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HYDROGEOLOGICAL MODELING TO SUPPORT THE MANAGEMENT OF GROUNDWATER RESOURCES IN ALPINE VALLEYS

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Abstract

The present PhD project deals with the development of methodologies and tools in order to support the management of groundwater resources from a quantitative and qualitative point of view. The work deals with a particular hydrogeological context such as the Alpine valleys aquifers, where groundwater/surface water interactions as well the wells pumping have a crucial role in the hydraulic behaviour of groundwater. Moreover, the hydrogeological setting of these aquifers makes groundwater highly vulnerable to the contamination by the human activities.

The work involves three main topics concerning specified issues affecting the Alpine valley aquifer of the Aosta Plain (Aosta Valley Region, N Italy).

The first topic is related to the modeling of the three-dimensional groundwater flow and its interaction with the surface water. This topic was addressed by the development of a numerical groundwater flow model of the Aosta Plain aquifer in order to identify groundwater/surface-water relationships and evaluate the overall effect of the pumping on water resources. The model was developed using MODFLOW2005 and the more recent Stream-Flow routine package (SFR2) to simulate the surface-water network. An inverse calibration procedure performed by the PEST code was used to obtain the steady-state and transient solutions. The quantification of the hydrogeological budget, the groundwater/surface-water interactions and the effect of well withdrawals on water resources were done using the model results.

The second topic deals with the management of groundwater hydrochemical data. This topic was addressed through the development of the online hydrochemical database called TANGCHIM which was joined with an existing hydrogeological database in order to provide an integrated platform able to manage, display and share water quality and quantity data.

The third topic takes into account a groundwater pollution related to a landfill site. Within this topic, two main aims were achieved. The first one is related to the definition of a methodology able to support groundwater managers to define the conceptual model of the site and to calculate the trigger levels as useful tool for monitoring landfill sites located in historical human-impacted areas. The second aim is related to the detection of the sources related to the groundwater contamination affecting the landfill site. The investigation was conducted using hydrochemical parameters, artificial sweeteners as tracers, multivariate statistical analysis and transport modeling. The source apportionment analysis was accomplished to distinguish the contribution of different sources of the leachate infiltration in order to improve the management of the landfill site and design a proper remediation system.

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1. Introduction

Water is a fundamental resource to preserve the life on the Earth. Its availability, in terms of quantity and quality, is at the same time a growth and limiting factor widely considered in the evolution of the human history. It was estimated that the total amount of water on the Earth is about 1 billion and 386 million km^3 of which about only 35 million is freshwater. The 68.7% of the freshwater is not available for the use since it is stored in glaciers and snow cover. Instead, the total available freshwater is about 30.37% of which groundwater represents the 30.1% whereas surface-water is about 0.27% (Shiklomanov, 1993).

Bringing in mind the relative availability in many areas of the planet, the low cost related to the well pumping, groundwater has acquired a key role on the human water supply and it has become the main water resource used for humans needs. However, in the more recent past, the industrialization processes have induced an increase both of population and human needs followed by a sharply increase of groundwater exploitation due to the well pumping and groundwater pollution due to direct/indirect infiltration of contaminants from waste, industry, agriculture, drugs and any other activity (Sophocleous, 2000).

Despite its significant advantages, groundwater is not an unlimited resource and its recovery time in the case of overexploitation and pollution problems could be decades and centuries, respectively (LHM et al., 1991). As a consequence, in the last decades, researchers and stakeholders have paid more attention to overexploitation, depletion and pollution problems affecting groundwater resources.

The protection of the water resources is one of the cornerstones of environmental protection in Europe. The EU directives 2000/60/CE (EC, 2000) and 2006/118/CE (EC, 2006), established a framework for Community action in the field of water policy, in particular on the protection of groundwater against depletion, pollution and deterioration, so protecting both quantity and quality of groundwater. Accordingly, groundwater management is an arduous challenge, since it should sustain, over the long term, the hydrogeological equilibrium, in particular between different interconnected water bodies and human supply. At the same time, many efforts should be spent in order to guarantee a good quality status of groundwater that is continuously threatened by human contamination.

2. Aims of PhD project

The main aim of the present project is to apply the academic research on the management of the groundwater resource. In particular, this work deal with the development of tools and strategies to support the management of the groundwater resource in order to ensure the preservation of its quantitative and qualitative status over the time.
The present PhD work involves three main general topics each of which developed on specified issues affecting the Alpine valley aquifer of the Aosta Plain. In particular:

I) **Groundwater/surface water interaction.** This topic was addressed by the development of the groundwater flow model of the Aosta Plain aquifer in order to identify groundwater/surface-water relationships and evaluate the overall effect of well pumping on water resources;

II) **Hydrochemical data management.** This topic was addressed through the development of the hydrochemical database called TANGCHIM which was joined with an existing hydrogeological database in order to provide an integrated platform able to manage, display and share water quality and quantity data;

III) **Landfill impact on groundwater quality.** This topic was addressed by combining the use of multivariate statistical analysis, emerging tracers (i.e. artificial sweeteners) and modeling approaches in order to obtain: the conceptual model of the groundwater contamination related to a landfill site located within the Aosta Plain, methodologies for its monitoring and the identification of the groundwater pollution sources in the landfill site.

The present PhD project arises from the collaboration between the Regional Environmental Protection Agency of the Aosta Valley Region (ARPA VdA) and the Department of Earth and Environmental Sciences of the University of Milano-Bicocca.

