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Nitrate contamination of groundwater in the western Po Plain (Italy): the effects of groundwater and surface water interactions

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ABSTRACT

This study aims to investigate the physical and chemical effects of interactions between groundwater and surface water (GW-SW) – particularly in streams – on nitrate contamination. The effects of GW-SW interactions are briefly reviewed, with a particular emphasis on processes and environments that influence increases or decreases in nitrate concentration. Then, this paper analyses nitrate concentrations in groundwater and surface water in the western Po plain (Northwestern Italy); this analysis includes the nitrate concentration profiles across the shallow aquifer and intersecting the main streams on the plain. The investigation highlights how the concentration trends are similar, even when nitrate levels in rivers and groundwater are not comparable. The maximum nitrate concentrations in the surface water were generally measured in areas with high nitrate levels in groundwater. An analysis of the nitrate concentration profiles highlighted the mutual influences of GW-SW. The most important streams on the plain (the Po River and Stura di Demonte River), both of them gaining streams, seem to reduce the nitrate concentrations of groundwater at a study scale.

The proposed conceptual model indicates how the near-stream environment (the riparian zone, wetlands, hyporheic zone and shallow organic-rich soils in the near-stream environment) and the groundwater flow systems in shallow and deep aquifers, from the recharge zone to the streams, could dramatically affects the nitrate concentrations.

Keywords

GW–SW interactions, nitrates, losing and gaining streams, denitrification, hyporheic zone, riparian zone, Po River

1. INTRODUCTION

High nitrate concentrations in groundwater are a worldwide problem (Strebel et al. 1989; Goss et al. 1998; Thorbum et al. 2003; Almasri et al. 2007; Debernardi et al. 2008; Burow et al. 2010; Li et al. 2010; Lasagna et al. 2015). Nitrate is soluble, highly mobile and potentially leaches from the unsaturated zone to groundwater (Pratt et al. 1978; Green et al. 2008; Liao et al. 2012). The global increase in the use of N-fertilizer (synthetic nitrogenous fertilizers and organic manure) over the last several decades has led to increased nitrate leaching and runoff, which threaten water quality, especially in agricultural areas. In fact, many studies have indicated a high correlation between agriculture and nitrate concentrations in groundwater (Agrawal 1999; Nolan and Stoner 2000; Harter et al. 2002; Debernardi et al. 2008). The extensive use of fertilizers for agricultural purposes is considered to be the main non-point source of nitrate contamination in groundwater (Liao et al. 2012; Postma et al. 1991; Baker 1992; Chowdary et al. 2005). Furthermore, point sources of nitrogen, such as septic systems, have been shown to contribute to groundwater nitrate pollution (Al-Agha 1999; Debernardi et al. 2008; MacQuarrie et al. 2001). Nitrate itself does not directly harm the human body. However, it can induce certain diseases, such as methemoglobinemia and cancer, when it transforms into nitrite (Hegesh and Shiloah 1989; Bukowski et al. 2001; Manassaram et al. 2010). Consequently, the US Environmental Protection Agency (US EPA) has established a maximum contaminant level (MCL) of 10 mg/L NO_3-N (50 mg/L NO_3) in drinking water (US EPA 2000). The Nitrates Directive (91/676/EEC), that aims to protect water quality across Europe by preventing nitrates from agricultural sources polluting ground and surface waters, requires Member States to identify groundwaters that contain more than 50 mg/L of nitrate or could contain more than 50 mg/L of nitrate if preventative measures are not taken. In addition, the Drinking Water Directive (98/83/EC) sets a maximum allowable concentration for nitrate of 50 mg/L. In Italy the maximum nitrate concentration in drinking water is 50 mg/L as well (Decreto Legislativo 31/2001). The recommended threshold value to achieve the good standard of groundwater chemical quality for nitrate is 50 mg/L (Decreto Legislativo 30/2009). This law indeed establishes criteria in order to ensure both good quantity and quality status of groundwater reservoirs before the end of 2015.

Processes such as denitrification and dilution may substantially decrease nitrate concentrations in water. Nitrate can be denitrified to produce nitrogen gas in the presence of chemically reducing conditions if a source of dissolved organic carbon is available. Denitrification in aquifers was observed at a variety of timescales and space scales (Gillham and Cherry 1978; Kölle et al. 1990; Postma et al. 1991; Korom 1992; Starr and Gillham 1993; Toda et al. 2002; De Bernardi et al. 2005; Lasagna et al. 2006; De Bernardi et al. 2008). Besides, dilution involves the mixing of water with different nitrate concentrations, which results in the lowering of contamination concentrations in the most polluted water. In groundwater, dilution plays a predominate role in decreasing nitrate concentrations; in particular, the higher the dilution capability of groundwater, the higher the nitrate concentration decrease (De Luca and Lasagna 2005; Lasagna et al. 2009). However this process, that is

omnipresent and is not affected by the biological and chemical conditions in groundwater, does not remove the contaminants from the system (Lasagna et al. 2013). The dilution process can also be achieved when groundwater and surface water come into contact (McMahon and Böhlke 1996; Kayabali et al. 1999; Winter et al. 1998; Lasagna 2006). Groundwater is a major component of streamflow and the quality of discharging groundwater can potentially affect the quality of the receiving stream in many hydrologic settings (Alley et al. 1999; Puckett et al. 2008). Streams interact with groundwater on all types of landscapes, and water can move in both directions between groundwater systems and surface-water bodies. Therefore, contaminants in surface water can be transported into adjacent groundwater systems, and groundwater contaminants can be transported into adjacent surface-water bodies.

Determining the contribution of ground water to the contamination of streams and vice versa is a critical step in developing effective water-management (Winter et al. 1998; Yang et al. 2014).

The aim of this paper is to provide a brief review of the physical (quantitative) and chemical (qualitative) effects of groundwater and surface water (GW-SW) interactions. The processes and environments that control GW-SW interactions and, consequently, enhance nitrate decrease or increase are emphasized. Several examples of previous worldwide studies are also reported.

Furthermore, this paper provides an example of the interactions between groundwater and streams in the Turin-Cuneo plain (Northern Italy). The Po River, the longest river in Italy, and the Stura di Demonte River flow in this plain and widely interact with groundwater. Furthermore, agricultural activities in this area are highly developed and nitrate contamination is widespread in the shallow aquifer. An investigation of nitrate concentrations in the groundwater and surface water in the Turin-Cuneo plain was conducted. Furthermore, nitrate concentration profiles are provided across the shallow aquifer, intersecting the main streams on the plain. These profiles are very useful to better understand the GW-SW interactions and to highlight how these relationships influence nitrate concentrations in this Italian plain. Finally, a conceptual model of the GW-SW interaction in the Turin-Cuneo Plain is presented and the effects on nitrate contamination are reported on the basis of existing data. The conceptual model is useful for clarifying the possible role of the denitrification environment (riparian zone, wetland, hyporheic zone, shallow organic-rich soils in near-stream environment) and of the flow systems (i.e., deep regional flow systems in the anoxic environment, shallow flow system in the oxic environment) on nitrate contamination in the near stream environment.

2. PROCESSES AND ENVIRONMENTS CONTROLLING GW-SW INTERACTIONS

Groundwater and surface water have been managed as isolated components for a long time, but they are hydrologically connected in terms of both quantity and quality (Winter 1999). The physical interactions between groundwater and streams primarily depend on two factors: 1) the geological context and permeability degree of an aquifer in comparison to a streambed; and 2) the relationship between the river water level and piezometric level in the vicinity of the river. Respective to the second factor, interactions take place in two basic ways (Winter et al. 1998) (Fig. 1): a) streams obtain water

from the inflow of groundwater through the streambed (a gaining stream); b) streams lose water to groundwater systems through outflow from the streambed (a losing stream). In some environments, streamflow gain or loss can persist; in other environments, flow direction can vary a great deal along a stream: so streams may be gaining in some reaches and losing in other reaches. Furthermore, the flow directions between groundwater and surface water can change seasonally as the altitude of the groundwater table changes in relation to the stream-surface altitude, or it can change over shorter timeframes when stream surfaces rise during storms and recharge the stream bank. In Italy, Botta et al. (2005) evaluated the interactions between surface water and groundwater using seepage-meters and minipiezometers. Tests were conducted at two sites on the Piedmont plain (Northern Italy) and indicated that the interactions were very different; indeed, situations in which streams receive groundwater, streams lose water to groundwater or "zero exchanges" were observed at the test sites a few metres away from each other.

Traditionally, the physical interaction between groundwater and surface water are presented using piezometric maps. Even if the overall water flow direction can be evidenced with these maps, especially at a regional level, sometimes the interactions between surface water and groundwater are very complex at a local scale. Many others methods of quantifying the physical interactions between groundwater and streams have been applied by researchers all over the world. The main measuring methods for groundwater and surface-water interactions were summarized by Kalbus et al. (2006), Brodie et al. (2007), Rosenberry and LaBaugh (2008), Bertrand et al. (2014).

