1 How can the role of leachate on nitrate concentration and groundwater

2 quality be clarified? An approach for landfills in operation (Southern

- 3 Italy)
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Abstract: Where the unique natural water resource is groundwater, the attention and the susceptibility of local communities and authorities to groundwater quality degradation risks can be so high to determine relevant problems to waste management, especially for landfills in operation or to be realised. A multi-methodological approach was suggested with the purpose to clarify the role of landfill leakage on groundwater quality degradation.

The selected study area (SSA) hosts some landfills in a narrow portion of a wide and deep coastal karstic aquifer, for these characteristics to be considered a case of high hydrogeological complexity and vulnerability. News concerning nitrate and secondly iron groundwater concentration anomalously high caused concern in the population and strong local opposition to landfills.

The multi-methodological approach includes: the hydrogeological site characterization; the chemical study and the multi-isotope characterization of groundwater and leachate; the land use analysis and the estimation of nitrogen contributions deriving from fertilizers; the mineralogical study of groundwater suspended particles to define the role of natural soil substances.

32 The hydrogeological site characterisation highlighted the local peculiarities of the 33 aquifer. The chemical study was used to define geochemical features, groundwater and 34 leachate characteristics and their macroscopic mixing.

The environmental isotopes of hydrogen, carbon, nitrogen, and oxygen were used to investigate the groundwater origin, the most relevant geochemical reactions, the existence of groundwater-leachate mixing, and the sources of anthropogenic NO₃. The land use analysis highlighted quantity and type of used fertilizers permitting to compare these with groundwater in terms of isotopic signature. The mineralogical study demonstrated the role of suspend natural particles due the presence of *terre rosse* (red or residual soils) in groundwater.

42 The approach confirmed that there are not the groundwater quality degradation effects

43 of landfills, contributing to reassure population and institutions, simplifying the waste

44 management.

45 Keywords: landfill, leachate, pollution, nitrate, isotopes, karstic coastal aquifer, Italy,
46 Apulia

47 **1. INTRODUCTION**

48 Municipal or urban landfill leachate consist generally of many different organic and 49 inorganic compounds that are either dissolved or suspended in the wastewater 50 (Mendoza et al., 2017). According to Mor et al. (2006), areas close to landfills have a 51 greater possibility of groundwater contamination because of the potential pollution 52 source of leachate which also contain heavy metals, including iron, and nitrogenous 53 solutes, including nitrate (Mendoza et al., 2017). Anomalous high groundwater 54 concentrations of these substances close to landfills can alarm population, highly 55 increasing opposition to landfills in operation and/or to landfill extensions.

56 Nitrogen-containing compounds are found in the organic substance, where nitrogen is 57 present, for example, in the amino acids that make up the proteins. In contrast, 58 lithospheric minerals containing nitrogen are generally very soluble, and therefore rare 59 (Appelo and Postma, 1996). Nitrogen is an important component of natural waters, 60 where it is present dissolved in different valences such as +5 in NO₂, +3 in NO₂, 0 in N₂ 61 and -3 in NH₄ (Appelo and Postma, 1996). The concentration of dissolved molecular nitrogen in water, in equilibrium at 25 °C with the atmosphere, is 5x10⁴ M (14 mg/L). 62 63 The natural groundwater nitrate concentration is generally low; concentrations greater

- 64 than 1 mg/L can be generally due to anthropogenic activities (Dubrovsky et al., 2010).
- 65 High-nitrate concentrations in groundwater are a worldwide problem (Burow et al.,
- 66 2010; Strebel et al., 1989; Thorburn et al., 2003).
- 67 Ingestion of high nitrate rate can cause many problems to humans; the World Health
- 68 Organization (WHO) states that the NO₃ concentration for drinking water should be less
- 69 than 50 mg/L (World Health Organization, 2011).
- 70 Potential sources of nitrate for groundwater include mineral fertilizers, septic waste,
- animal manure, and landfill leachate (Heaton, 1986).
- As all crops are not able to use all the added mineral fertilizer, the use of nitrogenous
- 73 fertilizer creates risk of increasing percolation and leaching of nitrates to groundwater,
- 74 which are very relevant in the case, almost frequent, of over fertilisation (Bijay-Singh et
- 75 al., 1995). Many studies have indicated a high correlation between agriculture and
- 76 nitrate concentrations in groundwater (Heaton, 1986; Sheikhy Narany et al., 2017).
- 77 Iron is a metal that can be considered almost common in natural soils and rocks.
- 78 Groundwater can transport iron as dissolved or suspended particles. The extent to which
- 79 iron dissolves in groundwater depends on dissolved oxygen and pH of water and not by
- 80 natural or anthropogenic iron sources (Appelo and Postma, 1996); the suspended
- 81 particles can be due the natural presence of residual soils (Moresi and Mongelli, 1988).
- 82 A low concentration of iron can be considered positive, as it is an essential nutrient for
- human, if natural (World Health Organization, 2011).
- 84 The aim of this paper is to clarify the existence or the absence of groundwater pollution

85 by landfill leachate mixing and, in the latter case, to explain the source of groundwater 86 quality degradation mainly focusing on the role of nitrate and secondly of iron. For this 87 purpose, a multi-methodological approach was proposed. A selected study area (SSA), 88 was considered with the purpose to testify the existence or excluding leachate effects on 89 groundwater quality. The SSA is a narrow portion of a wide and deep coastal karstic 90 aquifer, for these characteristics to be considered a case of high complexity and 91 vulnerability. Five landfills have operated from 1975, one after the other, using 92 increasing safety and technological devices to reduce risks due to leachate leakages. 93 Mainly nitrate and secondly iron groundwater concentration were considered 94 anomalously fearing the population, worried about the potential effects of landfills. For 95 this reason, some landfills were seized by public authorities, hypothesizing a huge role 96 of these in the groundwater quality degradation.

