# The use of multilevel sampling techniques for determining shallow aquifer nitrate profiles

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## ABSTRACT

Nitrate is a worldwide pollutant in aquifers. Shallow aquifer nitrate concentrations generally display vertical stratification, with a maximum concentration immediately below the water level. The concentration then gradually decreases with depth. Different techniques can be used to highlight this stratification. The paper aims at comparing the advantages and limitations of three open hole multilevel sampling techniques (packer system, dialysis membrane samplers and bailer), chosen on the base of a literary review, to highlight a nitrate vertical stratification under the assumption of (sub)horizontal flow in the aquifer. The sampling systems were employed at three different times of the year in a shallow aquifer piezometer in northern Italy. The optimal purge time, equilibration time and water volume losses during the time in the piezometer were evaluated.

Multilevel techniques highlighted a similar vertical nitrate stratification, present throughout the year. Indeed nitrate concentrations generally decreased with depth downwards, but with significantly different levels in the sampling campaigns. Moreover the sampling techniques produced different degrees of accuracy. More specifically, the dialysis membrane samplers provided the most accurate hydrochemical profile of the shallow aquifer and they appear to be necessary when the objective is to detect the discontinuities in the nitrate profile. Bailer and packer system showed the same nitrate profile with little differences of concentration. However the bailer resulted much more easier to use.

# 1. INTRODUCTION

Nitrate is one of the most abundant pollutants in groundwater throughout the world (Strebel et al. 1989; Thorbum et al. 2003; Almasri 2007; Burow et al. 2010; Li et al. 2010; Lasagna et al. 2016) and has potentially harmful effects on human and environmental health (Hegesh and Shiloah 1982; Bukowski et al. 2001; Manassaram et al. 2010). Nitrate is soluble and highly mobile, and it potentially leaches into groundwater from the unsaturated zone (Pratt et al. 1978; Green et al. 2008; Liao et al. 2012). In rural areas the extensive use of fertilisers for agricultural purposes is considered the main non-point source of nitrate contamination in groundwater (Postma et al. 1991; Chowdary et al. 2005). Furthermore, point sources of nitrogen, such as septic systems, can contribute to groundwater nitrate pollution (Al-Agha 1999; MacQuarrie et al. 2001).

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 (EEC 1991), which aims to protect water quality across Europe by preventing agricultural nitrates from polluting ground and surface waters, requires Member States to identify groundwater aquifers that contain greater than 50 mg/L of nitrate or could contain more than 50 mg/L of nitrate if preventative measures are not taken. Following the EU Directives (676/91/EC and 98/83/EC), the Italian Law (Decrees 31/01 and 30/09) established a nitrate threshold value of 50 mg/L.

Most shallow groundwater in Italy is affected by nitrate contamination (Capri et al. 2009). Nitrate has been recognised as the most widespread shallow groundwater contaminant in the Piedmont plains (NW Italy) (Lasagna 2006; Lasagna et al. 2015, 2016). A study based on isotopic techniques, particularly nitrogen and oxygen isotopes, determined that the nitrate contamination in some areas of the Piedmont plain is associated with synthetic nitrogen fertilisers/manure and septic tank effluents (Debernardi et al. 2008).

Nitrate concentrations are generally vertically stratified in shallow aquifers (Ronen et al. 1986; Dasika and Atwater 1995). A typical nitrate concentration distribution can be represented by a curve with a maximum immediately below the water level. The curve then gradually decreases with depth. The nitrate contaminated plume can extend variously in the aquifer: e.g Pickens et al. (1978) observed a rapid decrease of the nitrate concentration to zero at approximately 4 m below the water table whereas Sontheimer and Rohmann (1986) observed nitrate contaminated plume extended approximately 25 m into an unconsolidated sand aquifer.

Vertical nitrate stratification in an aquifer is related to the contamination sources and geological heterogeneities (Lasagna 2006). Contamination sources are located beneath the ground surface and are responsible for nitrate leaching toward the aquifer. In addition, geological heterogeneities almost always exist in aquifers. Layers with different hydraulic conductivities cause various contaminant and major chemical compound distributions in the aquifer.

Different techniques have been used to highlight the presence of nitrate stratification in aquifers. The most techniques involve open hole multilevel sampling systems.

This paper reviews the most common open hole multilevel sampling systems that are used for nitrate sampling and profiling in groundwater. Moreover, three different open hole multilevel sampling systems (packer system, bailer and dialysis membrane samplers) were used to analyse the existence of a vertical nitrate distribution during different times of the year based on piezometer measurements from the shallow Cuneo plain aquifer (NW Italy). The features and results of the open-hole multilevel sampling systems are compared to highlight the advantages and limitations of each technique. Despite the large amount of available nitrate contamination data, the vertical nitrate distribution in groundwater has never been studied in this plain. However, the Piedmont plain aquifer is the most important water reservoir in the Piedmont Region due to its size, deposit characteristics and recharge potential (Lasagna et al. 2013). Therefore, aquifer pollution studies can provide knowledge for groundwater management and preservation in the Cuneo Plain.

## 2. PREVIOUS STUDIES ABOUT MULTILEVEL SAMPLING TECHNIQUES FOR NITRATE SAMPLING

Beginning in 1970, several authors have studied nitrate contamination in groundwater and highlighted vertical nitrate distributions in aquifers. The studies were conducted in two main manners: a) by sampling wells and piezometers drilled to various aquifer depths at the regional scale and b) by using multilevel sampling techniques in a single borehole.

Regional scale studies allow for the analysis of nitrate concentrations versus well/piezometer depths. Numerous regional scale investigations have been conducted (Piskin 1973; Spruill 1983; Detroy 1986; Hudak 1999, 2000; Debernardi et al. 2008; Lasagna et al. 2015). These studies have observed an inverse relationship between the groundwater nitrate concentration and well depth. Nevertheless some authors highlighted

that concentration data obtained from a pumping well do not reflect the vertical variability in the composition of groundwater in the aquifer where the well screen is located. Thus these sampling cannot provide adequate information about groundwater quality for management purposes (Netzer at al. 2011).

Conversely the use of multilevel sampling techniques provides insight regarding aquifer stratification, especially nitrate distributions. Moreover closely spaced vertical sampling are also useful to adequately quantify processes as denitrification in aquifer (Smith et al. 1991; Frapporti et al. 1995).

Multilevel sampling installations can be grouped into three construction methods (Weaver et al. 2007) (Fig. 1):

(a) Multiple monitoring boreholes at one site (well cluster);

(b) A single monitoring borehole with multiple piezometers installed at different depths (nested well); and

(c) A single monitoring borehole with a single long screen ("flow-through" or "open-hole").

Multiple monitoring boreholes at one sampling point or multiple piezometers in a single monitoring borehole generally provide the best techniques for assessing chemical-physical parameter distributions with depth and ensuring that cross contamination does not occur. However, these systems are very expensive to construct and install. Thus, several techniques have been developed for multilevel sampling in a single open-hole monitoring borehole, that can be used to determine the actual nitrate distributions in shallow unconsolidated aquifers. According to some authors, open borehole methods carry the risk of obtaining poor or unrepresentative samples (Lerner and Teutsch 1995). Indeed open boreholes are known to act as a short circuit, allowing groundwater to flow from one aquifer layer to another. However the effect is more severe with stronger vertical gradients, that in the study area can be neglected.

Examples of open-hole multilevel sampling systems include packer systems, bundled piezometer systems, diffusive gel/dialysis membrane samplers, depth specific samplers, separation pumping and baffle systems. Further special equipment were used to provide insights on spatial and temporal variability of water head and hydrochemistry in bedrock aquifers (Chapman et al. 2015).

Multilevel sampling techniques can be classified as "active methods" or "passive methods".

## 2.1 Active sampling methods

Multilevel sampling techniques can be are considered active sampling methods when they collect groundwater samples over a relatively short period of time (minutes) using mechanical equipment. Active samplers control borehole flow by only allowing the water from a specific level of the aquifer to reach the sampling port via pumping (Nilsson et al. 1995a).

Active sampling methods include packer system, depth specific samplers, baffle systems, separation pumping systems and bundled piezometer systems.

### 2.1.1 Packer system

Packer systems are used to isolate a specific sampling zone in an open borehole. The system involves lowering one or more inflatable packers to a desired depth and then inflating the packer(s) to seal off the flow of water at that depth. To avoid problem of mixing or short-circuiting, the correct method of sampling is to leave a permanent packer in the borehole, and only collect the samples after the borehole has stabilised (Weaver et al. 2007).

