at the hydrogeological basin scale and in 10 out of 12 at the catchment scale, the nitrogen load from agricultural sources exceeded 20 t/year; at the catchment scale, in 7 out of 12 municipal districts,

60 t/year (Table 3). Both at the catchment and hydrogeological basin scales, the nitrogen loads due synthetic fertilizers dosage per hectare (respectively, 75 and 78 kg/ha/year) are lower than the European Community recommendation limits (170 kg/ha/year).

Livestock dimensions, in number of heads, are indicated in Table 4. The nitrogen loads from manure ranged from a minimum of 0 t/year in AN, CL and MA municipal districts to a maximum of 15.4 t/year in CO at the hydrogeological basin and from a minimum of 0 t/year in MA to a maximum of 22.3 t/year in CO at the catchment scale; only in CO, at the catchment scale, the nitrogen load exceeded 20 t/year (Table 4).

Only 7 out of 12 municipal districts occurring into the catchment, and 6 out of 10 at the hydrogeological basin scale, collect and purify their wastewaters in major municipal treatment plants, being the wastewaters from the other districts treated in minor treatment plants as septic tanks or imhoff. At the catchment scale, the nitrogen load from municipal treatment plants ranged from a minimum of 0 t/year in AA, AN, CL, TO and TR to a maximum of 30 t/year in MA; in the remaining municipal districts it never exceeded 15 t/year (Table 5). At the hydrogeological basin, the nitrogen load ranged from a minimum of 0 t/year in AA, AN, CL, TO and TR to a maximum of 30 t/year in MA.

Thirty-one septic tanks have been presently recorded in the River Vibrata hydrographic basin and 8 at the hydrogeological basin surface, distributed, respectively, in 5 municipal districts out of 12, and in 3 out of 10 (Table 5). At the catchment scale, the nitrogen load from septic tanks ranged from 0 t/year in AA, AN, MA, SE, SO, TO and TR to 5.8 t/year in CO; at the hydrogeological basin scale, the nitrogen load ranged from 0 t/year in AA, AN, CV, MA, SE, SO, TO to 2.1 t/year in CO (Table 5).

Six industrial sewages have been recorded in five municipal districts in both the hydrogeological and hydrographic basin (CO, NE, SE, SO, TO): three from industrial laundries, two from textile and one from food industry, being the nitrogen loads from the food industry the highest. The industrial nitrogen loads never exceeded 9 t/year (Table 5).

Together with synthetic fertilizers, nitrogen loads from other anthropogenic sources affected the hydrogeological and the hydrographic basins with comparable values (Fig. 6). At both scales, synthetic fertilizers clearly represented the main sources of nitrogen load in each municipal district, with the exception of MA and CV (as far as the hydrogeological basin is concerned), which are affected by higher amount of nitrogen from municipal wastewater treatment plant discharges. At both scales, nitrogen loads from livestock and major wastewater treatment plants exhibited comparable values in SE, SO and CO districts; industrial loads shared similar values in

Table 3 Calculated nitrogen loads from synthetic fertilizers per municipal district at catchment scale (C) and at hydrogeological basin scale (HB)

Municipal district code	% municipal district area		Vineyard (ha)	Olive (ha)	Fruit trees (ha)	Wheat (ha)	Corn (ha)	Pulse, forage (ha)	Grass (ha)	Vegetables (ha)	N load (t/year)	
	C	HB									C	HB
	AA	88.5									53.75	15.91
AN	37.9	1.39	120.66	70.78	8.30	173.21	175.90	110.86	46.05	1.41	35.1	1.3
CV	11.0	2.10	24.60	191.28	22.18	524.25	668.30	383.04	158.17	8.33	29.6	5.7
CL	51.7	1.82	133.98	148.68	76.57	294.42	217.55	113.61	32.72	47.14	75.0	2.6
CN	50.8		260.31	170.40	49.94	202.20	255.93	172.68	112.23	24.04	76.9	
CO	98.6	58.90	93.16	167.26	58.45	452.89	368.83	253.95	2.46	79.28	202.9	121.2
MA	4.7	3.24	68.41	57.57	74.95	64.17	89.82	0.27	71.32	43.99	2.6	1.8
NE	100.0	54.43	17.84	67.65	6.74	56.89	86.99	91.65	4.59	1.34	42.0	22.9
SE	56.9	39.18	10.76	66.07	5.77	183.31	470.55	94.08	55.80	7.37	81.0	55.8
SO	31.1	24.01	29.20	125.80	6.90	423.10	440.42	239.41	31.31	103.95	63.1	48.8
TO	100.0	17.52	119.37	104.36	15.25	281.90	174.81	105.78	0.40	4.74	117.4	20.6
TR	11.8		82.54	189.27	9.66	288.79	174.91	168.97	19.95	18.60	15.6	
N uptake (kg × ha/year)			100	180	25	180	200	0	25	120		