97 The approach considers each potential source of nitrate, considering the type of local
98 land use: mineral fertilizers, septic waste, animal manure and landfill leachate.

99 The approach includes the use of nitrogen, oxygen and tritium isotopes as tracers for100 evaluating contamination of the landfill.

101 The use of δ^{15} N is based on the distinct isotopic composition that characterizes nitrate of

102 different origin (Aravena et al., 1993). For the commercial fertilizers, typical $\delta^{B}N$ values

103 range from -2% to +4%, for soil organic nitrogen nitrate the values range from +3% to

104 +8% and + 10% to +20% for human and animal waste nitrate (Freyer and Aly, 1974;

105 Kreitler, 1975; Gormly and Spalding, 1979; Heaton et al., 2012). In the case of ¹⁸O,

106 synthetic fertilizers are characterized by enriched ¹⁸O values (+ 18% to +22%), since the

107 source of oxygen for these chemicals is atmospheric oxygen whose value is ¹⁸O=+

108 23.5‰ (Amberger and Schmidt, 1987). This method was successfully used for the
109 resolution of different groundwater nitrate sources in Australia, identifying a leachate
110 derived source down gradient from landfill (Moreau and Minard, 2014).

111 The method based on the determination of the stable isotopes ²H and ¹⁶O, useful to 112 support the hydrogeological conceptualisation (Mook, 2000), is able to highlight 113 leachate contamination of groundwater, i.e. due the enrichment of ²H due to extensive 114 methanogenesis (Hackley et al., 1996).

115 Tritium (³H) is a radioactive isotope of hydrogen, occurring in very low quantity in the 116 natural waters (Tazioli, 2011). Tritium levels in municipal solid waste landfill leachate 117 can be several orders of magnitude greater than background groundwater levels due to 118 the presence in the waste of some items containing high levels of tritium, such as 119 luminescence paints and watches (Robinson and Gronow, 1996; Hackley et al., 1996; 120 Tazioli, 2011) as verified in municipal landfills throughout the world (Fritz et al., 1994; 121 Robinson and Gronow, 1996; Hughes et al., 2011; Raco et al., 2013). Because of this, 122 tritium may be a sensitive indicator of leachate impacts on groundwater samples 123 (Kerfoot et al., 2003).

124 Other isotope used for prevention and control of groundwater pollution is the $\delta^{\mu}C$ of 125 total dissolved carbon. In general, the range of $\delta^{\mu}C_{\mu\nu}$ in the groundwater may be very 126 wide, the most common values range from -25% to -10%, (Boutton, 1991).

127 Under reduction conditions (similar to those present in landfill environments), δ^{13} C is

highly enriched ($\delta^{13}C > +10\%$) (Wimmer et al., 2013). The positive value of $\delta^{13}C$ is due

129 to the production of methane under anaerobic conditions (Wimmer et al., 2013).

130 Focusing on leachate-impacted groundwater, $\delta^{\mu}C$ of major carbon compounds

131 highlights attenuation due to biogeochemical reaction from dilution as a result of

132 advective dispersion (Mohammadzadeh and Clark, 2011).

133 2. SELECTED STUDY AREA

134 The SSA is located in the municipality of Conversano, close to Bari, the main town in

the Apulia region (Fig. 1). The SSA elevation ranges from 100 to 175 m a.s.l., with a

136 mean land surface slope of 1.3% from west to east (seaward). The SSA is a rural area.

137 Agriculture is the main activity, namely mainly due to vineyards cultivation, orchards,

138 olive trees, and arable crops.

139 The study area includes 5 solid urban waste landfills, distinguished from I to V in

140 chronological order of realisation, which are located roughly at 5 km northwest from the

141 town of Conversano (Fig. 1b and 1c).

142 Landfill I collected wastes from 1975 to 1982, for about a year in 1989 and for about

143 100 days in 1996, less than 10 years as total. This landfill was not sealed by capping.

144 The leachate tapping system was not realized.

The Landfill II operated from 1993 and was closed in 1996; the landfill post-mortem was terminated. It was equipped with a definitive capping realized with HDPE geomembrane and other typical urban waste tools, to nullify leachate leakage risks. The

148 landfill II top now hosts a photovoltaic system. The leachate tapping system is now

- 149 completely unuseful and unusable.
- 150 Roughly 1,465,000 m³ of wastes were disposed from 1996 to 2011 in the landfill III. At
- 151 the present, the top of the III has been realised by a capping of HDPE geomembrane.

152 The Progetto Ambiente Bacino BA/5 landfill system is made up of two sectors or tanks,

153 landfills IV and V (Fig. 1c). Roughly 200,000 m³ of waste were disposed from March

- 154 2011 to April 2013, temporally covered by soil layer in landfill IV, while the V was
- 155 realised but is still unused.
- 156 The landfills from II to V were built with a very low permeability bottom with different

157 solutions which include a clayey layer as minimum to hold back the leachate, collecting,

- 158 tapping and treating it. Contrarily, the oldest landfill (I) has not waterproofing liners at
- 159 the bottom; after closure, the landfill I was not sealed by impervious capping to prevent
- 160 rainwater infiltration, nor precautions were taken to collect leachate, limiting the
- 161 leakage toward groundwater.
- Landfills III, IV and V were sized by authorities. Merging all boundary conditions, itwas possible to sample only the leachate of landfill IV.

