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Effect of the dilution process on the attenuation of contaminants in aquifers

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ABSTRACT

This paper discusses the effects of the dilution process on levels of aquifer contamination attenuation, developing analytical equations for application in theoretical and practical cases. The key finding is that, in aquifers, the dilution process causes a reduction of the contaminant concentration. Analytical equations for the assessment of the contaminant attenuation capacity, by means of the dilution process in an aquifer, are put forward. In particular, the attenuation of the contaminant concentration in an aquifer, and thus the dilution, are described by the volumetric flow rate per unit width perpendicular to the flow direction (q_u). Moreover, a classification of q_u was developed, considering six classes of attenuation capacity due to dilution.

For the equations validation, nitrate contamination attenuation due to dilution was analysed in two sample areas in Piedmont (North-West Italy). The results confirmed the hypothesis, evidencing high nitrate concentrations in areas with low q_u values, connected to low dilution rate of the contaminant in the groundwater; *vice versa*, low nitrate concentrations were evidenced in areas with high q_u values, due to a high nitrate dilution rate.

Key words: contaminant attenuation, dilution, groundwater resources, nitrate, Italy

List of abbreviations

b = aquifer thickness (m)

C_{ae} = contaminant concentration in the cell input (mg/l)

C_i = contaminant concentration in the infiltration water (mg/l)

C_u = expected contaminant concentration in the cell output (mg/l)

C_w = actual nitrate concentration in the groundwater (mg/l)

i = hydraulic gradient (dimensionless)

I_e = infiltration rate (m/year)

k = hydraulic conductivity (m/year)

L = cell length (m)

P = cell width (m)

Q = volumetric flow rate (m^3/s)

Q_{ae} = groundwater flow rate used for cell input (m^3/year)

Q_i = infiltration flow rate (m^3/year)

Q_u = groundwater flow rate in cell output (m^3/year)

q_u = volumetric flow rate per unit width, perpendicular to the flow direction (m^2/s)

S = area of the cell (m^2)

T = transmissivity (m^2/s)

1 INTRODUCTION

In soil and unsaturated zones, contaminants are subjected to a series of transformations and chemical, physical and biological processes that, under favourable conditions, act to reduce the mass, toxicity, mobility, volume and concentration of contaminants. These processes include biodegradation, sorption, volatilisation and the chemical or biological stabilisation, transformation or abatement of contaminants.

If the contaminant reaches an aquifer, further attenuation phenomena can occur, and the quality of groundwater resources depends on the efficiency with which these processes manage to abate the contaminant concentration.

Dilution in particular has been found to play an important role in determining the degree of contamination in the case of conservative nonreactive and nonsorbing solutes (Bekesi and McConchie 2002; De Luca and Lasagna 2005; Lasagna 2006; Stigter et al. 2006; Debernardi et al. 2008; Farooq et al. 2011; Nishikiori et al. 2012).

2 THE DILUTION PROCESS

From a physical point of view, dilution is the reduction of the concentration of a chemical substance as it is dissolved into a larger volume of solvent (Kitanidis 1994). In aquifers, the dilution process causes a reduction of the contaminant concentration and takes place through diffusion and, above all, dispersion mechanisms. Molecular diffusion is the spontaneous migration of substances from regions characterised by a higher concentration to areas where concentration is lower, up to reach the equilibrium. The dispersion process involves the mixing of contaminated fluids, as they flow through a porous media, with uncontaminated water. The result is the dilution of the contaminant.

The dilution process causes a reduction of the contaminant concentration, but it does not remove the contaminants from the system. However, in contrast to other processes, this phenomenon is omnipresent and is not affected by the biological and chemical conditions in groundwater. For these reasons, dilution can be considered a key factor in determining groundwater contamination, and it has been found to play an important role in lowering contamination levels in different parts of the world (Bekesi and McConchie 2002; De Luca and Lasagna 2004; Stigter et al. 2006; Lasagna 2006; Debernardi et al. 2008; Lasagna et al. 2009; Farooq et al. 2011; Nishikiori et al. 2012). According to Todd (1980), dilution may be the most important mechanism for attenuation after the pollutant enters the groundwater system. Consequently, a higher degree of dilution results in a lower vulnerability of the groundwater to contamination. However, the traditional methods for vulnerability analysis generally do not involve an analysis of physical processes in aquifers, such as dilution. The result is a lack of correlation between vulnerability indexes and contaminant concentrations in groundwater. For example, several studies on nitrate, which is a conservative pollutant, have provided evidence of high groundwater vulnerability in areas with medium-low nitrate concentrations and low vulnerability in areas with high nitrate levels (GAO 1992; Evans and Maidment 1995; Debernardi et al. 2008). Stigter et al. (2006) performed groundwater vulnerability mapping of two areas in the south of Portugal with the DRASTIC (Aller et al. 1987) and SI (Ribeiro 2005) methods. Using the DRASTIC method, essentially no correlation has been found between the groundwater vulnerability and the nitrate concentrations in the most vulnerable and contaminated areas. According to the authors, this lack of correlation is mainly the result of underestimating the dilution capacity and overestimating the attenuation potential of the unsaturated zone and aquifers. The SI method, which derives from the DRASTIC method, provides much better results, although in many areas the vulnerability is overestimated.

Aller et al. (1987) recognised that when dilution plays an important role in contamination levels, it can lead to erroneous results in the DRASTIC method, as dilution is not accounted for.

Mishima et al. (2011) modified the DRASTIC method, selecting six of the seven original DRASTIC factors (the depth to water D, net recharge R, soil media S, topography T and impact of vadose zone media I) and using them to explain the vertical movement of contaminants to the aquifer. Moreover the rating for the net recharge factor was modified to a dilution factor for contaminants, rather than as a transporter. They suggest that the modified DRASTIC method, considering the dilution process, is applicable for fertilizer application management in upland fields.

Therefore, if vulnerability assessment is used in groundwater resource management and protection, the negative consequences of dilution underestimation could be avoided by considering the dilution process.

3 THE CONCEPT OF VOLUMETRIC FLOW RATE PER UNIT WIDTH

The contaminant concentration in an aquifer is strictly connected to dilution; in particular, the attenuation of a contaminant concentration in an aquifer, and thus the dilution, can be described by the volumetric flow rate per unit width perpendicular to the flow direction (q_u) (Lasagna 2006; Debernardi et al. 2008). This parameter depends on specific aquifer factors, particularly hydraulic conductivity, hydraulic gradient and aquifer thickness. Considering an equal contaminant input in groundwater, the q_u is directly proportional to the aquifer’s ability to reduce the contaminant concentration:

$$q_u = \frac{Q}{P} = k \cdot b \cdot i = T \cdot i \qquad (1)$$

where

q_u = volumetric flow rate per unit width perpendicular to the flow direction (m^2/s)

Q = volumetric flow rate (m^3/s)

P = width of the aquifer (m)

k = hydraulic conductivity (m/s)

b = aquifer thickness (m)

i = hydraulic gradient (dimensionless)

T = transmissivity (m^2/s)

The higher the q_u, the greater the aquifer's ability to reduce the contaminant concentration through the dilution process (Debernardi et al. 2008). In contrast, low q_u values correspond to areas with a low ability to reduce the contaminant concentration by means of the dilution process and, therefore, with a high hydrogeological potential for contamination.

The q_u value has great importance for studies on a regional scale designed to identify areas which are more prone to groundwater contamination. A comparison between areas with different q_u values can show which zones have a low dilution potential due to a low hydraulic conductivity, a low hydraulic gradient and a low aquifer thickness (sometimes these features are concomitant). In these areas, particular safety measures must be taken to prevent possible groundwater contamination.

Thus, the use of the parameter q_u as a planning tool can guarantee advantages for groundwater management and preservation.

3.1 VARIATION OF q_u BASED ON AQUIFER-SPECIFIC PARAMETERS

The volumetric flow rate per unit width perpendicular to the flow direction (q_u) varies distinctly as a consequence of the aquifer's specific parameters, such as hydraulic conductivity, hydraulic gradient and aquifer thickness.

Considering the ranges of hydrogeological parameters most frequently found in alluvial plains ($k = 10^{-2}$-10^{-5} m/s, i = 0.1-0.001, b = 10-100 m), q_u varies from a minimum value of 10^{-7} m^2/s to a maximum value of 10^{-1} m^2/s.

The minimum q_u value (i.e., 10^{-7} m^2/s) can be obtained by assuming the occurrence of a series of conditions unfavourable for contaminant dilution. These conditions might be low hydraulic conductivity, a low hydraulic gradient or a thin, shallow aquifer.

In the same way, a high q_u value (i.e., 10^{-1} m^2/s) can be obtained by assuming the occurrence of a series of conditions favourable to dilution, such as high hydraulic conductivity, a high hydraulic gradient or a thick, shallow aquifer. However, the q_u values that are most frequently found in alluvial planes range between 10^{-4} and 10^{-5} m^2/s due to intermediate hydrogeological conditions.

3.2 THE INFLUENCE OF HYDRAULIC CONDUCTIVITY ON q_u

The hydraulic conductivity (k) in saturated media is an important parameter for predicting the movement of water and contaminants dissolved in the water. The hydraulic conductivity of sedimentary aquifers is a function of rock porosity. In contrast to porosity, the hydraulic conductivity in an aquifer varies within a wide range of several orders of magnitude. Consequently, it is crucial to estimate the value of this parameter. Hydraulic conductivity has both negative and positive effects on groundwater quality. It has negative effects because an increase of the hydraulic conductivity rises the groundwater velocity, thereby causing the contaminant to be carried away at a faster rate; hence, the groundwater-contaminated area can become larger. In contrast, the hydraulic conductivity has positive effects because increasing the hydraulic conductivity raises the q_u and, therefore, contaminant dilution. Consequently, the contaminant concentration is reduced in the groundwater. Moreover, high hydraulic conductivity can be associated with a shorter average time for the renewal of groundwater, so it determines the contaminant persistence in the flow system. Thus, high hydraulic conductivity results in a lower vulnerability to contamination. However, the most widely used methods for vulnerability assessment either ignore this parameter (e.g. the GOD method (Foster and Hirata 1988; Foster et al. 2002) or they consider and emphasise only negative effects (e.g. the DRASTIC method (Aller et al. 1987).

Therefore, these approaches for groundwater vulnerability evaluation are incomplete, and new methods that also take into account the positive effects of hydraulic conductivity should be studied.