Nitrogen uptake for each crop is indicated in bold

AA Alba Adriatica, AN Ancarano, CL Colonnella, CO Corropoli, CN Controguerra, CV Civitella, MA Martinsicuro, NE Nereto, SE Sant’Egidio alla Vibrata, SO Sant’Omero, TO Torano Nuovo, TR Tortoreto

Table 4 Livestock head numbers and calculated nitrogen loads for municipal district, from bovine, ovine-caprine, swine and poultry livestock

Municipal district code	Bovine (heads)		Ovine-caprine (heads)		Swine (heads)		Poultry (heads)		Total N load (t/year)	
	C	HB	C	HB	C	HB	C	HB	C	HB
	AA	133	104	3	3	34	25	0	0	7.7
AN	44	0	0	0	56	0	0	0	3.0	0.0
CV	39	39	386	311	0	0	0	0	4.0	3.7
CL	132	0	0	0	15	0	2,800	0	8.7	0.0
CN	110		6		97		0		7.2	
CO	366	250	6	6	196	150	0	0	22.3	15.4
MA	0	0	0	0	0	0	0	0	0.0	0.0
NE	80	53	0	0	0	0	0	0	4.4	2.9
SE	27	27	910	910	0	0	0	0	5.9	5.9
SO	232	231	0	0	26	26	0	0	13.0	13.0
TO	80	32	8	0	32	14	0	0	4.8	1.9
TR	44		0		0		0		2.4	
N load per head (kg/head/year)	54.8		4.9		11.3		0.48			

Nitrogen load produced by each livestock typology is also indicated

C catchment, HB hydrogeological basin, AA Alba Adriatica, AN Ancarano, CL Colonnella, CO Corropoli, CN Controguerra, CV Civitella, MA Martinsicuro, NE Nereto, SE Sant’Egidio alla Vibrata, SO Sant’Omero, TO Torano Nuovo, TR Tortoreto

the municipal districts in which they occur; nitrogen loads from minor wastewater treatment plants were poorly represented. At the hydrogeological scale, nitrogen loads from agricultural sources (synthetic fertilizers and manure) exceeded nitrogen loads from non-agricultural

sources in 7 municipal districts out of 10 and in 10 out of 12 at the catchment scale. At the hydrogeological basin scale, nitrogen loads from agricultural sources were comparable to those deriving from non-agricultural sources in NE.

Table 5 Calculated nitrogen loads, per municipal district, from non-agricultural sources occurring, respectively, at the catchment scale (C) and at the hydrogeological basin scale (HB)

Municipal district code	N load (t/year) from m.w.t.p.		No. minor treatment plants		T.C. (p.e.)		N load from minor treatment plant (t/year)		W		C (p.e./W)		N load from industry (t/year)	
	C	HB	C	HB	C	HB	C	HB	C	HB	C	HB	C	HB
	AA	0.0	0.0	0	0	0	0	0.0	0.0	0	0	0	0	0.0
AN	0.0	0.0	0	0	0	0	0.0	0.0	0	0	0	0	0.0	0.0
CV	14.0	14.0	3	0	239	0	1.0	0.0	0	0	0	0	0.0	0.0
CL	0.0	0.0	7	1	536	95	2.3	0.4	0	0	0	0	0.0	0.0
CN	12.0		6		432		1.9		0		0		0.0	
CO	11.0	11.0	7	3	1,330	380	5.8	2.1	45	45	17	17	2.8	2.8
MA	30.0	30.0	0	0	0	0	0.0	0.0	0	0	0	0	0.0	0.0
NE	12.0	12.0	8	4	755	375	3.3	1.6	135	135	17	17	8.4	8.4
SE	6.0	6.0	0	0	0	0	0.0	0.0	60	60	17	17	3.7	3.7
SO	14.0	14.0	0	0	0	0	0.0	0.0	90	90	17	17	5.6	5.6
TO	0.0	0.0	0	0	0	0	0.0	0	20	20	98	98	7.2	7.2
TR	0.0		0		0		0.0		0		0		0.0	