### 2.1.2 Depth specific sampler

Depth specific samplers consist of plastic or metal tubes or vessels. The sampler is lowered to the desired depth using a rope or cable and an inlet valve is opened to allow the borehole water to enter the sampling vessel. The device is then retrieved and the sample is poured into a sampling bottle. The most common depth specific sampler is the bailer, of which several types exist (Trick et al. 2008). A bailer consists of a rigid tube made of PVC, stainless steel or Teflon, with a ball valve at the bottom and an open top. Bailer sampling techniques require a gentle lowering of the bailer into the water column of the well, to reduce potential problems due to fluid turbulence, and a proper transfer of water from the bottom of the bailer to sample containers (Lee 2002). Bailers, when properly used, are an acceptable sampling tool. The bailer is considered a suitable sampler for groundwater nitrate concentrations. However, although the method is common for depth specific sampling, it is not very accurate and is not recommended for accurate sampling in multilayered aquifers (Weaver et al. 2007). This is especially due to possible groundwater mixing or short-circuiting, especially in aquifer with vertical gradients. The result is a  potential ambiguity about the source of the water in multilevel sampling. Finally, it can be difficult to accurately determine the depth at which each sample was collected (Trick et al. 2008).

### 2.1.3 Baffle system

Baffle systems consist of a packer with a penetrating inner tube (baffle) of slightly smaller diameter than the borehole. A production pump is operated above the baffle element to cause a vertical flow inside the borehole and through the baffle. In this way a perfectly horizontal radial flow should develop around the borehole and level-accurate groundwater samples can be obtained just above the packer in the annulus between the baffle and the borehole screen. For this purpose a small pump is operated at low flow rates so as not to disturb the horizontal flow. More specifically the sample pump must be pumped at a lower flow rate than the rate of inflow through the screen (Nilsson et al. 1995a, 1995b). Repositioning the packer and baffle enables sampling at different levels. More details are reported in Lerner and Teutsch (1995).

### 2.1.4 Separation pumping system

Separation pumping is a three-pump technique. The two main pumps (flow control pumps) are positioned at the top and bottom of the borehole, while a sample pump is positioned in the middle. The flow control pumps separate the borehole water flow into two components, thus creating a water flow divide. A flow meter is used to locate the position of the water divide and the sample pump is positioned at this depth. Flow at the water divide is assumed to be horizontal. Pumping the sample pump at a very low rate (less than 1% of the total rate) allows a groundwater sample to be collected from a discrete aquifer depth where the water divide is located. The method requires accurate prior knowledge of the aquifer transmissivity and specific borehole capacity, as well as a high level of operational skill (Weaver et al. 2007). It is useful especially when the vertical flow inside open borehole is important. This method is also limited by the borehole diameter, which may not be wide enough to accommodate the three pumps (Nilsson et al. 1995a, 1995b; Jones and Lerner 1995).

### 2.1.5 Bundled piezometer system

Bundled piezometer systems consist of a number of narrow tubes installed at different depths in an open borehole. The tubes may be bundled together (Powell and Puls 1993) or strapped to the outside of a rigid support casing (Taylor et al. 2000). When connected to a vacuum and manometer, the advantage of this method is that it can be used to derive a vertical profile of water quality and hydraulic head measurements. Purging and sampling

volumes can be minimised with very small tubing and this can be constructed using readily available and cheap PVC tubing. However, this method is suitable only for shallow unconfined and sandy aquifers. It requires an experienced person to construct and install and is time consuming. Additional information on the bundled mini-piezometers construction and installation can be obtained from Acworth (2007). According to Weaver et al. (2007), this method does not completely resolve issues associated with vertical borehole flow and ambiguous hydrogeochemical results.

## 2.2 Passive samplers

ITRC (2005) defined a passive sampler as a device that is able to acquire a sample from a discrete location or interval in a well without the active transport associated with a pump or purge technique. Passive methods rely on the well water reaching equilibrium with the formation water. Passive samplers generally allow pollutant sampling in monitoring wells without creating active groundwater transport and without external energy sources (INERIS 2013). Passive sampling is based on the free flow of analyte molecules from the sampled medium to a collecting medium as a result of a chemical potential gradient (Gorecki and Namiesnik 2002). The flow of molecules will last until equilibrium is reached between the two media or until the sampler is retrieved (INERIS 2013). Numerous passive sampler designs exist, but most include a barrier between the sampled medium and the receiving phase. The barrier determines the sampling rate at which contaminant of a given concentration are collected. Thus, the barrier can be used to selectively permit or restrict various classes of chemicals from entering the receiving phase (Vrana et al. 2005). In the following diffusive gel/dialysis membrane samplers are described.

### 2.2.1 Diffusive gel/dialysis membrane samplers

Diffusive gel/dialysis membrane samplers (DMS) are based on the principle of diffusion or dialysis and accumulate dissolved species for chemical analysis. The dialysis process simultaneously occurs in both directions through the regenerated cellulose membrane. The well water ions diffuse inward and equilibrate inside the sampler while the deionised water slowly diffuses outward in an attempt to dilute the aquifer to deionised water. No pumping is required. Several diffusive gel units or dialysis units may be installed at the desired sampling depths in an open borehole. High spatial resolution of the hydrochemical vertical profile is enabled. However dialysis membrane techniques may face challenges associated with vertical borehole flow.

The DMS allowed to equilibrate with the dissolved species in the groundwater over a period of time and then recovered to analyse the accumulated solutes from each unit. The amount of time that DMS should be left in the piezometer prior to recovery depends on the equilibration time, which is the time required by the sampler to equilibrate with the ambient water and well conditions. Imbrigiotta et al. (2007) defined the equilibration time as the time required for the concentration inside the dialysis sampler to reach at least 95% of the ground water test solution concentration outside the sampler. DMS should not be left in a well for an extended period and should generally be retrieved within three to four weeks. Samplers left longer (more than 4-6 weks) can be compromised by biological activity.

Previous laboratory tests have shown that equilibration times range from a few days to several weeks, depending upon the contaminant (ITRC 2006). Harter and Talozi (2004) observed that specific conductance and nitrate equilibration was attained after 1-4 days at 21 ºC in 43 wells. Imbrigiotta et al. (2007) performed laboratory equilibrium tests, determining that dialysis samplers reached equilibrium within 1 day for bromide, chloride and nitrate at 21 ºC.

Moreover, previous studies have demonstrated a gradual sampler water volume loss during the equilibration period in wells with high ionic strength groundwaters (Vroblesky et al. 2002; Vroblesky and Pravecek 2002; Vroblesky et al. 2003). In some cases the lost water volume was severe enough to warrant the use of a rigid support inside the regenerated cellulose membrane, limiting the collapse of the sampler to a set volume. Lasagna (2006) hypothesised that the water loss may be connected to the pressure that the outer protective layer of the low-density polyethylene mesh exerts on the membrane.

Purported dialysis samplers limitations due to biodegradation and water volume loss over time in high ionic strength waters were not significant for equilibration times of one to two weeks (Imbrigiotta et al. 2007).

DMS have been successfully tested in the lab (Ehlke et al. 2004), in the field (Ronen et al. 1986; Dasika and Atwater 1995; Tunks et al. 2000; Vroblesky et al. 2002; Vroblesky and Pravecek 2002; Vroblesky et al. 2003) and some authors tested it both in lab and in field (LeBlanc 2003; Harter and Talozi 2004; Imbrigiotta et al. 2007) for a variety of water-quality parameters, including volatile organic compounds, major cations and anions, nutrients, trace metals, specific conductance, total dissolved solids, dissolved organic carbon, dissolved gases, sulphide and explosive compounds. Ronen et al. (1986) used a dialysis cell sampler to measure multilevel electrical conductivity and major anion concentrations (chloride, nitrate and sulphate) at 3-cm intervals just below the water table

in an open borehole. The dialysis cells were filled with distilled water and allowed to equilibrate for 30 days before analysing the equilibrated solutions. Dasika and Atwater (1995) adopted a multilayer sampler based on the dialysis membrane technique described by Ronen et al. (1986). The sampler was used to passively sample nitrate concentrations in two unconfined aquifers in British Columbia, Canada. They observed vertical nitrate stratification and recommended the dialysis membrane technique for obtaining detailed groundwater chemistry profiles. Harter and Talozi (2004) found that nitrate and specific conductance were equally well sampled by dialysis samplers and using a conventional purging method. Imbrigiotta et al. (2007) agreed with the results of Harter and Talozi (2004), observing a good agreement between nitrate concentrations collected using dialysis samplers and low-flow purging. However, low bromide and nitrate concentrations (above the detection limit of 0.1 mg/L) were often higher in the low-flow purge samples than in the corresponding dialysis samples.

# 3. MATERIALS AND METHODS

## 3.1 Site description

Open hole multilevel sampling systems were used to analyse the existence of a vertical nitrate distribution in a shallow aquifer at the Cuneo plain test site (NW Italy). Samples were collected from a piezometer located in Racconigi (Fig. 2). The piezometer diameter was 4 inches. The piezometer depth reached 25 m with screens between 12 and 24 m. The schematic stratigraphy of the borehole is illustrated in Fig. 3. The Racconigi piezometer was chosen because it is located in a nitrate contaminated area, already recognized and described in a previous study (Lasagna et al. 2016).