4. SIMPLIFIED APPROACH TO EVALUATING DILUTION IN A SUPERFICIAL AQUIFER

The dilution potential in groundwater varies according to several hydrogeological factors, and it is strongly dependent on q_u. To verify the relationship between dilution and q_u with an analytical approach, a simplified model was used (Fig. 1). This model analyses a flow net with quadrangular cells in which groundwater contamination already exists in the input to the cell (C_{ae}) and a contaminant concentration is associated with the infiltration water (C_i); thus, it is possible to evaluate which parameters influence the contaminant concentration in the cell output (C_u).

For the mass balance:

$$Q_{ae} \cdot C_{ae} + Q_i \cdot C_i = C_u \cdot Q_u \tag{2}$$

with $Q_u = Q_i + Q_{ae}$ (3)

Q_{ae} = groundwater flow rate in the cell input (m^3/year)

C_{ae} = contaminant concentration in the cell input (mg/l)

Q_i = infiltration flow rate (m^3/year)

C_i = contaminant concentration in the infiltration water (mg/l)

Q_u = groundwater flow rate in the cell output (m^3/year)

C_u = expected contaminant concentration in the cell output (mg/l)

Consequently:

$$C_u = \frac{(Q_{ae} \cdot C_{ae} + Q_i \cdot C_i)}{(Q_i + Q_{ae})} \tag{4}$$

Using Darcy’s law,

$$Q = k \cdot i \cdot b \cdot P \tag{5}$$

with

P = width of the cell (m)

and, finally,

$$Q_{ae} = k_{ae} \cdot i_{ae} \cdot b_{ae} \cdot P \tag{6}$$

and $Q_i = I_e \cdot S$ (7)

with

I_e = infiltration rate (m/year)

S = L * P = cell area (m^2)

L = cell length (m)

Then,

$$C_u = \frac{\left(k_{ae} \cdot i_{ae} \cdot b_{ae} \cdot P \cdot C_{ae}\right) + \left(I_e \cdot S \cdot C_i\right)}{\left(I_e \cdot S + k_{ae} \cdot i_{ae} \cdot b_{ae} \cdot P\right)} \tag{8}$$

Dividing numerator and denominator by Ie·S and simplifying the equation:

$$C_u = \frac{\left(k_{ae} \cdot i_{ae} \cdot b_{ae} \cdot C_{ae}\right) + \left(I_e \cdot L \cdot C_i\right)}{\left(k_{ae} \cdot i_{ae} \cdot b_{ae} + I_e \cdot L\right)} \tag{9}$$

and supposing that

$$q_u = k_{ae} \cdot i_{ae} \cdot b_{ae} \tag{10}$$

q_u = volumetric flow rate per unit perpendicular to the flow direction (m^2/year)

then

$$C_u = \frac{\left(q_u \cdot C_{ae}\right) + \left(I_e \cdot L \cdot C_i\right)}{\left(q_u + I_e \cdot L\right)} \tag{11}$$

Equation 11 takes into account the following assumptions:

a) the contaminant is a nonreactive and nonsorbing solute;

b) the contaminant input from the topsoil is continuous and has a constant concentration over a long period of time (equal to at least 10 years) so that a permanent flow can be considered;

c) the contaminant’s transverse dispersion is negligible;

d) a superficial aquifer is not connected with deep aquifers;

e) no degradation processes, which can produce a further reduction in contamination, occur in the groundwater.

These assumptions are conservative for evaluating the contaminant concentration in the cell output (C_u).
Equation 10 demonstrates that C_u, with all other factors being equal, is highly related to dilution and depends on specific aquifer parameters. In particular, the aquifer’s ability to reduce the contaminant concentration is strongly conditioned by the volumetric flow rate per unit width (q_u).

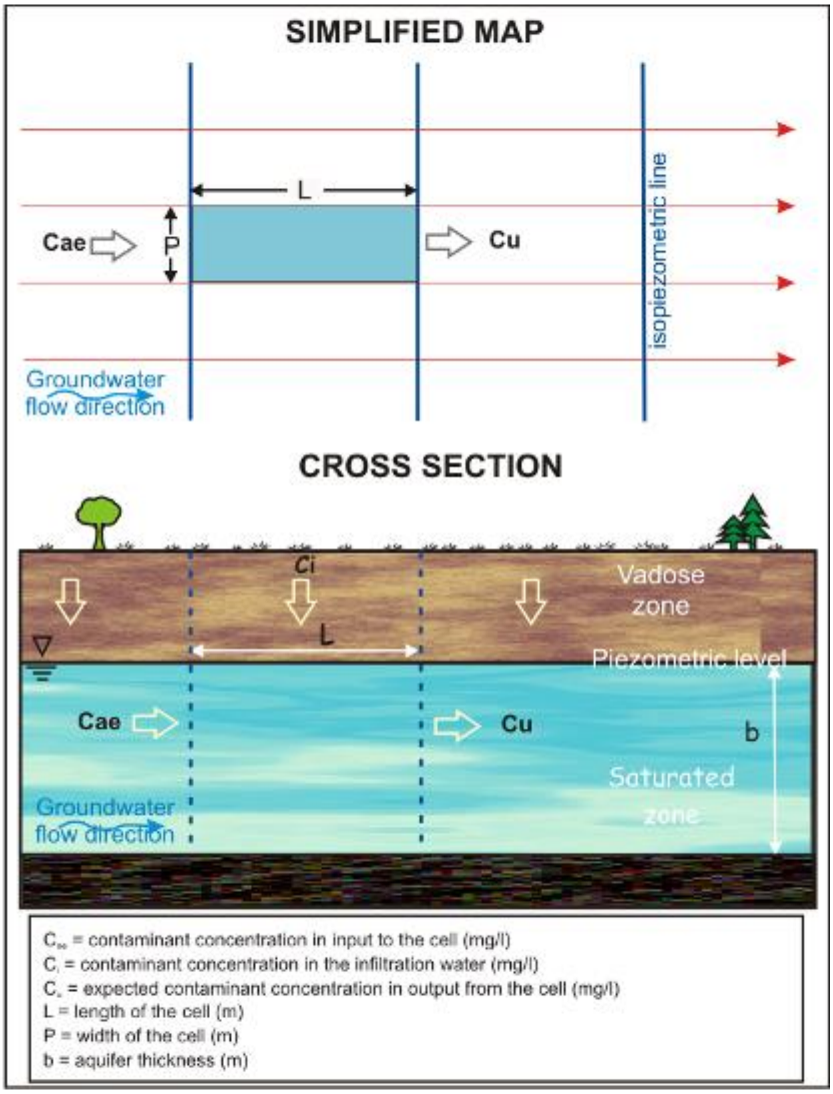

Fig. 1. Reference model schematisation for the assessment of C_u considering a single cell of the related flow system (modified from De Bernardi et al., 2008).

4.1 BORDERLINE CASES

In this section three borderline cases, which can be used in different environmental situations, are presented to simplify equation 11.

Equation 11 can be written as:

$$C_u = \left(\frac{q_u \cdot C_{ae}}{q_u + I_e \cdot L} \right) + \left(\frac{I_e \cdot L \cdot C_i}{q_u + I_e \cdot L} \right) \tag{12}$$

Supposing that L = 1 m, then

$$C_u = \left(\frac{q_u \cdot C_{ae}}{q_u + I_e} \right) + \left(\frac{I_e \cdot C_i}{q_u + I_e} \right) \tag{13}$$

The first term in equation 13 describes the effects of the contaminant concentration in the input to the cell used for the cell input (C_{ae}) on C_u; the second term clarifies the effects of the contaminant concentration in the infiltration water (C_i) on C_u.

Hereinafter some examples of implementation of the equation will be described.

4.1 CASE 1: INFILTRATION RATE (Ie) EQUAL TO ZERO

If the infiltration rate (Ie) is equal to zero, equation 10 can be simplified to:

$$C_u = C_{ae} \tag{14}$$

Equation 14 demonstrates that if any contaminant comes from the soil because of a lack of infiltration, the contaminant concentration in the cell output (C_u) is equal to the concentration in the cell input; in this context, no dilution takes place.

4.2 CASE 2: CONTAMINANT CONCENTRATION IN THE INFILTRATION WATER (Ci) EQUAL TO ZERO

If the contaminant concentration in the infiltration water (C_i) is equal to zero, so that no contamination derives from the soil, equation 11 can be simplified to:

$$C_u = \left(\frac{q_u \cdot C_{ae}}{q_u + I_e} \right) \tag{15}$$

This equation describes the effects of the contaminant concentration in the cell input (C_{ae}) on C_u. The dilution process takes place and reduces C_{ae}. Thus, the contaminant in the input to the cell is diluted with the available water of the system (i.e., volumetric flow rate per unit width plus infiltration rate).

In this situation, infiltration has only positive effects on the groundwater quality; in fact, the non-polluted infiltration water increases the discharge and, as a result, C_u is reduced in the groundwater because of dilution.

4.3 CASE 3: CONTAMINANT CONCENTRATION IN THE CELL INPUT (C_{ae}) EQUAL TO ZERO

In the case of point-source contamination, the contaminant concentration in the input to the cell (C_{ae}) can be equal to zero and the groundwater contamination is due to the polluted infiltration water. If the contaminant concentration in the input to the cell (C_{ae}) is equal to zero, equation 11 can be simplified to:

$$C_u = \left(\frac{I_e \cdot C_i}{q_u + I_e} \right) \tag{16}$$

This equation describes the effects of the contaminant concentration in the input to the cell coming from the soil (C_i) on C_u, where C_u depends on the infiltration rate, the concentration in the input from the soil and q_u.

Equation 16 demonstrates that infiltration has both a positive and negative effect on groundwater quality. In fact, infiltration increases the discharge and, as a result, C_u in the groundwater is reduced because of dilution. At the same time, the infiltration water can leach into the groundwater, thereby negatively affecting groundwater quality.

4.4 RELATIONSHIP BETWEEN C_u AND q_u

To evaluate the influence of q_u (volumetric flow rate per unit perpendicular to the flow direction) on C_u (contaminant concentration in the output from the cell), a study of the relationship between C_u and q_u was conducted with a sensitivity analysis. In particular, the C_u values were calculated with equation 11 by varying the q_u values.