Groundwater/surface-water interaction

In natural condition, the recharge and discharge of an aquifer are balanced, however, the human groundwater exploitation can affect this equilibrium.
In particular for groundwater/surface-water interconnected systems, wells pumping can increase the amount of the outflow discharged from an aquifer inducing both a decrease of the groundwater availability and rivers depletion, especially in the dry season when the streamflow is mainly constituted by the base flow component (Feinstein, 2012). Indeed, rivers are commonly the primary receptors of groundwater discharge and the latter is often the primary component of river discharge as base flow. As a consequence, the evaluation of the interactions between groundwater and surface-water, taking also into account the effect of wells pumping, should be mandatory, however, it is still challenging for hydrogeologists. (Alley et al., 2007; Zhou, 2009).
In this context, the storage capability of the aquifer plays a key role. Indeed, the initial water pumped by a well comes from the water stored in the aquifer (Sanz et al., 2011) and the release of this water continues until the well capture zone reaches another more accessible water. This water abstraction can originate a reduction of the natural outflow of the aquifer or an increase of the natural or artificial inflow to the aquifer from other connected water bodies. In the first case, the pumping subtracts water that, otherwise, would have flowed to other interconnected systems (e.g. river, pound, wetland). In the second case, the pumping can induce a water leakage from the connected surface-water bodies up to invert the type of existing relationship between them, especially in the case of a gaining river (Fetter, 2001). The above-mentioned behaviours induced by pumping results in streamflow depletion and/or groundwater overexploitation.
The effect of the well pumping is quite fast on groundwater rather than on surface-water where it may be evident only many years after pumping begins (Barlow and Leake, 2012). River discharge depletion due to pumping has to become an important water-resource management issue since these negative impacts may affect the aquatic system, surface-water availability and the quality and aesthetic values of the rivers.

Many different approaches based on hydrochemical, hydrogeological and numerical modeling can be used to investigate groundwater and surface-water interactions. The first two mentioned approaches include methodologies based on heat tracers, hydrochemical tracers, isotopes, mixing models, mass balance approaches and Darcy's law (i.e. study of the hydraulic gradient), nevertheless more reliable results arise only by the combined use of more than one of the previously listed methods (Mencio´ et al., 2014). These methodologies may help to depict the whole complexity of the groundwater/surface-water interactions. However, since they neglect the pumping effects and they are unable to consider the transient conditions occurring within an aquifer, the possibility to evaluate the impact of well pumping over the time, in terms of groundwater overexploitation and river depletion on the water resources, is prevented.

On the contrary, the numerical modeling approach provides powerful tools for quantifying the effects of the well pumping on both groundwater and surface-water, allowing to of well abstraction, groundwater exploitation and river depletion.

The numerical groundwater models can be developed and solved through two main approaches which are the finite difference method (FDM) and the finite element method (FEM).
The FDM leaves the physical model unchanged discretizing the differential equations of the problem under investigation. Using the FDM the model user establishes a regular grid over the model area that subdivides the total model area into rectangular subdomains where the differential equations are solved. Constant system parameters are then assigned to each cell as cell value. Unknown variables (e.g. hydraulic head for groundwater flow model) are calculated as discrete values at the grid node or at the central points of the cells (Spitz and Moreno, 1996). The effectiveness of the finite difference method increases with the increase of the number of the points (where the function is unknown) on which the related equation is solved. The FDM is able to solve complex problems (for example Numerical Fluid Dynamics). However, if the geometries of the system become very irregular or particular boundary conditions occur this method could be challenging to be applied.
The FEM differs from the FDM model by approximating the flow equation through and integration rather than a differentiation. In the case of FEM, the model area is subdivided into subareas, called elements, that usually are triangular elements. Since there are basically no restriction on the shape of the elements, the discretization of the modeled area is more flexible with respect to FDM. The general approach used by FEM is to approximate the solution of the unknown variable (e.g. hydraulic head for groundwater flow model) by piecewise linear functions and its distribution is approximated for each element by a linear function (Spitz and Moreno, 1996). The idea of the approximation used by the FEM is to approximate the true trend of the unknown function with some other functions of which the trend is known.

The two main codes used to develop three-dimensional groundwater flow models are MODFLOW and FEFLOW. MODFLOW is a free code developed by U. S. Geological Service. It is a FDM modular code able to simulate the groundwater flow within the aquifer using a block-centered finite-difference approach. MODFLOW code have a modular structure that consists of a main program and a series of highly independent "packages." Each package deals with a specific feature of the hydrologic system which is simulated. The division of the program into modules permits the user to examine specific hydrologic features of the model independently. This also facilitates the development of additional capabilities because new modules or packages can be added to the program without modifying the existing modules or packages (Harbaugh, 2005; Harbaugh et al., 2000; McDonald and Harbaugh, 1984).

FEFLOW is a proprietary and not freely available FEM code which uses a finite element (triangular) mesh to represent the model domain. The triangular mesh can be more easily adapted to variable stratigraphy such as sloping or pinch outs, and allows for versatile discretization of non-rectangular model domains (Trefry and Muffels, 2007).

The FEFLOW provides a better representation of anisotropy since it is based on FEM where each node which composes a triangular element of the mesh have own coordinates. Conversely, MODFLOW is based on a regular grid composed of regular cells on which the distribution of the aquifer propriety and the solution of the groundwater flow equation is discretized. However, the use of a code based on FEM does not guarantee the local mass conservation and there can be some discontinuous velocities at the element boundaries. Lastly, FEFLOW uses more generic boundary conditions to simulate different elements of the hydrogeological system (e.g., river, drain, well, no-flow zone, etc.).

The MOFLOW code is an international standard used by hydrogeologists to develop groundwater flow model. The main advantage of the MODFLOW code is that the obtained solution is mass conservative, accordingly, the analysis of the groundwater mass-balance computed by the code is more reliable. Moreover, as stated above, MODFLOW uses various packages to simulate different elements of the hydrogeological system.