164 3. GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

165 The Murgia Plateau, which represents the central part of the Apulian carbonate 166 platform, is made up of a Cretaceous carbonate succession in which the Bari Limestone 167 Formation (Valanginian-Early Turonian) and the Altamura Limestone Formation 168 (Coniacian-Early Campanian) can be distinguished (Spalluto, 2012). An unconformity

169 marked by a bauxite horizon and red soil or terra rossa deposits separates the two

170 Cretaceous formations (Borgomano, 2000). The Bari Limestone Formation, roughly 2

171 km-thick, outcrops in SSA (Fig. 1b).

Red soil is produced by limestone weathering: when limestone weathers, mainly by dissolution, the clay contained in the rocks is left behind, along with any other nonsoluble rock material. The red soil is typical of karstic Mediterranean areas (Bates and Jackson, 1987). The main minerals of red soil are illite, kaolinite, and oxides and hydroxides of iron; minor components are quartz, feldspars, micas, oxides and hydroxides of aluminium, and oxides of titanium (Moresi and Mongelli, 1988).

178 The Murgia Plateau emerged since Late Cretaceous until Pliocene (Pieri et al., 1997), 179 creating a major unconformity covered by thin (<100 m in thickness) Pliocene to 180 Quaternary deposits. These deposits consist of Middle Pliocene-Lower Pleistocene 181 calcarenite (Gravina Calcarenite) and Quaternary alluvial deposits, silt and red soil, that 182 fill the bottom of very flat and large karstic valleys, in SSA. The thickness of calcarenite 183 and alluvial deposits is low and, in any case, their role is certainly negligible for the 184 scopes of the paper. A narrow outcrop of marine silico-clastic unit of Middle 185 Pleistocene age lies above Calcarenite di Gravina Formation at the north-western side of 186 SSA. It includes fine sands and brownish silts in the lower part and by sandy clays and 187 greenish and grey clays in the upper part, reaching a maximum thickness roughly equal 188 to 15 m.

189 The plateau, greatly affected by paleo-tectonic and neo-tectonic movements (Pieri et al.,

190 1997) shows intense karstification with karst features at various scales, including 191 swallow holes, dolines, dry valleys, and poljes. The saturated groundwater flow happens 192 only in the deep and wide karstic aquifer which includes the whole Murgia Plateau 193 (Cotecchia et al., 2005). The inland portions of Murgia constitute the recharge area; the 194 natural outflow happens along the coasts of both the Adriatic and Ionian Sea (Polemio, 195 2005; Zuffianò et al., 2016). The aquifer is of coastal type, with relevant seawater 196 intrusion effects (Polemio, 2016). Different quality and quantity degradation effects 197 affect this aquifer, as well known by time (Polemio and Limoni, 2006).

198 Pure fresh Murgia groundwater shows typically salinity less than 0.5 g/L with chemical

199 characteristics determined by water-carbonate rock interaction (Polemio et al., 2009).

Focusing on SSA, groundwater flows toward the Adriatic coastline, with a general flow
direction towards NNE. The piezometric depth is high, from 120 to 137 m, feature this

that complicates any type of survey. Excessive groundwater exploitation, especially for
 irrigation, is still increasing the effects of seawater intrusion.

204 4. MATERIALS AND METHOD

A multi-methodological approach was tested in SSA. The test involved a survey squared area of 6 km of side centred on the landfill group. 18 water wells or piezometers were selected; the majority is used for irrigation the rest for landfill monitoring (Fig. 1b).

209 The approach merges in unique framework of knowledge: the hydrogeological site 210 characterization; the chemical study of groundwater and leachate; the multi-isotope

characterization of groundwater and leachate; the land use analysis and the estimation of nitrogen contributions deriving from agricultural activities, focusing on the use of fertilizers; and the mineralogical study of groundwater suspended particles to define the origin of the iron in the water samples.

The purpose of the hydrogeological study is to confirm the hydrogeological conceptualization of the study area bounding aquifers and aquitards, assessing hydraulic conductivity, recognising main three-dimensional groundwater flow paths, guiding sampling and data discussion, using a wide set of methods, the systemic description of which is outside the paper scope (Custodio and Llamas, 1996). Climatic gauge data, including rainfall and air temperature measurements as minimum, should be considered mandatory.

The groundwater potentiometric head measurement within wells under no-pumping conditions (static head) was realized seasonally in SSA, using a larger network (using some wells outside), and hourly with automatic probes, using a group of wells and piezometers close to the five landfills. The automatic probes measured groundwater temperature and electrical conductivity, apart from potentiometric head.

Multiparametric logs of all available wells, tracer tests, pumping tests, and the use of a climate gauge completed the hydrogeological set of determinations. Multi-parametric well logs of electrical conductivity (EC, defined as electrical conductivity at 25 °C), pH, temperature (T), salinity or TDS (estimated by EC and T), redox potential (Eh) and dissolved oxygen (DO) could highlight the existence of natural quality trend and/or

232 anomalous effects to be related to anthropogenic effects and seawater intrusion 232 (0, t, t) is the 1000

233 (Cotecchia et al., 1999).

The sampled well was purged using a flow cell and a multi-parametric probe with EC,

T, pH, TDS, Eh, and DO sensors, withdrawing 3 water-well volumes at least pursuinglow flow conditions, after that sampling when the steady groundwater trend of each

- 237 parameter is observed.
- After sampling, on site procedures included: (1) storing EC, T, pH, TDS, Eh, and DO values of sampling; (2) assessing the alkalinity in the field, by means of titration with HCl; (3) acidifying samples for cation analysis by the addition of HNO₃ to a pH < 2; 4) filtering water samples for metals determination through a cellulose acetate membrane (pore size 0.45 μ m) and then acidifying by HNO₃ to a pH < 2.

