Identification of groundwater pollution sources in a landfill site using artificial sweeteners, multivariate analysis and transport modeling

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Abstract

In this study, sources of groundwater pollution in a landfill site were identified, using artificial sweeteners as chemical tracers, multivariate statistical analysis and a quantitative analysis of the groundwater flow system through particle tracking and transport modeling. The study area, located in northern Italy, hosts an older unlined landfill and a newer lined municipal solid waste landfill placed downstream of the former. Groundwater, surface water, treated wastewater, and leachate samples were

collected in March 2017 for analysis of the artificial sweeteners saccharin, cyclamate, acesulfame and sucralose together with major cations and anions, inorganic nitrogen compounds, total phosphorus, COD and some further parameters. The interpretation of the results suggests that two main leachate leaks/spills are affecting the study area. The first one concerns leachate probably spilling out of the leachate collection system serving the younger lined landfill, the other one involves leachate from the older unlined landfill that also seems to affect an area downstream of the lined landfill. Direct leachate leaks from the lined landfill seem unlikely, although they cannot be definitively excluded.

This work underlines the importance of a multi-methods approach, which integrates here chemical tracers, multivariate analysis and transport modeling, for assessing groundwater pollution sources generated from complex landfill sites, where multiple and different sources may exist. In particular, this work highlights how artificial sweeteners can be used for tracing leachate plumes from landfills. The methodology applied in this study can have a broad applicability also in other polluted landfill sites worldwide.

Keywords: groundwater quality, leachate pollution, environmental tracers, cluster analysis, factor analysis, particle tracking.

1. Introduction

During the last decades, industrialization and population growth brought, as a side effect, an increase of the amount of wastes produced. The impact of landfills on the environment and human health is a concern for environmental managers and citizens worldwide (Asase et al., 2009; Assamoi and Lawryshyn, 2012; Fatta et al., 1999).

Groundwater pollution caused by leaks from landfills is frequently reported in literature (de Medeiros Engelmann et al., 2017; Giusti, 2009; Laner et al., 2012; Mor et al., 2006; Nigro et al., 2017; Öman and Junestedt, 2008; Srivastava and Ramanathan, 2008). Accordingly, landfill leachate represents one of the most critical threats for groundwater quality, since it can contain a wide range of pollutants (Christensen et al., 2001; Mor et al., 2006).

In the past, unlined landfills were widely used with the undesirable consequence of leachate infiltration into groundwater (Reyes-López et al., 2008). In response, to better protect environmental resources, many countries (e.g. member states of EU) imposed requirements to build landfills with lined systems at their bottom and collection systems to recover and treat the landfill leachate (e.g. the Landfill Directive; EC, 1999). Unfortunately, these systems may fail over time with negative effects on groundwater quality (Lee and Jones, 1994; Sizirici and Tansel, 2015).

In order to assess the impact of landfills on groundwater, various methods can be used, such as the analysis of major ions (Han et al., 2013), emerging tracers (Clarke et al., 2015), or stable isotopes (Castañeda et al., 2012; Nigro et al., 2017), microbiological analyses (Preziosi et al., 2019), multivariate statistical analysis of hydrochemical data (de Medeiros Engelmann et al., 2017; Kim et al., 2012; Rapti-Caputo and Vaccaro, 2006; Singh et al., 2008) and transport modeling (Christensen et al., 1998; Cozzarelli et al., 2011; Han et al., 2013; Van Breukelen et al., 2003).

The topic of the identification of groundwater pollution sources is a complex and critical issue. For instance, in most urban environments, new lined landfills have been built in areas already covered by older unlined landfills, making the proper identification and apportionment of pollution sources challenging. An inadequate knowledge of pollution sources affecting a site would lead to inefficient remediation

strategies or complex legal disputes. The identification of groundwater pollution sources, including their extent, locations and dynamics, plays a key role in the management and remediation of polluted sites (Ayvaz, 2010). Various techniques and methods for identifying groundwater pollution sources are reported in literature, based on multivariate statistical analysis (Tariq et al., 2008), isotopic analysis (Alberti et al., 2017; Grimmeisen et al., 2017) and transport modeling (Ayvaz, 2010). However, a multi-methods approach which integrates various investigative techniques is less-commonly used, likely due to the higher costs associated with the analysis of multiple parameters, the implementation of various tools and the fact that different expertise is required.

Artificial sweeteners can be used to trace leachate pollution from municipal solid waste (MSW) landfills (Roy et al., 2014). They may also support the identification of leachate sources. Artificial sweeteners were used in the last decades worldwide as sugar substitutes in beverages, food, drugs and personal care products (Lange et al., 2012), consequently, they can be found also in wastewater (Buerge et al., 2009; Van Stempvoort et al., 2011) and domestic wastes (Clarke et al., 2015; Roy et al., 2014). They can be considered as new emerging tracers of human impacts on water resources (Lange et al., 2012). Buerge et al. (2009) showed that artificial sweeteners, in particular acesulfame, are good markers of domestic wastewater. Furthermore, the sweetener saccharin may also end up in soil via manure after its use as an additive in piglet feed. Saccharin is a soil metabolite of certain sulfonylurea herbicides, and may thus eventually be leached into groundwater (Buerge et al., 2011). Artificial sweeteners contained in solid and liquid wastes (e.g. food wastes) were found in landfill leachate (Clarke et al., 2015; Roy et al., 2014; Van Stempvoort et al., 2011), they can thus be used as tracers of leachate leaks/spills in groundwater. Artificial sweeteners were

introduced onto the market in different years, and their analysis may thus allow to distinguish leachate plumes originating from landfills with different age. To this end, Roy et al. (2014) proposed the use of saccharin (SAC), cyclamate (CYC), acesulfame (ACE) and sucralose (SUC) that, in European countries, were approved in 1977, 1984, 1984 and 2000, respectively (Mortensen, 2006).

The present study involves the investigation of a landfill site with groundwater that is affected by leachate pollution and the identification of its sources. This site, located in northern Italy, hosts an older unlined landfill and a newer lined MSW landfill, thus making the assessment of pollution sources a challenging task. A preliminary hydrochemical characterization of the area (Stefania et al., 2018a, 2019) showed that the old unlined landfill likely affects groundwater quality, however, other unknown sources have to be considered as well, and properly identified to address remediation strategies.

The main aim of this work is to identify the sources of leachate pollution affecting the study area using a multi-methods approach, which integrates the use of artificial sweeteners as tracers with standard hydrochemical measurements, multivariate statistical analysis and transport modeling. More specifically, this methodology involved: a) an initial overall groundwater quality classification, made by cluster analysis of artificial sweeteners together with the other hydrochemical data; b) the pollution sources identification, done by the interpretation of artificial sweeteners, in particular ACE, factor analysis and groundwater particle tracking and transport modeling.

2. Materials and methods

2.1 Study area

The study area is located in an Alpine valley in northern Italy (Fig. 1a), more precisely, in an alluvial plain close to the town of Aosta (Aosta Valley Region). This plain has a length of ~13 km from west to east and its average width is ~2 km (Fig. 1b). It is made up of an unconfined aquifer composed of alluvial, fluvioglacial and lacustrine deposits. The texture of aquifer sediments ranges from coarse to medium (i.e. gravels to sands) with local and discontinuous silty layers. A deeper confined aquifer, not exploited by water wells, is found below the unconfined aquifer (Stefania et al. 2018b). These two aquifer units are separated by a lacustrine silty aquitard. A schematic of the aquifer system is represented by the cross-section in Fig. 1c. The thickness of the unconfined aquifer ranges from 20 to 90 m. The lacustrine silty aquitard is about 40 m thick. The available well-logs (TANGRAM database; Bonomi et al., 2014) reveal the presence of a discontinuous silty layer of about 5 m thickness in the eastern part of the plain, that subdivides the main aquifer in an unconfined (~20 m thick) and a semi-confined (between 12 and 25 m in thickness) part (Bonomi et al., 2015a; Novel et al., 2002; Triganon et al., 2003). The regional groundwater flow is from west to east following the slope of the valley. The main regional river (Dora Baltea River) flows along the plain from west to east changing from losing to gaining along its path (Bonomi et al., 2015b; Stefania et al., 2018b, 2018c).