In regard to chemical GW-SW interactions, where surface water and groundwater flow systems interact, groundwater and surface water chemistry cannot be dealt with separately (Winter et al. 1998). In fact, the movement of water between groundwater and surface water increases chemical transfer. In particular, streams can create favourable conditions for lowering or increasing a contaminant, e.g. for nitrates, in groundwater and so the stream effect is fundamental in the development and propagation of contamination in groundwater. A river can dilute contamination in groundwater by mixing surface water and groundwater; in contrast, a watercourse can be a linear source of contamination when streams have a greater pollution load than groundwater. Additional significant variations in water nitrate contamination are caused by hyporheic zones and the interfaces of aquifers with silt and clay confining beds or riparian zones adjacent to streams, where significant denitrification has been observed.

Next, a description of the physio-chemical interactions and the possible impacts on nitrate contamination in different contexts (gaining and losing streams, riparian zones and hyporheic zones) is reported.

2.1 The impact of gaining and losing streams on nitrate contamination

The impact of GW-SW interactions on nitrate concentrations is different in gaining and losing streams.

Losing streams are responsible for two different situations, depending on the relationship between nitrate concentrations in groundwater and surface water. If nitrate concentrations in streams are higher

than in groundwater, the groundwater and surface water mixing causes increased contamination in the aquifer; this increase is more elevated in zones adjacent to streams. Kayabali et al. (1999) studied the influence of a heavily polluted urban river on an adjacent aquifer in Turkey. The river that recharged the adjoining aquifers influenced the groundwater quality; however, the groundwater contaminants were attenuated with respect to distance due to their dilution, and this effect was particularly substantial with nitrates.

In contrast, if nitrate concentrations are higher in groundwater than in streams, the nitrate pollution in aquifers can be reduced, especially near the stream. Bourg and Bertin (1993) used nitrate and dissolved oxygen as an environmental tracer; they observed the changes in chemical concentrations over short distances as water from the Lot River (losing stream) in France moved into its contiguous alluvial aquifer. In detail, the nitrate concentrations and dissolved oxygen in water decrease from the river to the groundwater because the biogeochemical processes during the infiltration of river water into the alluvial aquifer. Next, nitrate further increases along the infiltration path because of mixing with nitrate-rich alluvial aquifer water.

A detailed study of nitrate dynamics in the Pajaro River, a nutrient-rich losing stream in central coastal California, indicated that denitrification is also an important process in losing streams (Ruehl et al. 2007). A time series analysis of river water chemistry indicated that nitrate concentrations decreased downstream while concentrations of other major ions remained unchanged. Therefore, the dilution process could not explain the removal of NO_3 during transport, and the denitrification process was considered the most significant NO_3 sink along the studied reach.

In **gaining streams**, the features of groundwater flow systems substantially affect the nitrate concentrations in rivers. Nitrate-rich groundwater that flows into oxygenated aquifers and does not pass through an environment where denitrification occurred (riparian zones, wetlands or shallow organic-rich soils in the near-stream environment) (Fig. 2) discharges upward into streams without major chemical modification. In a study of two drainage basins in Maryland (USA), Böhlke and Denver (1995) observed that, when groundwater follows a relatively deep flow path in an oxic aquifer, nitrate removal by wetlands, forests or shallow organic-rich soils in a near-stream environment are largely insignificant if groundwater converges and discharges rapidly upward to the streams. In this situation, the presence of nitrate-poor groundwater that discharges into rivers can be connected to relatively old waters with low initial nitrate concentrations.

In contrast, nitrate contaminated groundwater that flows into a relatively thin aquifer beneath a shallow riparian zone or encounters reduced lithologies or an environment in which denitrification occurred (Korom 1992; Seitzinger et al. 2006) discharges upward to the streams with decreased nitrate concentrations (Fig. 3a). Denitrification can also occur when groundwater flows into an environment with depleted oxygen, following a deep regional flow system before discharging into a gaining stream (Fig. 3b).

2.2 The role of the riparian zone

Riparian zones represent the green interface between land and a flowing surface water body (Fig. 3a). These corridors have a very diverse selection of vegetation that provide numerous benefits to the streams they border; in particular, riparian buffer zones can mitigate the effects of non-point source pollution on water quality, particularly removing contaminants from groundwater before they enter surface-water bodies (Clement et al. 1993; Haycock et al. 1993; Gilliam 1994; Hill 1996; Alley et al. 1999; Puckett 2004; Seitzinger et al. 2006). However, not all riparian zones are equally efficient at removing NO_3^- from groundwater before it reaches stream channels (Hill 1996; Puckett et al. 2002; Puckett and Hughes 2005). The ability of riparian buffer zones to remove pollutants, particularly nitrate, from groundwater is primarily related to the presence of reducing conditions in the organic-rich, saturated sediments that commonly occur in riparian buffer zones. In reducing conditions, nitrates can be converted into N_2O, thus into N_2 (gas) through the microbially mediated process of denitrification (Korom 1992). Furthermore, abatement processes beneath the soil surface are also due to plant absorption of nutrients (nitrogen and subordinately phosphorous) in groundwater; the water level permitting this phenomenon has to be near the soil surface to improve interactions between the roots and nitrates in groundwater.

The most important characteristics affecting the performance of riparian buffer zones are their width and strip composition. In plain areas, nitrate abatement in riparian buffer zones can be very high, exceeding 80% of the original concentration in groundwater (Borin and Bigon 2002). Moreover, the effectiveness of riparian zones in removing a significant portion of the total groundwater N load depends to a large degree on the proportion of the groundwater that comes in contact with these zones (Bohlke and Denver 1995). McMahon and Böhlke (1996) reported that a net decrease in NO_3^- concentrations in the South Platte River, CO, was a result of denitrification in the riparian zones. Hill (1996) summarized the efficiency of stream riparian zones in regulating the transport of nitrates in groundwater flowing from uplands to streams. The removal rates ranged from 0 to 99% over a wide range of streams, with most sites exceeding 80% removal. Balestrini et al. (2011) evaluated the nitrogen buffering capacities of two narrow riparian strips along irrigation ditches located in a typical flat agricultural watershed on the alluvial plain of the Po River (Northern Italy). The results indicated elevated nitrate removal efficiency in both riparian areas due to the denitrification process and elevated groundwater residence times. Moreover, they indicated the joint role of riparian vegetation in both ecohydrological and biological processes. In fact, the water uptake by trees affects the subsurface flow pattern and contributes to the complete removal of nitrate in the riparian zone.

2.3 The role of hyporheic zone

In gaining and losing streams, water and dissolved chemicals can move repeatedly over short distances between the stream and the shallow subsurface below the streambed. The resulting subsurface environments, which contain variable proportions of water from ground water and surface

water, are referred to as hyporheic zones. This zone, consisting of saturated sediments beneath and beside the active channel in which groundwater and surface water mix, has size and geometry that vary greatly in time and space (up to several metres in depth and hundreds of metres in width) (Alley et al. 1999). The hyporheic zone has an enhanced biogeochemical activity compared to groundwater and surface water (Winter et al. 1998; Edwardson et al. 2003; Jonsson 2003; Kazezyılmaz-Alhan and Medina 2006; Seitzinger et al. 2006; Puckett et al. 2008). This is a result of the flow of oxygen-rich surface water into the subsurface environment, where bacteria and geochemically active sediment coatings are abundant. This input of oxygen into the streambed stimulates a high level of activity by aerobic microorganisms, if dissolved oxygen is readily available. It is not uncommon for dissolved oxygen to be completely used up in hyporheic flow paths at some distance into the streambed, where anaerobic microorganisms dominate the microbial activity. Thus, anaerobic bacteria can use nitrate, sulphate, or other solutes in place of oxygen in metabolism (Fig. 4). Therefore, the hyporheic zone acts as an active site of biogeochemical transformations, regulating the flux of nutrients between ecosystems (Jones et al. 1995; Hedin et al. 1998; Dahm et al. 1998; Duff et al. 1998; Baker and Vervier 2004, Triska et al. 2011). More specifically, the hyporheic zone may serve as a sink for NO_3^-, both in the streams and in the groundwater before it reaches the surface-water bodies (Lowrance et al. 1984; Pinay et al. 1994; Jones and Holmes 1996; McMahon and Böhlke 1996; Hedin et al. 1998; Hill et al. 1998; Hill 2000; Hinkle et al. 2001; Schade et al. 2002; Sabater et al. 2003; Vidon and Hill 2004; Pretty et al. 2006; Puckett et al. 2008). Hydrologic exchange as a pathway for nutrient retention is maximized in sinuous, unconstrained rivers (Dahm et al. 1998; Malard et al. 2006). However, other authors found that the hyporheic zone plays a role as an N source to surface waters, especially in relatively pristine N-limited streams (Duff and Triska 1990; Holmes et al. 1996; Duff and Triska 2000; Triska et al. 2011). These studies support the conceptual model hypothesized by Jones and Holmes (1996), stating that hyporheic zones in NO_3^--rich streams may act as NO_3^- sinks, whereas in NO_3^- poor streams may act as NO_3^- sources. Hyporheic exchange has been observed in rivers gaining groundwater (Bayani Cardenas 2009), in base flow–influenced rivers such as low-order mountain streams (Harvey and Bencala 1993), and in streams losing net water, such as in semiarid climates (Dent et al. 2007; Harvey et al. 2003).