The chemical study was focused on main ions along with some minor significant ion (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁺, NH₄⁺, Li⁺, F⁻, Fe²⁺, and Mn²⁺) to define: geochemical features, supporting the hydrogeological conceptualisation; groundwater and leachate characteristics; and macroscopic mixing (Custodio and Llamas, 1996; Syafalni et al., 2014).

All these procedures were applied to all 18 wells and the leachate of landfill IV. Survey and sampling were realised during November 2014 (distinguished with * throughout this paper), March (**) and June 2015 (***). The unique exception is at point 4 of the sampling procedure: a former fraction of groundwater samples was not filtered but was acidified before chemical analysis. This choice was due to the scope to explain some

anomalously high iron contents that were detected in previous determinations in SSA.

254 The latter fraction was filtered to tap suspended particles from filters to be studied with

- the scanning electron microscopy. The scope of both fractions was to verify if they can explain a dissolved metal enrichment in the case of sampling without filtering before acidifying as was realised in some previous determinations.
- Water chemistry analyses were carried out at the chemical laboratory of DiSSPA. Anions (F, Cl, NO_{3} , SO_{4}^{2}) and ammonium ion (NH_{4}^{2}) were analysed by ion chromatography, while Li, K, Na, Ca, Mg, Fe and Mn by means of ICP-OES spectrometry.
- The charge balance errors for the analyses was mandatory within 5%. Ion chromatography results and the water classification are shown in Fig. 2.
- 264 The descriptive statistic for groundwater and leachate is shown in Table 1 and Table 2.
- 265 The multi-isotope characterization of groundwater and leachate was focused on $\delta^{\mu}O$, 266 $\delta^{2}H$, ${}^{3}H$, $\delta^{\mu}C$, $\delta^{\mu}N$ -NO₃ and $\delta^{\mu}O$ -NO₃. Water sampling and storing for isotope 267 determinations do not require any specific pre-treatment apart for the dissolved 268 carbonate $\delta^{\mu}C_{\mu c}$, $\delta^{\mu}N$ -NO₃ and $\delta^{\mu}O$ -NO₃. The sample for the dissolved carbonate $\delta^{\mu}C_{\mu c}$ 269 was acidified with orthophosphoric acid, according to Atekwana and Krishnamurthy 270 (1998). The sample for $\delta^{\mu}N$ -NO₃ and $\delta^{\mu}O$ -NO₃ was acidified with hydrochloric acid to a 271 pH < 2.
- It could be suggested a refrigerated storing of the polyethylene bottles of tritium (³H)
 water samples until the laboratory analysis starts. The whole set of determinations were

realised in SSA (Table 3).

275 The isotopic content of δ^{15} N-NO₃ and δ^{18} O-NO₃ was determined also considering the

276 main used commercial fertilizers, using the result of land use analysis (Table 4).

277 Stable isotope values of δ^{18} O and δ^{2} H were measured by Wavelength-Scanned Cavity

278 Ring Down Spectroscopy technology. The uncertainty of the measurements is $\pm 0.2 \delta$

279 % for δ^{18} O and $\pm 1 \delta$ % for δ^{2} H (Table 3). The isotopic ratio δ^{13} C_{DIC} is measured by mass

280 spectrometry IRMS with a Finnigan MAT250. The uncertainty of the measurements is

 $281 \pm 0.2 \ \delta \ \% o \ for \ \delta^{\tiny 13}C_{\tiny DIC} \ (Table \ 3).$

Groundwater and leachate ${}^{\circ}$ H level was determined at the Hydroisotop Schweitenkirchen GmbH Laboratory (Germany), by liquid scintillation counting (LSC), proceeded by electrolytic enrichment (Table 3). Due to the low level of tritium in groundwater, each groundwater sample was subjected to an electrolytic enrichment process before the measurement. The analytical precision for tritium was 0.5 TU (1 σ criterion/analytical errors), which can vary from ±0.59 to ±0.96 TU.

The analysis of nitrogen and oxygen were carried out at the ISO4 laboratory of Torino (Italy). For nitrogen and oxygen isotopic analysis, the dissolved nitrate was concentrated using anion exchange columns filled with resin. Nitrate were then eluted with HCl and neutralized with Ag₂O, filtered to remove the AgCl precipitate, then freeze-dried to obtain solid AgNO₃, following a modified method from Silva et al. (2000). Two aliquots of this salt were separated and then combusted in sealed quartz tubes with different reagents, in order to produce N₂ for $\delta^{\mu}N$ analysis and CO₃, which is

cryogenically purified and analysed for its oxygen isotope composition. The analysis of

296 gases was carried out by means of IRMS (Finnigan MAT 250). The 1σ analytical

297 precisions for δ^{15} N-NO₃ and δ^{16} O-NO₃ are ±0.5% and ±1%, respectively.

The land use analysis should recognize potential nitrogenous sources in the SSA, using a wide set of methods, the systemic description of which is outside the paper scope. In the case of mainly cultivated areas, an affordable choice is to use remote sensing maps, refined by on site GPS observations, and technical interviews. On this basis, it is possible to recognize cultivation, acquiring data on fertilizer loads and types (Table 4).

This approach was used in SSA: merging satellite images, land use maps, and direct observation on site, using GIS tools and interviews, it was possible to characterize in details the use of fertilizers in an area equal to 8 km² around the landfill group. The current land use in the study area comprises mainly vineyards cultivation; orchards, mainly cherries; olive trees; and arable crops, mainly horticultural crop.