More specifically, the study area is situated in the eastern part of this plain with a landfill site of approximately 0.55 km^2 that is bordered on the southern side by the main regional river. Before the introduction of environmental regulation, this area was used as an uncontrolled disposal site of waste that progressively formed an unlined landfill. During the 80's, a new lined MSW landfill was built downstream of the old unlined

146 landfill (Fig. 2). The liner system consists at least of a 1 m thick clay layer at the
147 bottom. During the early 90's, the unlined landfill was closed and a capping was placed
148 on top of the landfill in order to prevent rain infiltration to the waste.
149 In the MSW landfill ~1,800,000 t of waste are deposited with an annual increase of
150 70,000 t. The wastes stored in the MSW landfill are domestic waste and sewage sludge,
151 whereas those in the unlined landfill are inert, plastic and urban wastes of different and
152 unknown composition. A leachate collection system serving the MSW landfill is
153 composed of 4 underground tanks (3 x 5 m and unknown depth), 3 leachate wells, and
154 related underground pipes that cross the western and southern sides of the area (Fig. 2).
155 The leachate is then pumped to a wastewater treatment plant (WTP) located in the
156 western part of the dumping area (Fig. 2) that serves ~115,000 equivalent inhabitants.
157 The landfill is located in the area where the main aquifer is subdivided into an
158 unconfined and a semi-confined unit (Fig. 1c). The leachate pollution affects only the
159 ~20 m thick unconfined aquifer, whereas the underlying semi-confined aquifer is free
160 from pollution since it is protected by the silty aquitard and, where this is absent (i.e. in
161 proximity of the river), the groundwater flow is directed upwards due to the gaining
162 behaviour of the river (Stefania et al., 2018b, 2018c). The site has been polluted for at
163 least a decade, as shown by some legacy data provided by the Regional Environmental
164 Protection Agency of Aosta Valley Region (ARPA VdA) that testify the prolonged
165 deterioration of the quality of surrounding groundwater: mean values of Cl^-
166 concentrations (399 samples over the period 2011-2017), electrical conductivity (EC;
167 811 samples over the period 2014-2017) and chemical oxygen demand (COD; 1969
168 samples over the period 2006-2017) were 134 mg/L, 1326 uS/cm and 66 mg/L,
169 respectively. The groundwater table depth beneath the landfill site is, on average
170 (variable topography), 5-6 m bgl. The entire landfill area is monitored by 38

piezometers with an average depth of 15 m bgl, thus tapping the sole unconfined aquifer. These piezometeres are located around the MSW and unlined landfills (Fig. 2).

2.2 Field survey

A field survey was performed during March 2017. Water samples were collected from groundwater (38 samples), surface water (5 samples), and treated wastewater from the effluent of the WTP (1 sample). A leachate sample from a leachate well serving the MSW landfill was also collected. In addition, local authorities provided data related to 3 leachate samples collected from the leachate wells in January 2017. The location of the sampling points is shown in Fig. 2. Static groundwater levels were measured in March 2017 from the monitoring piezometers before sampling. Groundwater was sampled after a piezometer purging by 3 volumes using the portable sampling pump Grundfos MP1. Grab samples of surface water and sewage effluent were taken at 30 cm below the water surface using a bucket. Leachate samples were collected from the underground leachate tanks using a bucket.

Temperature (T), EC, and pH were measured in the field for all samples using portable instruments. Groundwater samples were analysed for nitrogen compounds (NH_4^+-N, NO_3^--N, NO_2^--N), COD, total phosphorus (P-tot), major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}) and the artificial sweeteners SAC, CYC, ACE and SUC. Surface water and sewage effluent samples were analysed for major ions and artificial sweeteners whereas nitrogen compounds, COD, P-tot, Cl^-, SO_4^{2-} and SUC (the latter, only for the sample collected in March 2017) were measured in leachate samples. Table S1 shows the list of sampling points with measured parameters.

Nitrogen compounds were analysed using the indophenol blue spectrophotometric method for NH_4^+-N (Bolleter et al., 1961), the Griess reagent spectrophotometric method for NO_2^--N (Barnes and Folkard, 1951), and ion chromatography for NO_3^--N (Leoni et al., 2014). A titration method was used to analyse COD whereas SO_4^{2-} and major ions were analysed by ion chromatography (Leoni et al., 2014). P-tot was determined by inductively coupled plasma mass spectrometry (ICP-MS; EPA, 2014). Artificial sweeteners (SUC, ACE, CYC and SAC) in groundwater and surface water were analysed by liquid chromatography tandem-mass spectrometry (LC-MS/MS) after online solid-phase extraction (Buerge et al., 2009), whereas SUC in leachate was analysed by gas chromatography-mass spectrometry (GC/MS; modified from Mead et al., 2009).

The limit of detection (LOD) was 2.5 mg/L for COD, 0.02 mg/L for NH_4^+-N, 0.014 mg/L for NO_3^--N, 0.0015 mg/L for NO_2^--N, 0.004 mg/L for P-tot, 0.1 mg/L for major ions, 1.0 µg/L for SUC with the LC-MS/MS method, 0.05 µg/L for SUC with the GC/MS method, 0.4 µg/L for ACE, 0.1 µg/L for CYC, and 0.3 µg/L for SAC. Results of chemical analyses were stored in the TANGCHIM database (Stefania et al., 2019).

2.3 Multivariate statistical analysis

Multivariate statistical analysis was applied on groundwater data considering 17 hydrochemical variables (i.e. EC, pH, COD, P-tot, NH_4^+-N, NO_3^--N, NO_2^--N, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, SAC, CYC, ACE and SUC) from 37 samples. Sample 28 was excluded since only major ions were measured. Concentrations below LOD were substituted with a value of LOD/2. Hierarchical clustering analysis (CA) and factor analysis (FA) were performed. The CA was done by means of the Ward method (Ward,

1963) using the Euclidean distance (Cloutier et al., 2008). In order to guarantee an equal weight for each variable in calculating the Euclidean distance matrix, the CA was made on standardized data (i.e. mean = 0 and standard deviation = 1; Judd, 1980). The FA was based on the calculation of the correlation matrix and was conducted using Varimax rotation (Kaiser, 1958). The selection of the significant factors was done on the basis of the eigenvalues matrix, in particular, only those factors with eigenvalues ≥1 were considered as significant factors (Kaiser, 1958).

2.4 Particle tracking and transport modeling

Particle tracking and transport modeling were based on the 3D steady-state groundwater flow simulation (January 2009) described in Stefania et al. (2018b) using MODFLOW2005 (Harbaugh, 2005). Details on groundwater flow model settings are reported in Sect. S3 of the Supporting Material. Particle tracking in forward and backward modes was done using MODPATH (Pollock, 2012), with the aim of estimating the potential area impacted by a leachate plume sourced from the old unlined landfill. The starting location of particles covered the entire area of the unlined landfill and they were placed on the top of the groundwater table.