In this context, surface-water can be simulated by using many types of boundary conditions and packages (e.g. GHB, RIV, STR, SFR2, Lake). Unfortunately, in order to understand the relationships between groundwater/surface-water, too simple and not specific boundary conditions are often used to simulate surface-water. This leads to an over-simplification of the dynamics occurring between groundwater/surface-water and wells pumping, limiting the model capability to understand their complex dynamics. In order to overcome this limitation, the Streamflow Routing (SFR2) Package (Niswonger and Prudic, 2000, 2010) can be used. In particular, SFR2 is able to compute and simulate the streamflow and stage of the river. So, using SFR2 water capture by pumping wells can make river segments dried or change the direction of the water exchange, gaining and losing river segments can be identified, river segment behaviour can respond to water-table oscillation, surface-water diversions can be simulated and unsaturated flow between river and aquifer can be computed.

Furthermore, the implementation of numerical models to manage aquifers system also provides the possibility to evaluate many other aspects related to groundwater. For example, the MODPATH code (Pollock, 2012) allows to track the advective component of the groundwater flow, whereas the

MT3DMS code (Zheng, 2010; Zheng and Wang, 1998) is able to simulate the fate of dissolved contaminants taking into account the advective-dispersive transport equation using the MODFLOW solution as a basis for groundwater flow.

The use of numerical modeling allows to consider, at the same time, different aspects that could have different weights on the evaluation of the quantity and quality status of the groundwater resource. Overall, groundwater model provides the chance, on one hand, to improve the comprehension of the behaviour of the system and, on the other hand, to implement more suitable management policies for the groundwater resource.
In the present PhD project, this topic was addressed by developing a three-dimensional numerical groundwater flow model of the Aosta Plain through the use of the SFR2 Package and MODFLOW 2005.

Hydrochemical data management

Groundwater is often felt as a relatively stable and well-protected water resource. However, a safe drinking water supply from groundwater is a complex task to assure. The understanding of the hydrological systems and the processes of pollutant transport is the basis of an efficient water management. This process should be based on the observations and scientific interpretation of the data collected in the field.

In order to do that, it could be possible to integrate tools and methodologies into informatic systems developed to manage field data stored in specified and well-structured database, providing outcomes for the water managers in an easily understandable and usable form. The integration of database and tools forms a decision support system (DSS) (Janža, 2015).

A DSS is a computer-based system that uses data stored in a connected and specific database, aiding the process of decision making (Sprague Jr and Carlson, 1982). Moreover, DSS utilizes data and models to solve unstructured problems in order to help decision makers (Finlay, 1994; Power, 2004). Considering the above definitions, DSS ranges from systems answering of simple queries to systems modeling of a complex human decision-making process (Nizetic et al., 2007).

In the context of groundwater resources, DSSs are often used to facilitate groundwater management in terms of suitable exploitation of the resources and to optimize groundwater remediation. Different examples of DDS are shown in literature. As for the quality management of groundwater, Track et al. (2008) developed a groundwater management tool coupled with an early warning system aimed at managing and controlling hazardous compounds in groundwater catchment areas. Ertel and Kirchholtes (2007) developed a tool focused on the optimization, evaluation and management of contaminated groundwater in urban area based on the cycling screening of groundwater hydrochemical data. Janža (2015) described a DSS for emergency groundwater management that was developed to improve activities after the discovery of pollution. The DSS is composed of a user-friendly graphical interface that enables water managers to utilize the database, numerical modeling techniques and expert knowledge, and thus gives them fast and easy access to supporting information for mitigating groundwater pollution.

As shown before, DSSs requires to implement at least one database that allows to store data. This database is the core of a DSS because it represents the source of data for all implemented tools. For this reason, the design of the structure and capabilities of the database represents an important task during a DSS developing.

In order to investigate and manage aquifer systems and groundwater contamination events, both new and historical hydrogeological and hydrochemical data have to be collect from fields surveys, institutional monitoring networks and well-drilling cores. However, these data are often difficult to obtain and share because they are managed by different public and/or private operators who store data in different formats and on different information supports. Moreover, databases are often designed each time as a simple "tank" for a specific project or specific study area.
Usually, hydrochemical databases are more difficult to manage with respect to the hydrogeological database. Indeed, in many cases, the number of the analysed chemical compounds and the groundwater sampling frequency are much higher than hydrological data. Besides, the name of a chemical compound can have more than one synonymous jeopardizing the integrity of the dataset by means of lack or duplication of data. As a consequence, many resources have to be spent to design, compile and join data from different sources in a new specific database. Moreover, this process, if not properly managed, could lead to redundancy as far to leak of data.

As stated before, both hydrogeological and hydrochemical data have to be considered in order to properly manage the groundwater resources. Moreover, it is desirable that these data can be easily recovered, used and shared. For this reason, an ever-increasing need in developing online integrated platforms is felt, in order to store, display and process different kinds of groundwater data. These online platforms, being easily accessible, could be used as a base to integrate tools or procedures able to analyse available data and providing a support system to decision-makers or scientists for a more effectiveness management and comprehension of water resources.
This topic was addressed in the PhD project by developing the on-line hydrochemical database called TANGCHIM.

Landfill impact on groundwater quality

Groundwater pollution is another key aspect that must be managed in order to guarantee the good quality status of groundwater. In this light, wastes represent one of the most important threats for groundwater quality, since they can contain a wide range of pollutants (Christensen et al., 2001; Han et al., 2013). Accordingly, quite some groundwater contamination events caused by leaks of leachate from landfills have been reported in literature (Christensen et al., 1998; Fatta et al., 1999; Giusti, 2009; Han et al., 2013, 2016; Laner et al., 2012; Lyngkilde and Christensen, 1992; Mor et al., 2006; Öman and Junestedt, 2008).

Especially in the past, wastes were disposed in the environment without paying any attention to probable leachate infiltrations toward soil and groundwater, building over the time many uncontrolled and unlined landfills that caused groundwater pollution. The environmental regulation partially reduced the uncontrolled disposal of waste by calling for rigorous prescriptions, such as a lined system able to avoid leaks and percolation of pollutants through soil and groundwater (Read et al., 2001).