The hydrogeological conditions analysed range between a dilution-positive condition (q_u = 10^{-1} m^2/s) and a dilution-negative condition (q_u = 10^{-7} m^2/s). Moreover, two situations were analysed: a situation with $C_i>C_{ae}$ (contaminant concentration in the infiltration water is greater than the one in the input to the cell) and a situation with $C_{ae}>C_i$. Different alluvial plain values of C_i and C_{ae} were chosen. I_e was assumed equal to 0.3 m/year.

Evaluating the C_u values based on q_u, the results showed the following:

- In the scenario with $C_i>C_{ae}$ (Fig. 2), the q_u-C_u values are represented by a curve with a hyperbolic trend. When q_u was increased, q_u-C_u values corresponded to a hyperbola asymptote, and the c_u concentrations decreased to C_{ae}. The hyperbola asymptote equation was $y = C_{ae}$. In contrast, with low q_u values, C_u assumed high values approaching C_i.
- In the scenario with $C_{ae}>C_i$ (Fig. 3), the q_u-C_u values formed a curve similar to the previous one. Increasing q_u, the C_u concentrations approached the C_{ae} concentrations; with low q_u values, C_u presented low values approaching C_i.

The area between the two curves comprises all possible situations resulting from different C_i and C_{ae} values.

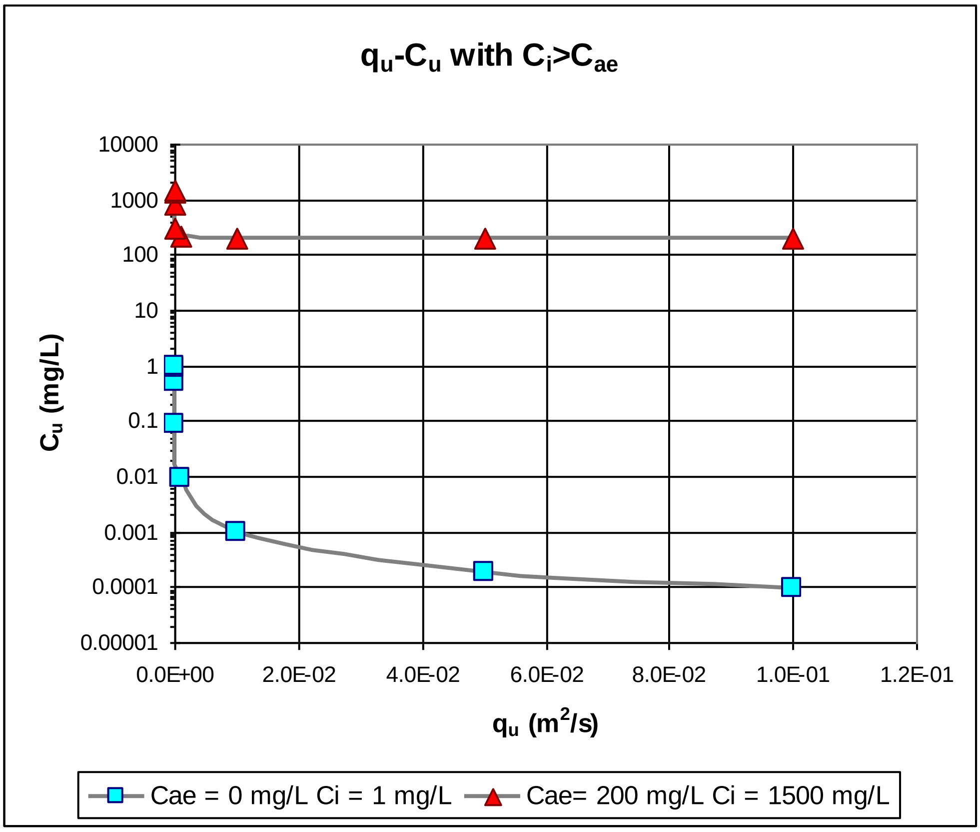

Fig. 2 - Variation of C_u depending on q_u: situation with C_i>C_{ae}.

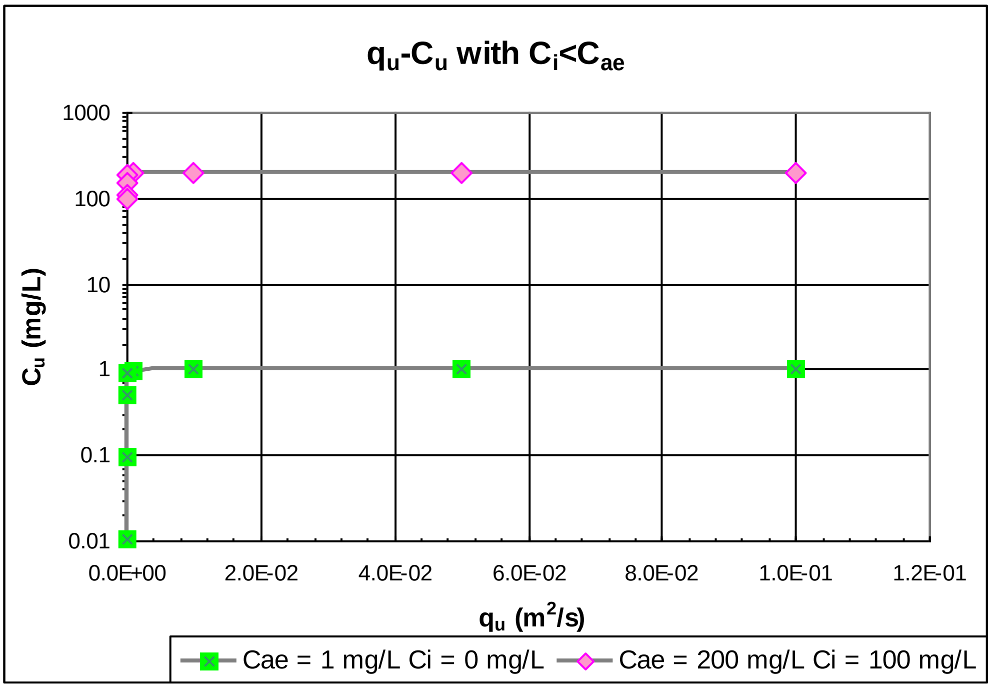

Fig. 3 - Variation of C_u depending on q_u: situation with C_i < C_{ae}.

5. AN APPLICATION OF THE VOLUMETRIC FLOW RATE PER UNIT PERPENDICULAR TO THE FLOW DIRECTION (q_u) IN A NITRATE-CONTAMINATED AREA

5.1 NITRATE ATTENUATION PROCESSES

There are various parameters that modulate the presence of nitrogen in the soil, including N-fertilisers and zootechnical effluent concentrations, the spreading procedure of fertilisers and the type of crop and cropping system. Once in the soil, nitrogen can be subject to numerous processes that reduce its concentrations: in fact the soil zone is the most active area of nitrogen cycling, both by microbial denitrification and plant uptake (Atxotegi et al. 2003; Buss et al. 2005). Most denitrification within the soil zone probably occurs in the uppermost 10-15 cm, where organic carbon concentrations are greatest from plant degradation and root exudates, and becomes less significant with depth (Burt et al., 1999). Also ammonia volatilisation (the loss of ammonia gas from the soil to the atmosphere) results in a net loss of nitrogen from the soil system; this process commonly takes place when nitrogen is in an organic form known as urea, and, indirectly it will result in less soil nitrogen being converted into the nitrate form (Killpack & Buchholz, 1993).

In the soil zone, moreover, the presence of allophone, imogolite and other poorly-crystallised oxide or hydroxide materials can induce nitrate sorption (Katou et al., 1996). Clay et al. (2004), for example, showed that nitrate was retarded relative to bromide in a smectitic clay-loam soil (the retardation factor for nitrate was approximately 1.37). In most cases, because of the absence of these minerals, nitrate behaves as a non-sorbing solute and move at the same velocity as the water in which it is dissolved (Buss et al. 2005). So, the nitrate concentration, still present in the system after being subjected to attenuation soil processes leaches vertically into the vadose zone toward the superficial aquifer with the infiltration water. The vadose zone generally does not eliminate nitrates but rather delays the introduction into the groundwater; this period can last decades or years. The transport period depends on the groundwater table depth, the vadose zone permeability or fessuration and the infiltration rate. In an alluvial plain, the nitrate velocity through the vadose zone ranges from 0.5 to 3 m/year (Pratt et al. 1978).

In the aquifer, nitrates can essentially be subject to three phenomena: denitrification, dissimilatory nitrate reduction in ammonium (DNRA) and dilution. In contrast to soil zone, in which nitrate sorption is active if specific minerals are present, examples of natural nitrate sorption in groundwater are not reported in literature.

Denitrification is a multi-step process that involves various nitrogen oxides (e.g., N_2O, NO) as intermediate compounds resulting from the chemically or biologically mediated reduction of nitrate to N_2 (Korom 1992).

Depending on the redox conditions, organisms will utilise different oxidised materials as electron acceptors in the general order of O_2, NO_3^-, and SO_4^{2-}. Microbial denitrification requires reducing conditions, and it does not occur in the presence of significant amounts of oxygen (Firestone 1982; Korom 1992; Thomasson et al. 1991; Enwright and Hudak 2009; Nishikiori et al. 2012).

The DNRA is another important process that results in nitrate concentration attenuation in groundwater systems, that is, the reduction of NO_3^- to NH_4^+. Tiedje (1982) hypothesised that DNRA is favoured when NO_3^- (electron acceptor) supplies are limited, while denitrification is favoured when carbon (electron donor) supplies are limited. This process also requires anoxic conditions. These processes, nevertheless, play a significant role generally within deep aquifers with nitrate contamination; in fact, anoxic conditions are common in deep aquifers (Debernardi et al. 2005; Debernardi et al. 2008).

The dilution process, in contrast, is not affected by the chemical conditions in groundwater. In agricultural and farming areas, characterised by diffuse nitrate contamination in groundwater due to ubiquitous use of synthetic N-fertilizers and zootechnical effluents, dilution phenomena can mask the net increase of nitrate in water (Stigter et al. 2011).

Compared with the denitrification process, it appears that the dilution process might play a more important role in nitrate concentration attenuation in shallow aquifers, given the same amount of N-inputs in groundwater (Bekesi and McConchie 2002; Stigter et al. 2006; Debernardi et al. 2008; De Luca and Lasagna 2005; Lasagna 2006).