3. Study area

The study area is located in Piedmont (Northwestern Italy) and correspond to the Turin-Cuneo plain. It has a maximum altitude of 600 m above seal level (a.s.l.) in the southern sector and a minimum altitude of 200 m a.s.l. in the eastern sector, corresponding to the confluence of the Stura di Demonte River and Tanaro River. This plain is underlain by an important groundwater resource due to its size, the characteristics of sediments and due to the relatively high rate of recharge in the region (Bove et al. 2005).

3.1 The hydrological and hydrogeological setting

Four superposed hydrogeological complexes, different in grain size and permeability of sediments, are present in the Turin-Cuneo plain. The following complexes occur from bottom to top: the pre-Pliocene complex (a and b in Fig. 5), the Pliocene marine complex (c and d in Fig. 5), the villafranchian transitional complex (e in Fig. 5), and the Quaternary alluvial deposits complex (f and g in Fig. 5) (Fig. 5; Fig. 6) (Bortolami et al. 1976; Comazzi M. et al. 1988; Bove et al. 2005; De Luca et al. 2007; Lasagna and De Luca 2008).

The pre-Pliocene complex consists of **alpine crystalline basement rocks** and **marine deposits of the Tertiary Piedmont Basin (TPB)**. The alpine rocks are mostly impermeable or slightly permeable by fissuration; locally karstic circuits can exist in calcareous rocks. The marine deposits of TPB consist of highly consolidated sediments, mainly comprised of marl, sand and clay, with gravel only found locally. These sediments, locally permeable by fissuration, have a notably low permeability and do not contain any significant aquifers.

The **Pliocene marine complex** (Lower-Middle Pliocene) consists of the Lugagnano Clay, with low permeability that forms an aquitard, and the Asti Sand, with a variable permeability, that constitutes a locally important aquifer.

The **villafranchian transitional complex** (Middle Pliocene-Lower Pleistocene), consisting of alternating clayey silt, sand and small gravel, forms a multilayer aquifer in which the sandy and gravelly permeable layers host significant semi-confined aquifers.

Finally, a shallow unconfined aquifer exists in the **alluvial deposits complex** (Middle Pleistocene-Holocene), formed by coarse gravel and sand, with subordinate silty-clayey intercalations, showing a generally high permeability. This complex represents an important aquifer whose water table is directly connected to surface drainage in the region.

The Poirino Plateau, located on the eastern side of the Turin-Cuneo Plain, is divided by Asti Hill on the east by a high terrace of approximately 100 m. The plateau has the same litho-stratigraphical sequences as Turin-Cuneo plain; however, the Quaternary alluvial deposits complex, with a thickness between 10 and 30 m, is constituted of silt and clay with rare gravely-sandy intercalations.

Grain size is variable and normally decreases from mountains to low plain along the Po River. The shallow aquifer, hosted in the alluvial deposits complex, is mainly supplied by direct rainfall and rivers at the outlet of the valleys on the plain. This hydrogeological complex has a general thickness ranging between 20 and 50 m; in spite of the variable thickness of the aquifer, it has a high productivity and has regional importance. The base of the shallow aquifer is generally well marked due to the textural variability of the deposits (Canavese et al. 2004; Bove et al. 2005). This base is usually identified by the presence of thick and relatively continuous layers of silt or clay-rich deposits. The deep aquifers are hosted in the villafranchian transitional complex and in the Pliocene marine complex.

In the Turin-Cuneo plain, the piezometric surface of the shallow aquifer normally follows the general topography of the land surface and isopiezometric lines are generally placed parallel to the Alps (Fig. 7). The groundwater generally flows from the southwest to northeast on the southern part of the plain,

and from south to north on the northern part. High terraces modify the morphology of potentiometric lines. In the southeastern sector of the Turin Plain (Poirino Plateau), the groundwater generally flows towards the west, i.e., towards the Po River, which represents the main watercourse of the study area. In detail, the groundwater flows from the north and from the south towards a minor stream (Banna S.), which is the most important local draining element.

In the northern sector of the Turin-Cuneo plain (Turin Plain), the hydraulic gradient of the shallow aquifer varies between 3%, e.g., at the edge of the Alps and 0.1% in the low plain. Along the transitional zone, from the higher to lower plain, a decrease in the hydraulic gradient, from 0.6% to inferior than 0.3% values, was generally observed and typical lowland springs (*fontanili*) emerge (De Luca et al. 2014). In the centre of the Turin-Cuneo plain, the hydraulic gradient normally ranges between 0.01% in the central sector and 0.25% near the Alps. On the south of the Cuneo plain, the hydraulic gradient is high near the Alps (0.2%) and decreases to 0.02% towards the central plain.

The depth to groundwater in shallow unconfined aquifers varies significantly, moving from the high plain to the low plain. On the low plain and near the rivers, the water table is generally less than 5 m deep, whereas it reaches depths of between 20 and 50 m close to the Alps. On the *fontanili line* (the transition zone from the high to low plain where *fontanili* occur), the depth to groundwater varies from 1 to 3 m. On the Poirino Plateau, the groundwater depth is generally low (0-5 m) and increases towards the south sector.

The main rivers on the Turin plain (Fig. 5) are the Po River and its tributaries, i.e., the Maira and Varaita streams on the Cuneo plain, and Pellice and Chisola streams on the Turin plain. The Tanaro River and Stura di Demonte River are very important watercourses on the Cuneo plain.

The shallow aquifer is strongly connected to the hydrographical net. Normally, the main watercourses appear to be losing rivers, giving water to the groundwater system, only close to the Alps. In the centre of the plain, the groundwater discharges into the main rivers (gaining streams). The Po River appears to be the most important gaining stream, based on size and flow rate, on the Turin-Cuneo plain. On the Poirino Plateau, the shallow groundwater discharges into the streams. In the south, near Cuneo, the main rivers are embedded between two high terraces and groundwater has a piezometric level that is higher than surface water; therefore, the Gesso River, Stura di Demonte River, Pesio River and Tanaro River receive water from the groundwater. Locally, the groundwater flows towards or away from the rivers and streams, depending on the relative water level in the groundwater and the surface water features.

Deep confined and semiconfined aquifers, hosted in the villafranchian transitional complex and in the Pliocene marine complex (Asti sand), have a flow direction generally similar to the shallow aquifer. Only locally the flow directions are very different, as reported in Lasagna et al (2014) for the Poirino Plateau.

Few studies have been conducted on the interaction between deeper aquifers and the shallow aquifer and most of all on its extent. In the Turin Plain, between the Alps and the Turin Hill, the presence of marine pliocenic and pre-pliocenic fine sediments (Lugagnano Clay and deposits of TPB) in the

subsoil likely favours the rise of deep groundwater (De Luca and Ossella, 2014). Moreover since the Po River and the Stura di Demonte River represent the base-level of the regional flow system, deep groundwater mixes with shallow groundwater near these rivers.

3.2 The land use

The study area consists of the plain comprised between Turin and Cuneo cities. It is essentially an agricultural zone (Regione Piemonte 2008), in which the main cropping systems are cereals and forages. Also livestock farming are highly developed, mainly cows and pigs.

In Bassanino et al. 2011, the Piedmont plain was divided in 5 Macro Land Units (MLUs) representing five different agro-environments. These MLUs are characterized by different soil properties, land uses, farming system attributes and main crop productivity. The Turin-Cuneo Plain is comprise in MLU3 for the central part of the plain, and MLU4 only for the zones located close to the Alps and the hills. MLU3 is a widely irrigated, highly productive maize-based area and MLU4 is a scarcely irrigated, but productive grass-based area. MLU3 and MLU4 represents the MLUs with highest livestock levels in Piedmont. Furthermore MLU3 shows a lower livestock density, but many more farms housing animals. This area is where swine, dairy cows, or bulls are bred in Piedmont. In MLU4 livestock husbandry is widespread, but with low farm stocking rates. Bovine breeding are conducted extensively on large grassy surfaces. Irrigation is not common due to a colder climate.

The main cities are Turin in the northern part of the plain, and Cuneo in the southern one. In the small towns domestic waste water is locally not connected to sewerage. Industrial areas are mainly located in the peripheral areas of Turin while mining areas are located near the main streams, especially the Po River, for the extraction of gravel and sand.

The land use in Turin-Cuneo plain is the cause of a diffuse nitrate contamination of groundwater, especially for the shallow aquifer. The cereals (maize and wheat), indeed, are generally fertilised with manure of intensive livestock production or synthetic nitrogenous fertilizers. It follows in an excess of nitrate in the soil and consequently in groundwater (Lasagna et al 2013). Previous studies of isotopic composition of NO_3 ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) in groundwater in two small areas of Turin-Cuneo plain indicated that nitrate contamination originates from the associated input of synthetic fertilisers and manure or septic tank effluents (Lasagna et al 2006; Debernardi et al 2008).

In Debernardi et al (2008) a study conducted in the Piedmont Region plain highlighted highest nitrate concentrations in areas characterized by mixed sowable land and alternated lawns, and by land sown with corn-wheat; medium nitrate levels were observed in urbanized areas, rice fields and areas where orchards, hazel grows and vineyards are planted; less important nitrate concentrations were detected in permanent lawns. The lowest nitrate concentrations (below 50 mg/l) were detected in areas where there are mixed broadleaf and poplar grove plantations.