Transport modeling was done using MT3DMS (Zheng, 2010; Zheng and Wang, 1999). The concentration of chloride, used as conservative tracer of landfill leachate, was simulated with the aim of testing whether Cl^- concentrations could be explained by the sole advective-dispersive transport from the old landfill to downstream of the MSW landfill, excluding possible additional leaks/spills sourced from the MSW landfill. The choice of the longitudinal dispersivity (α_L) value was driven by a sensitivity analysis since the simulated plume was expected to be fairly sensitive to changes of this

parameter (Han et al., 2013). The initial value of 15 m, calculated with the Mercado equation (Mercado, 1967) considering a length of the polluted aquifer (from the unlined landfill to the river) of 220 m, was varied using four multipliers: 0, 0.1, 1 and 10. Once selected the proper longitudinal dispersivity, the values of transversal (α_T) and vertical (α_V) dispersivities were calculated using the well-known constant ratios (Gelhar et al., 1992), i.e. α_L/α_T and α_T/α_V = 0.1. The source of chloride was simulated by imposing a constant concentration boundary at the cells corresponding to piezometers located upstream of the lined landfill and assigning the average measured Cl^- concentration (Table S2) calculated for each piezometer on the legacy data (over the 2011-2017 period) provided by ARPA VdA. The use of average measured Cl^- concentrations, rather than measured Cl^- in March 2017, was chosen since a) the simulated groundwater flow in January 2009 (on which the transport model is based on) represents average hydrodynamic conditions (Stefania et al. 2018b) and b) some variations in the groundwater flow direction occurred between January 2009 and March 2017 (see Sect. 3.1), so the use of measured Cl^- in March 2017 would be incongruous. Accordingly with the use of Cl^- as a conservative tracer (Christensen, 1992; Han et al., 2013), no physical and/or chemical reactions were simulated. A period of 365 days was used as total transport simulation time. This allowed to reach a quasi-steady-state for simulated concentrations downstream of the MSW landfill. The advective term of the transport was solved using the total variation diminishing (TVD) scheme since it is more accurate in solving advection-dominated problems and minimizing numerical dispersion (Zheng, 2010; Zheng and Wang, 1999).

3. Results and Discussion

3.1 Groundwater flow

Fig. 2 shows the piezometric map obtained by ordinary kriging interpolation of groundwater levels measured in March 2017. Fig. 2 also reports the simulated piezometric map by Stefania et al. (2018b) for January 2009. Groundwater mainly flows from west to east; however, the flow direction shifts toward south-east in proximity of the river due to its gaining behavior (PIAHVA, 1996; Stefania et al., 2018b). The effect of the gaining river on groundwater flow is more evident in the map for March 2017. This could be related to the fact that the simulated map for January 2009 comes from a regional model (covering the entire ~25 km^2 of the Aosta Plain; Stefania et al., 2018b), therefore it could not consider local variations of flow direction occurring at the site-specific scale of the landfill (0.55 km^2) as the detailed groundwater level survey of March 2017 can do. Moreover, some variations in the hydrodynamic conditions may have occurred between January 2009 and March 2017. The gaining behavior of the river nearby the landfill is kept throughout the year, even during the early summer when the river has its highest discharge due to snow melting (Stefania et al., 2018b).

On the basis of the groundwater flow, piezometers 26-30 can be considered located downstream of the old unlined landfill and piezometers 2-4B and 19-22 downstream of the MSW landfill.

3.2 Artificial sweeteners

Fig. 3 shows the spatial distribution of measured concentrations of artificial sweeteners in groundwater and surface water. In general, ACE was the most frequently detected artificial sweetener, whereas SUC was the least detected (note the higher LOD for

289 SUC). This is consistent with previous studies in other urban environments worldwide
290 (Lee et al., 2015; Tran et al., 2014; Van Stempvoort et al., 2011; Wolf et al., 2012).

291 ACE was measured above the LOD in 7 groundwater samples, with maximum
292 concentrations found in piezometers 1 (9.69 µg/L) and 17 (5.15 µg/L), located close to
293 the leachate well L1. Relevant concentrations were measured also in piezometers 27
294 (4.55 µg/L) and 28 (0.68 µg/L), located downstream of the older unlined landfill, in
295 piezometers 19 and 20 (1.71 and 1.51 µg/L), located downstream of the MSW landfill,
296 and in piezometer 11 (0.82 µg/L), close to the leachate well L3.

297 CYC confirmed these results, with highest concentrations in piezometers 1 and 17
298 (29.56 and 1.05 µg/L, respectively), followed by piezometer 27 (0.85 µg/L) and 11
299 (0.14 µg/L), although it was not detected in piezometers 19, 20, and 28. SAC was
300 detected in piezometers 1 and 17 (5.44 and 0.68 µg/L, respectively), moreover, it was
301 also detected in two piezometers in the eastern part of the area, downstream of the
302 unlined and MSW landfills, that are piezometers 22 (1.28 µg/L) and 24 (0.50 µg/L).
303 SUC was only detected in piezometer 1 (3.0 µg/L).

304 Concerning surface waters, SUC, ACE and CYC were detected in the main regional
305 river (3.21, 4.93 and 0.12 µg/L, respectively), but only just downstream of the discharge
306 of treated effluent from the WTP that showed concentrations of 3.43, 7.05, 0.32, and
307 0.53 µg/L for SUC, ACE, CYC, and SAC, respectively. Therefore, the concentrations
308 measured in the river seem to be related to the discharge of the WTP rather than the
309 gaining of polluted groundwater from the landfill site.

310 SUC was detected in the leachate sample L3 (0.15 µg/L). This indicates that SUC can
311 be used to trace pollution in groundwater by leachate from more recent landfills, as it
312 may be the case in piezometer 1 (see Sect. 3.4.1 for an in-depth discussion).

3.3 Groundwater quality classification

An overall characterization of the groundwater quality in the site can be obtained from the results of CA that combined the artificial sweeteners with the other measured hydrochemical parameters. The CA showed that groundwater samples can be grouped into three main clusters, called C1, C2 and C3. The location of piezometers composing each cluster is shown in Fig. 2, the histogram of centroids for the three clusters is shown in Fig. 4, and the CA dendrogram is shown in Fig. S1.

Cluster C1 groups 3 sampling points, piezometer 27, located downstream of the old unlined landfill, and piezometers 1 and 17, located upstream of the MSW landfill and close to the leachate well L1 (Fig. 2). Cluster C1 is mainly characterized by high values of ACE, COD, K^+, Mg^{2+}, Na^+, Cl^-, P-tot and EC (Fig. 4) ranging between 4.55 and 9.69 µg/L, 172 and 572, 124 and 434, 40 and 81, 219 and 634, 360 and 736, 0.25 and 1.84 mg/L and 1180 and 6260 µS/cm, respectively. All these parameters, in particular COD, K^+ and the tracer ACE, are indicators of groundwater contamination by landfill leachate (Christensen et al., 2001; Mor et al., 2006; Öman and Junestedt, 2008; Roy et al., 2014), therefore their high concentrations reveal that piezometers forming cluster C1 (i.e. 27, 17 and 1) are affected by a severe leachate pollution. It can be assumed that these piezometers are likely located close to some considerable leachate spills or leaks (i.e. main pollution sources of the site). It is noted that NO_3^--N values have a large variation in C1 ranging from <LOD in piezometer 1 to 455 mg/L in piezometer 27; this may indicate the presence of different types of pollution sources within this cluster (see Sect. 3.4 for a more detailed discussion).

Cluster C2 groups piezometers located in three different zones of the landfill site (Fig. 2): a) piezometer 11 is close to the leachate well L3, b) piezometers 29 and 30 are downstream of the unlined landfill and c) piezometers 4B, 19, 20 and 21 are located downstream of the MSW landfill, along its south-eastern side. Cluster C2 is mainly represented by higher values of NO_2^--N and NH_4^+-N. The former ranges between 0.04 and 0.20 mg/L whereas the latter varies from 9.4 to 118.0 mg/L. The hydrochemical features of cluster C2 can be related to ongoing degradation of organic compounds and its attenuation along groundwater flow paths (Christensen et al., 2001; Cozzarelli et al., 2011). High NO_2^--N values indicate an ongoing nitrification, i.e. NH_4^+ (the product of degradation of organic N) is oxidized to NO_3^-. The lower concentrations of COD, P-tot, and major ions with respect to cluster C1 could be related to attenuation (i.e. dilution/dispersion/degradation) processes during the transport of leachate in groundwater (Appelo and Postma, 2004; Christensen et al., 2001). Cluster C2 groups piezometers that can be considered affected by a moderate leachate pollution. This could be related to some leachate spills/leaks less intense than for C1 or to the transport of main leachate plumes (originating close to piezometers forming C1) that evolve their chemical composition along groundwater flow paths.

Cluster C3 groups the remaining 27 piezometers of the groundwater monitoring network of the landfill site. Since all measured parameters have lower values here, it can be stated that this cluster represents the baseline hydrochemistry of the area.