The mineralogical study of groundwater suspended particles could be easily realized distinguishing the particles trapped by filters (cellulose acetate membrane with pore size of 0.45 μ m), used for groundwater sampling for dissolved metal determinations, by means of SEM (scanning electron microscopy). It was previously used to recognise the source of chromium contamination of groundwater in a natural soil (Scott et al., 2011). This method was applied in SSA specially to define the origin of the iron in the groundwater samples (Table 5).

315 The particles of twelve filter of cellulose acetate membrane (pore size $0.45 \ \mu m$), used

for the sampling of the metal dissolved in groundwater, were analysed at laboratory of Scienze della Terra e Geoambientali of University of Bari by means of scanning electron microscopy with an energy-dispersive X-ray spectrometry (SEM-EDS). SEM and EDS analysis were recorded by using EVO-50XVP (Leo-Zeis); microanalyses were achieved with an X-max (80 mm²) silicon drift Oxford detector supplied with a Super Atmosphere ThinWindow ©.

322 **5. RESULTS AND DISCUSSION**

323

324 5.1 Hydrogeology

The hydrogeological study confirmed the conceptualization: SSA correspond to a unique, karstic, wide, and deep (hundreds of meters) aquifer, the groundwater of which mainly flows in a direction roughly orthogonal to the coastline (SSO-NNE). The potentiometric variations are deeply influenced by daily and seasonal exploitation needs for irrigation, with relevant difference between wells.

330 A typical example of well multi-parametric log of a Murgia well in almost natural 331 conditions is in Fig. 2: almost steady temperature (apart from shallower portion), 332 roughly 17 °C, low and almost steady EC and salinity (with typical values of pure fresh 333 groundwater), pH slightly greater than 7, positive values of DO and Eh (Cotecchia et 334 al., 1999). Typical deviation by this trend were observed for the deeper portion of some 335 wells in terms of greater values of EC and TDS and decrease almost to zero of DO and 336 Eh, as it could be the effect of upconing due to well overexploitation (Polemio et al., 2009). 337

338 26 well tests or pumping tests were available for SSA. The hydraulic conductivity 339 determined by these tests was in the range 5 10° to 4 10° m/s, with mean value equal to 340 4 10° m/s, which is typical of aquifers of good hydrogeological characteristics 341 (Cotecchia et al., 2005).

A mobile downhole fluorometer was used to check if relevant vertical flow components exist into surveyed wells, realising tracer tests with fluorescein (Polemio and Mitolo, 1998; Polemio and Limoni, 2009): the results showed the negligible role of vertical and flow components in the available wells.

346

347 5.2 Chemical composition

348 Physical-chemical characteristics of leachate samples depend mainly on waste 349 composition and water content of waste. The characteristics of the leachate samples of 350 landfill IV are in Table 2. The pH range is from 7.90 to 8.20. The values of EC (21.80-351 26.50 mS/cm), BOD (335-450 mg/L), COD (2240.0-5210.0 mg/L), and high values of 352 ammonium (range from 1603.0 to 2636.0 mg/L) indicate the presence of inorganic 353 material in the leachate. The BOD/COD ratio is considered an indicator of organic 354 matter degradation in a landfill. Low BOD, low BOD/COD ratio (0.12 as mean value), 355 high ammonium and pH 8.1 (mean values) are the characteristic conditions of 356 methanogenic phase (Lo, 1996).

357 Considering the sampled groundwater, pH is from 6.73 to 7.44 and EC is 0.68 to 2.91 358 mS/cm. The highest electrical conductivity values were measured at well 1, the deepest

359 (300 m in depth), reasonably due to the seawater intrusion.

The chemical groundwater classification could be based on the Langelier-Ludwig diagram (Fig. 3): the first group of samples (right-bottom) shows a Ca-Mg-HCO₃ composition, with TDS from 671 to 936 mg/L, while the second group shows a Ca-Cl-SO₄ composition, with TDS from 1147 to 1925 mg/L; the salinity increase from the former to the latter group is coherent with an almost proportional sea water mixing (Custodio and Llamas, 1996; Polemio et al. 2009).

366 The well 17 and its samples can represent the pure fresh groundwater; these samples 367 and the sea water sample should be considered the two end members of the mixing line 368 plotted in Fig. 3, along which all the groundwater samples are dispersed, confirming the 369 idea that the well-known mixture of pure fresh groundwater and saline water due to 370 seawater intrusion is the dominant phenomenon in SSA, as well-known at regional scale 371 (Polemio et al., 2009). Using the Langelier-Ludwig diagram (similar results were 372 obtained with other purely chemical diagrams, as suggested by (Custodio and Llamas, 373 1996), the chemical study does not show macroscopic leachate effects on groundwater, 374 the variable characteristics of which seems mainly due to pure mixing with sea water. 375 The chemical study, almost simple and inexpensive, confirms its utility, as in previous 376 experiences (Syafalni et al., 2014).