As regards of the waste management, nowadays, the European legislative referent is the 99/31/EC Landfill Directive (EC, 1999) that aims to prevent or reduce the negative effects of landfills on soils, surface-water and groundwater. It establishes a list of requirements for a proper groundwater monitoring network in landfill sites and specifically imposes the definition of trigger levels to identify significant adverse environmental effects on groundwater, of course on the basis of a proper conceptual model of the site. As regards of the trigger level, the Directive provides a general guideline for their determination related to new landfills built in an unpolluted site, whereas no methodologies are suggested for landfills built in historically human-impacted areas.

In order to evaluate the impact of human activities on the quality of groundwater and surface-water, recent studies have paid attention to the use of new emergent contaminants, tracers and isotopes (Buerge et al., 2011; Clarke et al., 2015; Eggen et al., 2010; Lapworth et al., 2012, Sui et al., 2015, Van Stempvoort et al., 2011). Water, nitrogen and carbon isotopes are well-known robust tracers typically used to depict the evolution of groundwater contamination related to leachate plume originate by landfills, septic tank, etc. (Caschetto et al., 2018; Van Breukelen et al., 2003). Although isotopes are considered robust tracers, they have high costs related to sampling and analysis.

Lange et al. (2012) found that the artificial sweeteners can be considered a new class of emerging traces in groundwater, since they are conservative and they were found in groundwater affected by leachate plume and sewage (Buerge et al., 2009; Lange et al., 2012; Van Stempvoort et al., 2011). Artificial sweeteners are usually used as sugar substitutes in foods, beverages, drugs and sanitary products. A Canadian study reported the use of different types of artificial sweeteners, selected on the basis of their approval and following introduction as a product additives, to trace leachate plumes

originated from different landfills (Roy et al., 2014), highlighting the possibility of using these compounds to trace different leachate plumes on the basis of the landfill age.
Broadly speaking, many works, regarding groundwater impacted by leachate plumes, focused on the description of the overall composition and behaviour of the groundwater leachate plume (Bjerg et al., 1995; Clarke et al., 2015; Cozzarelli et al., 2011a; Han et al., 2016). Christensen et al. (2001) summarizing the main involved processes governing contaminants in leachate affected aquifer such as dilution, sorption, ion exchange, precipitation, redox reactions and degradation. The authors underlined that the redox-processes and the related zonation always occur in a groundwater leachate plume. For this reason, the comprehension of the redox zone distribution is an important task to understand. Moreover, the contaminants patterns in a leachate plume change as the leachate migrates away from landfill. These process are promoted by microbial communities (Christensen et al., 1998) that use the dissolved organic carbon, that composes the leachate (Fatta et al., 1999; Mor et al., 2006), as substrate to maintain the microbial redox processes (Ludvigsen et al., 1998).
Although the COD is usually monitored in landfill site to evaluate the likely infiltration in groundwater of leachate, and thus organic matter, its content is also affected by other reduced species like Fe, Mn or H_2S that can significantly contribute to it. More reliable indicators of the presence of organic carbon in groundwater which could be considered when studies are focused on the redox-zonation of a leachate plume are DOC (Dissolved Organic Carbon) or TOC (Total Organic Carbon) because their quantification are not affected by the presence of redox-sensitive species. Moreover, the DOC coupled with other tracers could allow to trace both the evolution of the oxidation of dissolved organic carbon and the three-dimensional extension of a landfill leachate plume (van Breukelen et al., 2003, Cozzarelli et al 2011). For this reason, the DOC or TOC detection should have to be imposed for the groundwater monitoring nearby landfill site by regulation, instead of COD.

A good characterization of a plume should consider the vertical quantification of the investigated contaminants, especially for the redox-sensitive species such as O_2, Fe, Mn, As, NH_4, etc (Colombani et al., 2015). This need arises from the evidence that water-quality samples collected from long-screen wells may be not representative of the quality of the water in the aquifer because of the vertical flows of water in the well induced by pumping. Vertical flows in a well can be increased by: high aquifer transmissivity, greater proximity to discharge or recharge zone, greater well volume and greater vertical/horizontal anisotropy (McMillan et al. 2014). In these cases, the water origin of the sample is sensitive to pump intake position, pumping rate and pumping duration. Furthermore, McMillan et al. (2014) showed that when vertical gradients are present, a sample bias is present even when the local vertical flow in the wellbore is less that the pumping rate. Appelo and Postma (2004) clarified the effect of the water mixing on a typical redox-species such as Fe^{2+} on a fully completed well, sampled without using multi-level methods. They have shown a typical vertical profile of Fe^{2+}

and O_2 in a sandy aquifer obtained by depth-specific sampling where a well-defined oxic zone is on top of an anoxic zone containing Fe^{2+}. The authors stated that if a piezometer fully screened is used, the obtained water sample will be representative of a mixing of both oxic and anoxic zone. Furthermore, the oxic water will react with the Fe^{2+} containing water and the concentrations of O_2 and Fe^{2+} will result alter. This behaviour induces as a result that the water sample collected without a multi-level sampling does not properly reflect the real conditions of the aquifer because the mixing of not contaminated and contaminated water, that originates from different screened portions of the aquifer, distorts the real concentrations of the investigated compounds (Church and Granato, 1996). For proper depth-specific sampling, dedicated systems are required. For example, new multiple nested piezometers or multiple-borehole piezometer may be drilled, otherwise removable packer or backfill system could be used to seal the borehole between monitoring zones to prevent the unnatural vertical flow of groundwater and maintain the natural distribution of fluid pressures and chemistry for existing piezometers (Nielsen, 2005). All of these aspects are abundantly discussed in previous works that constitute the main references for the geochemical characterization of groundwater and related pollution (Appelo and Postma, 2004; Christensen et al., 2001; Church and Granato, 1996).