Fig. 5 shows the scatter plot of Cl^- *vs* K^+ for groundwater, surface water and sewage effluent samples. The ions Cl^- and K^+ are useful tracers of MSW leachate pollution since they are conservative and typically found at high concentrations in MSW leachate (de Medeiros Engelmann et al., 2017; Devic et al., 2014; Kim et al., 2016; Panno et al., 2006; Rotiroti et al., 2015a, 2015b; Singh et al., 2008). K^+ is contained in vegetal

361 wastes, e.g. paper (Naveen et al., 2017), while Cl^- is contained in domestic salts
362 (Rotiroti et al., 2017). In general, the Cl^- *vs* K^+ plot confirms the groundwater
363 classification resulting from CA. Indeed, samples from C1 were the most polluted,
364 followed by samples from C2 and then by C3 with the lowest values. Within the latter,
365 representing the baseline hydrochemistry, a sub-classification can be done. Some points
366 exhibit lower concentrations (Cl^- < 21 and K^+ < 5 mg/L) attributable to the natural
367 baseline (i.e. piezometers 35-38 located outside of the landfill site) whereas for the other
368 points with higher concentrations, an anthropogenic baseline, accounting for all human
369 activities at the site over time, can be considered, as for piezometers 8, 31 and 32 that
370 reach Cl^- concentrations around 200 mg/L. However, for these piezometers, a slight
371 influence of the leachate collection system serving the MSW landfill cannot be excluded
372 since they are all located close to an underground leachate tank (Fig. 1). The samples
373 from cluster C1 together with sample 28, that has high Cl^- and K^+ concentrations, but
374 was excluded from the CA (see Sect. 2.3), show a good linear correlation between Cl^-
375 and K^+ (r^2 = 0.98). This leads to the following two considerations: a) sample 28 likely
376 has similar hydrochemical features with respect to the samples forming cluster C1, so it
377 can be considered as part of this cluster b) all these four piezometers are affected by the
378 same landfill pollution evidenced by CA results.

379 Fig. 5 shows that concentrations of Cl^- and K^+ in surface water samples were similar to
380 groundwater samples from cluster C3. This suggests that, at the time of sampling, the
381 main regional river was not affected by the landfill although it gains groundwater
382 crossing the landfill site. This could be due to attenuation (i.e.
383 dilution/dispersion/degradation) occurring along groundwater flow paths and within the
384 river. The highest concentrations of K^+ and Cl^- in surface water were found just
385 downstream of the discharge of treated wastewater from the WTP.

386

387 **3.4 Identification of pollution sources**

388 The groundwater classification (Sect. 3.3) allowed to identify those piezometers
389 affected by more severe (cluster C1) and moderate (cluster C2) pollution. However, this
390 classification was not able to differentiate between possible pollution sources of the
391 area, that are a) the old unlined landfill, b) the MSW landfill, c) the leachate collection
392 system serving the MSW landfill and d) a combination of these. The attribution of a
393 pollution source to each cluster or sub-group of piezometers is discussed in the
394 following.

395

396 **3.4.1 Severely polluted groundwater**

397 The identification of pollution sources attributable to piezometers with severe pollution
398 (cluster C1) was supported by the FA made on groundwater samples.

399 The FA identified 4 significant factors (FAC1-4) explaining a total cumulative variance
400 of 86.8% (Table S3). FAC1 explains 45.8% of the total variance. The original variables
401 that represent FAC1 (i.e. loading value > |0.7|) are NO_3^--N, Ca^{2+}, SO_4^{2-} and Na^+. FAC2
402 explains 22.9% of the variance and is represented by the four sweeteners SUC, CYC,
403 SAC and ACE. FAC3 explains 11.2% and is mainly represented by P-tot and EC. FAC4
404 explains 7.0% and is only represented by $NH4^+$-N.

405 Fig. 6 reports the loading and score plots for FAC1 *vs* FAC2 and FAC1 *vs* FAC3. Fig. 6
406 shows that FAC1 is able to separate the samples forming cluster C1: piezometer 27 is
407 polluted by leachate having higher NO_3^--N, Ca^{2+}, SO_4^{2-} and Na^+ whereas piezometers 1
408 and 17 have lower concentrations of these species. Considering the location of

piezometer 27 (Fig. 2), FAC1 may represent pollution by leachate leaking from the older unlined landfill. The higher values of NO_3^--N and SO_4^{2-}, that characterize FAC1, seem consistent with leachate coming from an older landfill. Indeed, Lee et al. (2010) reported an increase of SO_4^{2-} in leachate from older landfills. The high SO_4^{2-} concentration could be related to higher O_2 due to rainfall infiltration and heterogeneous mixing of wastes (Chofqi et al., 2004) that promote oxic conditions, preventing sulfate reduction (Abd El-Salam and Abu-Zuid, 2015). Ziyang et al. (2009) analyzed nitrogen compounds in leachate samples from landfills with different ages (2-12 years), observing a decrease of NH_4^+-N and an increase of NO_3^--N over time.

Fig. 6 shows that FAC2 and FAC3 distinguish piezometer 1 from piezometer 17. FAC2 highlights the highest concentrations for all the four measured sweeteners found in piezometer 1. In particular, the most relevant contribution of SUC to FAC2 indicates that this factor may represent pollution by leachate from the younger MSW landfill. This is confirmed by the detection of SUC in the leachate sampled from the leachate collection system serving the MSW landfill (see Sect. 3.2). The location of piezometer 1 indicates that this pollution is likely originated from the leachate well L1 and/or its related underground tank. FAC3 underlines that piezometer 17 has higher P-tot and EC. High values of these parameters are consistent with the chemical features of leachate from younger landfills (Christensen et al., 2001; de Medeiros Engelmann et al., 2017; Han et al., 2013; Mor et al., 2006; Van Breukelen et al., 2003; Van Breukelen and Griffioen, 2004; Vodyanitskii, 2016) that also typically shows lower concentrations of NO_3^- and SO_4^{2-} (Aziz et al., 2010; Lee et al., 2010; Ziyang et al., 2009). Therefore, considering that piezometer 17 is located close to and downstream of piezometer 1, it can be argued that both these piezometers may be affected by a leachate spill from the leachate well L1 serving the younger MSW landfill.

A confirmation of this interpretation can also be given by the plot of SO_4^{2-} *vs* Cl^- (Fig. 7), measured also in leachate samples from the leachate collection system of the MSW landfill. Groundwater samples 1 and 17 plot towards the leachate samples that have high Cl^- and low SO_4^{2-}, thus strengthening the idea that leachate leaking, from the well L1 serving the younger MSW landfill, is polluting surrounding groundwater.

In summary, the identification of pollution sources for those piezometers classified as severely polluted revealed that piezometers 27 and 28 (the latter associable to the severely polluted group (Sect. 3.3) and located close to the former, as shown in Fig. 2) are likely affected by leachate leaking from the older unlined landfill, whereas piezometers 1 and 17 are likely affected by a leachate spill from the leachate well L1 serving the MSW landfill.

3.4.2 Moderately polluted groundwater

The understanding of the sources of pollution for piezometers forming cluster C2 (moderately polluted groundwater) was supported by the use of the sweetener ACE as tracer, followed by a quantitative analysis of the groundwater flow system through particle tracking and transport modeling.

The sweetener ACE gave more comprehensive information than the other sweeteners, indeed, characterizing cluster C1, it was able to trace the two main leachate spills/leaks (from the leachate well L1 serving the MSW landfill and from the unlined landfill) and, being detected in piezometers 11, 19 and 20 of cluster C2, it also allowed to identify groundwater classified as moderately polluted; this is consistent with its conservative properties (Buerge et al., 2009; Van Stempvoort et al., 2011). According to this, the interpretation of ACE concentrations can be a valid support for understanding what

causes the moderate pollution in piezometers 11, 19, and 20. The identification of the pollution source for piezometer 11 seems quite easy since its proximity to the leachate well L3 and the absence of any other possible sources upstream indicate, with little doubt, that some modest spills from well L3 are affecting piezometer 11. Conversely, the understanding of the cause of pollution in piezometers 19 and 20 could be challenging. Indeed, these piezometers might possibly be affected by a) the old unlined landfill, b) the MSW landfill or c) a combination of the two. The distribution of ACE concentrations, with higher values in piezometer 27 and lower values in piezometers 19 and 20, seems to sustain the idea that these piezometers could be affected by a leachate plume sourced from the old unlined landfill. This may also be the case for piezometers 4B and 21, that were classified as moderately polluted too (Sect. 3.3), and are located downstream of the MSW landfill, close to piezometers 19 and 20.

