

Chapter 4

Natural Groundwater Background Levels of Nitrate and Landfill Effects (Apulia, Southern Italy)



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Abstract High nitrate concentration of fresh groundwater of a coastal karstic aquifer, not far from the Apulian regional capital (Southern Italy), caused public concern and alarm from the authorities. The attention of local communities focused on the effect of a group of landfills, the use of which started from 1975, using improved technological and safety devices to reduce groundwater pollution risks.

This chapter describes a simple approach based on the spatial and temporal variability of groundwater nitrate concentration (GNC) able to answer to public concern, circumscribing the main source of contamination, discussing of natural background values and spatial/temporal variability of GNC. For this purpose, a wide spatial and temporal range of data were discussed from 2006 to 2018. A regional survey of 2006–2007 was used to define background values or almost natural values of groundwater nitrate concentration (GNC). In the landfill sector, a monthly time series from 2007 to 2013 showed the GNC seasonality and the relationships with rainfall, and the periodical surveys of 2014–2018 showed the geochemical groundwater characteristics and the spatial variability of GNC, in both cases at the detailed scale of the study area.

The results show the source is diffuse and should be related to the intensive agriculture activities in the area. The results correspond perfectly with the results obtained using a multimethodological complex and expensive approach based on the use of several parameters, including nitrogen isotopes.

Keywords Nitrate · Natural background nitrate · Nitrate pollution · Landfill karstic coastal aquifer · Apulia · Italy

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4.1 Introduction

Natural soil and rock minerals containing nitrogen are generally very soluble and, therefore, rare (Appelo and Postma 1996). In contrast, compounds containing nitrogen can be found in organic matter, such as in amino acids of proteins. The natural nitrate concentration of groundwater is worldwide low; concentrations greater than a few milligrams per litre can be generally due to anthropogenic activities (WHO 2011).

High nitrate concentration of groundwater is a worldwide concern (Strebel et al. 1989; Burow et al. 2010; Thorburn et al. 2003). Potential anthropogenic sources are usually septic waste systems, inorganic fertilizers, animal manure and leachate of landfill. The correlation between agriculture activities and nitrate groundwater content is considered high in the literature (Heaton 1986; Sheikhy Narany et al. 2017).

The evolution from traditional agricultural practices to the intensive cultivation forms and the development of the chemical products has determined the spread of nitrogenous fertilizers.

As leachate contains heavy metals and nitrogenous solutes, the surrounding landfill areas have a greater probability of groundwater pollution due to the risk of leachate leakage (Mor et al. 2006). High nitrate concentration was highlighted as anomalously high, alarming the local communities and leaving them worried about the landfill activity, especially after 2011, when the latest landfill became operative.

Natural background levels of nitrate in the groundwater should be commonly used to serve as references when assessing the contamination status of groundwater units (Lucon et al. 2018; Parrone et al. 2019). This chapter depicts a simple spatial temporal method, based on the discussion of groundwater nitrate concentration (GNC), assessing if groundwater nitrate pollution by landfill leachate mixing exists and, in the negative case, suggesting alternative anthropogenic sources of nitrate. The approach is validated selecting a site for which a previous study was done. It used complex and expensive chemical and isotope parameters of groundwater and leachate, analysis of land use and the assessment of the role of nitrogen deriving from inorganic fertilizers, and mineralogical analysis of groundwater suspended particles and showed that the role of landfills in the area on the groundwater quality was null or insignificant (Cossu et al. 2018). High GNC, somewhere higher than the standard threshold, was explained as the effect of inorganic fertilizers.

4.2 Geological and Hydrogeological Settings

Four main hydrogeological structures (HSs), Gargano, Tavoliere, Murgia and Salento, can be distinguished in Apulia (Fig. 4.1) (Polemio 2016). Apart from Tavoliere, which corresponds to a shallow porous aquifer, the remaining HSs constitute wide coastal karstic aquifers, offering high-quality groundwater resources:

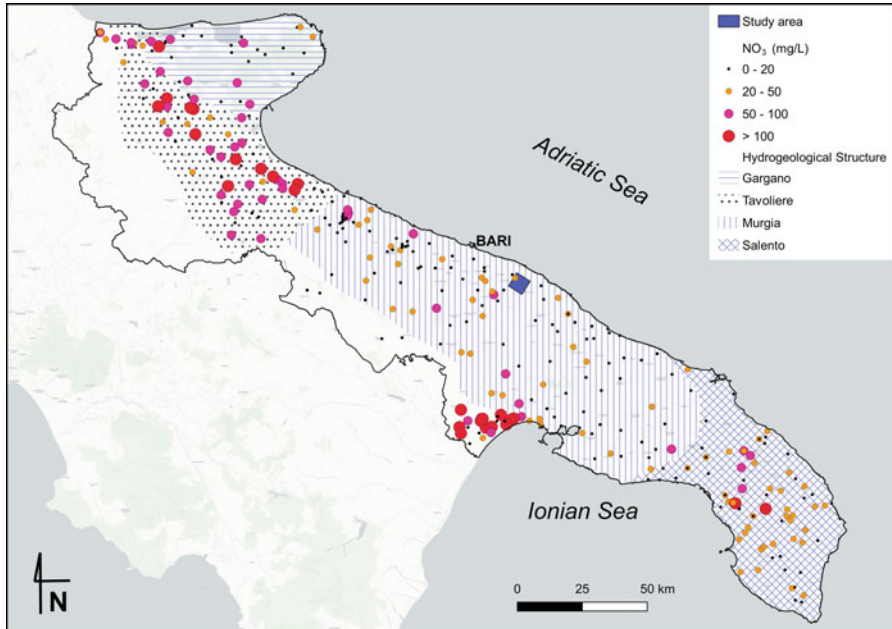


Fig. 4.1 Boundaries of main hydrogeological structures of Apulia and groundwater nitrate concentration of 2006–2007, from the regional nitrate survey of the Apulia region (Ancona et al. 2010)

Gargano, Murgia and Salento. HSs show common characteristics: they consist of Mesozoic calcareous and/or calcareous-dolomitic rocks; the permeability, which is heterogeneous and anisotropic due to the karst and the fracturing, is from medium to high.

Focusing on the Murgia HS, it is the central part of the Apulian carbonate platform, in which can be distinguished the Mesozoic limestone formation called ‘Calcarei di Bari’, roughly 2 km thick, which outcrops in the area (Fig. 4.2). The Mesozoic limestone formation was involved by paleo-tectonic and neo-tectonic movements (Pieri et al. 1997). It shows surface and deep karstic features, that is, poljes, swallow holes, dolines and dry valleys. These rocks outcrop widespread also if are locally overlapped by subsequent formations, constituted by calcarenite, sandy clay and alluvial deposits. The groundwater saturated flow involves predominantly the limestone formation, which is part of a deep karstic aquifer, involving the whole Murgia HS (Cotecchia et al. 2005). The recharge area includes inland portions of the Murgia HS (Polemio 2005); the outflow happens along the Adriatic coast and the Ionian coast (Zuffianò et al. 2016). Serious seawater intrusion effects are known for this coastal aquifer (Polemio 2016). Several degradation effects of groundwater quality and quantity of this aquifer were observed (Polemio and Limoni 2006).

The salinity threshold of pure fresh groundwater of the aquifer was assessed equal to 0.5 g/L, value mainly due to water–carbonate rock interaction (Polemio et al. 2009).

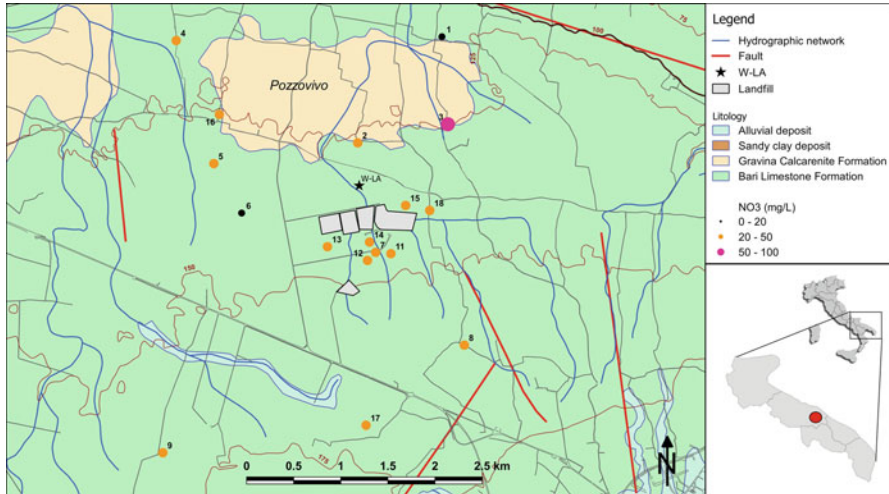


Fig. 4.2 Geological map of the study area, landfills and groundwater sampling points (W-La, 1-18)