m.w.t.p. municipal wastewater treatment plants, *TC* cumulative tanks capacity, *p.e.* population equivalent, *C* industrial coefficient, *W_i* number of workers belonging to the *i*-industry, *AA* Alba Adriatica, *AN* Ancarano, *CL* Colonnella, *CO* Corropoli, *CN* Controguerra, *CV* Civitella, *MA* Martinsicuro, *NE* Nereto, *SE* Sant'Egidio alla Vibrata, *SO* Sant'Omero, *TO* Torano Nuovo, *TR* Tortoreto

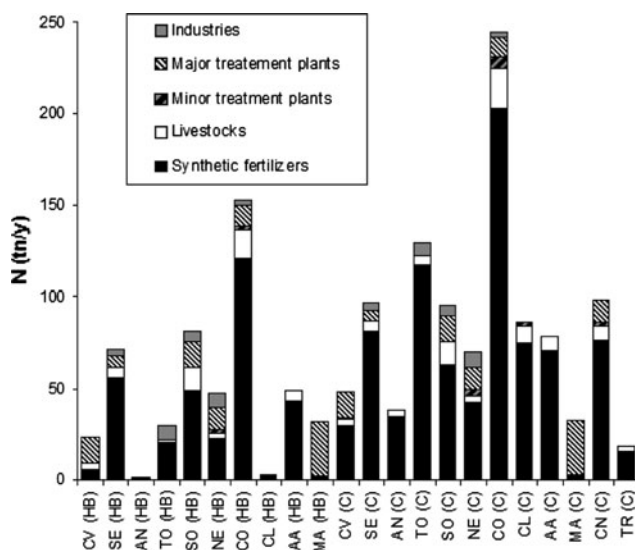


Fig. 6 Nitrogen loads from different anthropogenic sources per municipal district (*AA* Alba Adriatica, *AN* Ancarano, *CL* Colonnella, *CO* Corropoli, *CN* Controguerra, *CV* Civitella, *MA* Martinsicuro, *NE* Nereto, *SE* Sant'Egidio alla Vibrata, *SO* Sant'Omero, *TO* Torano Nuovo, *TR* Tortoreto) at catchment scale (C) and at hydrogeological basin scale (HB)

The total input of nitrogen to the aquifer has been estimated at about 491 t/year: 324 t/year derives from synthetic fertilizers (Table 3), 49 t/year from livestock (Table 4), 87 t/year from major wastewater treatment plants, 28 t/year from industrial wastewater discharges and 4.1 t/year from minor wastewater treatment plants (Table 5). The total input of nitrogen to the catchment was estimated at about

1,036 t/year: 812 t/year derives from synthetic fertilizers (Table 3), 83 t/year from livestock (Table 4), 99 t/year from major wastewater treatment plants, 28 t/year from industrial wastewater discharges and 14 t/year from minor wastewater treatment plants (Table 5).

Isotope approach

The isotope data for NO_3^- obtained in both sampling surveys are listed in Table 6. The isotope composition of NO_3^- dissolved in the Vibrata alluvial aquifer ranged from 4.9 to 22.8 ‰ in July 2007 and from 3.8 to 18.9 ‰ in November 2007 for nitrogen (data referred vs. AIR), and from 1.3 to 11.0 ‰ in July 2007 and from 3.7 to 14.7 ‰ in November 2007 for oxygen (data referred vs. SMOW).