Unfortunately, the multi-level sampling is not a widespread practice, especially for the routine monitoring done by both managers of contaminated-site and environmental control agencies. Indeed, a multi-level sampling would sharply increase the cost of the monitoring.
Furthermore, neither European or extra-European legislations require multi-level sampling, therefore both managers and control agencies, in their ordinary activities, usually neglect the vertical sampling. On this basis, it is required to find and develop tools and methods to effectively use available data from routine monitoring.

Groundwater affected by the landfill leachate plume is a crucial issue for a safe drinking supply. Consequently, in these cases one of the most important tasks to properly design a remediation system is the identification and quantification of the points from which leachate infiltrates toward underlying aquifer. In order to support the identification of the sources, statistical methods, modeling and emerging tracers can be used. Usually they are used in a separate way. However, the combined use of the above mentioned tools could improve and increase the reliability on the identification of the likely position where the infiltration of pollutant (e.g. leachate) is occurring.
In a landfill site, leaks of leachate could be related, for examples, to a deficiency of the landfill liner systems, to problems with the leachate collection system or to a previous landfill built in the same area with no environmental prescriptions. Accordingly, the location of the pollution sources should be correctly recognized.

Indeed, inadequate knowledge regarding groundwater pollution sources either leads to decrease the efficiency of remediation strategies or increase the remediation costs. Therefore, the detection of the exact sources of the groundwater pollution is a critical issue in groundwater management. Thus, the estimation of the pollution source characteristics including numbers, locations, and release histories becomes a key task for efficiently managing the groundwater systems and polluted sites (Ayvaz, 2010).

This topic was addressed in the present PhD project using different approaches in order to define the conceptual model of pollution, a methodology to calculate trigger levels and the identification of the sources of leachate infiltration in a landfill site affecting the Aosta Plain aquifer.

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3. Study area

The study area is a portion of the Aosta Plain, an Alpine valley floor in the Aosta Valley Region (Northern Italy). The elevation of the Aosta Plain ranges from 700 to 530 m above sea level (asl) and it is bounded on the south and north by mountains slopes that sharply reach more than 2500 m asl. The study area is about 13.5 km from west to east and 2.5 km from south to north (fig. 1). The geographical location joined with its elevation guarantee the presence of a dense surface-water network with a nivo-glacial regime. The main regional river is the Dora Baltea River that flows from west to east in the middle of the plain.

The Alpine valley aquifer of the Aosta Plain lies over a deep impermeable crystalline basement rock which was first eroded by the Balteo glacier and, later, progressively filled by deposits whose origin may be fluvioglacial, alluvial and lacustrine. The aquifer consists of a high transmissive unconfined aquifer, locally layered though low permeability lenses and limited at the bottom by a silty-clay lacustrine layer. More recently, new data showed a deeper unexploited aquifer below the lacustrine layer, which seems to be discontinuous. Groundwater flows from west to east, showing close relationships with the Dora Baltea River. The recharge of the Aosta Plain aquifer firstly depends from snow-melt and secondly by the Dora Baltea River which contributes to the sharp and wide seasonal water-table oscillations. Within this hydrogeological context, groundwater is the main source of water supply which is supported by the high transmissivity of the aquifer.

The coarse deposits and the absence of impermeable layers, especially in the shallow part of the aquifer, make groundwater quality highly vulnerable to contamination by waste deposits, industry and agriculture.

Typically, the configuration of the Alpine valley aquifers allows the interaction between groundwater and surface-water in terms of losing and/or gaining behaviour of the river. In this light, the Dora Baltea river changes its behaviour from losing to gaining, flowing from upstream to downstream of the Aosta Plain. In particular, in the upstream area, its losing segments contribute to the rising of the water table, whereas in the downstream area the draining stretches reduce the amplitude of water-table oscillations. Accordingly, from west to east, the depth of the water-table changes from about 20 to 2 m and, similarly, seasonal water-table oscillations change from 7 to 1 m. For these reasons, the hydrogeological setting of the Alpine valley aquifer, such as that of the Aosta Plain, is the typical one that offers the opportunity to study the groundwater/surface-water interactions.

The geomorphological context which characterizes the Aosta Valley Region forced the population to live and develop their activities within the major valleys (e.g. Aosta Plain) since here the lower slope of the ground surface joined with the easy availably of water resources. However, this process has caused the concentration of human activities in restricted areas, inducing inevitable impacts on both availability and quality of the water resources.