The study area is not far from Bari, the capital town in the Apulia region (Figs. 4.1 and 4.2), in the Conversano Municipality. The land surface is a vast rural area in which agriculture is largely prevalent. Vineyards, orchards, olive trees and arable crops cultivations are very diffuse. The study area includes five solid urban waste landfills, which are located roughly at 5 km northwest from the town of Conversano, where the closest rainfall gauge of the regional network is located (Fig. 4.2). As the rest of the Murgia HS, the study area is dominated by limestone outcrop (Fig. 4.2). The local groundwater flow is towards the Adriatic Sea (6 km away, north–north-east). The depth of piezometric level from ground surface, 120–137 m, is so high to complicate any type of survey. Local groundwater overexploitation for irrigation purposes seems worsening seawater intrusion effects.

4.3 Materials and Methods

Groundwater nitrate concentration (GNC) data of 361 sampling points were considered for the period 2006–2007, involving all Apulian HSs (Fig. 4.1). The sampling points were selected for the Regional Nitrate Plan, including wells of the Regional Groundwater Monitoring Network of the Apulia region (Ancona et al. 2010). Period and wideness of this surveyed area were selected to define background or almost natural GNC values respect to fearing news published after 2011.

Moving to the detailed scale of the study area, the well W-LA was used to study the GNC monthly time series from 2007 to 2013, showing the GNC seasonality and the relationships with monthly rainfall, using the closest gauge of the monitoring

Table 4.1 Descriptive statistics for physical–chemical parameters of groundwater

	EC (mS/cm)	T (°C)	pH (–)	DO mg/L	Eh (mV)
Min.	0.68	12.07	6.73	1.39	–52.00
Average	1.18	16.75	7.14	4.35	147.18
Max	3.17	19.48	7.58	8.25	346.00
Std. dev	0.52	1.03	0.20	1.73	79.12

EC electrical conductivity at 25 °C, T temperature, DO dissolved oxygen, Eh redox potential

network of the Apulia region (5 km from landfills, very close to the SE corner of Fig. 4.2).

A total of 18 groundwater samples (Fig. 4.2) were collected between November 2014 and January 2018 during four surveys. Before sampling, each well was purged, and groundwater samples were collected using a flow cell, connected to the pumping system, and a multiparametric probe. Each groundwater sample was taken only after constant values of electrical conductivity (EC), pH, temperature (T), dissolved oxygen (DO) and redox potential (Eh) were established after purging (Zuffanò et al. 2018). The descriptive statistic for physical–chemical parameters is shown in Table 4.1.

On-site measurements of EC, pH, T, DO and Eh were conducted during sampling. The water samples were filtered (pore size 0.45 µm) using a membrane of cellulose acetate and then acidified adding HNO₃ to a pH < 2 for cation analysis, avoiding negative precipitation or absorption effects. The sample for anion analysis was unacidified. Moreover, alkalinity (as HCO₃[–]) was determined by titration with HCl.

The chemical study focused on GNC and some ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl[–], NO₃[–], SO₄^{2–}) to define the geochemical features, operating by means of ICP-OES spectrometry and ion chromatography. The maximum accepted error of charge balance was mandatory within 5% for each analysed sample. Figure 4.4 shows the analysis results and the water classification.

The discussion was supported by classical statistical, geostatistical and time series tools, assessing main statistical parameters and frequency distribution of spatial GNC at aquifer or regional scale, cross-correlation and trend.