Nitrate in soils originates from different sources, which include mineralisation of soil organic nitrogen, synthetic fertilizers, organic residues from leakage of septic tanks or sewage and atmospheric deposition. This different sources produce nitrate with distinct isotopic composition, as displayed in the $\delta^{18}\text{O}/\delta^{15}\text{N}$ graph (Fig. 7). The majority of groundwater samples falls into the range commonly attributed to synthetic fertilizers based on NH_4^+ , corresponding with intensively farmed areas showing elevated nitrogen concentrations and characterised by the use of ammonium salts fertilizers. Deviations from this main isotopic composition of synthetic fertilizers towards more positive values due to nitrogen isotope fractionation in soil reactions (e.g. ammonia volatilisation) have been frequently observed (Kreitler 1979; Green et al. 1998). In fact,

Table 6 Isotopic composition of nitrate ($\delta^{15}\text{N}$ AIR and $\delta^{18}\text{O}$ SMOW) in the water samples from the Vibrata alluvial aquifer measured in July 2007 and November 2007

Well code	$\delta^{15}\text{N}$ (vs. AIR) July 2007	$\delta^{18}\text{O}$ (vs. SMOW) July 2007	$\delta^{15}\text{N}$ (vs. AIR) November 2007	$\delta^{18}\text{O}$ (vs. SMOW) November 2007
W1	6.4	4.3	5.9	5.6
W2	4.9	4.9	3.8	4.7
W3	22.8	11.0	10.3	6.7
W4	5.9	1.3	6.1	7.2
W5	n.m.	n.m.	n.m.	n.m.
W6	5.0	2.7	4.5	3.7
W7	5.3	1.3	5.2	4.4
W8	5.8	3.8	5.7	5.4
W9	14.1	5.4	11.0	5.4
W10	5.3	3.7	18.9	13.7
W11	12.6	8.8	4.3	7.0
W12	6.5	5.4	14.7	10.7
W13	6.6	6.1	5.3	7.1
W14	12.3	7.8	n.m.	n.m.
W15	10.3	6.5	16.4	14.7
W16	6.6	4.8	n.m.	n.m.
W17	11.5	7.4	11.5	8.5
W18	19.6	10.1	9.3	9.1
W19	12.6	8.6	n.m.	n.m.
W20	n.m.	n.m.	11.6	13.6

Wells are scheduled according to the distance from the coastline, W1 being the most distant and W20 the closest to the coastline. Location is in Figs. 1 and 3

n.m. not measured

some samples fall in the area of animal and sewage waste sources, showing also a tendency toward denitrification processes (Fig. 7). Denitrification is a biologically driven process, requiring specific environmental conditions (Korom 1992; Böhlke 2002), and implying a lowering of NO_3^- concentration along with an increase in heavy nitrogen and oxygen isotope contents.

Denitrification is generally described by a Rayleigh process and is predicted by the classic equation:

$$\delta^{15}\text{N} = \delta^{15}\text{N}_0 + \varepsilon \ln(C/C_0)$$

By comparing the $\delta^{15}\text{N}$ values from both sampling surveys (Fig. 8), a group of sampling sites showed a steady isotope composition (mirrored also by $\delta^{18}\text{O}$ values). The $\delta^{15}\text{N}/[\text{NO}_3^-]$ graph (Fig. 9), showed a stability of nitrate concentration and isotope values in the Upper Valley from both sampling surveys, while in the Lower Valley a higher $\delta^{15}\text{N}$ value, along with a lowering in NO_3^- concentrations, has been observed in the second survey.

Discussion

According to chemical data, in the sampled wells, Cl^- and SO_4^{2-} showed an increase downgradient, toward the coastline. On the basis of the observed correlation among EC, Cl^- and SO_4^{2-} , Cl^- and SO_4^{2-} can be considered as descriptors of the groundwater hydrochemistry of the aquifer, sharing a common origin that predominantly contributed to the total content of dissolved salts, with possible contribution by coastal and/or deep waters, as suggested by previous studies (Desiderio et al. 2007). In contrast, nitrate concentrations showed a very poor correlation with Cl^- and SO_4^{2-} values, suggesting a different origin, which cannot reconstitute a simple leaching process of the aquifer sediments. The alluvial aquifer of the River Vibrata is undoubtedly highly polluted by nitrates, as NO_3^- concentrations exceeded 50 mg/L in 15 out of 20 wells sampled in July 2007 and in 9 out of 16 wells sampled in November 2007.