The hypothesis that a leachate plume sourced from the unlined landfill, moving downstream, affects piezometers 4B, 19, 20 and 21 was tested by particle tracking and transport modelling. Results of particle tracking showed that a leachate spill from the old unlined landfill could affect the south-eastern part of the study area, between piezometers 3 and 5B (Fig. 8). The estimated travel time required for groundwater to move from the unlined landfill to these downstream piezometers is ~160 days. The simulation suggested that piezometer 19 is not affected by the plume from the unlined landfill. However, particle tracking was based on the simulated groundwater flow for January 2009 (see Sect. 2.4 for details), and piezometer 19 may nevertheless be affected by the plume from the old landfill. Indeed, the potentiometric map obtained from March 2017 data clearly shows that piezometer 19 is downstream of the unlined landfill along a groundwater flow line (Fig. 2). Therefore, piezometer 19 can also be considered as affected by a leachate plume sourcing from the unlined landfill. The particle tracking

pointed out that also piezometers 29 and 30, classified as moderately polluted (Sect. 3.3), may be affected by leachate spills from the unlined landfill.

Results of particle tracking, together with groundwater level data of March 2017, showed that piezometers 4B, 19, 20 and 21 could be affected by a leachate plume from the unlined landfill but do not exclude any possible leachate spills from the MSW landfill. This can be elucidated by results of the chloride transport modeling. This modelling was aimed at testing if Cl^- concentrations in piezometers downstream of the MSW landfill can be explained by the advective-dispersive transport of Cl^- sourced upstream of it or whether additional leaks/spills from the MSW landfill contribute to the observed pollution. Fig. 9 and Table 1 show the results of this modeling. Fig. 9a depicts results of the sensitivity analysis on longitudinal dispersivity through simulated breakthrough curves of chloride in piezometer 4B. The curve obtained using a α_L value of 1.5 m fits with the travel time of 160 days estimated by particle tracking, so this value was used for modeling. Fig. 9b shows the map of the simulated Cl^- plume and indicates which piezometers were used as pollution point sources and pollution targets (the latter are the piezometers located downstream of the MSW landfill). In the target piezometers 3, 4B and 19, the simulated Cl^- concentrations were comparable to average measured concentrations, in piezometers 4, 20 and 21 even higher (Table 1). This indicates that unaccounted additional sources, i.e. leachate leaks/spills from the MSW landfill, seem unlikely. Nevertheless, this conclusion based on chloride transport modeling does not allow to definitively exclude leachate spills/leaks from the MSW landfill. In particular, the NH_4^+-N concentrations found in March 2017 were significantly higher in piezometers 19 and 20 (118 and 116 mg/L, respectively) than in piezometer 27 (2.3 mg/L), and exceeded the trigger level for identifying significant adverse environmental effects caused by the MSW landfill that was estimated by

Stefania et al. (2018a) to be 9 mg/L for this area (calculation based on legacy data from 2006 to 2010). The assessment of possible impacts from the MSW landfill is thus still an open issue and further monitoring of these piezometers is needed.

In summary, the identification of the pollution sources for those piezometers classified as moderately polluted revealed that piezometers 4B, 19, 20, 21, 29 and 30 are likely affected by a leachate plume sourced from the old unlined landfill, whereas piezometer 11 is likely affected by a leachate spill from the leachate well L3 serving the MSW landfill. Table 2 summarizes the pollution phenomena identified in the site, for each of which the names of affected piezometers are listed and the composition of affected groundwater is reported through their mean concentrations. Direct leachate spills/leaks from the MSW landfill seem unlikely, although they cannot definitely be excluded, in particular, nearby piezometers 19 and 20.

3.5 Recommendations for improving groundwater quality in the landfill site

Once identified the source of pollution for each piezometer in the studied landfill site, some recommendations can be given in order to improve the groundwater quality. This work showed that the main pollution sources affecting the area are related to a) the old unlined landfill and b) the leachate collection system serving the MSW landfill. Therefore, the recommendations are: a) to check the sealing of the leachate collection system in order to identify and repair the spills of leachate and b) to implement a drainage system just downstream the old landfill in order to prevent the migration of leachate toward the MSW landfill; this, in turn, would allow to better monitor the MSW landfill itself making the identification of possible future leachate spills from it easier.

4. Conclusions

This work presented a detailed identification of pollution sources for groundwater in a landfill site. For each monitored point affected by leachate pollution, the likely source and cause of pollution was assessed. This was done using a multi-methods approach which integrates the use of artificial sweeteners as tracers of leachate pollution, multivariate statistical analysis, particle tracking and transport modelling.

This work highlights that a multi-methods approach allows to overcome gaps and limitations related to each single method, supporting a more comprehensive understanding of the pollution phenomena affecting the study area. Artificial sweeteners are confirmed to be useful tracers of leachate plumes from MSW landfills, moreover, due to their different commercialization years, they may give some indication on the age of the leachate; in particular, the presence of SUC indicates that the leachate is sourced from a landfill containing recent (after 2000) wastes. The sweetener ACE, due to its conservative properties, gives more comprehensive information on leachate pollution affecting the study area. However, a better understanding of the system under analysis can be given combining the use of artificial sweeteners with other tracers/parameters, for example through a multivariate statistical analysis, and implementing other investigative techniques, such as transport modelling. The detailed identification of pollution sources for each cluster or sub-group of monitored sampling points leads to suggest effective and specific actions for remediation and improving groundwater quality in the study area.

This work presented a local case study for attributing groundwater pollution sources in a landfill site, however, the methodologies used here can be applied to other polluted landfill sites worldwide.

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Appendix A. Supplementary material

Supplementary material to this article can be found online at ...

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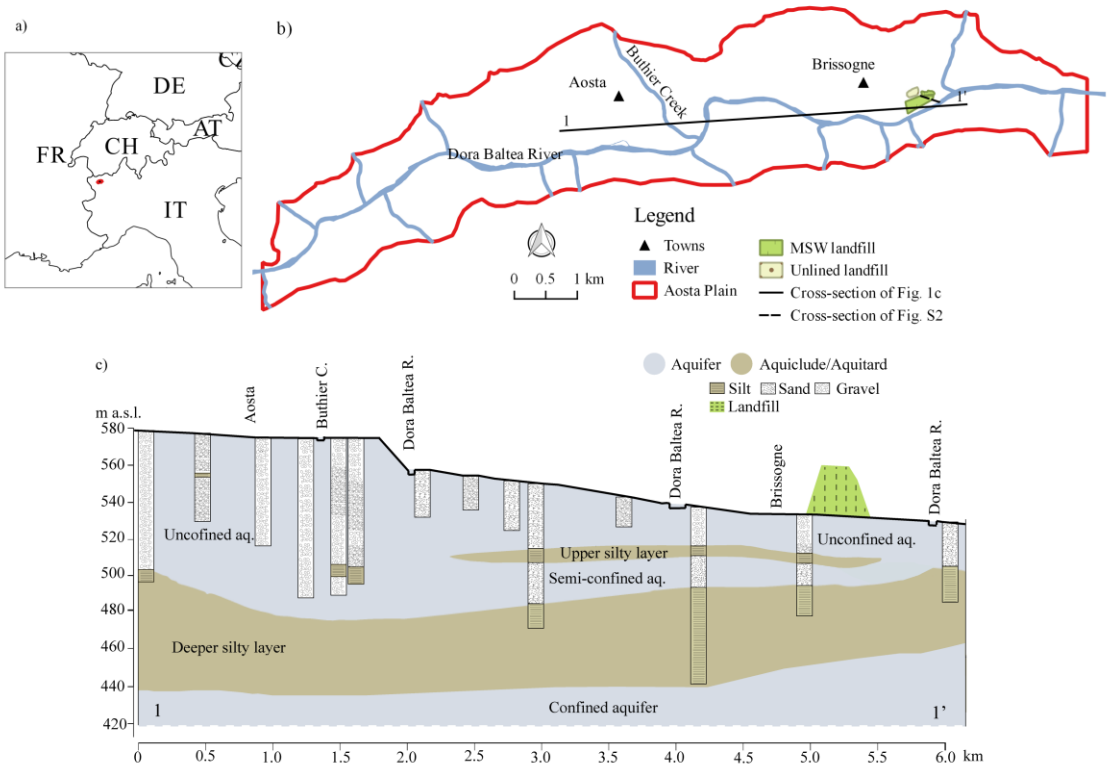

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855 Fig. 1 - a) Location of the Aosta Plain. b) The Aosta Plain and location of the landfill site. c)
856 Cross-section showing a schematic of the hydrogeological settings of the Aosta Plain.