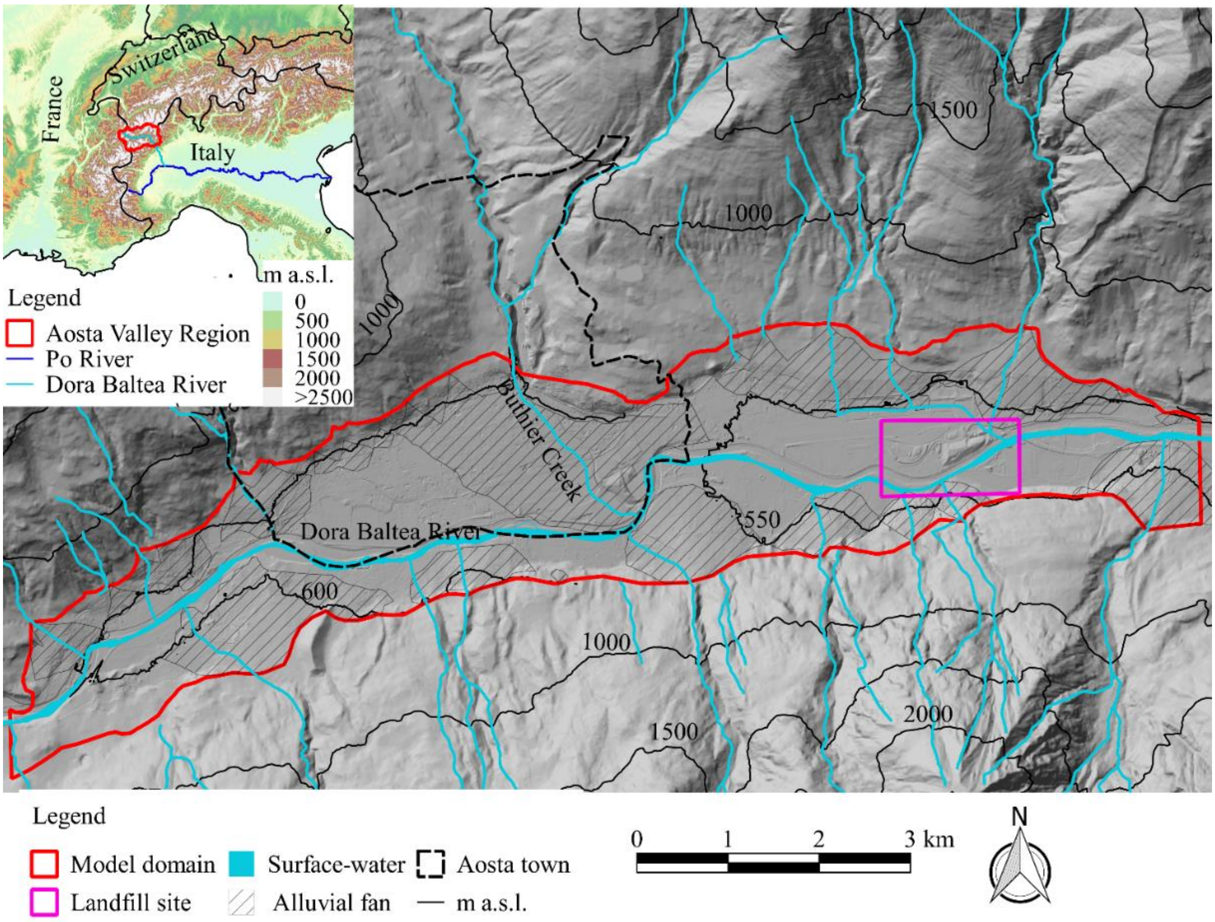

Fig. 1 – Study area: Aosta Plain. Red line represents the aquifer bounds which were used as the domain of the three-dimensional groundwater flow model. Violet line represents the landfill site.

The landfill site involved in the present PhD project is located in the eastern part of the Aosta Plain (fig. 1) and it is composed of two main landfills: an old unlined landfill and a new lined and controlled landfill.

4. Thesis structure

The present PhD project consists of four main sections:

- Section I: Groundwater/surface-water interaction modeling;
- Section II: Hydrochemical data management;
- Section III: A methodology to define landfill trigger levels;
- Section IV: Sources detection of the leachate infiltration in a landfill site.

4.1. Groundwater/surface-water interaction modeling

This first section deals with the implementation of the hydrogeological numerical model of the Aosta Plain aquifer aimed at simulating the three-dimensional groundwater flows, groundwater/surface-water interactions and the impact of the pumping wells on water resources.

The main aim of the model is to evaluate the impact of groundwater pumping on groundwater and surface water resources, where the main regional river is changing from losing (upstream) to gaining (downstream). Other related purposes are: (1) to reproduce the wide seasonal fluctuations of the water table (2) to understand the dynamics between groundwater/surface-water, and (3) to improve the knowledge of the Aosta Plain aquifer.
The numerical groundwater model was implemented using MODFLOW2005, whereas surface-water were simulated using SFR2 Package which allows both to simulate the changing behaviour of the main river and evaluate the impact of the pumping on the water system. Based on the aim of the model, measured monthly withdrawals were assigned to wells. An inverse method through the PEST code was used to calibrate both steady-state and transient models using both head and flux targets. Different scenarios were simulated in order to characterize losing and draining segments of the river as a function of water-table oscillations and pumping. A quantification of the hydrogeological budget, groundwater/surface-water interactions and the effect of well withdrawal on water resources were done by the interpretation of MODFLOW mass balance outputs.

The results of this section of the PhD project are summarized in the following published paper:

Modeling groundwater/surface-water interactions in an Alpine valley (the Aosta Plain, NW Italy): the effect of groundwater abstraction on surface-water resources.

Stefania, G.A.[(1)], Rotiroti, M. [(1)], Fumagalli, L. [(1)], Simonetto, F. [(2)], Capodaglio, P.[(2)], Zanotti, C.[(1)], Bonomi, T.[(1)].

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REPORT

Modeling groundwater/surface-water interactions in an Alpine valley (the Aosta Plain, NW Italy): the effect of groundwater abstraction on surface-water resources

Gennaro A. Stefania[1] · Marco Rotiroti[1] · Letizia Fumagalli[1] · Fulvio Simonetto[2] · Pietro Capodaglio[2] · Chiara Zanotti[1] · Tullia Bonomi[1]

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4.2. Hydrochemical data management

The second section shows the implementation of the hydrochemical database called TANGCHIM which was connected to an existing hydrogeological database that, on the whole, form an integrated platform able to store, process and share all groundwater data related to wells and piezometers;

The TANGCHIM idea arises from the need to provide an online platform able to: 1) easily manage hydrochemical time series keeping the connection with the hydrogeological data; 2) manage data derived from different geographical contexts, authorities, projects or private companies; 3) provide an easy access to the data without losing data confidentiality; 4) provide database access by using whatever devices that support an internet connection (e.g. personal computer, tablet, smartphone). Currently, TANGCHIM stores more than 115,000 hydrochemical data subdivided between about 430 chemical compounds. It also manages synonyms of chemical compounds to avoid data duplication by providing well-structured data. Data export can be performed through many types of queries, based on chemical compounds, well name, temporal period and location. Moreover, TANGCHIM is able to compute simple statistical reports (i.e. descriptive statistics), boxplots and concentration time-series graphs. A practical use of TANGCHIM was shown in supporting the development of the preliminary conceptual model of the groundwater contamination induced by the landfill area located in eastern part of the study area.