Taking into account the above-mentioned chemical data, the River Vibrata discharge, the nitrate content, and the different behaviour of the hydrographic and the hydrogeological basins, a preliminary conceptual model of the nitrogen cycle can be inferred.

The River Vibrata discharge (Fig. 3) at SW1 shows a steady-regime mainly supported by a mean groundwater contribution of about 100 L/s. The river discharge increases downstream (SW2) as reflection of the intense runoff in this stream sector, with sharp seasonal differences. This is due to the large outcrop of low-permeability sediments in this part of the basin. The groundwater contribution to the base flow from this sector is negligible, because summer discharge shows only minimal increase in comparison to the upstream discharge, which allows water persistence along the river.

At the same time, nitrate content in the stream is clearly lower at SW1 (4 mg/L in average), while at SW2 it is about 13 mg/L, decreasing to 8 mg/L at SW3, where the discharge was not measured. In addition, an inverse correlation between nitrate content and discharge is shown at SW1 (Fig. 3) while nitrates related to SW2 do not show clear correlation with discharge.

The basin shows a different behaviour along the Valley (Fig. 2): in the Upper Valley the river is mainly fed by groundwater coming from the alluvial aquifer; the catchment of the Upper Valley is not significantly larger than the hydrogeological one (Fig. 1) and runoff fairly contributes to the river discharge only during rainy season; conversely, in the Lower Valley, runoff becomes prevalent, due to the large extension of the hydrographic basin having low permeability (Fig. 2); contribution from the aquifer to the river discharge is limited because of limited outcrop extent

Fig. 7 Scatterplot of the $\delta^{15}\text{N}$ (AIR) versus the $\delta^{18}\text{O}$ (SMOW) of the dissolved nitrate in the water samples collected in the two sampling campaigns in the Vibrata alluvial aquifer. The fields of the different nitrate sources are drawn as reported by Silva et al. (2000)

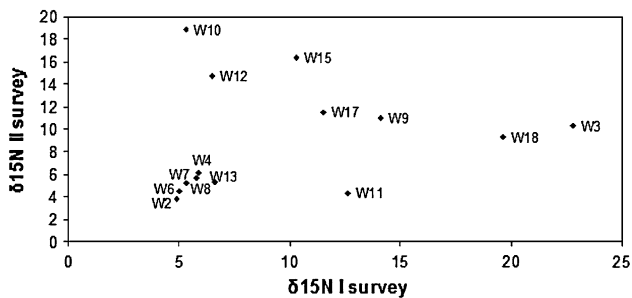
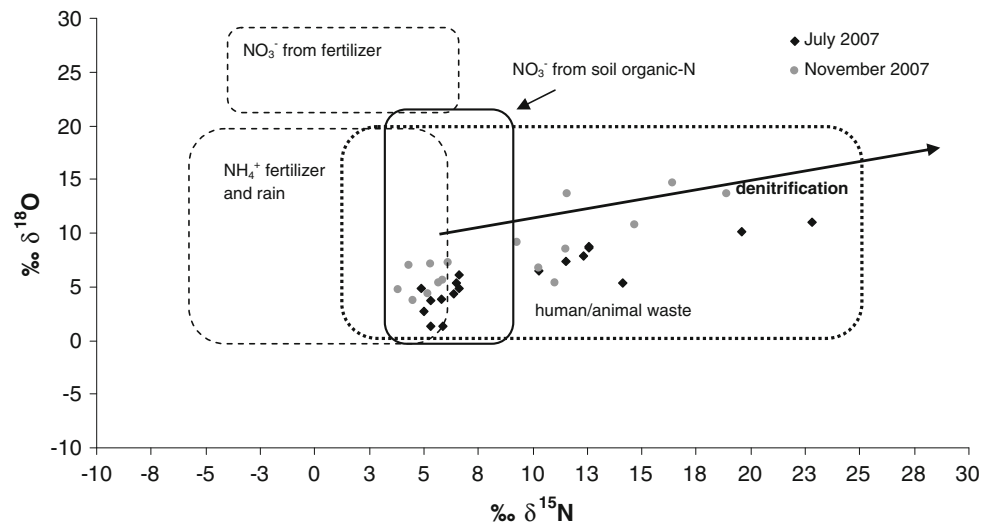