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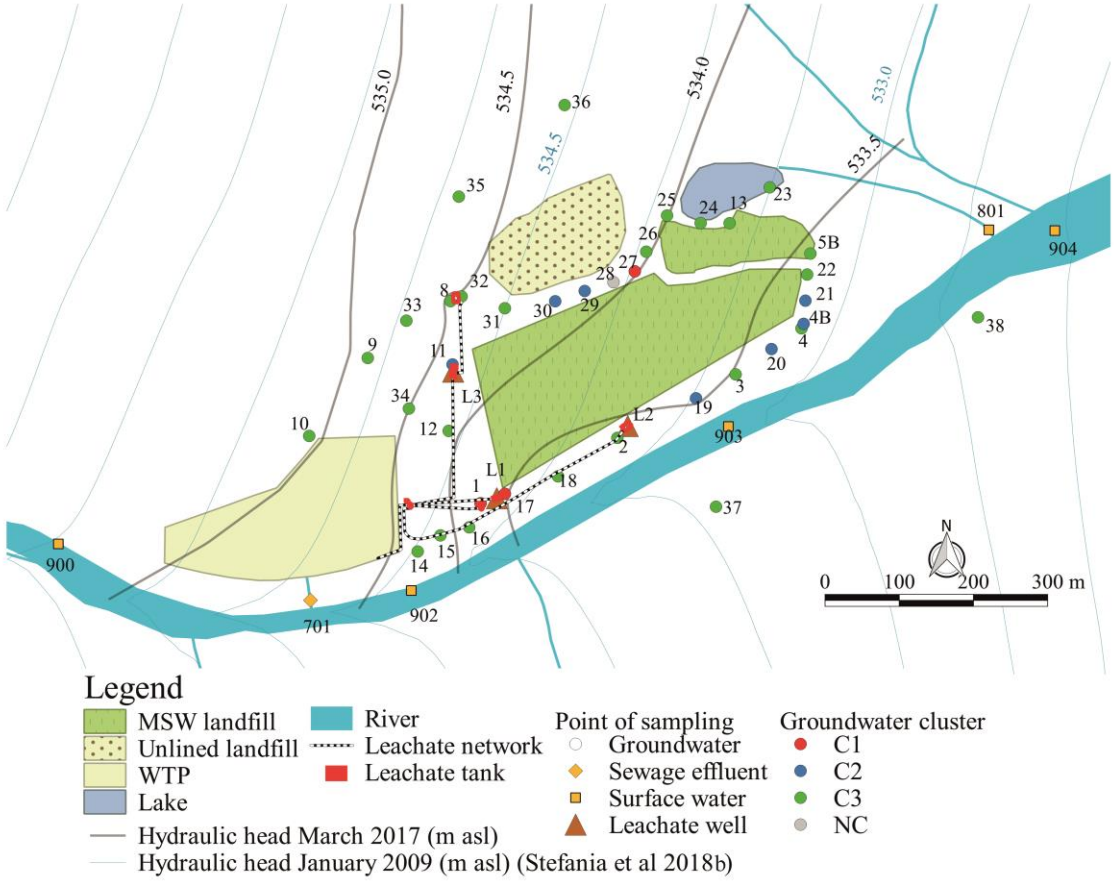

858

859 Fig. 2 - Map of the study area showing piezometric maps for January 2009 and March
860 2017 and locations of landfills, leachate collection system and sampling points
861 (numbers are point IDs; L*n* is for the leachate wells); groundwater sampling points are
862 grouped into the 3 clusters resulting from the cluster analysis (C1, C2 and C3). MSW:
863 Municipal Solid Waste, WTP: Wastewater Treatment Plant, NC: Not Classified.
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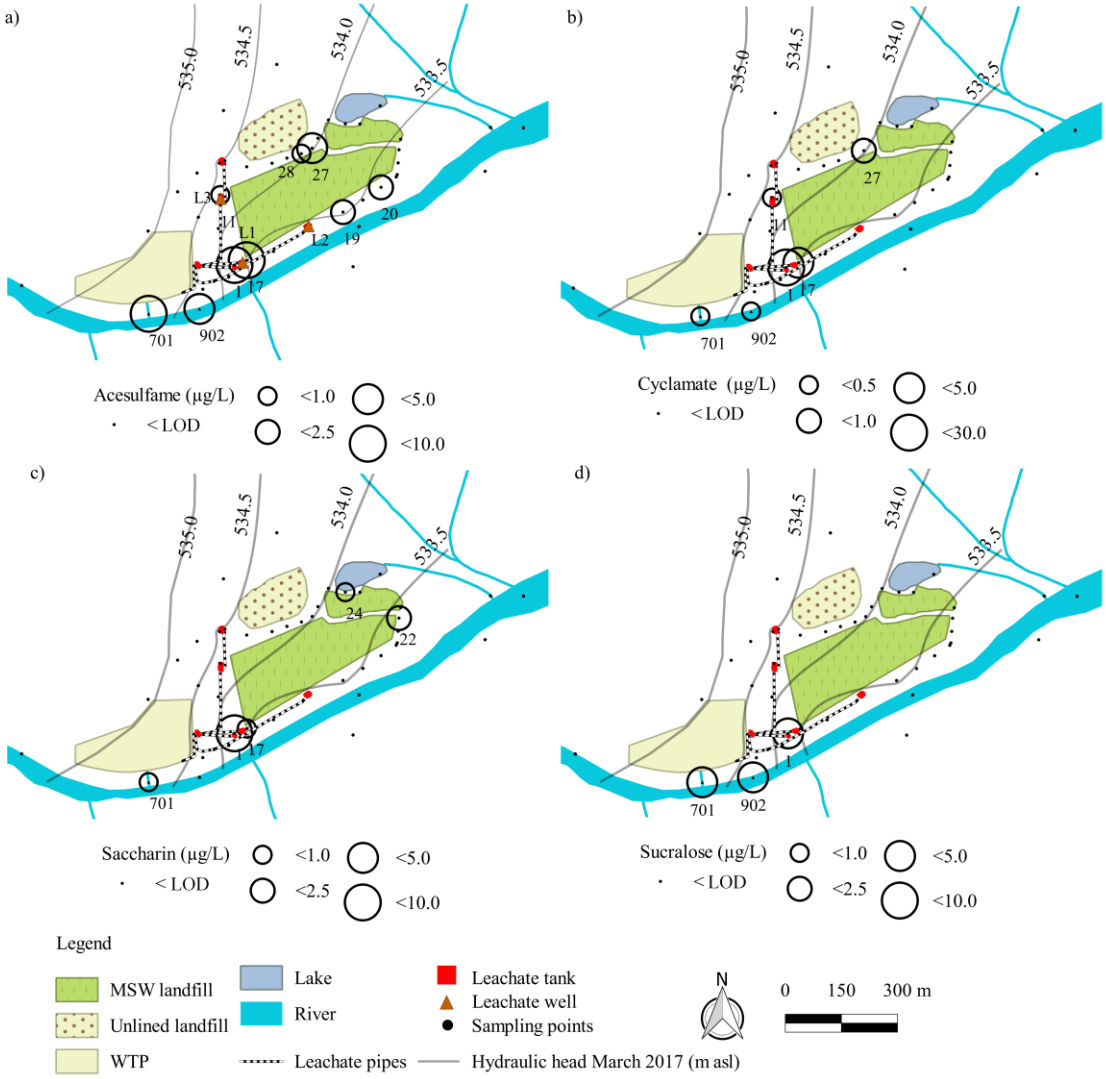

865

866 Fig. 3 - Maps of measured concentrations of artificial sweeteners (March 2017); sample IDs are
867 reported for points with concentrations >LOD. a) Acesulfame. b) Cyclamate. c) Saccharine. d)
868 Sucralose.