According to the map of the shallow unconfined aquifer (D.G.R. 34-11524/2009), the piezometer is located within the shallow aquifer. Four hydrogeological units are located in the Turin-Cuneo plain. These units possess different grain sizes and sediment permeabilities. From bottom to top, the units include the pre-Pliocene units (a and b in Fig. 2), the Pliocene marine unit (c and d in Fig. 2), the Villafranchian transitional unit (e in Fig. 2) and the Quaternary alluvial deposits unit (f and g in Fig. 2) (Bortolami et al. 1976; Bove et al. 2005; De Luca et al. 2007, 2014, 2015; Castagna et al. 2015a, 2015b). The shallow unconfined aquifer exists in the Quaternary alluvial deposits unit (Middle Pleistocene-Holocene), which is characterised by coarse gravel and sand with subordinate silty-clayey intercalations. The unit possesses a relatively high permeability ($5*10^{-3}$-$5*10^{-5}$ m/s). This

unit represents an important aquifer whose water table is directly connected to surface drainage in the region. The grain size varies and normally decreases from the mountains to the low plain along the Po River. The thickness of this hydrogeological unit ranges from 20 to 50 m. In spite of the variable aquifer thickness, the aquifer is highly productive and regionally important. The base of the shallow aquifer is generally well marked by the presence of thick and relatively continuous silt layers or clay-rich deposits (Bove et al. 2005).

Some characteristics of the Poirino plateau alluvial deposits unit differ from the rest of the unit. This area is composed of silt and clay with rare gravely sandy intercalations. Moreover, the unit thickness ranges from 10 to 30 m.

On the base of the described hydrogeological situation and in absence of any pumping well or other disturbance, the aquifer flow in the study area can be assumed as (sub)horizontal.

The Cuneo plain is a largely agricultural zone (Regione Piemonte 2008) in which the main crops include cereals and forage crops. Livestock farming is also highly developed, particularly cows and pigs. These areas represent the most intensely managed areas in the Piedmont (a highly productive maize-based area and with ample livestock) and are characterised by the highest soil nutrient loads (Bassanino et al. 2011). Moreover, sewer services are locally lacking, especially in isolated areas. The plain's land use characteristics are the cause of diffuse nitrate contamination in groundwater, especially within the shallow aquifer.

**3.2 Water sample collection using multilevel sampling techniques**

Among the multilevel sampling techniques described in the review of the literature, in this study the three best considered systems to be applied to the nitrate stratification problematic were selected. More specifically a packer system, a bailer and dialysis membrane samplers were chosen. In this way both active and passive systems were tested for the evaluation of vertical nitrate stratification in Cuneo shallow unconsolidated aquifer. In fact, under the assumption of (sub)horizontal flow in the aquifer, separation pumping system and baffle system, adapted to situations where vertical flow inside the open borehole cannot be neglected, were not selected in this study. Moreover bundled piezometer systems were avoided because of the reported problems of vertical borehole flow and ambiguous hydrogeochemical results.

Groundwater sampling campaigns were conducted at the Racconigi piezometer in October 2013 (SC1), March 2014 (SC2) and September 2014 (SC3).

SC1 used the packer system multilevel sampling technique. Multiparameter logging was performed to evaluate the temperature (T), electrical conductivity (EC), dissolved oxygen concentration (DO) and pH distributions with depth using a Hydrolab Quanta G multiprobe meter (Fig. 4A). The multiprobe meter includes a transmitter with a 4.4-cm (1.75-in) diameter and 37.1-cm (14.6-in) length, making it suitable for the piezometer's 2-inch casing. Temperature, electrical conductivity (EC), pH and dissolved oxygen (DO) were analysed. The temperature measurement accuracy was ± 0.2 °C and resolution was 0.01 °C. The dissolved oxygen measurement accuracy was ± 0.2 mg/L ≤ 20 mg/L and ± 0.6 mg/L > 20 mg/L, and the resolution was 0.01 mg/L. The EC measurement accuracy was within 1% of the reading and the resolution included 4 digits. The pH measurement accuracy was ± 0.2 units and resolution was 0.01 units.

SC2 used dialysis samplers, a bailer and a packer system.

SC3 used a packer system.

The sampling period, the sampling systems and the chemical analyses performed on the groundwater samples are presented in Tab. 1.

The use of the packer system in three sampling campaigns permitted to highlight variations in ions concentration during the year. Moreover the use of three sampling systems during the SC2 campaign allowed to compare the results obtained using different techniques.

The chemical groundwater analyses were performed by the Hydrochemical Laboratory of the Earth Science Department (Turin University). Alkalinity was measured via a titration method using 0.1 N HCl. The major anions ($NO_3^-$, $SO_4^{2-}$ and $Cl^-$) were determined using ion chromatography (Metrohms 709, 732, 733, 752 and 863). The major cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$) and metal cations were determined via ICP-AES (Perkin Elmer, Optima 2000DV).

### 3.3 The packer system

The packer system consisted of a submersible pump with double packers (Fig. 4B). The system was lowered into the piezometer at different depths and aquifer intervals were isolated by inflating the double packers. The submersible pump was then started and groundwater samples were collected. This packer system was specifically built for this study, but it is suitable for piezometer diameters ranging from 2.5 to 4.5 inches and depths

of up to 58 m. The distance between the two packers was 1 m. Consequently, each groundwater sample corresponded to an aquifer interval of approximately 1 m. The packer system was equipped with a submersible pump (MP1 Grundfoss). The submersible pump was used during the SC1, SC2 and SC3 sampling campaigns at depths of 13 m, 16 m, 19 m and 21 m below the surface. Sampling was performed after the piezometer was purged for a time considered "optimal" for the collection of a representative groundwater sample. The optimal purge time was determined based on various purge times in pilot piezometers, water-quality indicator parameter measurements and nitrate concentrations. The six pilot piezometers possessed identical characteristics (diameter, installation features, etc.). Purging was performed at a low flow, with the pump located within the saturated-screened interval. The water-quality indicator parameters (purge parameters) included pH, electrical conductivity (EC), dissolved oxygen concentration (DO) and temperature (T). A Hydrolab Quanta G multiprobe meter was used to analyse the water-quality indicator parameters. The purging parameters were monitored at specific time intervals, commonly every three to five minutes. According to Yeskis and Zavala (2002), sampling commenced after three successive stabilised water-quality indicator parameter readings. The same procedure was applied at different depths in the piezometers.

### 3.4 The dialysis membrane samplers

The dialysis membrane samplers used in this study consisted of small diameter bags produced from 15 m of flat width regenerated cellulose membrane tubing (Cellu·Sep® T2, Membrane Filtration Products, Inc.). Unlike native cellulose, which is highly crystalline and rigid, regenerated cellulose is largely amorphous and swells when saturated. The swollen areas act as pores, permitting sufficiently small solute molecules to pass through the membranes. The membranes are flexible and transparent, with good chemical and pH resistance and a high temperature tolerance. The DMS used in this study were characterised by a molecular weight cut off (MWCO) of 6000 to 8000 Daltons. The MWCO of the membrane represents the molecular weight of the smallest solute for which the permeation is 10% or less (at least 90% is retained during the tests). The DMS in this study included a flat width of 100 mm, a diameter of 63.7 mm and a volume/length ratio of 31.8 mL/cm.

Individual bags were prepared and handled using latex gloves. Each bag was cut from the membrane tubing and measured approximately 20-cm long. The membranes were washed in deionised water to remove preservatives. The clean tubing was filled with

deionised water and sealed at both ends (Fig. 4C). The DMS were prepared in the laboratory the day before use and were stored in a plastic container filled with deionised water. The complete DMS assembly was performed *in situ*. The dialysis membrane samplers were covered with an outer protective layer of low-density polyethylene mesh to avoid scraping along the monitoring well casing and to protect against surface contamination during the placement and extraction of the sampler. The membrane were then linked to each other and suspended in the piezometer using a polyethylene rope. They were separated using an attached weight to overcome buoyancy and were positioned at different depths to construct a hydrochemical and nitrate profile of the shallow aquifer. The DMS were only located at intervals with piezometer screens and were separated by at least 1 m, between 12 and 23 m below the ground level. Moreover, the samplers were separated by rubber foam cylinders to provide insulation and prevent mixing or short circuits in the water column.

This study performed experimental laboratory equilibration time and volume loss evaluations for the DMS. According to the results of these tests and previous studies, the membrane were left in the piezometer for 12 days, which was deemed long enough to achieve a chemical equilibrium with groundwater while avoiding membrane biodegradation. The DMS were pulled out of the well, removed from the mesh and clipped with scissors after 12 days. The water was then pressed out of the bag and sampled using plastic bottles.