In Bassanino et al. 2011, the nutrient budgets were calculated for each MLUs. Conceptually, the nutrient budget is a mass balance between nutrients exported with the harvested crops and forages,

and nutrient inputs to the soil from both natural and agricultural sources. As expected, the highest nutrient surpluses were detected in the most intensely managed area (MLU3).

4. Materials and methods

In this study, nitrate concentration both in shallow aquifer and in rivers are used to create nitrate concentration profiles. All data are referred to March - April 2004, because of the completeness and representativeness of the database.

Shallow groundwater data were sampled from 341 monitoring points. Particularly 155 groundwater sampling points are referred to wells and piezometers of the Monitoring Network of the Piedmont Region, managed by the Regional Agency for the Protection of the Environment (ARPA Piemonte). The piezometers have generally screens extended over the full saturated thickness of the shallow aquifer. The wells, mostly private, were selected for the regional monitoring network according to their features, compatible with the use (depth, screens, location, density of observation wells...) (De Luca et al, 2004). The chemical analysis of nitrate, also determined by ARPA Piemonte, are part of a larger half-year monitoring campaign, performed in the shallow aquifer of the whole Piedmont region, in order to evaluate the quality of groundwater.

The remaining 186 points correspond to private wells, sampled and analysed by the Earth Sciences Department of Turin University. All groundwater sampling points are referred to the shallow aquifer, according to the map of the bottom of the shallow unconfined aquifer (Deliberazione della Giunta Regionale 34-11524 del 3 giugno 2009) and are screened in the shallow aquifer system. The location of the groundwater sampling points (Fig. 8) was chosen at a distance not less than 1 km from the rivers, to avoid pumping wells that draw surface water.

The water sampling methods and analytical techniques are reported in APAT - IRSA (2003).

The nitrate levels data, homogeneously distributed in the study area, permitted to delimit nitrate-contaminated areas in the shallow aquifer.

The chemical analyses of surface water were performed by ARPA Piemonte as part of a monthly monitoring campaign in Piedmont rivers. The reported chemical analyses correspond to 12 rivers (Banna, Chisola, Gesso, Grana, Maira, Pellice, Pesio, Po, Sangone, Stura di Demonte, Tanaro and Varaita). The data inserted in Fig. 8 are referred to as the average nitrate concentration for a period from March to April 2004.

Finally, six nitrate concentration profiles were developed, connecting groundwater sampling points intersecting the main streams on the Turin-Cuneo plain. Three profiles were located on the southernmost part of the plain, intersecting the Varaita, Maira, Grana, Pesio and Stura di Demonte rivers; three additional profiles cross the northern sector of the plain, intersecting the Chisola, Lemina, Po, Varaita and Maira rivers. In the profiles, the nitrate concentrations, the piezometric level of the shallow aquifer and the intersections of the profile with streams are reported. Therefore, the profiles allowed for the assessment of nitrate levels in groundwater and the mutual influence of GW-SW.

5. Results

5.1 Distribution of nitrate in groundwater and surface water

In shallow aquifer, the nitrate concentrations are very different. The map of nitrate distribution is reported in Fig. 8. In Italy the maximum nitrate concentration in drinking water is 50 mg/L (Decreto Legislativo 31/2001). Most of the contaminated groundwater is located in Poirino Plateau where the nitrate concentration exceeds 100 mg/L and reaches up to 320 mg/L, and in the sector on the right banks of the Stura di Demonte River, where shallow groundwater introduces nitrate concentrations higher than 90 mg/L. Nitrate concentrations ranging between 50 mg/L and 75 mg/L were measured on the left banks of the Stura di Demonte River, in the area along the Stura di Demonte River and Varaita Stream, in the sector connecting the towns of the Savigliano and Racconigi, and locally downstream from Pinerolo town.

Nitrate concentrations in groundwater generally increase from the Alps to the low plain. More specifically, in the Turin-Cuneo plain, as in the entire Piedmont plain, the maximum nitrate concentrations are always measured at monitoring points that are located at low altitudes; in contrast, low concentrations are measured at sampling points that are at both low and high altitudes (Debernardi et al. 2008).

In surface waters, nitrate concentrations are very variable. The maximum yearly concentration in rivers in 2004 never exceeded 50 mg/L. The medium nitrate concentration in surface water, measured between March - April 2004, ranged between 2 mg/L and 27 mg/L. Even if the nitrate concentrations in rivers and groundwater are not comparable, the concentration trend is similar. In fact, the maximum nitrate concentrations in the surface water are generally found in areas with high groundwater nitrate levels. Specifically higher nitrate concentrations in surface waters are present in Poirino Plateau and in the sector connecting the towns of Savigliano and Racconigi. Moreover, nitrate concentrations in rivers increase from higher altitudes near the Alps to the plain: e.g., the nitrate concentrations rise from 2.5 mg/L to 13 mg/L in the Stura di Demonte River, from 7.7 mg/L to 18 mg/L in the Po River, and from 5 mg/L to 24 mg/L in the Maira Stream. The nitrate enrichment from the Alps to the low plain is common in both surface water and in groundwater. It is due to the high input of nitrogenous fertilizers (synthetic N-fertilizers and organic manure) applied. The nitrate input from agricultural activities is heavier on the lower plain (discharge zones) than in the elevated zone (recharge areas) (Bassanino et al. 2011). Therefore, a progressive increase in dissolved nitrate in the groundwater can be observed due to the constant build-up of nitrates, continuously added by the transport and nitrification of fertilizers.

5.2 Nitrate concentration profiles

The six nitrate concentration profiles (Fig. 8 and Fig. 9) in only the Po River and the Stura di Demonte River, the most important gaining stream of Turin-Cuneo plain in terms of dimension and discharge, show an effect on the nitrate concentration in groundwater at the study scale. In the alluvial deposits close to the rivers, the groundwater exhibits lowering nitrate levels. Other rivers do not indicate, at the study scale, attenuation or increases in nitrate concentrations in the groundwater. Specifically, in the profile A-A', located in the high Cuneo plain close to the Alps, the groundwater nitrate concentrations are lowered coming from Cuneo plain (approximately 30 mg/L) to the areas close to the Stura di Demonte River (3 mg/L). In the stretch of the river crossed by the profile, the nitrate level is approximately 6 mg/L. In the profile B-B', low nitrate concentrations (approximately 20-25 mg/L) are highlighted at the ends of the profile, corresponding to the plains near the Alps. In the centre of the plain, characterized by significant agricultural activity and the accompanying intensive N-fertilizer use, nitrate concentrations are high and very high, up to 73 mg/L. In the area close to the Stura di Demonte River that exhibits a nitrate concentration of approximately 7 mg/L, the nitrate levels are substantially lower. The C-C' profile exhibits the same nitrate concentration trend as the B-B' profile. In the D-D' profile, elevated nitrate concentrations (higher than 50 mg/L) are present at the end of the cross section, corresponding to the central part of the Turin plain. In the two areas, one downstream from the town of Pinerolo and one close to the town of Racconigi,, there are significant agricultural activities. Lower nitrate concentrations (10-15 mg/L) are highlighted approaching the Po River, which in this stretch has a nitrate concentration of approximately 20 mg/L. The E-E' profile crosses an uncontaminated area, with nitrate concentrations lower than 5 mg/L, on the left banks of the Po River and a highly polluted area, with nitrate concentrations up to 84 mg/L, on the right banks. The Po River has nitrate concentrations of approximately 19 mg/L. The F-F' profile exhibits a trend similar to the E-E' profile. However, crossing the Poirino Plateau, it highlights very high nitrate levels, up to 135 mg/L. Close to the Po River, the nitrate concentration in the groundwater is very low at less than 5 mg/L.

6. Discussion

An investigation of the nitrate concentrations in groundwater and surface water in the Turin-Cuneo plain highlights that even if the nitrate levels in rivers and groundwater are not comparable, the concentration trends are similar. More specifically, nitrate concentrations increase from the Alps to the low plain in both surface water and groundwater. Therefore, maximum nitrate concentrations in surface water are generally measured in areas with high nitrate levels in groundwater. Nitrate concentrations are particularly high in the low plain agricultural areas, where an elevated input of nitrogenous fertilizers (synthetic N-fertilizers and organic manure) is applied. Bassanino et al. (2011) described these areas as the most intensely managed areas in Piedmont (highly productive maize-based area and with high livestock levels), characterised by the highest nutrient surpluses to soil.

The situation described refers to a period distinguished by a large amount of nitrate level data both in groundwater and in rivers. Franchino et al. (2014) highlighted that the area distribution and levels of nitrate pollution in groundwater remained quite the similar from 2000 to 2012. The authors observed

that nitrate concentrations in the Piedmont plain aquifers exhibited no statistically significant trends over time in the study period. Therefore, this paper is consistent with the current situation of contamination in groundwater.