5.2 STUDY AREA DESCRIPTION

Most shallow groundwater in Italy is affected by nitrate contamination. In Piemonte Region (North-western Italy) nitrate has been recognised as one of the most important pollutants of shallow groundwater (Debernardi et al. 2005; Lasagna 2006; Lasagna and De Luca 2008). In this area, increasing amount of synthetic nitrogenous fertilizers and organic manure are used for agricultural purposes and it results in a diffuse pollution by nitrate compounds in groundwater. In Piemonte Region the correlation between the amount of nitrogen fertilizer applied and the nitrate content in groundwater has been recognised (Lasagna 2006; Debernardi et al. 2008). Moreover, regional investigation of the impact of farming on shallow aquifers in the fluvial deposits has found evidence for vertical hydrochemical distribution of nitrate in the shallow aquifer (Lasagna, 2006; Lasagna and De Luca, 2006). The relation between dilution and q_u, analytically demonstrated above (eq. 11), was verified in a study of nitrate contamination in two areas of Piemonte Region (fig. 4), namely the Cuneo plain (Area A) and the Alessandria plain (Area B).

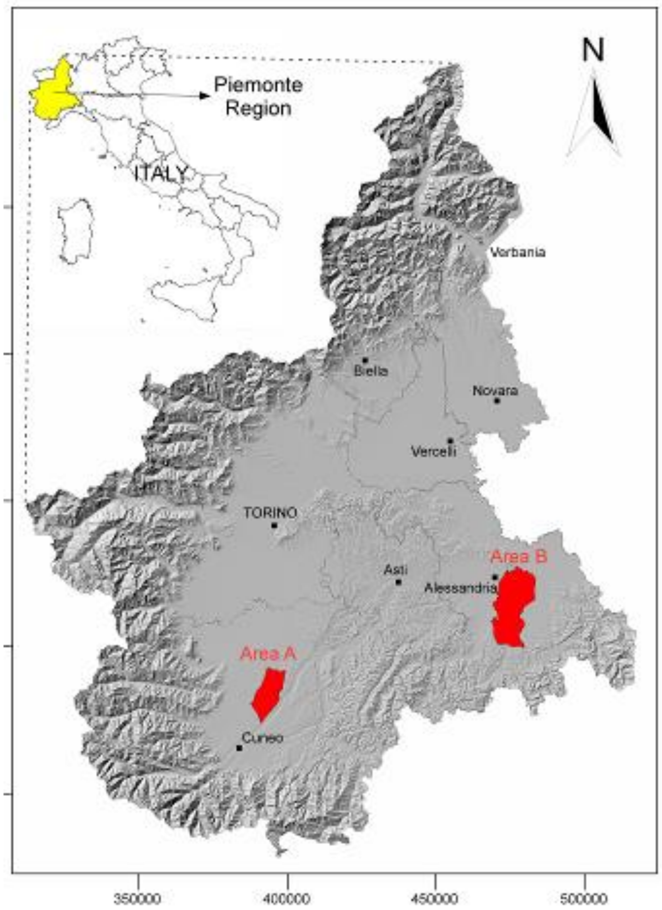

Fig. 4 – Study areas in the northwest of Italy: Area A corresponds to a portion of the Cuneo plain, and Area B corresponds to a portion of the Alessandria plain.

Area A is located in the middle of the Cuneo plain and covers 120 km². In the region, farming is well developed, with a prevalence of orchards, cereals, forage and vegetable growing. Animal husbandry (mainly pigs and sheep) is also a widespread activity.

Area B is situated in the Alessandria plain and covers 300 km². This area is also characterised by industrial activities. Regarding soil exploitation, 80% of the plain is planted mainly with corn and wheat; the remaining part of the plain is cultivated with vineyards, orchards, hazel groves and grass.

Area A and Area B are essentially agricultural zones, in which farming and zootechnical activities are highly developed. Thus, a large amount of synthetic nitrogenous fertilizers and organic manure are used for agricultural purposes. It follows in an excess of nitrate in the soil and consequently in groundwater.

5.3 GEOLOGY OF THE STUDY AREAS

The analysed areas are included in the Ligure-Piemontese Basin, a continuous sedimentary post-orogeneous succession settled on Western Alps structures, which develop in depth (Irace et al. 2009; Irace et al. 2010). The Ligure-Piemontese Basin, after remarkable subsidence, was affected by an important terrigenous sedimentation, with the settlement of conglomerates, sand, clay, silt, marl, clayey marl and chalk (Pre-Pliocene). A series of tectonic corrugation processes caused the rising of hills and separation in various basins (Pieri and Groppi 1981; Mosca 2006). The series ends with the deposition of marine sediments (Pliocene), lacustrine and deltaic deposits of the "Villafranchiano" complex (late Pliocene – early Pleistocene) and continental sediments, with both fluvioglacial and fluvial alluvium (Medium Pleistocene-Holocene) (Carraro 1996; Mosca 2006; De Luca et al. 2007). The crystalline basement of the Alps and the sediments of the Torino hill plunge under this succession of sediments. The thickness of these sediments is strongly affected by the tectonic processes that have occurred.

Area A borders the southern sectors of the Torino plain to the north and is bounded by the hills to the east and by the Alps to the south and west. The area is located at the end of large alluvial fans and it is covered by coarse deposits (pebbles, gravel and sand). These deposits can have a thickness ranging between 20 and 80 metres (Servizio Geologico d'Italia, 1931).

Area B lies on the plain of Alessandria. The area represents the filling of the Tortona-Alessandria basins by rivers coming from the Alps and the Apennine mountains. In fact, this plain is characterised by a series of large alluvial fans, which, starting from the valleys, open like fans towards the north, touching each other. The deposits of these fans are mainly connected to coarse materials. In the Alessandria plain, these conoids are deeply terraced as a consequence of the succession of erosive-depositional cycles due to tectonic and climatic factors (Servizio Geologico d'Italia, 1970). In the north of Area B, the alluvial deposits are thin (20 metres), but in the remaining area of the Alessandria plain, the alluvial deposits are thicker (60 metres).

5.4 HYDROGEOLOGICAL SETTING OF THE STUDY AREAS

The Piemonte plain sector is the most important water reservoir of the Piemonte Region due to its size, the characteristics of its deposits and the possibility of recharge. This plain has an unconfined aquifer in alluvial deposits (late Pleistocene mid-Holocene), lain on a confined multi-aquifer system in the fluvial-lacustrine deposits of ''Villafranchiano'' successions (late Pliocene–early Pleistocene), which lies on a confined aquifer in marine deposits (early Pliocene–Pliocene). The aquifer systems are recharged by local precipitation and, mostly, by considerable losses of rivers coming from the Alpine valleys.

5.4.1 Piezometric reconstruction of the shallow aquifer

The groundwater levels in the shallow unconfined aquifer were monitored from January to August 2005 in Area A and from May to November 2005 in Area B. The measurement points were irrigation wells and domestic wells, piezometers and rivers: 49 wells and 5 measurements of river water were utilised in Area A, while 64 wells, 2 piezometers and 9 measurements of river water were used in Area B. The piezometric maps are shown in Fig. 5 and 6. The piezometric surface contour maps were created using Surfer 9 software (Golden Software, Golden, CO), based on water heads in meters above sea level. A kriging algorithm was used to interpolate the piezometric data. In both areas, the maps demonstrate an identical piezometric morphology in the two measurement areas. In the northern sector of Area A, the isopiezometric lines have a regular trend and are sub-parallel. The average hydraulic gradient is 0.005, and the flow direction is from SW to NE. The SE sector of Area A shows closer piezometric lines, with an average hydraulic gradient of 0.007. The NE sector is heavily affected by topography because of the presence of a 30-m-high terrace. In this area, the average hydraulic gradient is 0.05. Groundwater is greatly influenced by the Stura di Demonte river, which is a gaining river. The Mellea river flows from SW to NE and is almost independent of the aquifer.

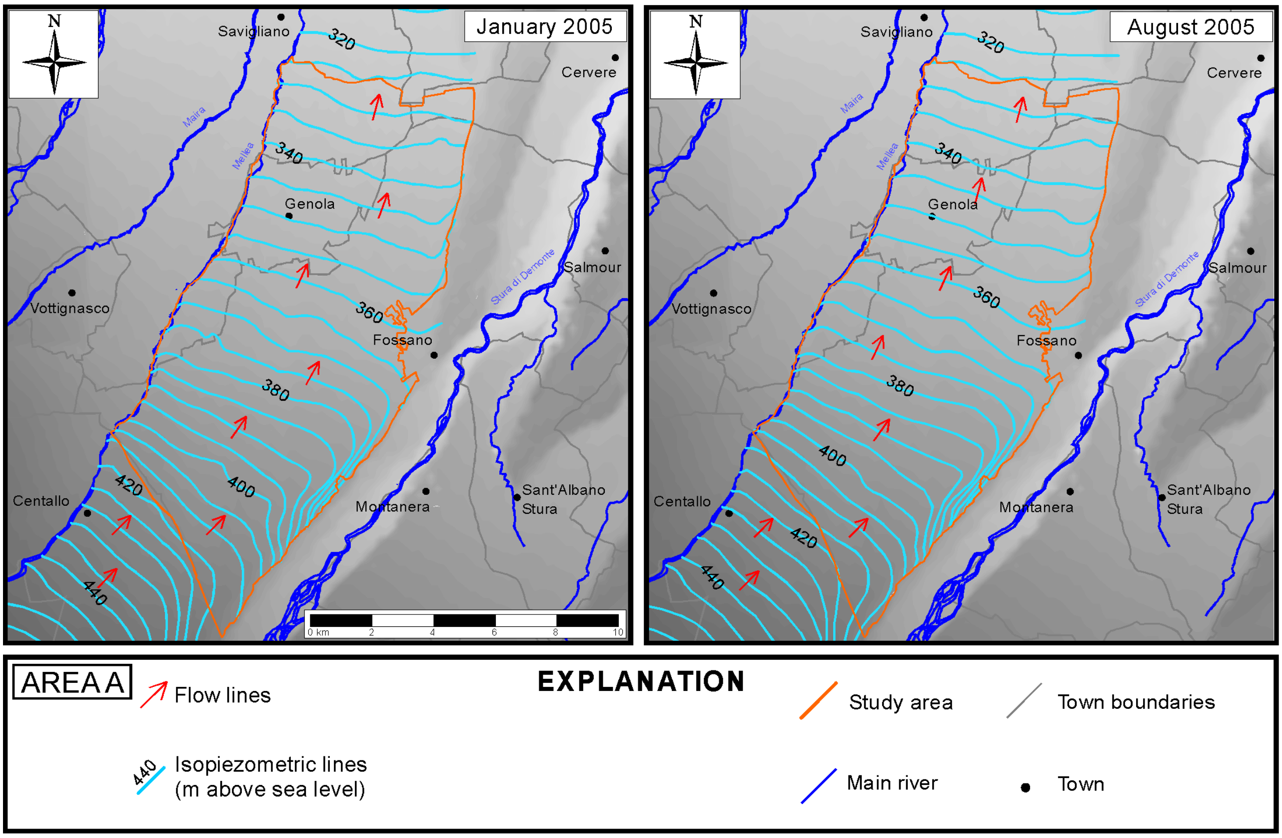

Fig. 5 - Piezometric maps of the shallow aquifer (January 2005 and August 2005) in Area A.