### 3.4.1 Experimental evaluation of DMS equilibration time

This study evaluated the DMS equilibration time for nitrate via laboratory investigations.

The three dialysis samplers in this study were filled with deionised water and inserted into a beaker filled with groundwater, with known nitrate (27.6 mg/L), chloride (7.7 mg/L) and sulphate (86.7 mg/L) concentrations. The anion concentrations in DMS_3, DMS_6 and DMS_9 were measured after 3 days, 6 days and 9 days, respectively. The test was conducted at a water temperature of 18 °C.

### 3.4.2 Experimental evaluation of volume losses

This study tested the DMS volume/weight-loss phenomenon via laboratory investigations. Three DMS were filled with deionised water, covered by a low-density polyethylene mesh outer protective layer and inserted into a plastic bin filled with 8 L of groundwater. The DMS were weighed at the beginning of the test and at 1 day intervals for 8 days.

The weight differences between the three dialysis samplers were then reported as a function of time and the percentage of volume loss.

## 3.5 The bailer

The depth specific sampler used in this study consisted of a plastic open top bailer with a one-way check valve at the bottom (Fig. 4D). The bailer fills with water when lowered into the piezometer below the water level. The check valve closes when the bailer is lifted to the surface. The 1 m long and 0.06 m diameter bailer was lowered to desired depths using a rope. The sampling depths were 13 m, 16 m, 19 m and 21 m below the ground level. These not too close depths were chosen because of the possible problems of fluids turbulence in the piezometer and the difficulties, highlighted by some Authors, to accurately determine the depth at which each sample was collected. The bailer is lowered to the required depth and groundwater flows up through the ball valve and out through the open top. The pressure of the water column closes the ball valve and seals the sample inside the bailer after the bailer remains stationary for a given period of time.

# 4. RESULTS

## 4.1 The optimal purge time

The water-quality indicator parameter readings recorded in the six pilot piezometers at different purge times and depths are listed in Tab. 2 and Tab. 3. Piezometer 3 corresponds to the Racconigi piezometer, in which the shallow aquifer hydrochemical and nitrate profiles were investigated using multilevel sampling techniques. Only nitrate concentrations were measured at different purge times and depths in piezometers 4, 5 and 6 (Tab. 3).

The purge parameter analyses suggest that both the water-quality indicators and nitrate concentrations minimally differ between the 3-minute and 10-minute purge times. Thus, the optimal purge time was established as 10 minutes. This time does not delay the measurement campaigns, but it is long enough to produce accurate measurements.

## 4.2 The DMS equilibration time

The laboratory test results (Tab. 4) permitted the evaluation of the nitrate, chloride and sulphate equilibration times. The water in dialysis sampler, analysed 3 days after the beginning of the test, exhibited anion concentrations equal to those in deionised water.

The water became enriched with anions after 6 days, but the concentrations were considerably different from groundwater anion concentrations, especially sulphate concentrations. The 9 day analyses exhibited nitrate, chloride and sulphate concentrations equal to those of groundwater. According to these results, a 9-day period is sufficient for reaching nitrate, chloride and sulphate equilibrium with groundwater. The DMS were left in the piezometer for 12 days, providing ample time for the DMS to reach chemical equilibrium with groundwater while avoiding membrane biodegradation.

## 4.3 Water volume losses during the equilibration period

Laboratory tests identified actual water losses in the DMS. Fig. 5 illustrates the weight differences in three dialysis samplers (DMS_1, DMS_2 and DMS_3) as a function of time. Assuming the density of water is 1 g/mL, the weight loss was expressed as a volume loss per unit time. The measured volume losses ranged from 12.9% (for DMS_3) to 49.1% (DMS_1) over 8 days. The lowest percentage volume loss was measured in the membrane with the lowest initial water content (DMS_3). Conversely, the highest membrane water loss was observed in the DMS with the highest water content at the beginning of the test (DMS_1). Moreover, the DMS_1 and DMS_2 water losses ceased after approximately 7 days. The DMS_3 water losses were lower, but they continued until the eighth day.

## 4.4 Hydrochemical and nitrate profiles

Multilevel sampling systems, specifically a packer system, DMS and bailer, were used to determine the hydrochemical and nitrate profiles in the Racconigi piezometer. Meaningful nitrate concentration variations were detected with depth.

Tab. 5 reports the water table depths in the Racconigi piezometer for the three sampling campaigns. During SC2, the packer system was again used and the dialysis samplers were positioned in the piezometer on the same day. In addition, the bailer was used on the day when the membrane samplers were recovered. Therefore, Tab. 5 gives the average piezometric level for SC2 based on the packer system and bailer data.

Multiparameter logging was performed during SC1. The temperature, electrical conductivity (EC), Dissolved Oxygen (DO) and pH distributions are reported in Fig. 6. These parameters significantly varied between the portion of tube without screens (from the water table to the screened depth) and the portion with screens. These variations are likely due to the lack of groundwater replacement in the piezometric tube without screens. However, parameters also varied with depth in the portion with screens. Specifically, T

varied from 13.7 °C to 12.83 °C, EC varied between 901 µS/cm and 872 µS/cm and OD ranged from 5.24 mg/L to 3.81 mg/L. All of the parameters decreased with depth, but abrupt EC and OD variations were observed at depths of approximately 16 and 19 m below ground level. Only pH remained relatively constant, ranging from 6.74 to 6.88.

Moreover, different groundwater samples were collected during SC1 using the packer system and they were analysed. The concentrations of $Mg^{2+}$, $Na^+$ and $HCO_3^-$ showed an initial lowering and then an increase (Fig. 7). The levels increased from the depth of 16 m for $Na^+$, and of 19 m for $Mg^{2+}$ and $HCO_3^-$. The ion $K^+$ highlighted constant concentration with depth. The concentrations of $Cl^-$, $NO_3^-$, $SO_4^-$ and $Ca^{2-}$ generally decreased with depth. This can be connected to an anthropic pollution from the soil and a dilution with depth.

SC2 utilised a bailer, a packer system and dialysis samplers. The packer system and bailer collected groundwater samples at depths where samples were collected during SC1. The DMS permitted a more detailed groundwater sampling at a sampling interval of 1 m. The bailer was used on the day that the membrane sampler was recovered. The anions are plotted versus depth in Fig. 8.

The nitrate, sulphate and chloride concentrations generally decrease with depth. Chloride concentrations range between approximately 25 and 22 mg/L for the three sampling systems. Nitrate varied from about 54 mg/L to about 45 mg/L, with very little differences of concentration using the three sampling techniques. Sulphate concentrations ranged from 70.3 to 67.3 mg/L in the DMS samples, remained relatively constant at approximately 66 mg/L in the packer system samples and varied from 77.6 mg/L to 71.7 mg/L in the bailer samples. The difference in sulphate concentrations could be due to the different time of sampling. Indeed the dialysis membranes were left in the piezometer 12 days longer than the packer system, while the bailer was used after DMS recovery. In the SC2 only the membrane samplers were able to observe the abrupt concentration variations, particularly the nitrate variation, at depths of 16 and 19 m.

The SC3 sampling campaign was conducted using the packer system. Chloride concentrations were similar to those observed during SC2, varying between 24.8 and 20.5 mg/L. Sulphate concentrations remained relatively constant at approximately 75 mg/L. Nitrate concentrations decreased with depth, ranging from 44.7 to 34.2 mg/L, with a clear variation at approximately 16 m.

# 5. DISCUSSION

The multilevel sampling techniques produced different vertical stratification profiles due to their operational differences. Tab. 6 presents the major features of the packer system, DMS and bailer.

**The packer system** strongly reduces groundwater pumping for the purge and requires only a short sampling period. Moreover, groundwater can be collected without volume limitations. However, this system represents the most expensive multilevel sampler, especially due to the initial equipment acquisition costs. The system requires some essential accessories, including a pump with a frequency convertor and current generator. The size and weight of the packer system reduce the tool's manageability. In addition, at least two operators are required to lower the pump and tubes into the piezometer and retrieve the system. Furthermore, the packer system can be used only in piezometers with dimensions (diameter and depth) that comply with the packer's technical features. The packer system used in this study requires a piezometer diameter between 2" ½ and 4 ", and a maximum depth of 58 m.