Fig. 8 Scatterplot of the $\delta^{15}\text{N}$ (AIR) of the dissolved nitrate in the water samples of the first survey versus the $\delta^{15}\text{N}$ of the second sampling survey in the Vibrata alluvial aquifer

and the position of water table. It can be assumed that the terminal part of the basin may have the same behaviour, being unavailable discharge data for SW3.

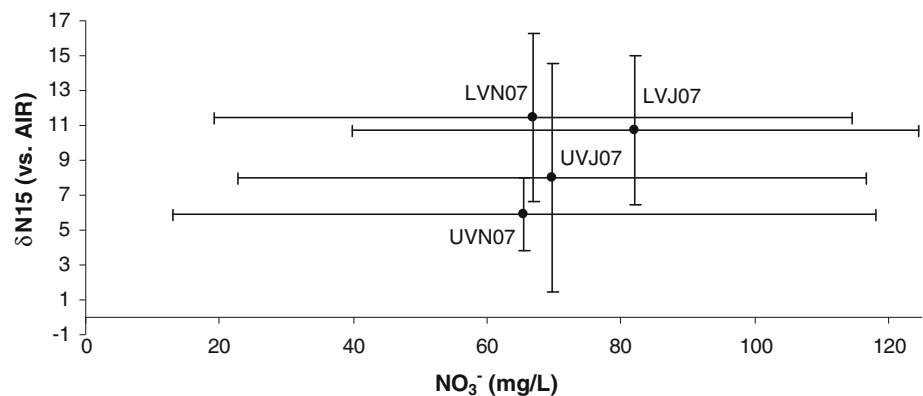
The limits between the Upper and Lower Valley can be located between wells W8 and W9 (Fig. 1), because samples from W1 to W8 showed EC lower than $1100 \mu\text{S}/\text{cm}$, while from W9 to W20 the EC was higher, except for W10 and W11 (Table 1). Taking into account the river/aquifer

interaction, the higher elevation of W1–W8 group, if compared to stream elevation in the same sector, may support the presence of seepage from the aquifer to the river; in the Lower Valley the relationships between groundwater and stream were observed varying with time, and water table and river have a comparable elevation (Table 1).

The nitrate isotope data validated this hydrological model: group W1–W8 corresponded to the isotope values related to the fertilizers field (Fig. 7; Table 6), except for W3, which is a very shallow well (5 m) located very close to the River Vibrata (10 m far from the river banks); this means that W3 chemistry can be influenced by both stream surface and hyporheic waters, being the riparian zone almost absent. Otherwise, samples W9–W20 located in the Lower Valley showed higher isotope values of both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, except for W13, with the highest mineralisation observed among all samples.

Changes in $\delta^{15}\text{N}$ between the two surveys (Fig. 8) evidenced that stable values correspond to the Upper Valley samples, except for W3, which, as mentioned before, is influenced by surface waters. Both nitrate content and nitrogen isotopes of this group only slightly changed during

Fig. 9 Box plots of the mean values of $\delta^{15}\text{N}$ (AIR) versus the nitrate concentration in mg/L of the dissolved nitrate in the water samples collected in the two sampling campaigns in the Vibrata alluvial aquifer. Bars indicate standard deviations. UVJ07 Upper Valley in July 2007, LVJ07 Lower Valley in July 07, UVN07 Upper Valley in November 2007, LVN07 Lower Valley in November 2007



the year, confirming a direct contribution from the aquifer (Figs. 8, 9). The remaining samples (located in the Lower Valley) showed higher variability in isotope compositions for both nitrogen and oxygen (Fig. 8; Table 6), accompanied by enrichment of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, along with a decrease in nitrate content, moving in average from 82 to 64 mg/L (Fig. 9).