4.4 Results and Discussion

All HSs show GNC values greater than 20 mg/L (Fig. 4.2). A global rough estimation of the upper limit for pure or natural groundwater could be considered 1 g/L (Dubrovsky et al. 2010). In the United States, the natural GNC was assessed less than 4–9 mg/L, depending on lithological situation under aerobic conditions (WHO 2011). For both the criteria, the whole Apulian region is characterized by too high GNC values, too high to be natural. The widespread quality degradation is clear due to a diffuse source: the use of fertilizers. High GNCs correspond to cultivation of crops for which a significant nitrogen surplus is commonly used (Serio et al. 2018). Serio

et al. (2018) report the negative effects of some cultivations such as of hard wheat in the Tavoliere HS, of fig trees in the Bari hinterland (Murgia HS), of sugar beets together with tobacco in some areas of the Salento HS, all areas in which, also due to the availability of irrigation facilities, intensive agricultural activities still exist. If the subset of data of the Murgia HS is considered, the range is 0.4–94.9 mg/L. The 2° quartile, equal to the median value, is 11.7 mg/L, while the 1° quartile is 3.0 mg/L: a preliminary assessment of the natural GNC of the Murgia HS could be considered not very much higher than 3.0 mg/L and in any case lower than 11.7 mg/L.

The well W-LA is downward if the landfill district is considered. The GNC monthly time series of the well W-LA permits to discuss NO_3^- variability, cross-checking this with monthly rainfall variability (Fig. 4.3). Data are available from January 2007 to March 2013 with some gaps.

The GNC range is from 18 (June 2007) to 192 (November 2012) mg/L, with mean value equal to 67 mg/L, showing that there is an almost continuous anthropogenic modification of GNC in this well. The very high GNC monthly variability shows a self-evident seasonality: if the mean monthly GNC is considered, the minimum values are in summer (from June to August the range is 33–45 g/L) and the peak values are from November (156 mg/L) and January (the range is 90–152 mg/L), the wet season in the area. After deseasonalizing, the trend GNC was analysed using the Mann-Kendall test, showing a significant decreasing trend (at 5%). This type of temporal pattern does not seem physically justifiable with the release of a leachate plume from landfill. The rainfall time series shows a seasonal pattern almost like that of GNC. The cross-correlation with rainfall shows that the peak cross-correlation, which is statistically significant, is for lag 0 (cross-correlation coefficient equal to 0.248). The rainfall excess is able to cause relevant infiltration, especially in this karstic aquifer: the result is an increase of the GNC.

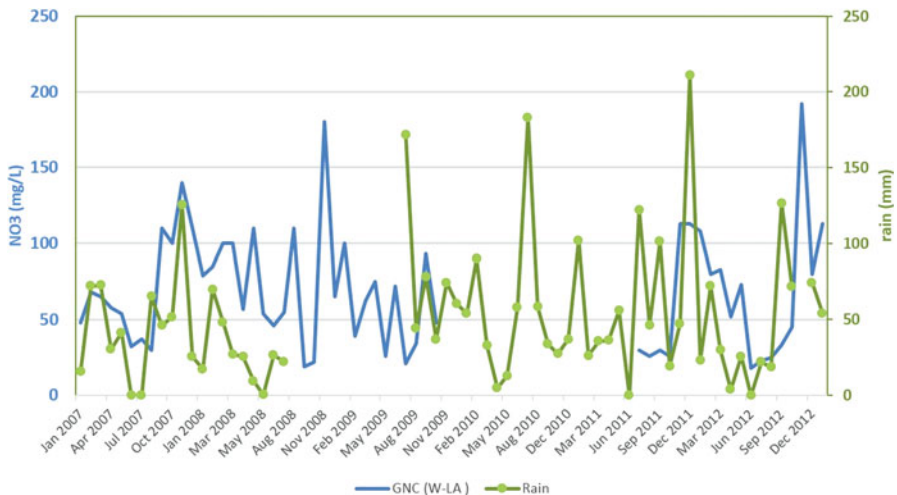


Fig. 4.3 Monthly GNC (groundwater nitrate concentration of well W-LA) and rainfall time series for the period 2007–2013

Four surveys were realized on site from 2014 to 2018 (Fig. 4.2). Statistics of on-site parameters of groundwater samples are reported in Table 4.1.

The EC range is from 0.68 to 3.17 mS/cm, 1.18 mS/cm as mean value. The peak EC was measured at the measuring point 1 (Fig. 4.2), corresponding to the highest well depth (300 m), which is reasonably the most exposed to the risks of upconing of brackish groundwater. pH is from 6.73 to 7.58, almost common values for this type of groundwater.