The results of this section of the PhD project are summarized in the following submitted paper:

The hydrochemical database TANGCHIM, a tool to manage groundwater quality data: the case study of a leachate plume from a dumping area.

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4.3. A Methodology to define landfill trigger levels

The third section deals with the development of a standard methodology useful to characterize and manage complex groundwater contamination induced by landfill sites. This methodology allows to calculate groundwater trigger levels, that are useful to monitoring landfill sites built in highly historical impacted areas.

The European 1999/31/EC Landfill Directive establishes a list of actions for a proper groundwater monitoring network in a landfill site. Between these, it specifically imposes the definition of trigger levels for identifying significant adverse environmental effects on groundwater generated by the landfill. However, no methodology is reported in the Directive. In order to fill this regulatory gap, a methodology based on multivariate statistical analysis was proposed. It involves four main steps: a) implementation of the conceptual model, b) landfill monitoring data collection, c) hydrochemical data clustering and d) calculation of the trigger levels.
The methodology was applied to the available historical dataset related to the landfill site located in the eastern sector of the Aosta Plain. Data were processed through multivariate statistical analysis (i.e. cluster analysis) in order to identify groups of monitoring points having similar hydrochemical features. The resulting groundwater clusters were then classified in suitable or not suitable for the determination of trigger levels. The final identification of the trigger levels involved the choice of representative parameters on the basis of the characteristics of the wastes stored in the landfill and then the calculation of the trigger value.

The results of this section of the PhD project are summarized in the following submitted paper:

Determination of trigger levels for groundwater quality in landfills located in historically human-impacted areas.

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Determination of trigger levels for groundwater quality in landfills located in historically human-impacted areas

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ABSTRACT

Landfills are one of the most recurrent sources of groundwater contamination worldwide. In order to limit their impacts on groundwater resources, current environmental regulations impose the adoption of proper measures for the protection of groundwater quality. For instance, in the EU member countries, the calculation of trigger levels for identifying significant adverse environmental effects on groundwater generated by landfills is required by the Landfill Directive 99/31/EC. Although the derivation of trigger levels could be relatively easy when groundwater quality data prior to the construction of a landfill are available, it becomes challenging

4.4. Identification of groundwater pollution sources in a landfill site

The fourth section addresses the identification of the sources of the leachate infiltration in the landfill site located in the Aosta Plain, using hydrochemical data analysis, artificial sweeteners and transport modeling.

Hydrochemical data from a field survey made in March 2017 were analysed in order to identify the likely points through which leachate infiltrates toward groundwater inducing a poor water quality. The hierarchical clustering approach was used in order to obtain a preliminary classification of the groundwater chemistry using hydrochemical groundwater data. Instead, major ions such as Cl, K, SO_4 and factor analysis were used to distinguish between distinct types of leachate sources which are affecting groundwater quality. Artificial sweeteners, such as saccharin, cyclamate, acesulfame and sucralose were analysed from groundwater and surface-water firstly to evaluate their occurrence in groundwater impacted by leachate and secondly to evaluate if their use could help to understand the origin and the fate of the plume. A transport model was implemented by using the MT3DMS code in order to test the hypothesis on the origin of the high concentration of chloride ion measured downstream of the landfill. Moreover, particle tracing analysis, by means of MODPATH code, were used to design a drainage barrier useful to control the contamination affecting groundwater beneath the landfill area.

The results of this section of the PhD project are discussed in the following later paper in preparation to be submitted.

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

Manuscript in preparation, to be submitted

5. Publications

The results of Ph.D work are summarized in four papers dealing with the qualitative and quantitative management of groundwater resource in the Aosta Plain aquifer:

- Modeling groundwater/surface-water interactions in an Alpine valley (the Aosta Plain, NW Italy): the effect of groundwater abstraction on surface-water resources.
- The hydrochemical database TANGCHIM, a tool to manage groundwater quality data: the case study of a leachate plume from a dumping area.
- Determination of trigger levels for groundwater quality in landfills located in historically human-impacted areas.
- Identification of groundwater pollution sources in a landfill site using artificial sweeteners, multivariate analysis and transport modelling

5.1. Modeling groundwater/surface-water interactions in an Alpine valley (the Aosta Plain, NW Italy): the effect of groundwater abstraction on surface-water resources

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Keywords: Groundwater management, Heterogeneity, Groundwater/surface-water relations, Italy, Numerical modeling

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Abstract

A groundwater flow model of the Alpine valley aquifer in the Aosta Plain (NW Italy) showed that well pumping can induce river streamflow depletions as a function of well location. Analysis of the water budget showed that ~80 % of the water pumped during two years by a selected well in the downstream area comes from the baseflow of the main river discharge. Alluvial aquifers hosted in Alpine valleys fall within a particular hydrogeological context where groundwater/surface-water relationships change from upstream to downstream as well as seasonally. A transient groundwater model using MODFLOW2005 and the Streamflow-Routing (SFR2) Package is here presented, aimed at investigating water exchanges between the main regional river (Dora Baltea River, a left-hand tributary of the Po River), its tributaries and the underlying shallow aquifer, which is affected by seasonal oscillations. The three-dimensional distribution of the hydraulic conductivity of the aquifer was obtained by means of a specific coding system within the database TANGRAM. Both head and flux targets were used to perform the model calibration using PEST. Results showed that the fluctuations of the water table play an important role in groundwater/surface-water interconnections. In upstream areas, groundwater is recharged by water leaking through the riverbed and the well abstraction component of the water budget changes as a function of the hydraulic conditions of the aquifer. In downstream areas, groundwater is drained by the river and most of the water pumped by wells comes from the base flow component of the river discharge.