Observed enrichment of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in samples coming from the lower part of the basin can be attributed to denitrification processes (Fig. 7), especially in wells where a lowering in nitrate content has been observed (e.g. W10, W12 and W15 in Fig. 8).

In this conceptual model, the Upper Valley is affected by minimal runoff contribution, due to the reduced extension of the catchment area, characterised by low permeability and the prevalence of permeable sediments of the aquifer (Fig. 4). The groundwater significantly contributes to river discharge and the lower EC indicates a shallow groundwater flow.

Nitrogen source is mainly represented by synthetic fertilizers based on NH_4^+ , which directly affected groundwater, due to the high permeability of the hydrogeological basin largely outcropping in the Upper Valley. High nitrate content is widespread observed in groundwater of the alluvial aquifer, except for local situation where interaction with river waters can lowering nitrate concentration by denitrification processes. In fact, the shallow W3, located close to the River Vibrata, shows relatively low nitrate content and isotope values plausibly altered by denitrification processes, testifying the contribution of the hyporheic and riparian zones in lowering the nitrate content in the Upper Valley. This role is limited to the areas located nearby the River Vibrata.

In the Upper Valley, nitrate contribution to the river surface water predominantly comes from groundwater by baseflow; the dilution of nitrate concentration recorded during high-discharge periods (Fig. 3) confirms that runoff does not contribute to the nitrogen amount in river waters. The main contribution of nitrogen loads to the river is given by the polluted aquifer, while runoff does not significantly produce nitrogen increase.

As a result, in the Upper Valley, nitrate content in groundwater is high and stable, while in discharge waters its amount is changing with time: during the dry season only groundwater contributes to the streamflow and nitrate content becomes higher than in rainy season, when a limited runoff contribution to the river discharge fairly dilutes its nitrate content.

According to the *Components Approach*, the Upper Valley is affected by a nitrogen load from synthetic fertilizers with about 295 t/year at the catchment scale and about 108 t/year at the hydrogeological basin scale. Infiltration is dominant and determines the transport of nitrogen

into the aquifer, as well as the high and steady nitrate content observed in wells W1–W8. Only close to the River Vibrata, buffering zones (e.g. the hyporheic zone) are likely able to locally reduce the nitrate content in groundwater, as demonstrated by nitrate isotope content in W3. Considering a base flow discharge of about 100 L/s due to groundwater and a mean nitrate content of 4 mg/L of the streamwater in the gauging station SW1, the total amount of nitrogen flowing into the River Vibrata at SW1 amounts to about 2.8 t/year, roughly corresponding to 1 % of the total nitrogen load of this area. By considering the high nitrate content in groundwater, it can be assumed that the bulk of nitrogen load is predominantly located in the alluvial aquifer, and the hyporheic zone likely might act as powerful buffer area preventing the severe contamination of the river flowing water.

In the Lower Valley, river/groundwater interaction is more difficult to be assessed. The nitrogen source due to synthetic fertilizers is directly connected with surface waters by runoff, which increases nitrate content of the River Vibrata at SW2. Nitrate content in stream water lowers at SW3, suggesting a possible dilution effect by runoff coming from non-agricultural slopes in the terminal part of the catchment. In groundwater, nitrate content shows high variability with time and space, due to infiltration of nitrogen in the hydrogeological basin and to the interactions with river waters. Nitrate isotope values are locally consistent with the existence of denitrification processes, with influence of seasonal changes and local situations diverging from this general trend.

Even if denitrification could be reasonably hypothesised for several samples in the Lower Valley, on the basis of both isotopic and geochemical data, this statement cannot be extended at the regional scale, but is limited to some location of the Lower Valley only. Sites for which denitrification was hypothesised are the ones with higher isotope composition, coupled to lower nitrate concentrations, located on the upper left side of the graph in Fig. 8 (W10, W12, W15). In more detail, denitrification can be inferred for W3 in the Upper Valley and for several wells in the Lower Valley. For these wells, it is worth mentioning that higher $\delta^{15}\text{N}$ values in the second survey are accompanied by a decrease in nitrate content (Fig. 9), while in wells for which a $\delta^{15}\text{N}$ lowering has been recorded in the second survey, an increase in nitrate concentration has also been observed. This observation quite fits with the proposed conceptual model, where denitrification in the lower basin does not show a general seasonal trend related to nitrogen inputs, depending on local situation, possibly related to river/groundwater interactions (e.g. W12), driven by aquifer/surface waters flow exchanges and by local chemical-physical conditions in the aquifer.