Piper diagram (Fig. 4.4) was used to show the geochemical facies and water types. Ca-HCO₃ and Ca-Mg-Cl are considered to be the main water types in the whole area surrounding the landfills: the former type is pure fresh groundwater (Polemio et al. 2009), whereas the latter type is due to the mixing caused by seawater intrusion (Custodio and Llamas 1996).

The samples 17 can represent the pure fresh groundwater in the study area: this sample together with the sea water sample should be considered the end members of the mixing (Fig. 4.4), focusing on the effect of seawater intrusion. Fig. 4.4 confirms graphically that the well-known mixture of pure fresh groundwater and saline water due to seawater intrusion is the phenomenon to be considered dominant in the study area (Polemio et al. 2009).

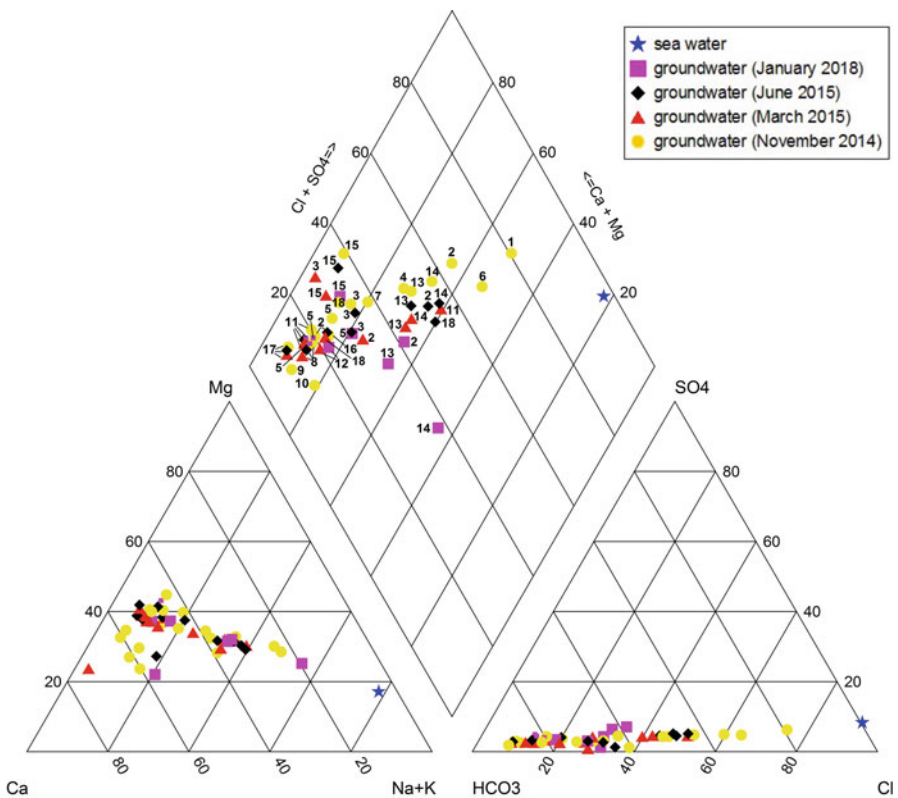


Fig. 4.4 Piper diagram of sampled groundwater

The GNC ranged from the minimum of 13.40 mg/L to the peak value of 59.90 mg/L (Fig. 4.2), with a unique sample slightly exceeding 50 mg/L, considered a worldwide upper value for good-quality waters. The spatial distribution is not affected by the position respect to landfills and confirms a diffuse effect of anthropogenic degradation of groundwater quality.

All results show that there is no evidence of negative effects of landfills on the GNC of the area. This result is with the previous results obtained with an innovative multi-methodological approach, including the use of more isotopes, as a nitrogen isotope (Cossu et al. 2018) showing the key role of the inorganic fertilizer utilization to justify the GNC in the study area.

4.5 Conclusions

Wide portions of main hydrogeological structures of Apulian region are characterized by high and unnatural GNC. High GNCs are due to anthropic effects, especially for the excessive use of fertiliser in agricultural.

The spatial temporal approach based on the discussion of groundwater nitrate concentration (GNC) was able to clarify the lack of groundwater pollution due to leachate leakage and mixing; it allowed to formulate realistic hypotheses, confirmed by the use of other methodologies or other studies, at different scales, on the main source of groundwater nitrate.

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Author Contributions Authors’ contribution should be considered equal.

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