The concentration of NO₃ of groundwater samples varied from 13.40 to 59.90 mg/L (Table 2), although only one sample mildly exceeded the permissible limit, equal to 50 mg/L (3 in Fig. 2b). The NH₄ concentration in the water samples was lower than the

- 380 instrumental detection limit (<0.1 mg/L).
- 381 The BOD and COD ranges were from 1.00 to 10.00 mg/L and from 5.00 to 51.20 mg/L
- 382 respectively. The mean groundwater BOD/COD ratio was equal to 0.5, significantly
- 383 different from the leachate ratio.
- 384 The groundwater samples were analysed for heavy metal such as Fe and Mn (Table 2).
- 385 Fe concentration in the groundwater samples varied from 0.01 to 1.79 mg/L while Mn
- 386 varied from 0.0001 to 0.02 mg/L.
- 387
- 388 5.3 Mineralogy of the suspended solids

The results of mineralogical analysis show that the filtered material is mainly composed of calcium oxides (26-93%), iron (8-84%) and silicon (2-47%), thus confirming the typical red clay composition present in suspension in the analysed groundwater samples. These results show clearly the iron concentration of unfiltered and unacidified samples was due the natural or background effect of suspended clay particles and not to anthropogenic activities. These results are coherent with previous experiences (Scott et al., 2011).

396

397 5.3 Isotopic composition

Stable isotopic compositions of groundwater range from -7.23 to -6.42‰ for δ^{18} O and from -42.83 to -39.27‰ for δ^{2} H. The mean δ^{2} H and δ^{18} O values for groundwater and leachate are -41.00 and -6.78‰ and 5.57 and -4.93‰ respectively (Fig. 4 and Table 3).

401 The isotope composition is very similar for all groundwater samples and completely 402 different respect to leachate samples. Fig. 4 shows the $\delta^{18}O/\delta^2H$ values compared with 403 the Global Meteoric Water Line (GMWL; Craig, 1961) and the Mediterranean Meteoric 404 Water Line (MMWL; (Gatt and Carmi, 1970); the groundwater samples are very close 405 to the Global Meteoric Water Line (GMWL; Craig, 1961), confirming the high impact 406 of the isotope characteristics of infiltrated rainfall (natural recharge) and secondly the 407 absolutely negligible role of leachate characteristics. Fig. 4 suggests a rapid infiltration 408 of meteoric water recharging the coastal aquifer, in a temperate weather (Mook, 2000). 409 The absence of groundwater point dispersion denotes that the sampled groundwater 410 belongs to a geographically narrow area of the same aquifer, as an effect of a narrow or 411 homogenous recharge area. These results are coherent with previous hydrogeological 412 knowledge on the aquifer and its groundwater (Tulipano et al., 1990; Polemio and 413 Mitolo, 1998) and do not show effects of groundwater-leachate mixing, coherently with 414 previous landfill studies (Syafalni et al., 2014).

The leachate tritium ranges from 182 to 235 TU (Fig. 5a). Tritium levels in groundwater samples range from <0.60 (lower detectable limit) to 3.1 TU. Comparing this range with rainfall data published by the Global Network of Isotopes in Precipitation of IAEA (http://www-naweb.iaea.org/napc/ih/IHS resources gnip.html), it can be considered the pure effect of radioactive decay of rainfall tritium (Tazioli et al., 2002). These tritium levels suggest that groundwater residence time in the carbonate aquifer is generally high, the leachate contamination seems unrealistic (Fig. 5a). These results are coherent

422 with previous experiences on the groundwater contamination due to leachate (Hughes et

423 al., 2011; Raco et al., 2013). Secondly, the significance of salinity variability, roughly

424 assessed by chloride, on TU variability seems negligible, showing the seawater425 intrusion cannot justify the low TU values of groundwater (Fig. 5a).

426 Even for $\delta^{B}C$ the isotopic variability of groundwater is rather low (-7.23 ÷ -11.28 ‰) 427 and typical of natural groundwater (Fig. 5b); these values are characteristic of 428 groundwater flowing within an aquifer constituted by carbonate rocks of marine origin 429 (Anders et al., 2014). δ ¹³C of leachate samples ranges from 21.85 to 22.77 ‰. The high 430 positive value of leachate $\delta^{B}C$ is due to a typical process which is well-known, the 431 methanogenesis process (Wimmer et al., 2013), that using the light isotope, leaves the 432 heavy isotope available for the formation of the percolated aqueous phase, which is 433 enriched in δ^{13} C. δ^{13} C results do not show effects of groundwater-leachate mixing, 434 coherently with previous landfill studies (Mohammadzadeh and Clark, 2011).

435 The groundwater isotopic compositions of dissolved nitrates range between +2.94 and + 436 11.06% vs AIR in δ^{15} N-NO₃ and between +6.4 and +16.64% vs SMOW in δ^{16} O-NO₃. In 437 order to identify the different sources of nitrate, samples were plotted in a diagram 438 displaying the δ^{15} N-NO₃ vs δ^{18} O-NO₃ concentration (Fig. 6). The nitrate content of all 439 groundwater samples is very well correlated to fertiliser effects. The three samples of 440 well 15 show δ^{15} N-NO₃ values greater than the rest and for this could seem an exception; 441 at the contrary, they highlight the effects of partial denitrification, which is typically 442 able to increase in δ^{18} O-NO₃ and δ^{15} N-NO₃ values along a path that is generally bounded

- 443 by the green lines of Fig. 6. These results are coherent with previous experiences on the
- 444 source of groundwater nitrate (Moreau and Minard, 2014).

445 6. CONCLUSIONS

The natural presence of suspended clay particles in groundwater, due to the natural presence in the aquifer limestone of red clay in thin levels or filling voids, explains the concentration of dissolved iron higher than true and so high to cause concern, as an effect of the not used optimal sampling procedures (sampling without filtering and acidifying).

The absence of leachate contamination was confirmed by all applied chemical and isotope methods. Where the SSA groundwater shows high nitrate concentration, somewhere higher than the standard threshold value, this should be considered an anthropic effect clearly due to the use of fertilisers.

The proposed multi-methodological approach offered all required answers concerningthe role of leachate on groundwater quality.