In Area B, groundwater generally has a radial and centripetal movement consistent with a paleosurface setting. In the eastern part of the studied area, the groundwater flows from south to north; in the western part, the flow is from SSW-NNE. From a morphological point of view, the piezometric level follows the topographic surface, and it is influenced significantly by the different degrees of permeability of deposits. The hydraulic gradient can vary greatly in the area of study; generally, it decreases from SE to NW. Regarding the relationship between the groundwater and shallow streams, the Bormida, Orba and Lemme rivers drain groundwater. Two field measurement campaigns were also performed in 11 monitoring points of piezometric levels throughout the year in the Area A and Area B. They exhibited a shallow fluctuation of piezometric level, especially in the Area A (inferior than 1 m).

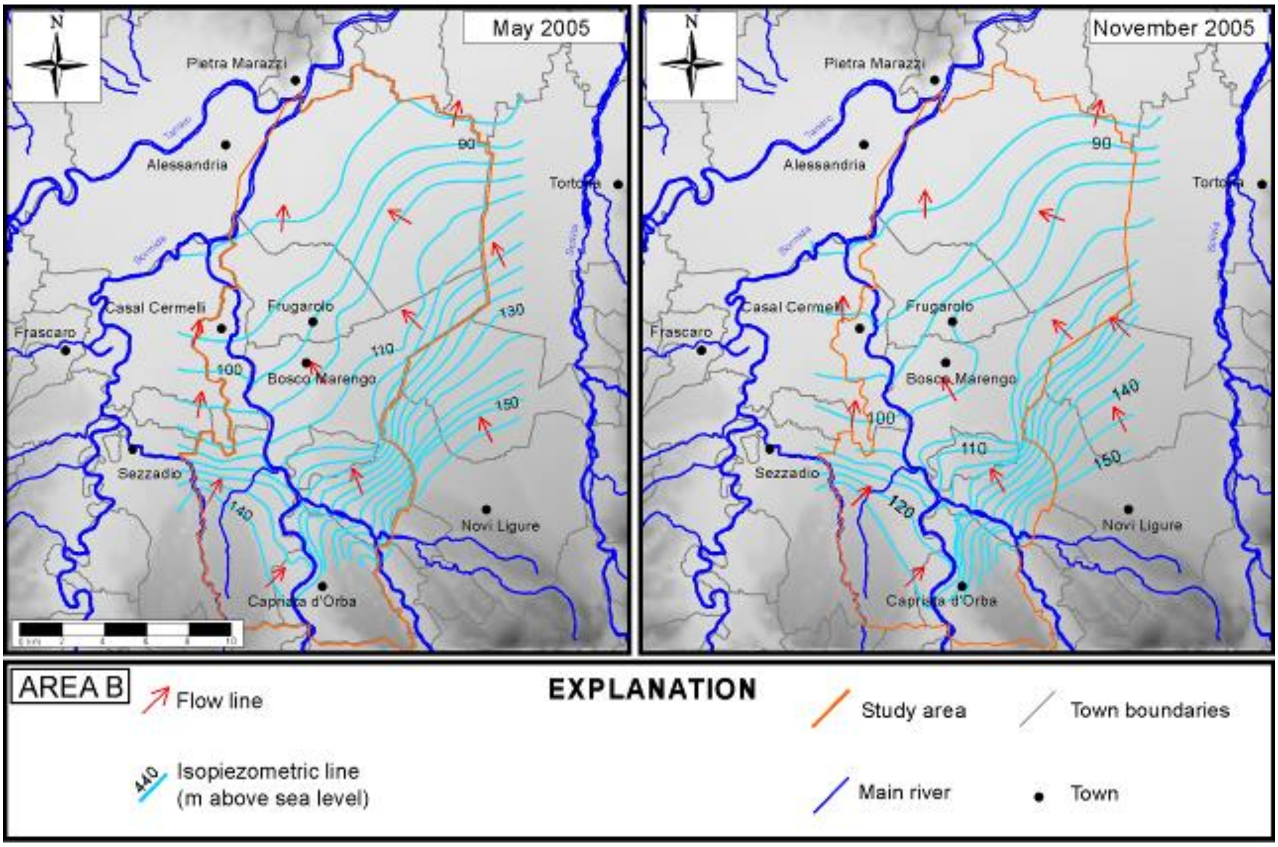

Fig. 6 - Piezometric maps of the shallow aquifer (May 2005 and November 2005) in Area B.

5.4.2 – The transmissivity of the shallow aquifer

To understand the characters of the shallow aquifer in the two areas of study, the transmissivity was assessed. The transmissivity values were evaluated using specific discharge for 44 wells in Area A and 170 wells in Area B; the wells filters existed only in the shallow aquifer. The transmissivity maps were created using Surfer 9 software (Golden Software, Golden, CO). The Kriging interpolation algorithm was used to interpolate the transmissivity data.

The aquifer transmissivity of Area A (Fig. 7) ranged from $5.0 \cdot 10^{-3}$ m^2/s in the western sector of the study area to $3.3 \cdot 10^{-2}$ m^2/s near the city of Fossano in the eastern part of the study area. The transmissivity map of Area B (Fig. 7) shows that the lowest transmissivity values can be found in the southern and eastern sector of the study area; these values are due to the presence of sand-silt-clay alluvium and heavily altered alluvium. The highest transmissivity ($2.8 \cdot 10^{-2}$ m^2/s) was found in the northwestern sector, where gravel-clay deposits exist, which have only moderate shallow alteration and, hence, good permeability.

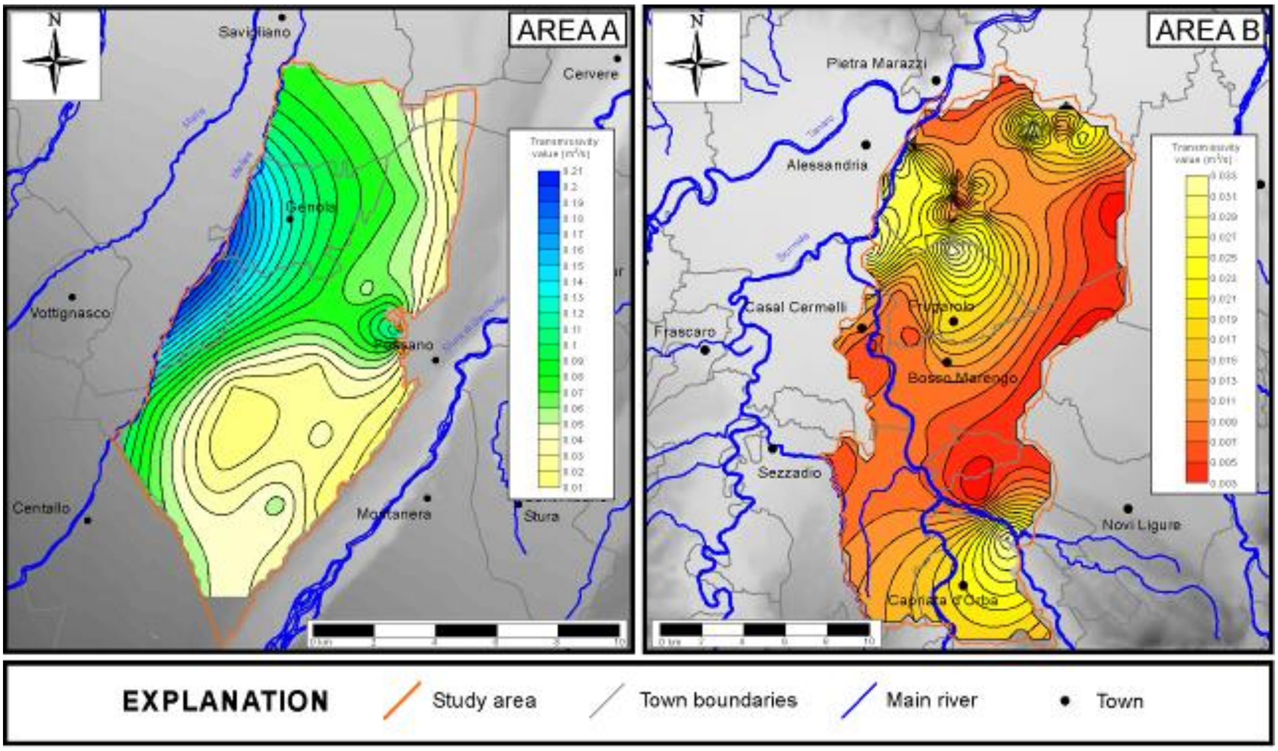

Fig. 7: Transmissivity maps of the shallow aquifer in Areas A and B.

5.5 – NITRATE CONTAMINATION IN THE SHALLOW AQUIFER

To emphasise the nitrate distribution in the shallow aquifer, two sampling campaigns were conducted in Area A (January and August 2005) and two in Area B (May and November 2005). In Area A, 24 wells and 4 rivers were sampled in January 2005, and 38 wells and 5 rivers were sampled in August 2005; in Area B, 32 wells and 7 rivers were sampled in May 2005, and 16 wells and 6 rivers were sampled in November 2005. Water samples were analysed for nitrate concentration in the laboratories of Earth Science Department (University of Turin).

The nitrate concentration maps were interpolated using the kriging method of Surfer 9 software (Golden Software, Golden, CO).