**The dialysis membrane samplers** (DMS) can be advantageously positioned close each other at distances of less than one metre. In addition, these samples can be placed along the entire screened portion of a piezometer, regardless of the piezometer diameter or length. Moreover, they do not require purging, so no purge water is produced during sample collection, transport or treatment. DMS also eliminate groundwater turbidity problems because water samples are clear and ready to be analysed, as particulates do not pass through the membrane. Nevertheless, the equilibration time is relatively long, encompassing at least 9 days for nitrate according to the experimental tests. Samplers left in a piezometer or well for longer periods of time can be compromised by biological activity. DMS are very manageable both in the laboratory and *in situ*. Only one operator is required for the lab activities (membrane rinsing and filling, experimental equilibration time tests, the removal of water from the membrane, etc.). In addition, only one operator is required for *in situ* procedures, including positioning the DMS in the piezometer. Therefore, the field time is minimised for field personnel, although membranes require two trips to the field (one to position and one to retrieve samplers). Another disadvantage is the relatively low groundwater sample volume, which depends on each DMS diameter and length (generally around ten mL). The membrane costs are lower than the packer system costs but higher than the bailer costs.

**The bailer** is the most inexpensive multilevel sampling technique. It is portable and very easy to use. Bailers require a single operator and possess a short sampling time. This technique generally does not allow piezometer purging, so no purge water is collected, transported or treated. A bore can be purged using a bailer only if a reasonably small volume of water is to be removed (Sundaram et al. 2009). Furthermore, bailers do not require an external energy source. However, potential problems due to fluid turbulence in well can take place if bailer is quickly lowered into the well. Moreover, because of the difficulties to accurately determine the depth at which each sample was collected, sample quality depends on effective and consistent bailer operation at multiple depths.

The hydrochemical and nitrate profiles in the Racconigi piezometer displayed some differences both throughout the year and based on the multilevel sampling technique.

Anion concentrations generally decreased with depth during SC1. Nitrate, sulphate and chloride displayed similar stratifications, with clear concentration variations at approximately 16 and 19 m. Sulphate and chloride did not display distinct concentration trends or clear stratification during SC2 and SC3.

The nitrate stratification profiles of the three sampling campaigns (Fig. 9) were compared, producing the following observations:

  a) *Vertical nitrate stratification is present throughout the year.*

Multilevel sampling techniques were used to observe vertical nitrate stratification during three sampling campaigns (SC1, SC2 and SC3). All of the results suggest that nitrate concentrations decrease with depth. Vertical nitrate stratification is evident throughout the year, although nitrate concentrations varied in the sampling campaigns. The maximum nitrate levels were registered during SC1 (October 2013), with concentrations of greater than 50 mg/L. The minimum nitrate concentrations, less than 50 mg/L at all measured depths, were observed during SC3 (September 2014). Intermediate concentrations, which were greater than 50 mg/L close to the surface and less than 50 mg/L below approximately 15-16 m, were observed during SC2.

  b) *Different multilevel techniques yield different degrees of accuracy.*

Three different multilevel sampling techniques (DMS, packer system and bailer) were used in association over a short time interval during SC2. The nitrate concentration profiles were comparable among all of the techniques. Specifically, the packer system and bailer displayed similar vertical stratifications with the same degree of accuracy. However, the dialysis samplers more accurately measured the hydrochemical characteristics of the shallow aquifer. These membranes can be positioned very close to each other and along

the entire screened interval of the piezometer, regardless of the piezometer diameter or length. The DMS observed significant nitrate concentration variations at depths of approximately 16 and 19 m (Fig. 9). The packer system and bailer did not observe the stratification in such an accurate manner in SC2, probably due to a scarce spatial resolution of sampling. Instead packer system pointed out the concentration discontinuities at 16 and 19 m in SC1 and SC3; it can be connected to a different stratification of nitrate in these sampling campaigns, and an easier identification of the discontinuities at the measured depths.

The analyses of physicochemical parameters (dissolved oxygen, electrical conductivity and temperature) can also be used to monitor with 1 m resolution the aquifer. These profiles could be used to calibrate a low-resolution nitrate profile more easily obtained with a bailer.

  *c) The shallowest portion of the aquifer lacks nitrate concentration data*

The Racconigi piezometer is screened between 12 and 24 m below ground level (b.g.l.). However, the water table depth varied from 3.20 m b.g.l. during SC2 to 5.88 m b.g.l. during SC1. Therefore, data could not be collected from the shallowest portions of the aquifer, which are generally significant for vertical nitrate stratification.


# 6. CONCLUSION

Multilayer multilevel sampling techniques are very important in hydrogeological studies because they provide detailed and accurate qualitative monitoring. Three different open hole multilevel sampling systems (packer system, bailer and dialysis membrane samplers DMS) were used throughout different times of the year in a shallow aquifer piezometer in northern Italy.

The goal of the study was to evaluate the presence of vertical nitrate stratification in the shallow aquifer, to test the three sampling techniques, also in association, and highlight the advantages and limitations of each multilevel sampling system. Moreover, the optimal packer system purge time and DMS equilibration time and water volume losses were evaluated, as a prerequisite for subsequent analysis. The optimal purge time was evaluated based on the purge times in various pilot piezometers. The purge parameter analysis results suggested that both the water-quality indicators and nitrate concentrations generally exhibited minimal differences between the 3-minute and 10-minute purge times.

Thus, the optimal purge time was established as 10 minutes. This time did not significantly delay the measurement campaigns but was long enough to provide accurate sampling.

The DMS equilibration time and volume/weight-loss phenomenon were tested in the laboratory. The experimental tests showed that nitrate, chloride and sulphate reached equilibrium with groundwater after a period of 9 days. The DMS were left in the piezometer for 12 days, which is long enough to reach chemical equilibrium with groundwater while avoiding membrane biodegradation. Regarding volume/weight-loss phenomenon, the tests highlighted a lowest percentage volume loss in the DMS with the lowest initial water content. Conversely, the highest water loss was observed in the membrane with the highest initial water content. Moreover, the DMS water losses ceased approximately 7-8 days after the tests began.

The use of multilevel sampling systems highlighted the presence of a vertical nitrate stratification in the shallow aquifer, with nitrate concentrations that generally decreased with depth downwards. The vertical nitrate stratification is present in all the sampling campaigns, but with significantly different nitrate concentrations.

The association of three different sampling techniques during a sampling campaign has allowed to compare the nitrate profiles and to point out the advantages and limitations of each multilevel sampling system. The multilevel sampling systems showed the same nitrate profile with little differences of concentration. The dialysis membrane samplers most accurately represented the hydrochemical profile of the shallow aquifer than packer system and bailer. Therefore they appear to be necessary when the objective is to detect the discontinuities in the nitrate profile. However the bailer resulted the cheapest technique and much more easier to use.

The advantages and disadvantages of each multisampling technique must be considered when choosing the most suitable method for a specific scenario. The ideal technique must maximise accuracy while minimising time, effort and cost requirements.