The results of the Components Approach for the Lower Valley shows a main input of nitrogen from synthetic fertilizers, with reference to ammonium salts. The nitrogen load is about 517 t/year of which 216 t/year is measured in the hydrogeological basin and 301 t/year in the low-permeability area. The nitrogen load in surface waters at SW2 is about 27.5 t/year, a contribution of more than 24 t/year higher if compared to the upper part of the river. This value represents 9.1 % of the total nitrogen load in the low permeability area of the Lower Valley.

Conclusions and management strategy

Monitoring results evidenced that synthetic fertilizers, mainly ammonium salts, are the major sources of nitrate in the Vibrata alluvial aquifer. By using an integrated approach, including surface water data, groundwater chemical data, components approach and nitrate isotopes, a conceptual model of the nitrate cycle at the catchment scale has been inferred. In the catchment, two different zones have been identified: the Upper Valley, where infiltration toward groundwater is dominant and nitrogen easily migrates into the aquifer; the contribution from the aquifer to the river discharge was dominant and constant values of nitrates affect both surface (4 mg/L) and groundwater, where concentrations frequently higher than EU requirements are recorded. Stable values of nitrogen isotopes confirm that pollution in the Upper Valley is widespread, requiring immediate and not easy countermeasures. Only close to the River Vibrata, denitrification processes, probably driven by the hyporheic zone, may help in lowering nitrate concentration in groundwater (e.g. W3) and, mainly, in surface waters (1 % of the total nitrogen load in the area).

In the Lower Valley, the nitrate content in surface waters is higher and runoff is significant, directly moving nitrogen loads to the river. In fact, about 9.1 % of nitrogen load can be found in surface waters. Interventions aimed at lowering nitrogen loads can probably have direct impact on nitrate content in this area. In addition, groundwater is found interested by denitrification processes, without clear seasonal trends. This condition may allow a natural decrease of nitrate content, often reaching acceptable values with respect to the law limits.

The European policy dealing with groundwater nitrate contamination (91/676/EC Directive) requires a decreasing in nitrate concentrations in *Nitrate Vulnerable Zones* (EC 1991, 2000) and recommends a maximum dosage of fertilizers (natural and synthetic) per hectare lower than 170 kg/ha/year (EEA 2009). According to the components approach herein applied, in the Vibrata Plain the estimated mean dosage of fertilizers per hectare is quite under the

European limits, both at catchment (75 kg/ha/year) and hydrogeological basin scales (78 kg/ha/year). By considering that the actual dosage of fertilizers is peer to that estimated, in order to minimize the runoff, local authorities should impose technical requirements as: (1) timing of fertilization, which is to be strictly limited to crop permanence period; (2) application of the most appropriate irrigation techniques according to soil typology (e.g. drip-irrigation or other appropriate techniques); (3) creation of a continuous buffer strip of spontaneous vegetation at field boundaries, which should be at least larger than 3 m (Paegelow and Hubschman 1991); (4) prohibition of the use of synthetic fertilizers inside the river banks. Moreover, different management strategies should be applied in the Upper and Lower Valley, respectively; in the Upper Valley, it is necessary to promote denitrification processes into the aquifer, possibly by introduction of buffering riparian zones along the agricultural fields (Cey et al. 1999). In the Lower Valley, the diminution of nitrogen loads can have direct and fast response on the aquifer, lowering nitrate content; in addition, the buffer strips along the River Vibrata can reduce the contribution of nitrate to streamwaters by runoff.

In the Vibrata Plain, users' consensus has not yet been fully reached; however, concentration tables and dissemination of information take place regularly. A programme for monitoring the effectiveness of the technical requirements should be implemented, aimed at defining the starting point for trend reversal, i.e. any statistically and environmentally significant decrease of nitrate concentration in groundwater and in streamwaters.

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