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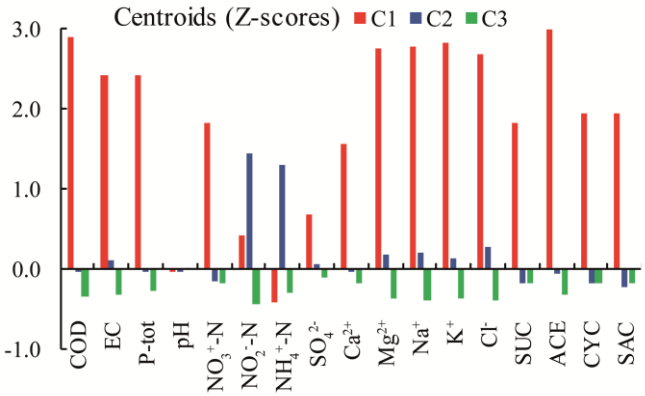

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872 Fig. 4 - Histogram of centroids for the three identified clusters in the cluster analysis (C1, C2
873 and C3).

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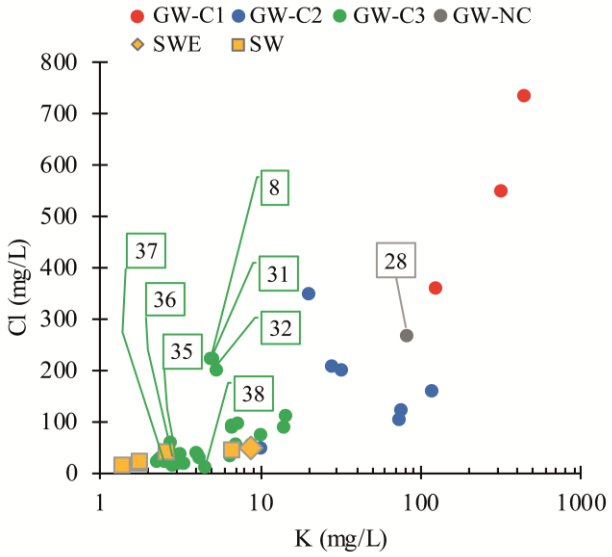

876

877 Fig. 5 - Scatter plot of Cl^- vs K^+ for groundwater (GW), surface water (SW) and sewage effluent
878 (SE) samples; numbers are sample IDs cited in the text; groundwater samples are grouped into
879 the three identified clusters (C1, C2 and C3); NC = not classified.

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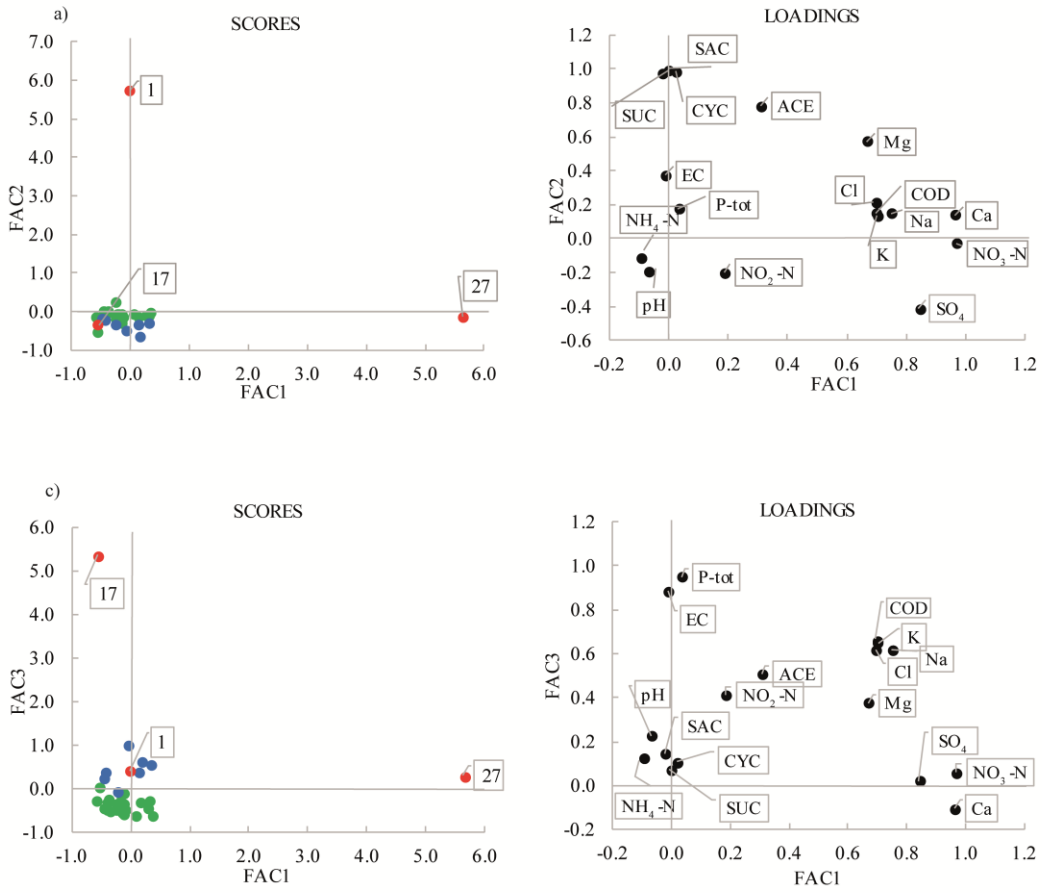

881

882 Fig. 6 - Score and loading plots resulting from the factor analysis of groundwater data; scores
883 are grouped into the three identified clusters (C1, C2 and C3); numbers are sample IDs cited in
884 the text. a) Plots of FAC1 *vs* FAC2. b) Plots of FAC1 *vs* FAC3.