457 Due to the scientific relevance and reliability of the single merged methods, the 458 approach offered an authoritative contribution to the reduction of public opposition to 459 landfill in operation or landfill extension.

This combination of techniques provides an approach which is able to attain detailed groundwater contamination understanding, offering a relatively cheap and fast support to waste management decisions. A relevant advantage seems the possibility to identify incipient pollution and provide early warning when chemical or biological indicators do

464 not yet give cause for concern. On the basis of results, costs reductions could be

465 pursued, i.e. minimizing the number of collected samples and/or considered parameters.

- 466 The successful current application of a multi-methodological approach which integrates
- the use of more isotopes with other methods could be considered a relevant forensic tool
- 468 to recognise potential sources of environmental contamination.

469 In terms of disadvantages, as the reactivity of the waste decreases, the stable isotope 470 fractionation could be reduced, reducing the significance of the isotope discussion. The 471 proposed multi-methodological approach could be theoretically applied worldwide but it 472 should be deeply validated in other natural and anthropogenic conditions. The 473 groundwater quality degradation could be justified as an effect of leachate 474 contamination in terms of many parameters, only some of which considered by the 475 proposed approach: to solve these limitations, it could be necessary integrating other 476 methods in the approach.

- 477 All these advantages can be reduced increasing research efforts and experiences, as it is
- 478 planned by authors for the immediate future.

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662 Figure 1. (a) Italy, Italian regions, and selected study area (SSA). (b) Geological and

663 hydrogeological map of SSA. (c) Aerial view of five landfills.

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666 Figure 2. Multi-parametric log of well number 8.







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Figure 6. Stable isotope composition of dissolved nitrates in groundwater and fertiliser

678 (modified after <u>Clark and Fritz, 1997; Kendall et al., 2007</u>). The rectangles highlight the

679 main types of nitrate sources.

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		EC (mS/cm)	T (°C)	рН (-)	DO mg/L	Eh (mV)	TOC (mg/L)	BOD _s (mgO ₂ /L)	COD (mg/L)
groundwater	Min.	0.68	12.07	6.73	1.71	-52.00	0.50	1.00	5.00
	Average	1.14	16.73	7.08	4.12	132.54	2.41	4.44	8.64
	Max.	2.91	19.48	7.44	8.25	242.00	5.10	10.00	51.20
	Std. dev	0.46	1.12	0.16	1.63	62.06	1.50	2.74	7.84
	Min.	21.80	n.d.	7.90	n.d.	n.d.	970.00	335.00	2240.00
leachate	Average	24.37	n.d.	8.10	n.d.	n.d.	1192.30	398.33	3376.67
	Max.	26.50	n.d.	8.20	n.d.	n.d.	1360.00	450.00	5210.00
	Std. dev	2.38	n.d.	0.17	n.d.	n.d.	200.66	58.38	1602.88

682 Table 1. Descriptive statistics for physical-chemical parameters of groundwater and

683 leachate. n.d. = not determined. EC was estimated at $25 \,^{\circ}$ C.

Reference to be cited: Raffaello Cossu, Livia Emanuela Zuffianò, Pier Paolo Limoni, Giorgio De Giorgio, Paola Pizzardini, Teodoro Miano, Donato Mondelli, Roberto Garavaglia, Carmine Carella, Maurizio Polemio, 2018. How can the role of leachate on nitrate concentration and groundwater quality be clarified? an approach for landfills in operation (southern italy). Waste Management, 77, 156-165. doi:10.1016/j.wasman.2018.05.014

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		Li∙	K∙	Na	N-NH.	Ca∗	Mg.	F	Cl	HCO	NOs	SO.*	Fe	Mn
	Min.	0.00	1.10	5.90	n.p.	87.20	25.90	0.10	22.60	378.30	13.40	3.90	0.01	0.0001
ter	Average	0.01	4.61	69.57	n.p.	115.69	54.62	0.19	159.34	459.56	32.26	22.49	0.19	0.00
andwa	Max.	0.02	20.00	333.80	n.p.	149.10	105.00	1.00	848.00	549.16	59.90	94.70	1.79	0.02
grot	Std. dev	0.00	3.92	70.28	n.p.	17.78	13.66	0.16	163.47	44.81	10.85	17.08	0.40	0.00
	Min.	0.02	1239.4	1720.00	1603.0	31.50	32.60	0.90	2725.60	10006.00	2.70	10.60	1.23	0.02
hate	Average	0.03	1505.13	2140.30	2082.7	45.50	41.70	2.23	3266.70	11633.92	41.20	29.37	3.46	0.04
leac	Max.	0.03	1807.20	2538.00	2636.0	55.50	51.08	3.10	3788.00	12813.80	115.00	58.80	5.45	0.05
	Std. dev	0.00	285.64	409.47	520.4	12.49	9.64	1.17	531.48	1456.53	63.93	25.81	2.12	0.01