In Area A (Fig. 8), the nitrate concentrations in groundwater C_w were generally high. Values greater than 50 mg/l, the maximum nitrate concentration accepted by Italian law (Decreto Legislativo 152/2006), were present in the central sector of the study area. The nitrate concentration in the Mellea river was approximately 15 mg/l in the winter, and it ranged between 15 and 30 mg/l in the summer. In Area B (Fig. 8), the nitrate levels were generally high, with a local concentration greater than 100 mg/l. The southern sector of the study area was not contaminated because farming activities are rare in this area. The rivers, where analysed, exhibited nitrate levels of less than 10 mg/l.

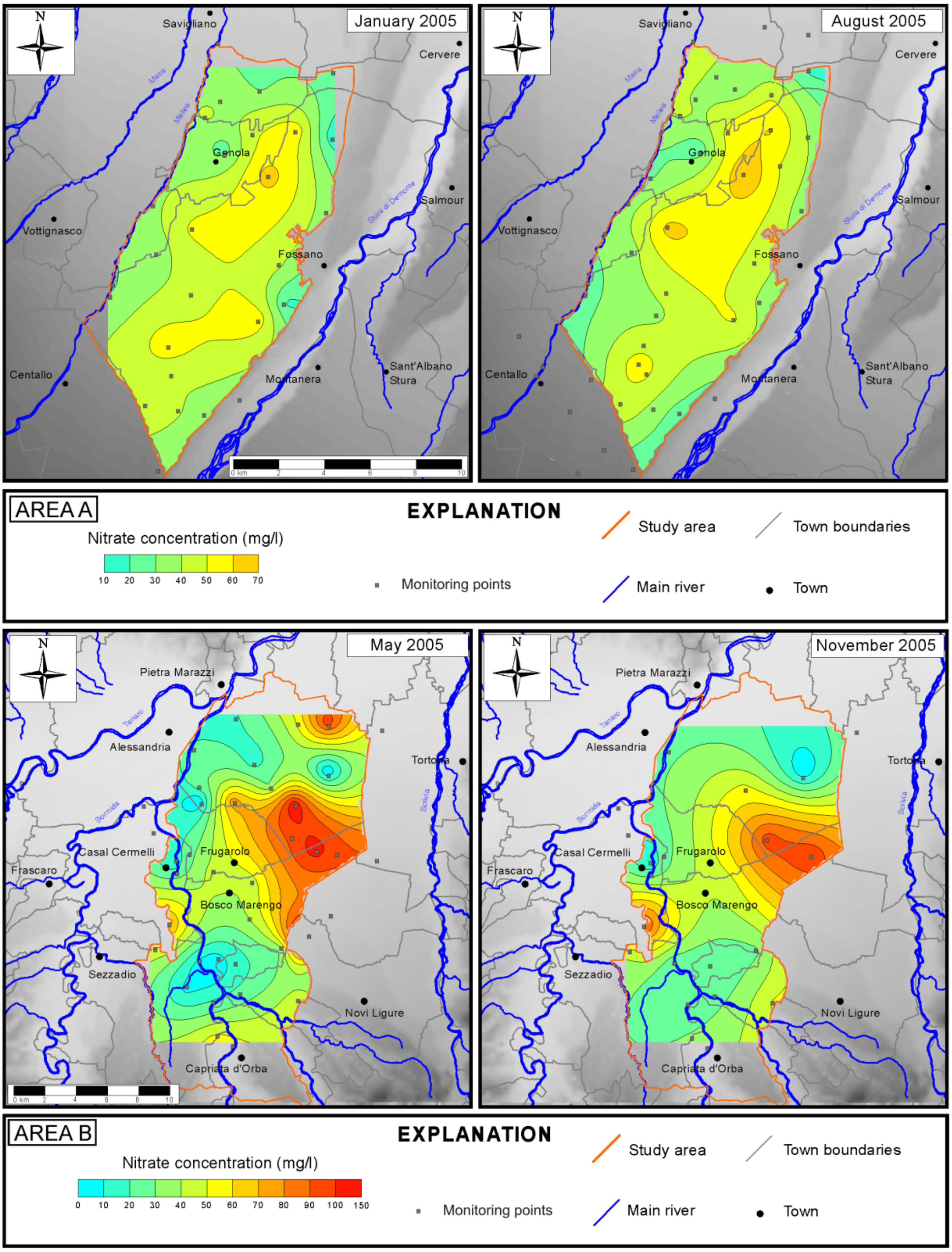

Fig. 8: Nitrate concentration maps in Area A (January 2005 and August 2005) and in Area B (May 2005 and November 2005).

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In addition, five monitoring wells for Area A and Area B were chosen to evidence the nitrate concentration variation over time. The sampling frequency was monthly over an entire year. In Area A the wells were sampled from January 2005 till January 2006, whereas in Area B monitoring wells were sampled from May 2005 till April 2006.

In area A (Fig. 9) the nitrate concentration in groundwater remains quite constant during the year in the monitoring wells. On the contrary, in Area B nitrate concentration shows a high variability during the year. In P6 and P13 monitoring wells, the highest values of nitrate concentration were measured in the period from June to August (irrigation period). In these agricultural areas nitrate is available for leaching because of the previous application of synthetic N-fertilizers and zootechnical effluents. During the months of winter and spring the concentration in nitrates is very low or absent. In P11, P32 and P38, the highest nitrate concentrations were observed in winter and spring, while during summer the concentrations were lower.

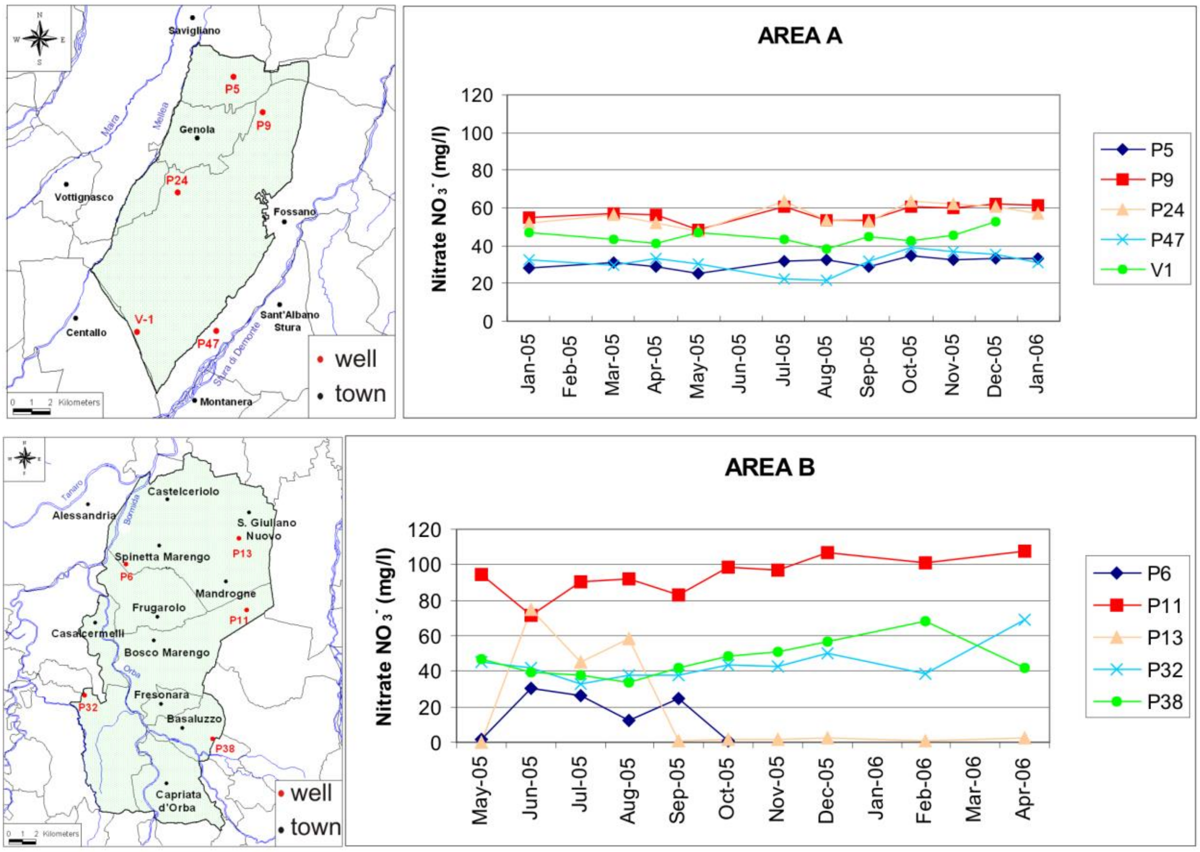

Fig. 9: Time series of observed NO_3^- concentration of five monitoring wells in Study Area A and in Study Area B, and their location.

5.6 EVALUATION OF q_u IN THE PIEMONTE PLAIN SAMPLE AREAS

To evaluate the aquifer's ability to attenuate nitrate through dilution, the volumetric flow rate per unit perpendicular to the flow direction (q_u) was calculated in Area A and Area B. In the two study areas, a flow net comprised of equal-length (L) 1-km cells was created; the cells were located along parallel flow tubes (Fig. 10). The q_u value was calculated for each cell in Area A and Area B (Fig. 11). Because q_u is proportional to the attenuation capability due to aquifer dilution, the map was created based on the division of q_u into various classes, as suggested in Table 1.