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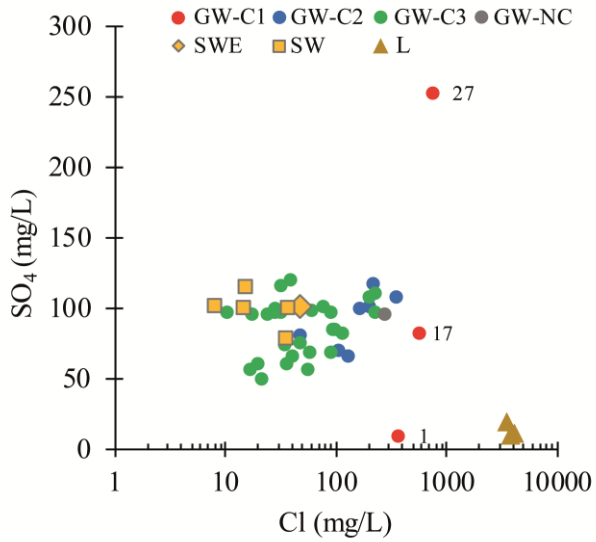
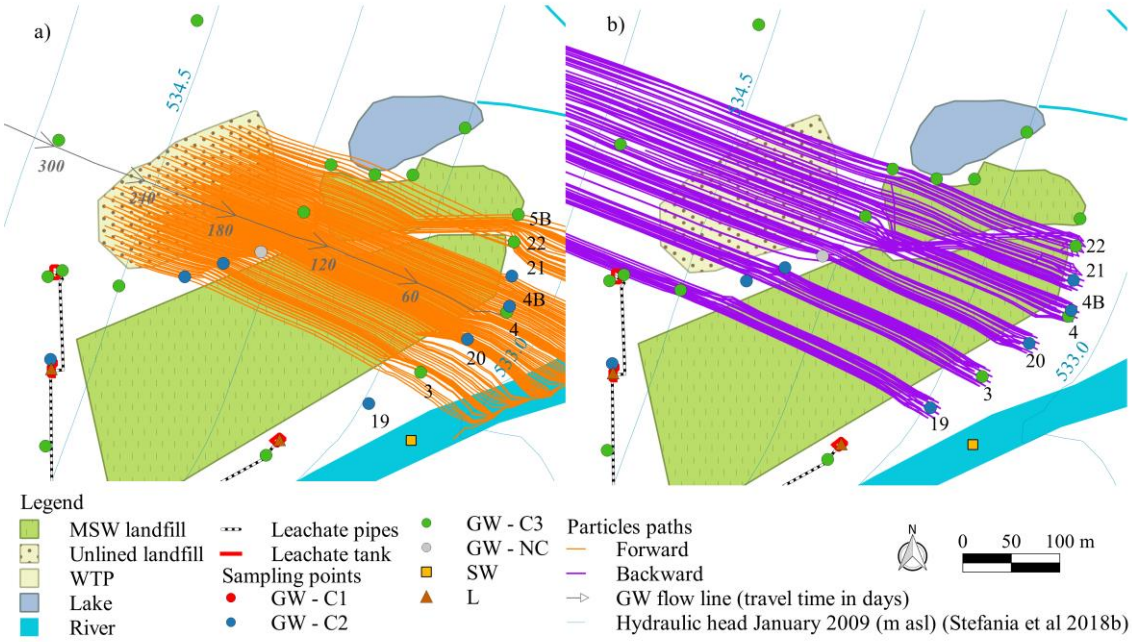


Fig. 7 - Scatter plot of SO_4^{2-} *vs* Cl^- for groundwater (GW), surface water (SW) sewage effluent (SE) and leachate (L) samples; numbers are sample IDs cited in the text; groundwater samples are grouped into the three identified clusters (C1, C2 and C3); NC = not classified.



899

900 Fig. 8 - Results of particle tracking. a) Extension of a hypothetical plume originating
901 from the whole old unlined landfill (forward simulation); the grey line represents the
902 groundwater flow passing through piezometers 27 and 4B, for which the travel time
903 (days) is expressed. b) Origin of groundwater passing through piezometers located
904 downstream of the lined landfill (backward simulation). L: Leachate Well.
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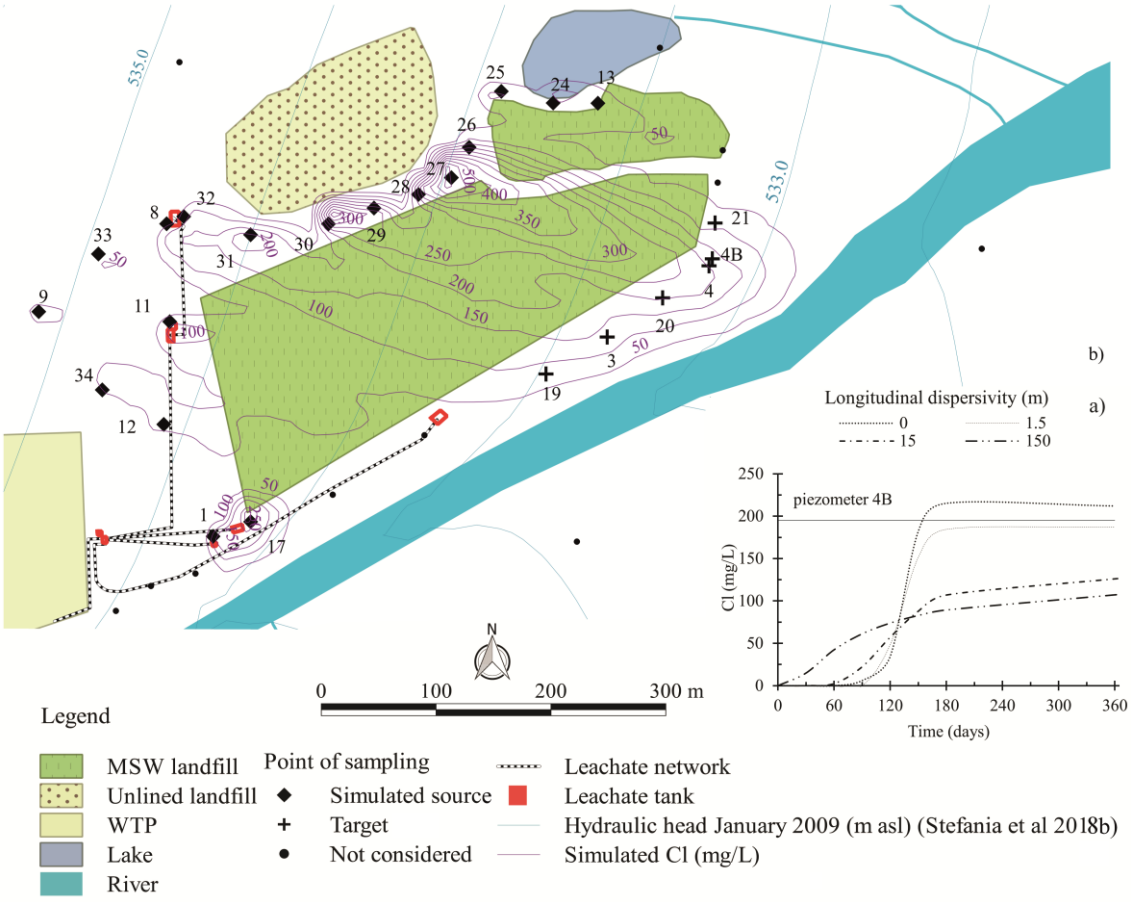

Fig. 9 - Results of the chloride transport model. a) Breakthrough curves of simulated Cl^- in piezometer 4B using the different values of longitudinal dispersivity tested in the sensitivity analysis. b) Map of the simulated Cl^- plume that indicates which piezometers were used as pollution sources and pollution targets.

Table 1 - Comparison of simulated against average measured Cl^- concentrations (mg/L) from 2011 to 2017; targets are referred to piezometers located downstream of the MSW landfill.

Piezometer	Average measured (mg/L)	Simulated (mg/L)	Residual (mg/L)	Residual (%)	Discrepancy (%)
3	114.5	116.3	-1.8	-1.5	-1.5
4	84.9	194.4	-109.4	-128.8	-78.3
4B	195.0	186.9	8.1	4.2	4.3
19	105.5	86.4	19.1	18.1	19. 9
20	92.4	202.7	-110.4	-119.5	-74.8
21	76.3	101.6	-25.2	-33.1	-28.4

937 Table 2 - Summary of the pollution phenomena identified in the site and average composition of
938 affected groundwater.

939

Pollution source	Old unlined landfill	MSW landfill leachate well L1	MSW landfill leachate well L3
Affected piezometers	4B, 19, 20, 21, 27, 28, 29, 30	1, 17	11
EC (µS/cm)	1300	4985	1580
COD (mg/L)	104	308	140
NO_3^--N (mg/L)	67.95	2.69	0.88
NO_2^--N (mg/L)	0.10	0.05	0.08
NH_4^+-N (mg/L)	44.51	0.76	54.00
P-tot (mg/L)	0.08	1.17	0.34
K^+ (mg/L)	95.8	218.0	116.6
Cl^- (mg/L)	252.7	454.3	160.5
SO_4^{2-} (mg/L)	114.5	46.8	101.2
SUC (µg/L)	<1.00	1.75	<1.00
ACE (µg/L)	1.22	7.42	0.82
CYC (µg/L)	<0.10	15.31	0.14
SAC (µg/L)	<0.30	3.06	<0.30

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