Nitrate levels in the deep aquifers are generally low, inferior than 50 mg/L in the whole plain. Lasagna et al. (2015), using a diagram of nitrate concentration versus well depth, highlighted that higher nitrate concentrations (>50 mg/L) are always present in superficial wells with depths lower than 50 m; on the contrary, in wells with depths higher than 50 m, nitrate concentrations are generally lower than 50 mg/L. Deep aquifers generally show low nitrate concentrations because of the high degree of natural protection from surface contamination compared with shallow aquifers and because of the role of denitrification occurring in the reducing conditions that normally take place in deep aquifers. Debernardi et al. (2005) analysed the Fe, Mn and NH_3 presence generally occurring in reducing waters, in Piedmont groundwater. More specifically, they investigated concentrations in the deep and shallow aquifers. Their study indicated that Fe, Mn and NH_3 are mainly characteristic of deep aquifers. The diagrams of Fe, Mn and NH_3 levels versus nitrate also highlighted an inverse correlation of these parameters: low Fe, Mn and NH_3 concentrations are usually associated with high nitrate levels and vice versa. However, the study of geochemical conditions also sustains the local presence of conditions supporting denitrification in the shallow aquifer. Debernardi et al. (2005) highlighted the establishment of reducing conditions, proven by the presence of Fe, Mn, NH_3 and NO_2 especially in the Poirino Plateau, and locally in the Turin-Cuneo Plain.

The role of the shallow aquifer of the Turin-Cuneo Plain in supporting the denitrification process was also highlighted in Lasagna et al (2006) and Debernardi et al (2008). In these studies the isotopic composition of NO_3 ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) in groundwater were used both to evaluate nitrate contamination sources and to identify geochemical processes (e.g. the denitrification) occurring in the shallow aquifer of two pilot sites. A pilot site was located in the Poirino Plateau, whereas the other one in the center of the Cuneo Plain, between the towns of Racconigi and Savigliano. These areas have very different hydrogeological features but very high nitrate concentration in aquifer, superior than 50 mg/L.

In the Poirino Plateau pilot site, six groundwater samples were collected in wells drilled in the shallow aquifer. The groundwater samples showed nitrate concentrations between 32 and 200 mg/L, δ15N between 5.9 and 16.6‰, and $\delta^{18}O$ between 8.8 to 14.7‰. The authors interpreted the isotopic composition as derived from the associated input of synthetic fertilisers and manure or septic tank effluents. Moreover, a significant denitrification phenomenon was assessed; particularly, it was possible to identify two samples as poorly denitrified (with a denitrified nitrate percentage of 5%) and two samples as highly denitrified, with a denitrified nitrate percentage up to 45% compared to the original composition.

In the Cuneo Plain pilot site, six groundwater samples were collected in the shallow aquifer. The nitrate concentration ranged between 81 and 132 mg/L, $\delta^{15}N$ between 7.6 and 11.3‰, and $\delta^{18}O$ between 6.5 and 12.2‰. Also in this pilot site nitrate in groundwater was interpreted as the

associated input of synthetic fertilisers and manure or septic tank effluents. However only one sample showed an isotopic composition connected to a denitrification process, with a denitrified nitrate percentage of 15%.

The role of the shallow aquifer in supporting the denitrification process was further confirmed by the correlation diagram between $\delta^{15}N$ and NO_3/SO_4. In the Poirino Plateau pilot site the diagram showed a progressive decrease of the ratio NO_3/SO_4 and an increase of the $\delta^{15}N$, typical of denitrification process. In the Cuneo Plain pilot site one sample of water showed this correlation.

Analysis of nitrate concentration profiles across the shallow aquifer in the Turin-Cuneo plain and the intersecting main streams highlighted the mutual influence of GW-SW. The most important streams on the plain, in terms of dimension and discharge, are the Po River and Stura di Demonte River, both gaining streams. Their presence appears to affect the nitrate concentration in groundwater at the study scale. In fact, groundwater exhibits lowering nitrate levels close to these rivers, reaching concentrations below 5 mg/L. Other rivers do not indicate, at the study scale, attenuation or increases in nitrate concentrations in groundwater. The nitrate concentration decreases close to the gaining streams on the Turin-Cuneo plain, which may be due to the flow path of groundwater discharging into the river. The deep groundwater recharge zone is located in areas close to the Alps (Bove et al. 2005), where agricultural activities are minimal (grass-based area; Bassanino et al. 2011); the unpolluted or low polluted groundwater follows a deep regional flow system before discharging into the rivers on the low plains (Fig. 10).

As the Po River and the Stura di Demonte River represent the base-level of the regional flow system, deep groundwater mixes with shallow contaminated groundwater near these rivers. Thus, the dilution process is able to decrease the nitrate concentrations. Moreover, deep groundwater, following a deep regional flow system, passes through an environment depleted of oxygen before discharging into the gaining streams and is thus prone to denitrification. Furthermore, shallow groundwater that is rich in nitrate flows beneath the riparian buffer zone, especially along the Po River, and can discharge upward to streams with decreased nitrate concentrations. The role of the riparian buffer zones in supporting denitrification in the alluvial plain of the Po River was also confirmed by previous studies (Balestrini et al. 2006; Balestrini et al. 2011). As a consequence, riparian buffer zones likely enhance the quality of groundwater.

Finally, the role of hyporheic zones, in which groundwater and surface water mix, is not negligible. More specifically, hyporheic zones could play a significant role in the removal of nitrogen from the Po River and the Stura di Demonte River due to denitrification and mixing between river water and groundwater in the riverbed sediments.

It is important to highlight that this conceptual model is based on a limited range of data and more research is needed to better define the actual role of the described processes and environments, especially the roles of riparian and hyporheic zones.

7. Conclusions

GW-SW interactions are of considerable importance in the study of nitrate contamination of aquifers because the rivers can create conditions that increase or attenuate nitrates in groundwater.

In this study, the Po River and the Stura di Demonte River act as gaining streams in the Turin-Cuneo Plain (Northwestern Italy). The proposed conceptual model suggests that the near stream environment and the way the groundwater flows before discharging into the stream highly affect nitrate concentrations. In fact, the presence of a denitrifying environment (riparian zone, wetland, hyporheic zone and shallow organic-rich soils in the near-stream environment) can influence the nutrient concentrations in groundwater, which discharge upward to the streams with decreased nitrate concentration. In fact, nitrate concentration profiles exhibit lowering nitrate levels close to these rivers.

However, knowledge about not only the near-stream environment but also about the flow system is important. On the Turin-Cuneo Plain, the deep groundwater recharge zone is located close to the Alps where agricultural activities are limited and groundwater is unpolluted. The groundwater then follows an anoxic deep regional flow system before discharging into rivers on the low plain. Next, contaminated shallow groundwater mixes with low nitrate deep groundwater and the dilution process decreases the nitrate concentration.

A complete understanding of the nitrate contamination phenomenon cannot be separated from proper knowledge about the processes in place. The proposed conceptual model is supported by abundant data about nitrate concentrations, especially in surface water and groundwater. However, no quantitative data are available for riparian and hyporheic zones or about the denitrification processes in these environments. Consequently, it is not possible to determine the real importance and the impact of each environment on nitrate concentrations. This topic should be the subject of further studies in other hydrogeological settings to clarify and deepen understanding of the role of GW-SW interactions in nitrate contamination processes.

Therefore, better understanding of the GW-SW interactions and near stream environment could provide key scientific insights for the integrated management of water resources.

8. References

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Captions:

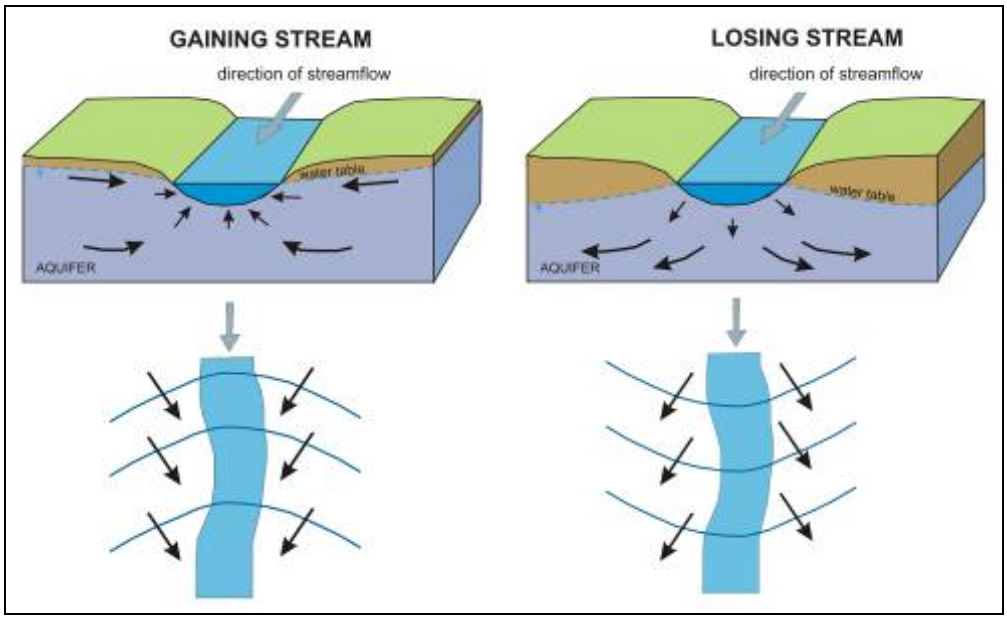

Figure 1: Schematic sketch (section and plan) of a gaining stream (a) and a losing stream (b).