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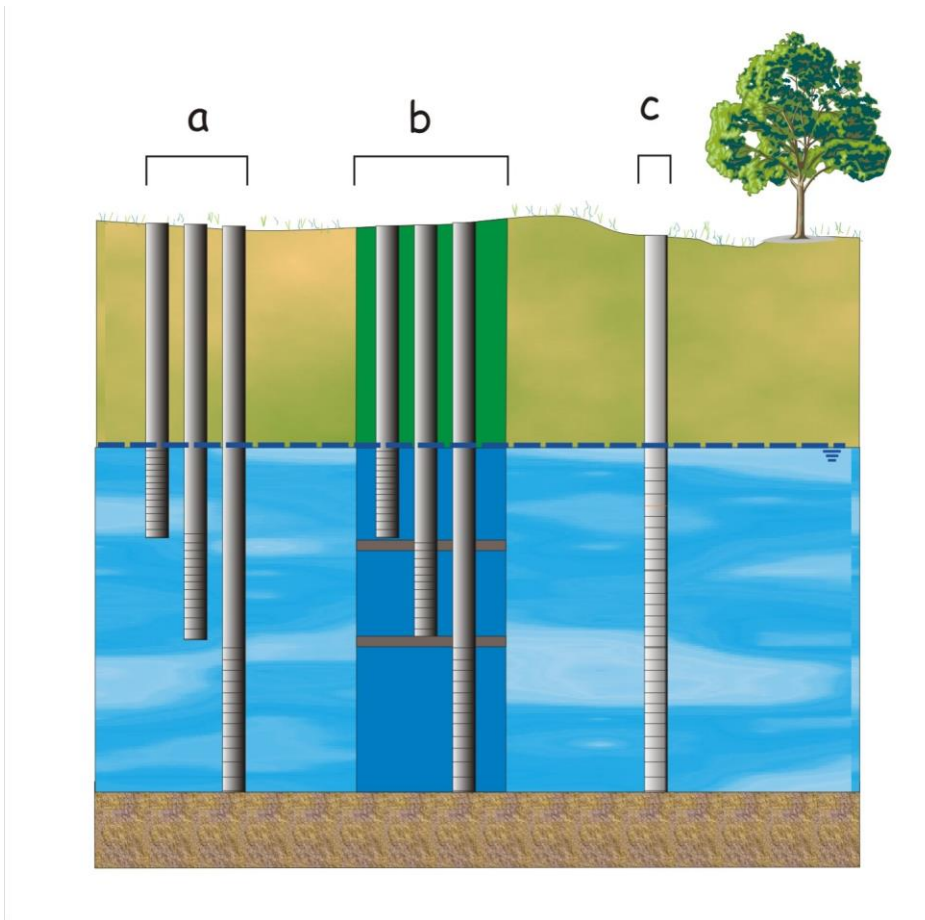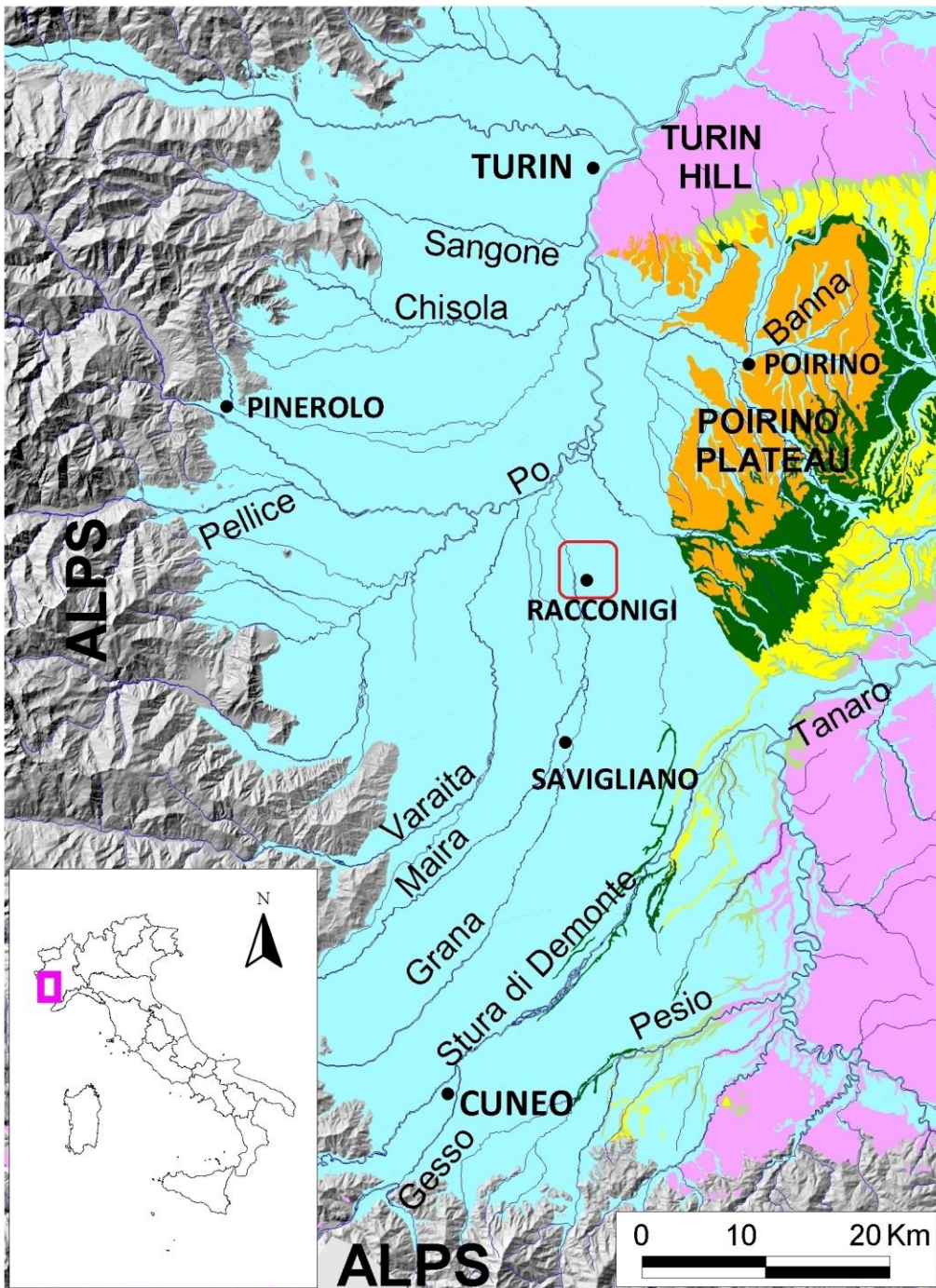
**FIGURE CAPTIONS**



Fig. 1. Types of monitoring boreholes: a) Cluster of piezometers in separate boreholes; b) nested wells; c) single monitoring borehole with a single long screen.

Fig. 2. Pilot site location (in the red square) and map of the Turin-Cuneo plain geological setting.
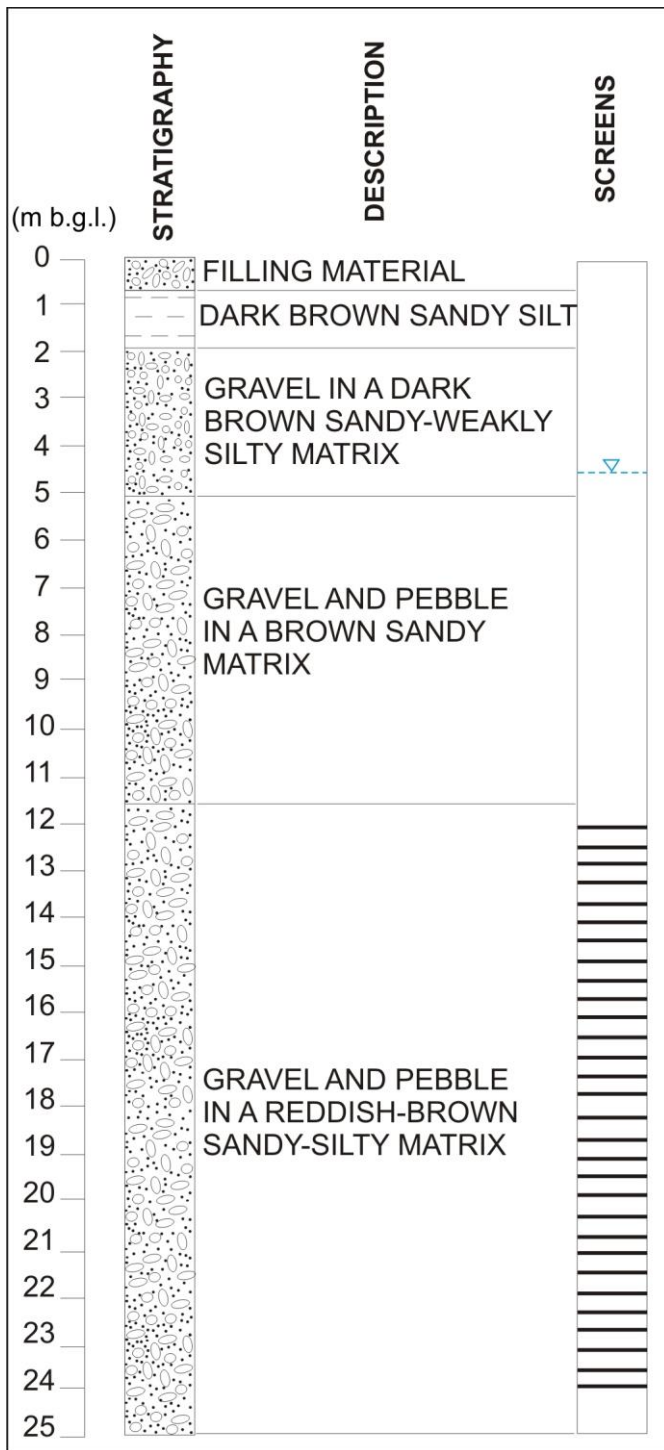
Fig. 3. Schematic stratigraphy of the Racconigi piezometer including the lithology and screen interval. The average piezometric level is denoted by the blue dashed line.