686 Table 2. Descriptive statistics for groundwater and leachate. Chemical composition in

 $687 mtext{mg/L}; mtext{ n.p.} = mtext{not present}.$

sample	date	δ ¹⁸ O (‰SMOW)	δ:H (%cSMOW)	δ ^{IS} C _{DIC} PDB	Tritium TU	δ ¹⁵ N _{N03} (%cair)	δ ¹⁸ O _{N03} (%0VSMOW)
1*		-6.64	-39.27	-8.69	<0.60	4.62	15.3
2*		-6.84	-40.70	-8.59	<0.60	3.06	9.6
3*		-6.47	-39.40	-11.28	0.90	3.12	9.6
4*		-6.70	-39.83	-9.31	<0.60	3.05	8.9
5*		-6.73	-40.28	-9.02	1.10	3.51	8.2
6*		-6.76	-39.89	-7.35	0.90	3.84	10.2
7*		-6.64	-40.37	-10.33	1.40	3.20	9.3
8*		-6.89	-42.16	-7.23	<0.60	4.62	12.6
9*		-6.73	-42.61	-9.32	0.60	3.87	8.7
10*	Nov	-6.82	-42.83	-9.21	0.70	5.58	12.7
11*	2014	-6.63	-41.89	-10.75	1.30	4.64	13.3
12*		-6.78	-41.93	-9.63	1.40	4.74	13.6
13*		-6.55	-41.25	-9.77	0.90	5.08	12.3
14*		-6.77	-40.94	-9.03	2.00	5.37	11.3
15*		-6.47	-40.23	-9.92	2.30	11.06	10.2
16*		-6.61	-40.35	-10.66	1.20	4.57	11.0
17*		-6.87	-41.55	-10.87	0.90	4.59	9.9
18*		-6.79	-41.59	-10.41	1.40	5.40	10.8
Leachate IV*		-4.81	9.89	21.85	235.00	4.22	<1
1**		-6.86	-41.21	-9.74	<0.60	4.57	16.6

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2**		-6.70	-40.92	-9.23	1.00	3.37	12.0	
3**		-6.42	-39.62	-11.08	0.70	2.94	12.3	
5**		-6.62	-40.73	-9.45	2.10	4.16	11.2	
8**		-6.75	-41.75	-10.45	1.00	4.95	11.8	
11**		-6.67	-41.11	-10.76	2.00	3.94	10.7	
12**	X 1	-6.87	-40.26	-9.31	2.00	4.46	11.7	
13**	March 2015	-6.76	-40.83	-9.95	1.60	5.30	11.6	
14**	2015	-6.89	-41.24	-9.55	2.20	5.60	10.0	
15**		-6.63	-39.83	-9.96	3.10	10.62	11.5	
17**		-6.94	-41.33	-11.01	1.10	4.47	11.4	
18**		-6.85	-41.42	-10.14	2.20	5.20	11.3	
 Leachate IV**		-5.22	-2.77	22.20	182.00	3.15	<1	
3***		-6.83	-40.07	-10.76	2.40	4.07	7.8	
11***		-7.15	-42.08	-10.76	2.50	4.37	8.0	
12***		-7.23	-42.23	-10.23	2.10	5.23	7.8	
13***		-7.01	-41.43	-9.21	1.70	3.68	7.1	
14***	June	-7.07	-41.97	-8.64	2.00	5.06	6.4	
15***	2015	-6.83	-40.58	-9.78	3.00	10.60	6.9	
18***		-6.98	-41.21	-9.48	2.00	4.63	7.1	
Leachate IV***		-4.75	9.60	22.77	225.00	4.06	<1	



Table 3. Isotopic composition of groundwater and leachate.

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δ ¹⁵ N _{NO3} (%cair)	δ18 Ο 303 (%0 VSMOW)			
0.15	-			
-0.53	-			
-0.22	-			
1.38	19.0			
	δ ^ω N _{xxx} (%cair) 0.15 -0.53 -0.22 1.38			

Table 4. Isotopic composition of commercial fertilizers in the area.

The original or published publication is available at https://doi.org/10.1016/j.wasman.2018.05.014

Reference to be cited: Raffaello Cossu, Livia Emanuela Zuffianò, Pier Paolo Limoni, Giorgio De Giorgio, Paola Pizzardini, Teodoro Miano, Donato Mondelli, Roberto Garavaglia, Carmine Carella, Maurizio Polemio, 2018. How can the role of leachate on nitrate concentration and groundwater quality be clarified? an approach for landfills in operation (southern italy). Waste Management, 77, 156-165. doi:10.1016/j.wasman.2018.05.014

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Sample	SiO ₂	TiO ₂	Al_2O_3	FeO*	ZnO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	SO ₃	Cl
2	13.35	n.d	5.59	0.07	n.d	n.d	3.75	73.26	0.32	0.56	n.d	n.d	2.46
3	31.03	n.d	12.64	23.42	n.d	n.d	4.06	26.55	n.d	0.74	n.d	0.72	0.84
5	7.36	n.d	n.d	22.06	1.18	n.d	6.07	61.87	n.d	n.d	n.d	n.d	1.46
8	46.89	0.31	22.17	7.9	n.d	n.d	4.67	15.3	0.09	2.55	n.d	n.d	0.13
11	13.49	n.d	5.02	35.84	1.01	n.d	5.51	38.65	n.d	n.d	0.49	n.d	n.d
12	23.72	0.19	8.82	36.38	1.44	n.d	1.99	26.58	0.21	0.68	n.d	n.d	n.d
13	2.31	n.d	n.d	n.d	n.d	n.d	5.66	90.54	n.d	n.d	n.d	n.d	1.48
14	11.7	n.d	0.22	61.46	0.29	n.d	2.98	16.78	2.53	0.19	2.3	n.d	1.57
15	18.44	n.d	4.41	45.13	4.31	0.17	2.1	21.07	0.43	0.55	1.34	1.49	0.55
17	n.d	n.d	n.d	n.d	n.d	n.d	6.16	93.84	n.d	n.d	n.d	n.d	n.d
18	12.39	n.d	3.33	75.2	n.d	n.d	1.36	5.57	0.06	0.32	1.67	n.d	0.1

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697 Table 5. Analysis results at SEM-EDS. *Iron expressed as sum of FeO+Fe₂O₃; n.d.=not

698 detectable.

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