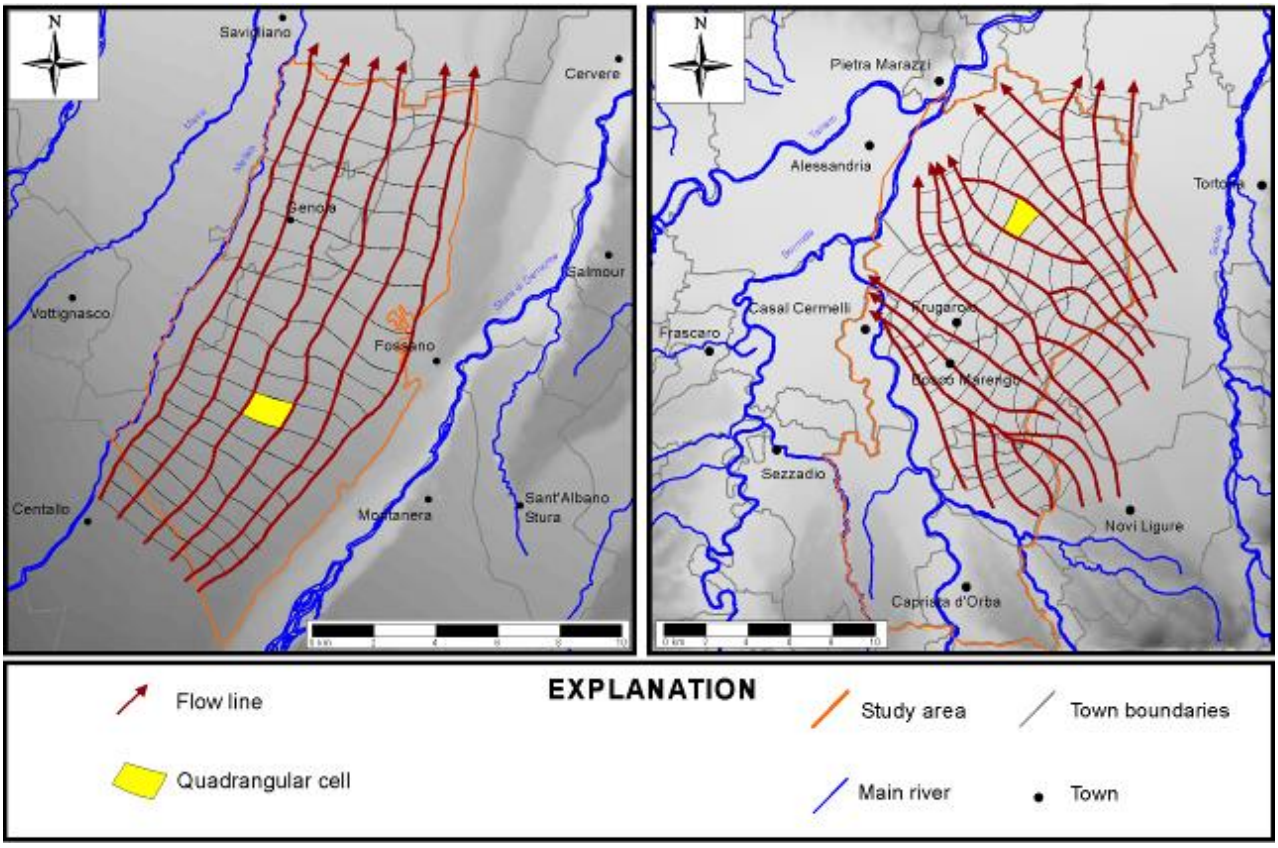

Fig. 10 - Division of Area A and Area B into a flow net with 1-km lengh cells.

q_u (m^2/s)	Class of attenuation capacity due to dilution
$>5*10^{-3}$	Very high
10^{-3}-$5*10^{-3}$	High
$5*10^{-4}$-10^{-3}	Moderate-high
10^{-4}-$5*10^{-4}$	Moderate-low
$5*10^{-5}$-10^{-4}	Low
$< 5*10^{-5}$	Very low

Table 1 – Division of the q_u value into classes according to the aquifer's ability to reduce the contaminant concentration through the dilution process (modified from Lasagna et al. 2009).

Studying the attenuation capability due to the aquifer dilution of Area A, it is evident that the q_u values range from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ m^2/s, probably due to the small dimensions of the study area and the low variability of the hydrogeological parameters. This result is well within the moderate-low class of attenuation capacity due to dilution. By contrast, the q_u parameter in Area B has a significant degree of variability, with values ranging from $5 \cdot 10^{-5}$ to $5 \cdot 10^{-4}$ m^2/s. Most of Area B is included in the very low class of attenuation capacity due to dilution ($q_u < 5 \cdot 10^{-5}$ m^2/s), thereby demonstrating a low dilution ability. However, the western areas and small southern sectors are different; they fall within the low class of attenuation capacity due to dilution. The areas in this class seem to have higher hydraulic conductivity values than the surrounding zones. The E-SE area is in the moderate-low class of attenuation capacity due to dilution, and the main feature of this class is a high hydraulic gradient. Sectors in the moderate-low and low classes of attenuation capacity due to dilution indicate a low-medium aquifer ability to reduce contaminant concentrations due to dilution.

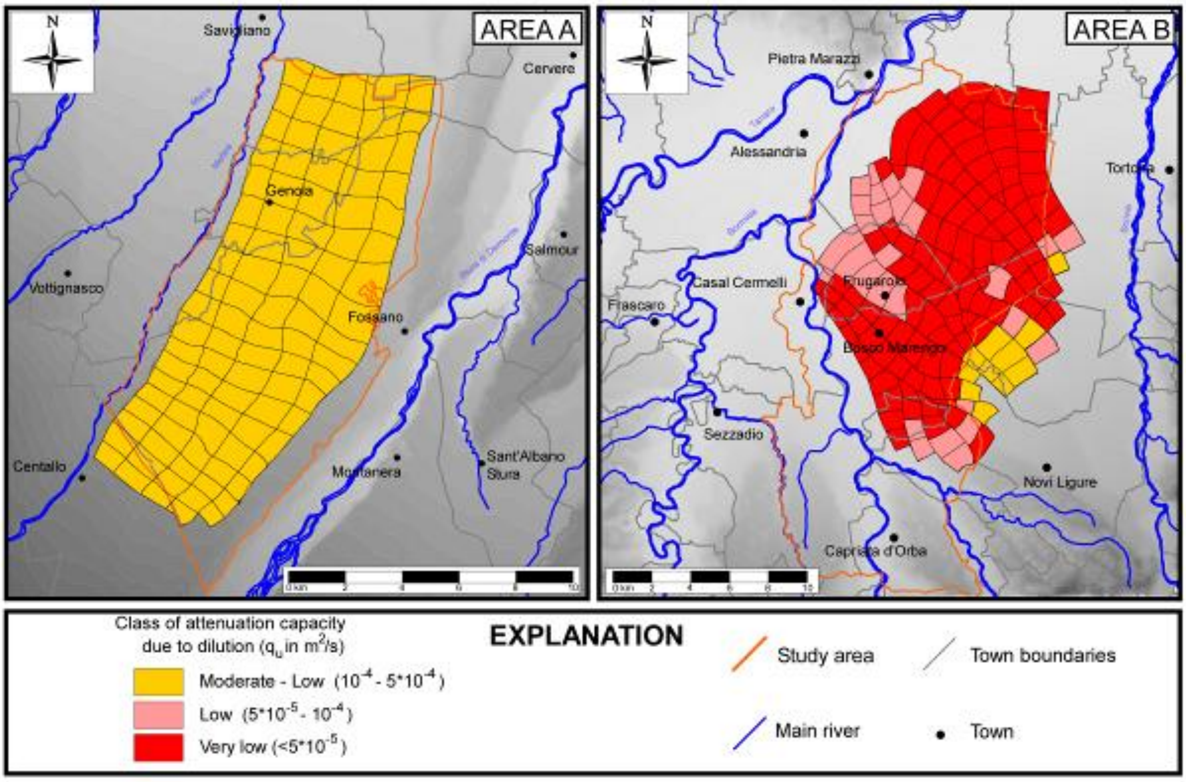

Fig. 11: Maps of the dilution attenuation capacity of the shallow aquifers (evaluated as q_u) in Area A and Area B.

5.6.1 CORRELATION BETWEEN THE ACTUAL NITRATE CONCENTRATION IN GROUNDWATER C_w AND q_u

To demonstrate the role of dilution in the shallow aquifer, the q_u values in the Piemonte plain sample areas were compared with the actual nitrate concentration values C_w. The C_w values were assessed using the nitrate distribution in the shallow aquifer in August 2005 (Area A) and in May 2005 (Area B) (Fig. 8). The nitrate distributions in the different seasons were similar for each area. The pairs of q_u and C_w values in each cell were then plotted on a Cartesian diagram, where the q_u values were drawn on the abscissa axis, and the C_w values were drawn on the ordinate axis (Fig. 12).

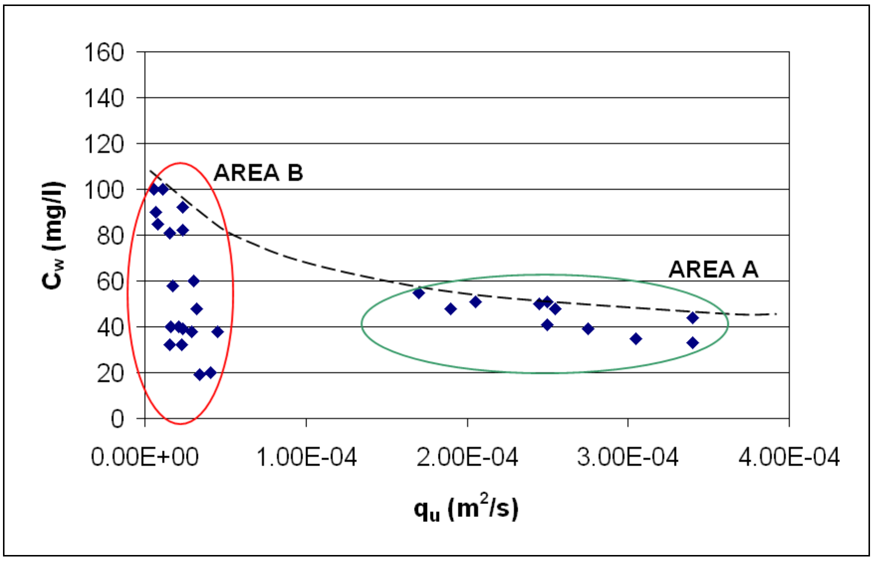

Fig. 12: Correlation between nitrate concentration in groundwater C_w and q_u in Area A and Area B. The dotted line connects the values of maximum nitrate concentration and corresponding q_u.

Based on the binomial q_u/C_w representation, a trend is observable connecting the values of maximum nitrate concentration and corresponding q_u. In particular, higher nitrate concentration C_w values (up to 100 mg/l) are found in areas with lower q_u values (Area B). On the other hand, nitrate concentrations are lower (up to 48 mg/l) in areas with higher q_u values (Area A). This is true despite of the fact that q_u/C_w ratio does not take into account the quantity of nitrate input from the soil. The anomalous points, especially in Area B, are probably due to this element. Furthermore the binomials q_u/C_w reflect the theoretical trend observed in Fig. 2. In the study areas, indeed, the nitrate concentration in the infiltration water is most of time higher than the input to the cell. This trend, as previously described, is connected to the dilution attenuation capability of the aquifer being proportional to the q_u of the aquifer itself; in fact, the lower the attenuation capability, the more difficult it is to dilute the contaminant, and consequently, the nitrate concentration in the groundwater is higher.