Fig. 4. Multilevel sampling devices used in the Racconigi piezometer. A) multiprobe meter for multiparameter logging. B) packer system. C) dialysis membrane sampler. D) bailer.
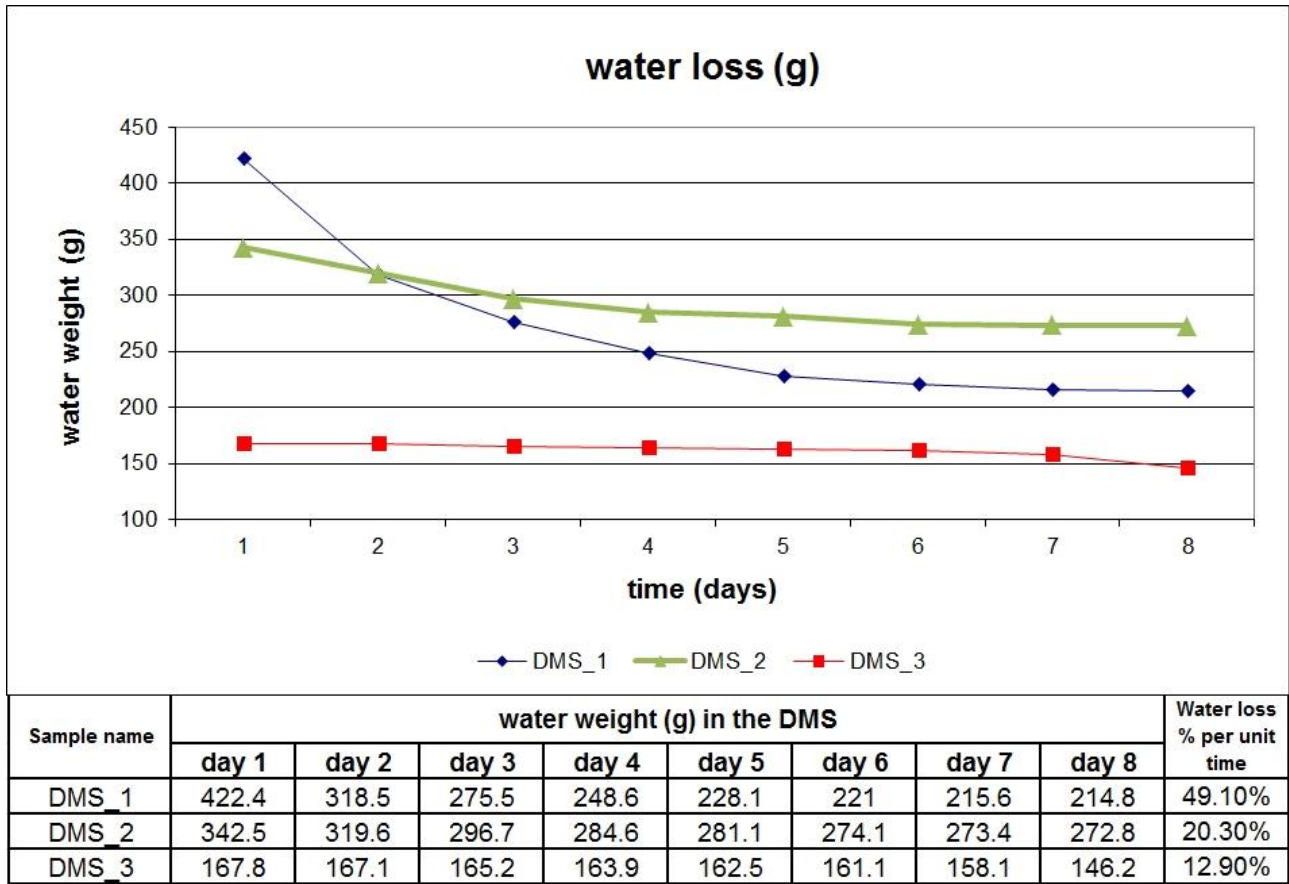
## water loss (g)

| Sample name | water weight (g) in the DMS | | | | | | | | Water loss % per unit time |
|---|---|---|---|---|---|---|---|---|---|
| | day 1 | day 2 | day 3 | day 4 | day 5 | day 6 | day 7 | day 8 | |
| DMS_1 | 422.4 | 318.5 | 275.5 | 248.6 | 228.1 | 221 | 215.6 | 214.8 | 49.10% |
| DMS_2 | 342.5 | 319.6 | 296.7 | 284.6 | 281.1 | 274.1 | 273.4 | 272.8 | 20.30% |
| DMS_3 | 167.8 | 167.1 | 165.2 | 163.9 | 162.5 | 161.1 | 158.1 | 146.2 | 12.90% |