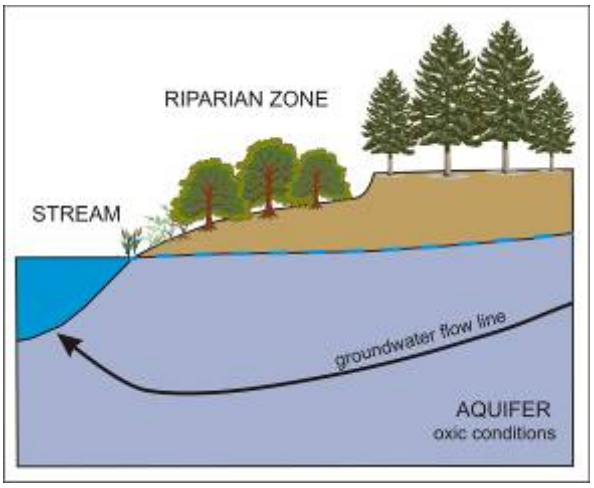

Figure 2: Nitrate-rich groundwater that flows into oxygenated aquifers discharges upward into streams without major chemical modification.

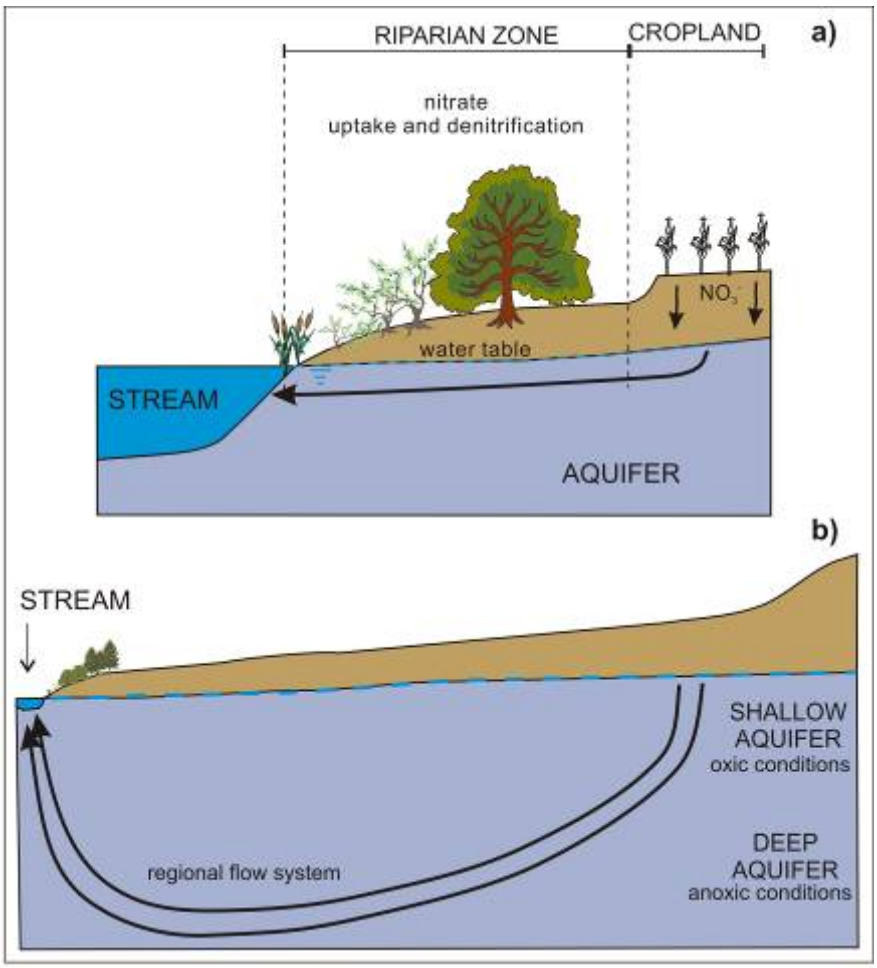

Figure 3: Situations that enhance the denitrification process and thus nitrate abatement: the riparian zone (a) and the deep regional groundwater flow system in an anoxic environment (b).

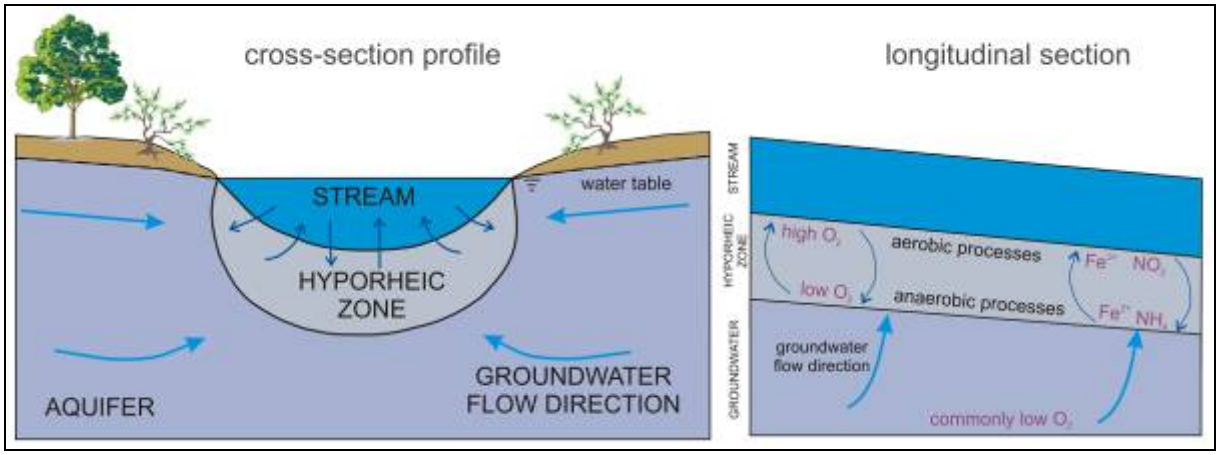

Fig. 4: In the hyporheic zone, surface water and groundwater mix, enhancing biogeochemical activity and improving water quality (modified form Winter et al. 1998).

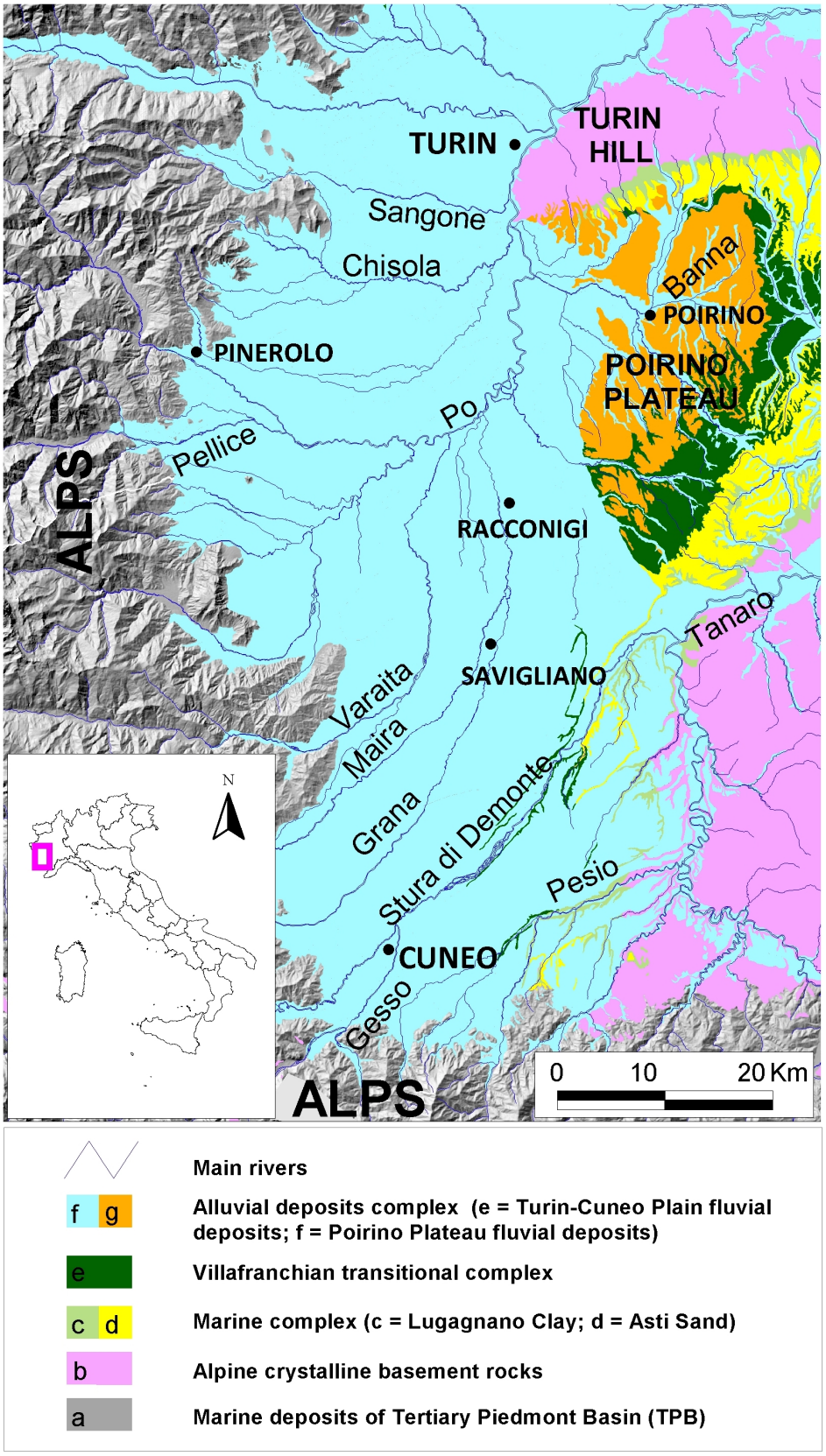

Figure 5: Simplified hydrogeological sketch of the Turin-Cuneo plain.