Based on these results, it is possible to assume that, at a regional scale, high nitrate concentrations in the output from the cells with low q_u values are due to low dilution rate of the contaminant in the groundwater. *Vice versa*, it is safe to assume that low nitrate concentrations in the output from the cells with high q_u values are due to a high nitrate dilution rate.

5.7 EVALUATION OF EXPECTED NITRATE CONCENTRATION IN GROUNDWATER

To evaluate the expected contaminant concentration in the output from the cell (C_u) in a flow net, equation 11 was applied in Area A and Area B (Fig. 13). In the two study areas, a flow net with constant length (L) equal to 1 km for the q_u evaluation was used.

The nitrate concentration in the infiltration water (C_i) was evaluated as:

$$C_i = \frac{NL}{I_e}$$

NL (kg N/ha) is the nitrogen (N) reaching groundwater due to leaching, that is, the amount of nitrogen fertiliser that reaches the aquifer (Grignani & Sacco 2005). NL depends on the amount of nitrogen fertilisers, the soil hydraulic parameters and the degradation processes in the atmosphere and soil. Ie is the infiltration rate (m/year). In Area A, the infiltration rate is evaluated as leached water below the soil profile (Grignani & Sacco 2005).

In Area B, Ie is calculated as the product of precipitation (Biancotti et al. 1998) plus irrigation (De Vecchi Pellati and Pesce 1986) and a coefficient that takes into account the geological context and soil features (American Petroleum Institute 1996).

The nitrate concentration in the input to the cell C_{ae} is represented in the shallow aquifer concentration maps of Area A (August 2005) and Area B (May 2005) (Figs. 8). In Area A, the minimum C_{ae} is equal to 12 mg/l, and the maximum C_{ae} is equal to 68 mg/l; in Area B, the minimum C_{ae} is equal to 5 mg/l, and the maximum C_{ae} is equal to 145 mg/l.

Comparing the map of expected nitrate concentration (C_u) with the map of the actual nitrate concentration (C_w) in groundwater (August 2005 for Area A and May 2005 for Area B), the maximum concentration areas demonstrate a high degree of consistency.

Moreover, the concentration data for both areas were plotted on an X-Y graph with the expected nitrate concentration (C_u) on the X axis and the actual nitrate concentration (C_w) in the groundwater on the Y axis (Fig. 14). A good correlation of the data is shown, namely the mean observational error between C_w and C_u is 6 mg/l in Area A and 5 mg/l in Area B. The coefficient of correlation (R^2) is 0.77 in both Area A and Area B. This result demonstrates a significant correlation between the two parameters.

These results show that the proposed model provides a good simulation of the actual situation, stressing the possible usefulness of this methodology.

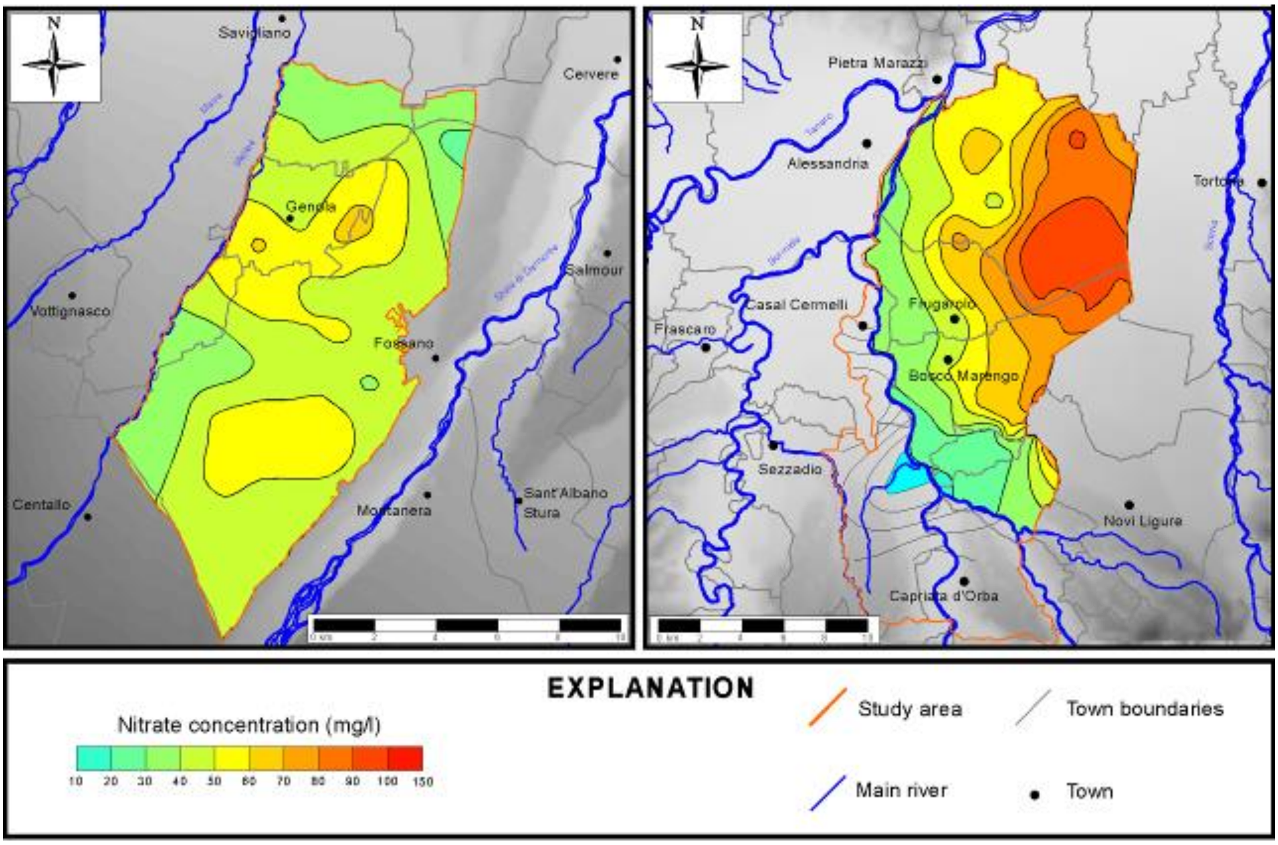

Fig. 13 - Map of expected nitrate concentration C_u in Area A and Area B.

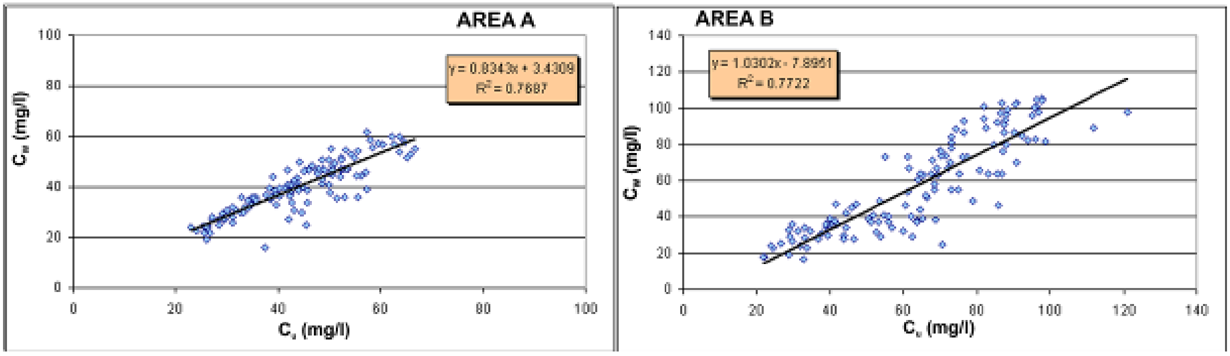

Fig. 14: Correlation between Cu (evaluated contaminant concentration in the output from the cell) and Cw (actual nitrate concentrations in the groundwater) in Area A and Area B.

CONCLUSIONS

In groundwater, the dilution process takes place everywhere irrespective of biological and chemical conditions. This process is very important because can cause contaminant reduction. As result, in areas with pollution from diffuse sources, dilution can prevent the net increase of contaminant in shallow aquifers along the groundwater direction. In some cases, dilution has been found to be the most important mechanism for the attenuation of nonreactive and nonsorbing solutes in groundwater systems.

The dilution potential of groundwater varies according to several hydrogeological factors, and it is potentially strongly dependent on the volumetric flow rate per unit perpendicular to the flow direction (q_u, m^2/s); q_u is a function of the hydraulic conductivity, hydraulic gradient and aquifer thickness.

To verify the relationship between dilution and q_u an analytical approach was used, considering a simplified model. The model is comprised of a flow net, in which groundwater contamination is already present in the input to the cell (C_{ae}) and the contaminant concentration comes from the infiltration water (C_i). The proposed equation demonstrates that the C_u (expected contaminant concentration in the cell output), with all other factors being equal, is strictly related to dilution and that it depends on specific aquifer parameters. In particular, an aquifer ability to reduce the contaminant concentration is highly dependent on $q_{u.}$ Furthermore a classification of q_u was proposed, considering six classes of attenuation capacity due to dilution.

The relationship between dilution and q_u was verified for nitrate contamination in two study areas of the Piemonte plain (Northern Italy). Even though the high concentration of nitrate generated from agricultural activities such as use of commercial fertilizer and manure from livestock farms, is identified, natural attenuation effectively offset this increased nitrate concentration coming into the specific study. This lack of concentration increase is the first signal of a nitrate attenuation phenomenon in aquifers. The q_u values evaluated in the two sample areas were compared to the nitrate concentration values C_w in the groundwater. Based on the binomials q_u/C_w, a regional trend is observable in that higher nitrate concentration C_w values are found in areas with lower q_u values. Viceversa, nitrate concentrations are lower in areas with higher q_u values. Moreover the binomials q_u/C_w also reflect the theoretical trend $q_u/C_{u,}$ based on the proposed equations. This trend is due to the dilution attenuation capability of the aquifer being proportional to the q_u of the aquifer itself.

Besides the equation to evaluate the expected contaminant concentration in the cell output (C_u) in a flow net was applied in the two study areas. Comparing the map of C_u with the map of the nitrate concentration actually found in groundwater (C_w), a significant correlation was found between these two parameters.

At last the parameter q_u can be used as a planning tool, with advantages for groundwater management and preservation.

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