Fig. 5. Water weight differences between three dialysis samplers (DMS_1, DMS_2 and DMS_3) as a function of time.
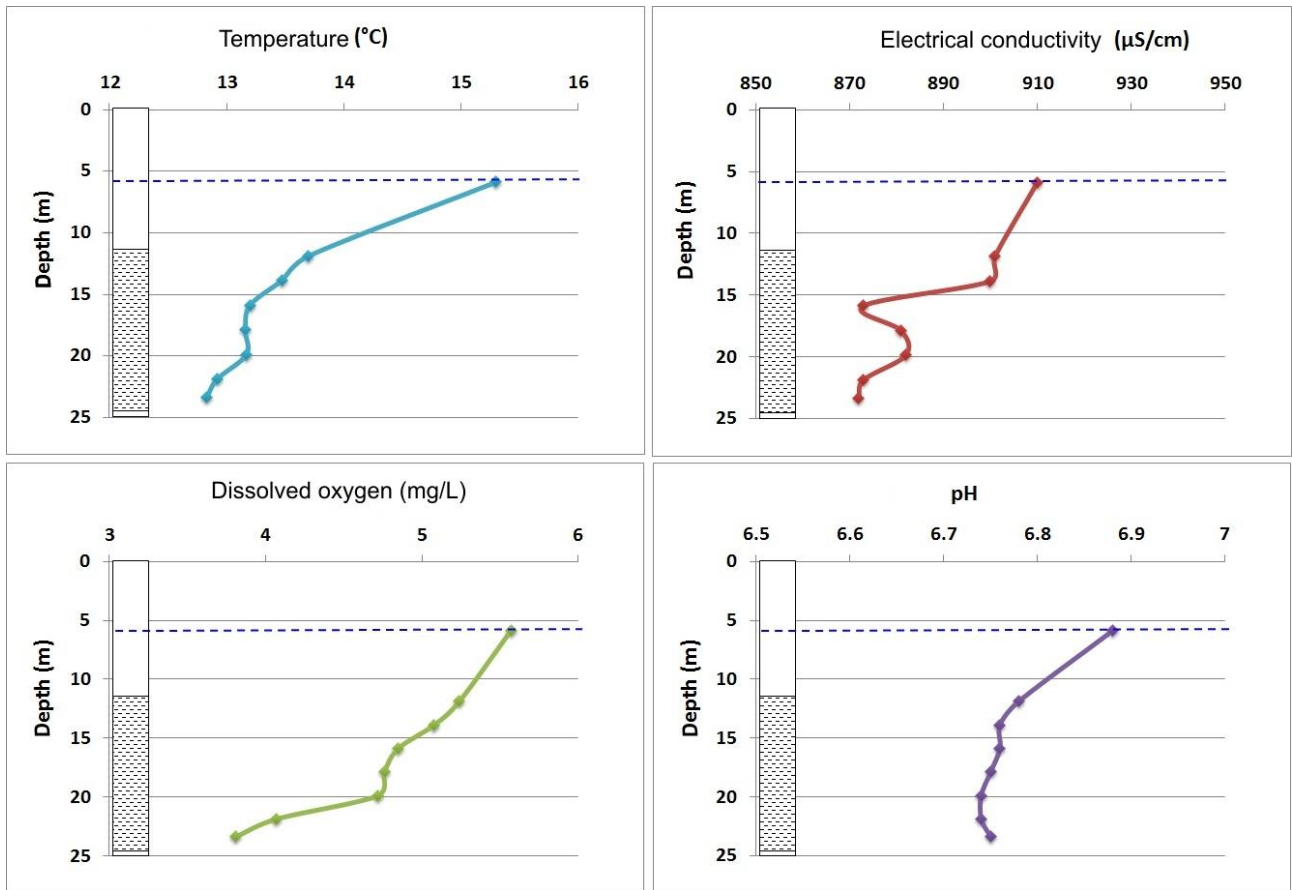
Fig. 6. Multiparameter logging performed in the Racconigi piezometer during the SC1 sampling campaign.
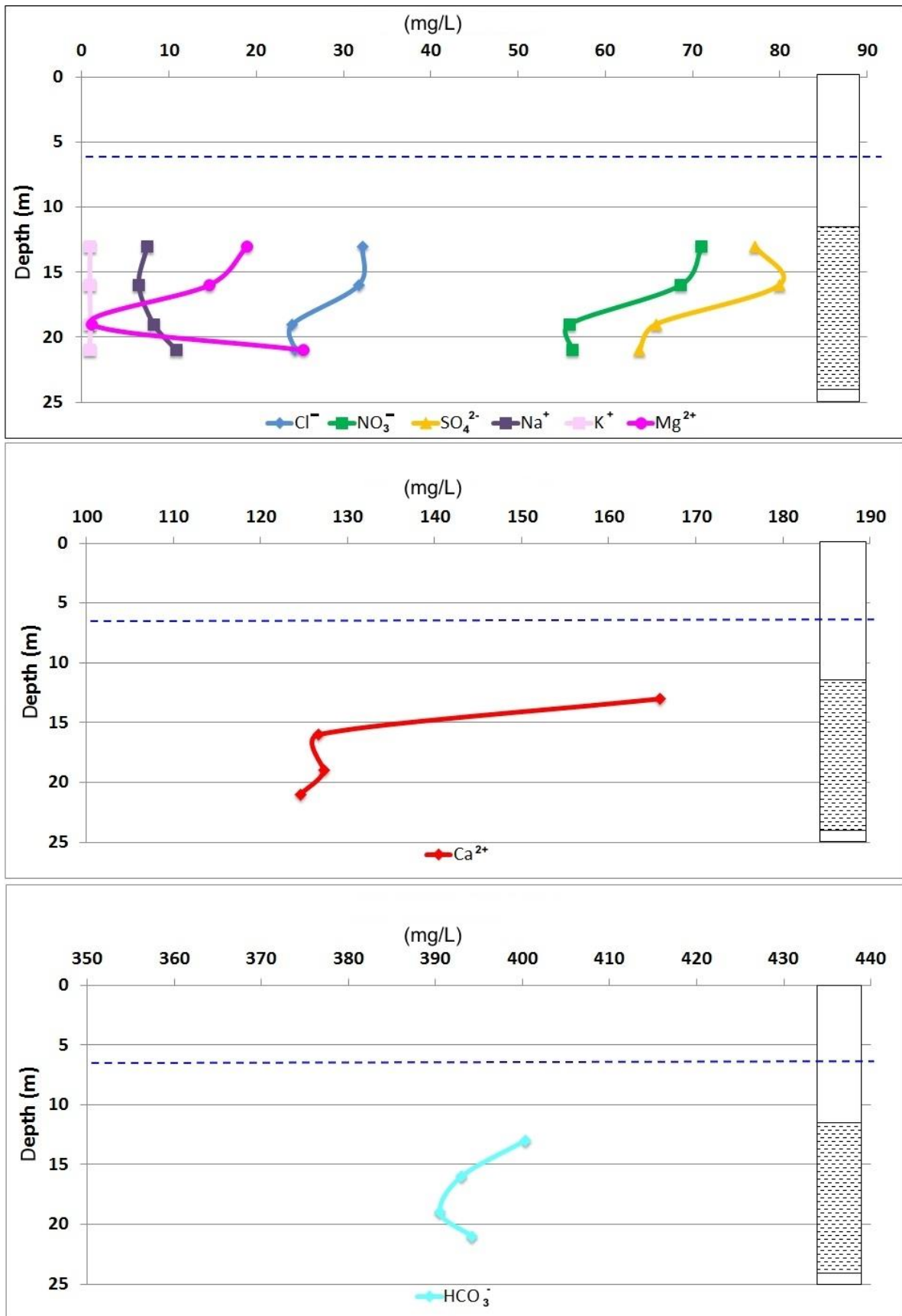
Fig. 7. Major ions vs depth during SC1 using the double packer multilevel sampling technique.
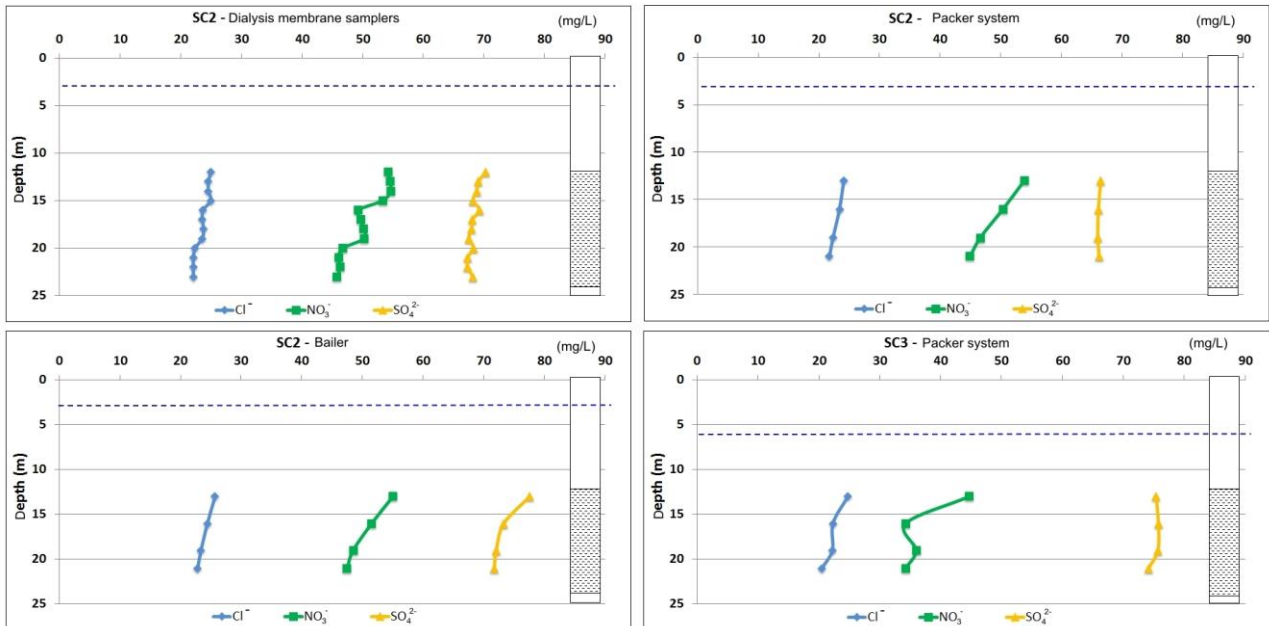
Fig. 8. Chloride, nitrate and sulphate concentrations vs depth during SC2 and SC3. The DMS, packer system and bailer multilevel sampling techniques were used during SC2, while the packer system was used during SC3.
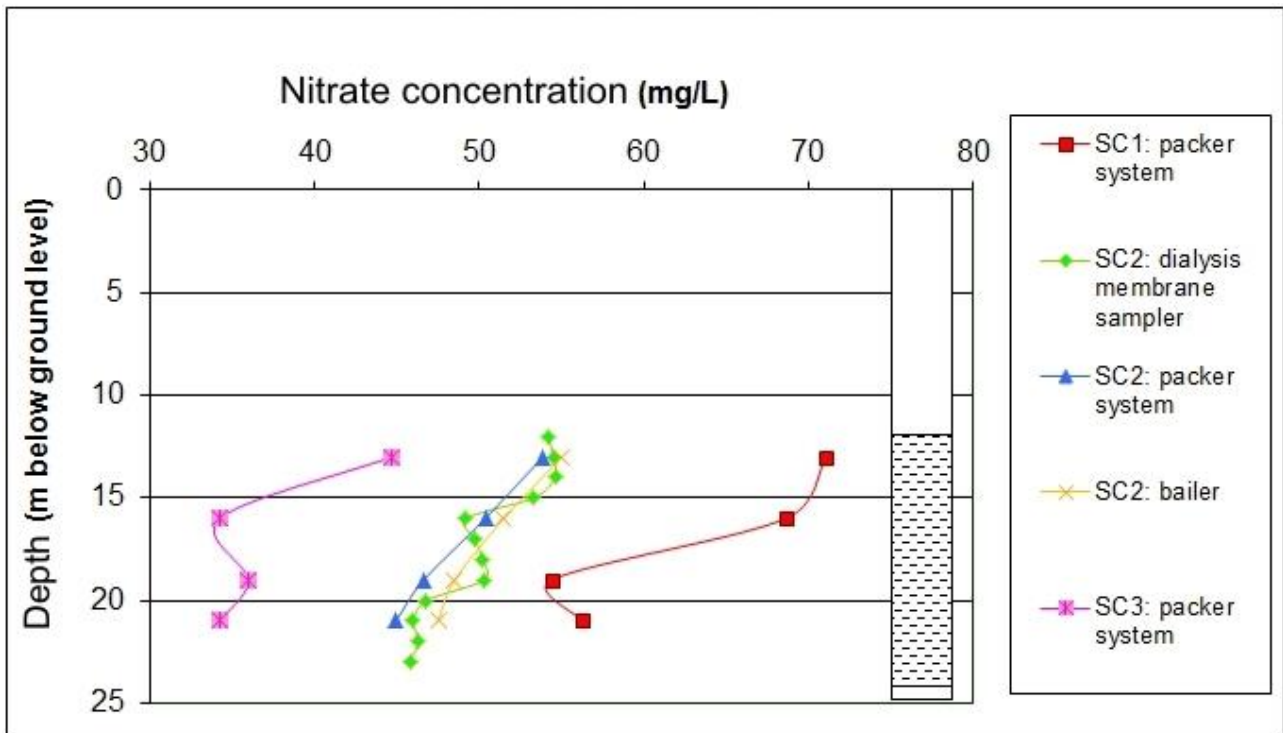


Fig. 9. Vertical nitrate stratification in the Racconigi piezometer using multilevel sampling techniques.