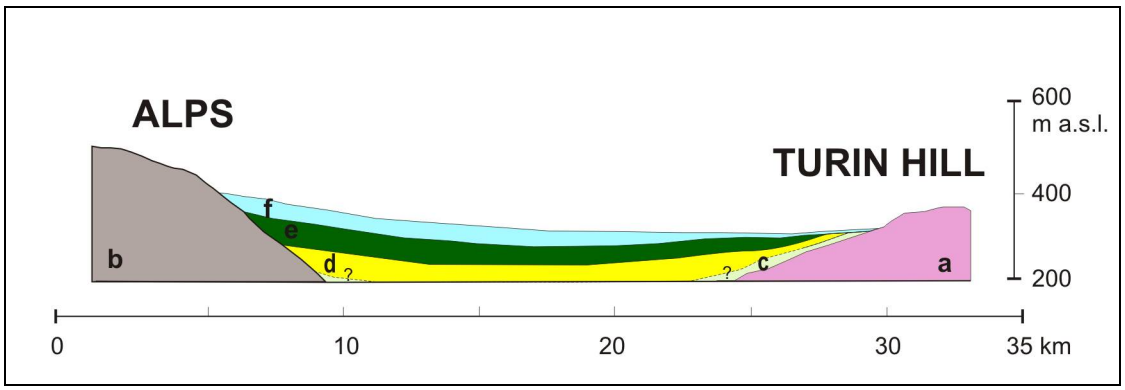

Figure 6: Simplified hydrogeological section of the Turin plain (the numbers are referred to in Fig. 5).

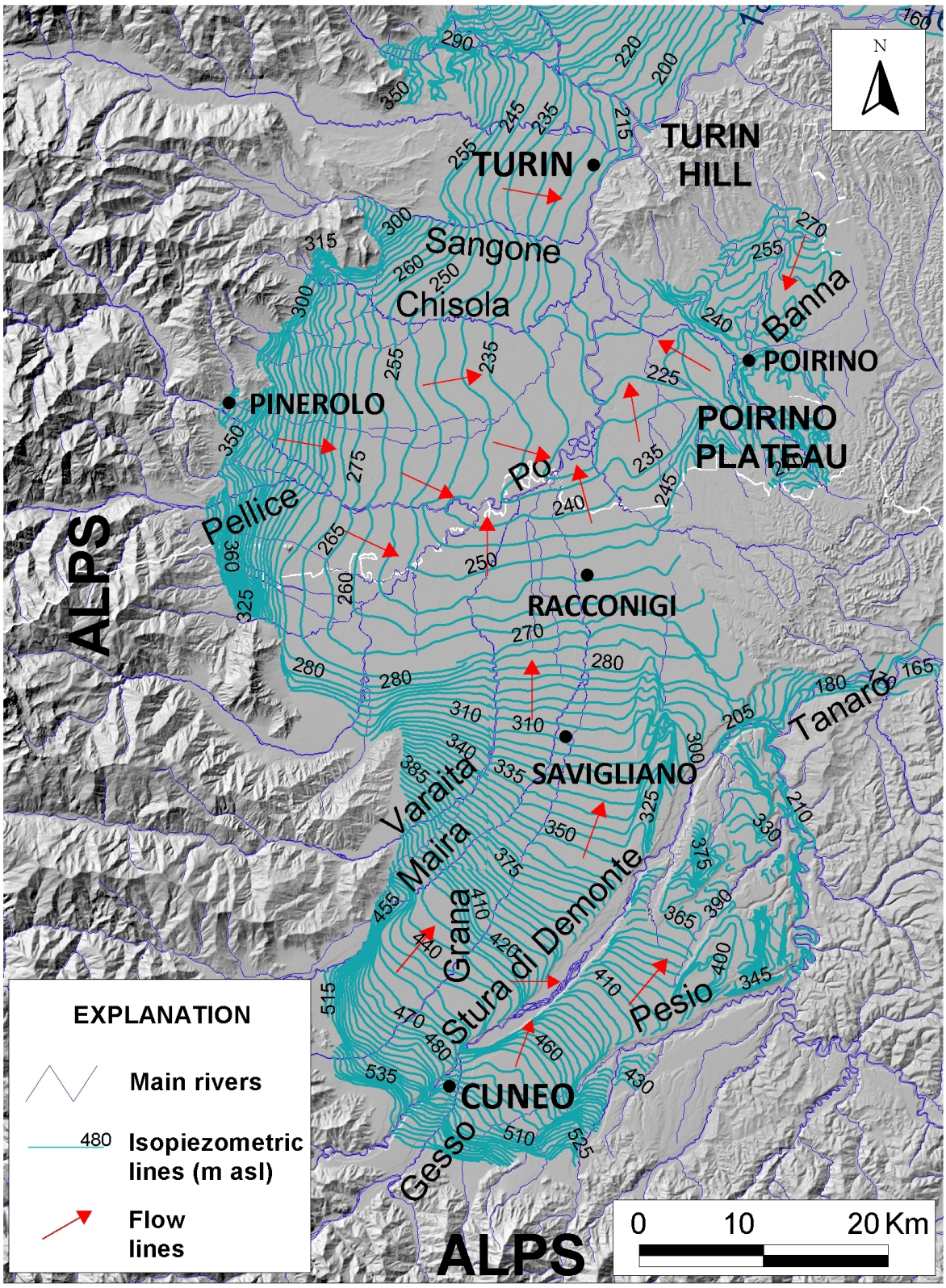

Figure 7: Water table map of the shallow unconfined aquifer on the Turin-Cuneo plain (June-July 2004).

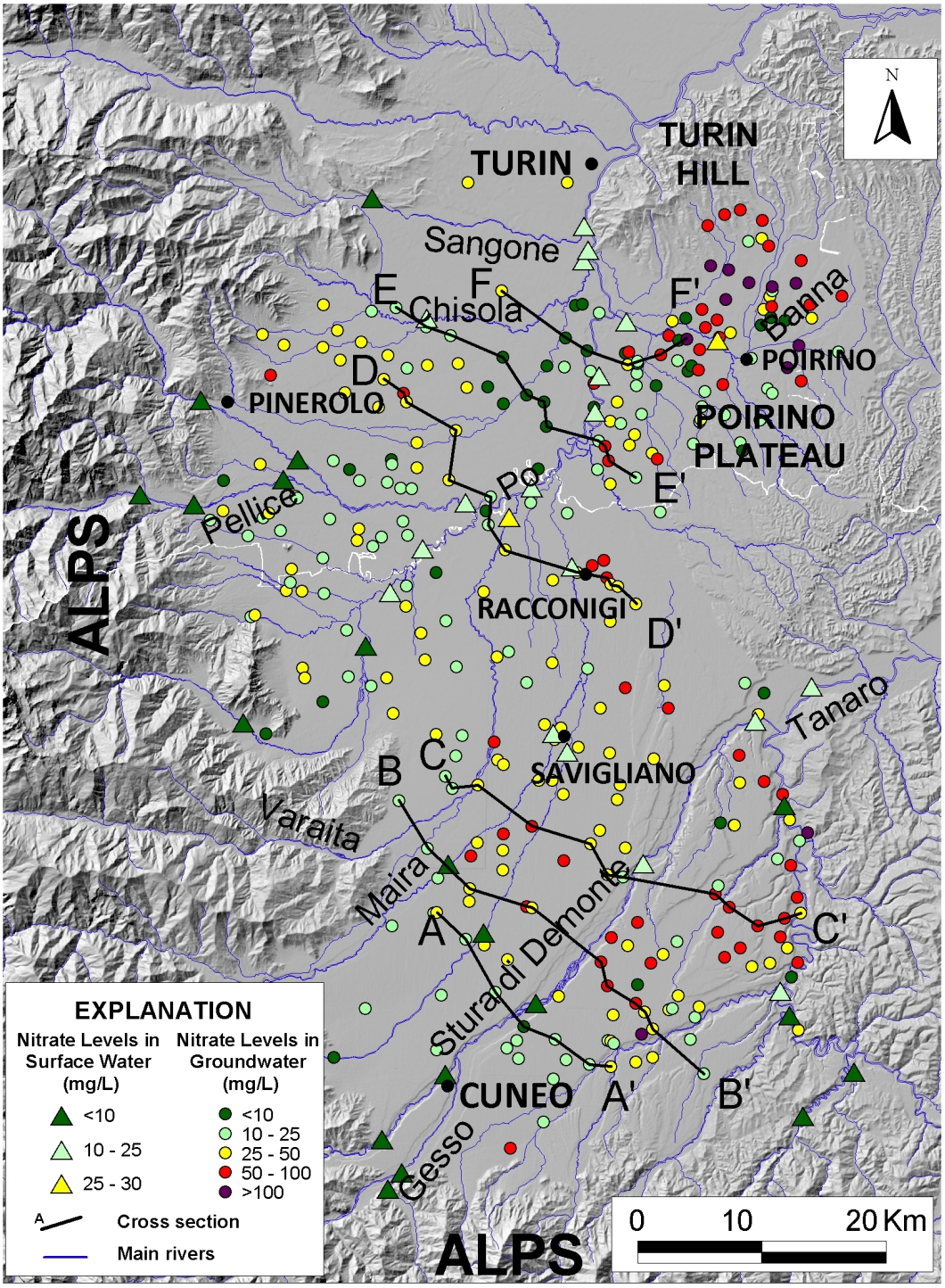

Fig. 8: Nitrate distribution in surface water and groundwater of the shallow aquifer on the Turin-Cuneo plain (March – April 2004). In the figure, the traces of six nitrate concentration profiles are reported.

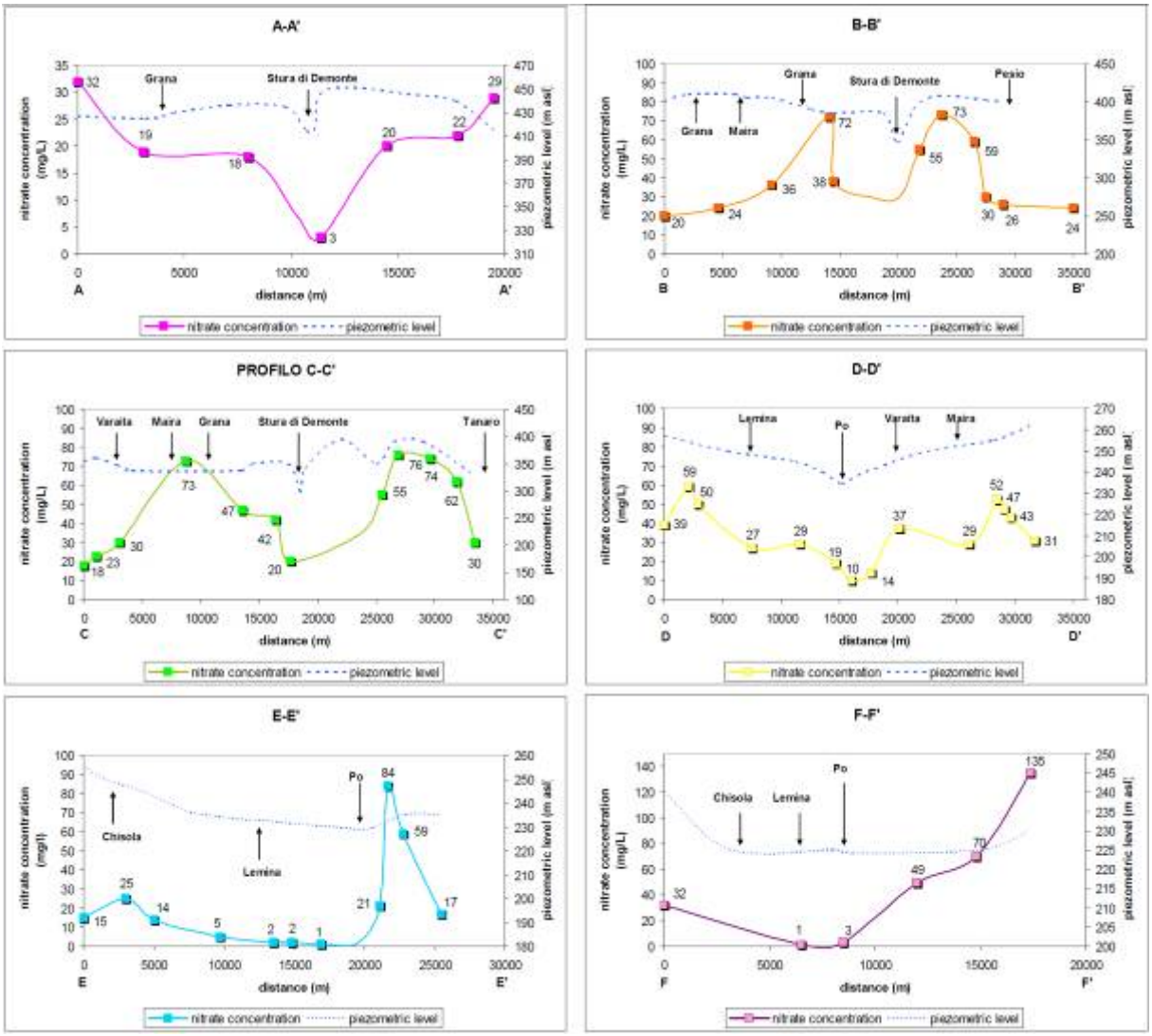

Figure 9: Nitrate concentration profiles in the shallow aquifer on the Turin-Cuneo plain; in the diagrams, the solid line represents nitrate concentrations in the spring of 2004; the dotted line represents the piezometric level in the summer of 2004; the arrows indicate the intersections between the profiles and watercourses.

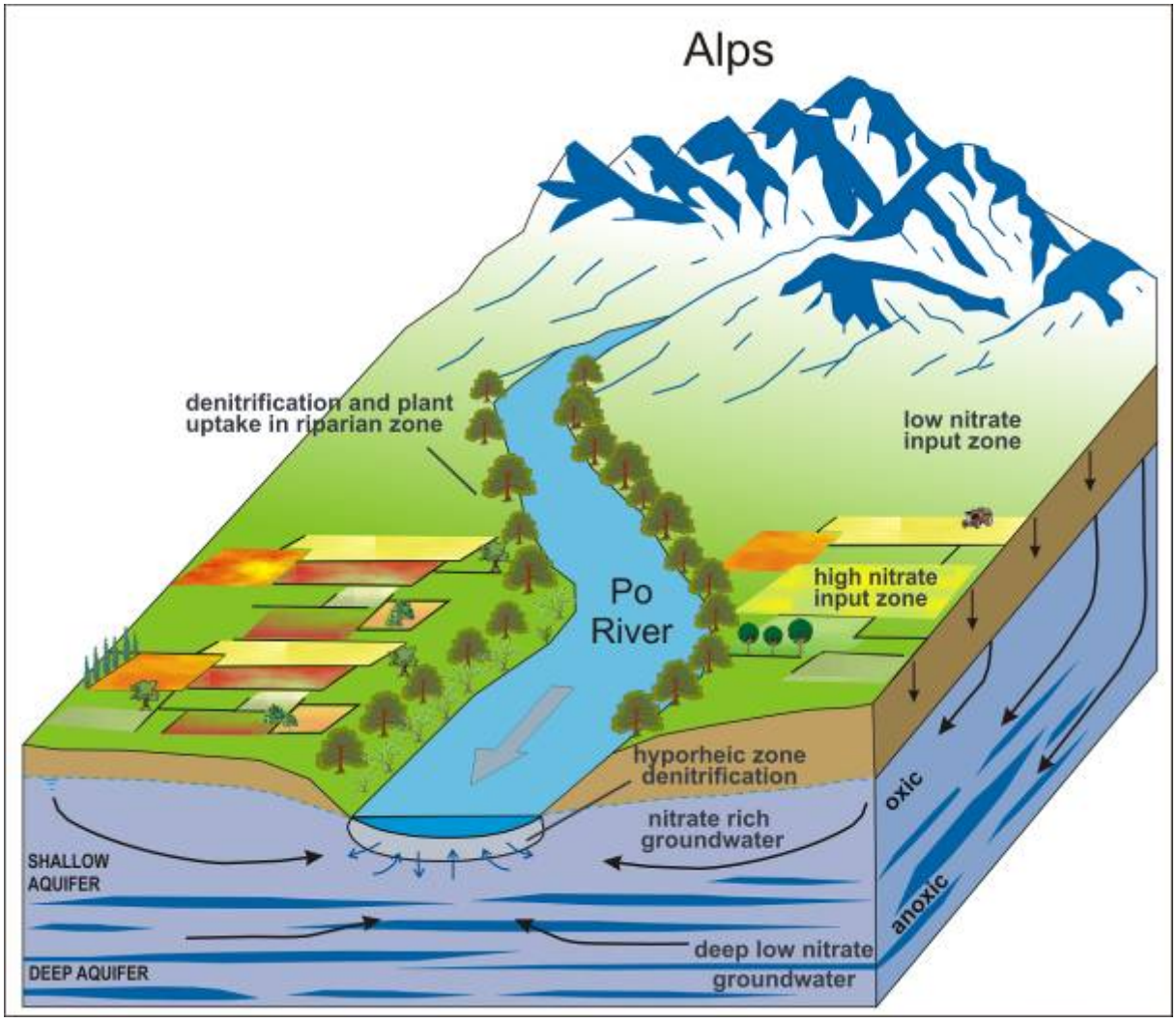

Fig. 10. Suggested conceptual model of the GW-SW interaction on the Turin-Cuneo Plain and the effects of nitrate contamination based on existing data.