I. Introduction

The interaction between groundwater and surface water (e.g., river, stream, lake, wetland, spring, etc.) is an important aspect of the water cycle since it can influence the utilization of water resources by humans. As remarked by Winter (1998), "*surface water commonly is hydraulically connected to ground water, but the interactions are difficult to observe and measure*". Along its path, a stream can be gaining, losing or both. Furthermore, along a reach, interactions between surface and groundwater bodies could change during the seasons (Alley et al. 1999). When groundwater and surface water systems are interconnected, the groundwater discharge may be an important component of the total flow in the surface water network and vice-versa. Another key aspect is the role of well withdrawal, influencing both the groundwater and surface water balance. In such interconnected systems, well pumping can have a strong influence on the amount of groundwater discharged to surface water bodies (Barlow and Leake, 2012; Sophocleous 2002). Well pumping induces some deformations on the water table that could affect the streamflow, especially in the dry season when the streamflow is mainly constituted by base flow. It follows that the identification of the impacts of well withdrawals on groundwater, surface water and their interactions should be of great importance (Alley 2007; Zhou 2009; Feinstein 2012). Furthermore, Sanz et al (2011) highlights the importance of taking into account the storage capability of the aquifer when an analysis of the impact of the well pumping on groundwater/surface-water interactions is carried out in non-steady-state systems. This aspect gains greater importance if the analysis considers the measured discharges of both wells and rivers.

In order to quantitatively evaluate groundwater/surface-water interactions, three-dimensional numerical modelling is often implemented. MODFLOW is one of the most employed numerical codes in hydrogeology studies to simulate the flow field of groundwater (Harbaugh 2005). This code is organized in various packages, and it is able to simulate the different elements constituting the hydrogeological system (e.g., river, drain, well, no-flow zone, etc.). In particular, the Streamflow Routing (SFR2) Package (Niswonger and Prudic 2005) was especially designed to simulate surface water and its exchanges with groundwater. The coupling of MODFLOW-2005 and SFR2 allows taking into account the possibility that groundwater and surface water might be directly connected through the streambed or separated by an unsaturated zone (Feinstein 2012). The SFR2 package has the following advantages with respect to the simpler and more commonly used River (RIV) Package (McDonald and Harbaugh, 1988): a) stream stage is computed, so that the case in which diversions and pumping make a stream go dry can be simulated, as opposed to RIV which keeps the river stage fixed, b) gaining and losing reaches respond to water-table oscillations and c) it is possible to add surface-water diversions and impose the river streamflow in the system to provide more information on conjunctive use of surface water and groundwater.

This work deals with the analysis of groundwater/surface-water interactions in an Alpine valley in NW Italy, more precisely in the Aosta Plain, located in the middle of the Aosta Valley Region. In this area, groundwater is the main source for public drinking water supply and industry. The investigated area contains an alluvial aquifer, commonly found in Alpine valleys, that has important relationship with the hydrographic network. The studied area is crossed by the Dora Baltea River (main river of the Region, a left-hand tributary of the Po River) which flows from west to east and has 16 tributaries mostly oriented perpendicular to its path. Previous studies found that the interaction between groundwater and surface water changes along the Aosta Plain. In particular, the Dora Baltea River changes from losing to gaining from upstream to downstream within the study area. (P.I.A.H.V.A. 1996; Triganon et al. 2003; Bonomi et al. 2013, 2015).
The main aim of this work is to evaluate the impact of well pumping on groundwater and surface water resources in the study area, where the main river is changing from losing (upstream) to gaining (downstream). Other related purposes are: a) to reproduce the wide seasonal fluctuations of the water table and to better understand the dynamics of groundwater/surface-water interactions b) to improve the knowledge of the Aosta Plain aquifer.
In order to achieve these goals, a numerical groundwater model, both in steady-state and transient conditions, was implemented using MODFLOW 2005 (Harbaugh 2005) and the SFR2 Package (Niswonger and Prudic, 2010) for simulating the Dora Baltea River and its tributaries. More specifically, the investigative approach included: a) the definition of the conceptual model of the Aosta Plain aquifer; b) the reconstruction of the 3D distribution of hydraulic conductivity by interpolation of coded data (Bonomi et al. 2009, 2013, 2014, 2015; Perego et al. 2014; Rotiroti et al. 2015; Stefania et al. 2015) extracted from the TANGRAM© database (Bonomi et al. 2014); c) the quantification of groundwater/surface-water interactions and the effect of well withdrawal on water resources by the interpretation of MODFLOW mass balance.
An innovative aspect of the present work is the application of the advanced package SFR2, that was previously used in a few studies (Feinstein et al. 2010; Masterson and Granato 2013; Leaf et al. 2015). Moreover, to the best of the authors' knowledge, no previous studies have used the SFR2 package to evaluate the effects of well pumping on groundwater/surface water interactions in complex hydrological systems such as the Alpine valleys.

II. Materials and Methods

Study area

The study area is a portion of the Aosta Plain, located in the Alpine region of Aosta Valley in northern Italy (Fig. 1). It stretches west-east for about 13.5 km, reaching a width of 2.5 km in the central part, near the town of Aosta, and its elevation ranges from 700 to 530 m above sea level (a.s.l). It lies in the mountain catchment area of the Dora Baltea River flowing from west to east (Fig. 1), with 16 tributary streams, the largest of which is the Buthier Creek. The study area is approximately 60 km², i.e. less than 2% of the whole Aosta Valley region, but includes 66,000 inhabitants (52% of the entire regional population) with a population density up to about 1,600 per km² in the town of Aosta. The water supply in the area is mostly from groundwater.

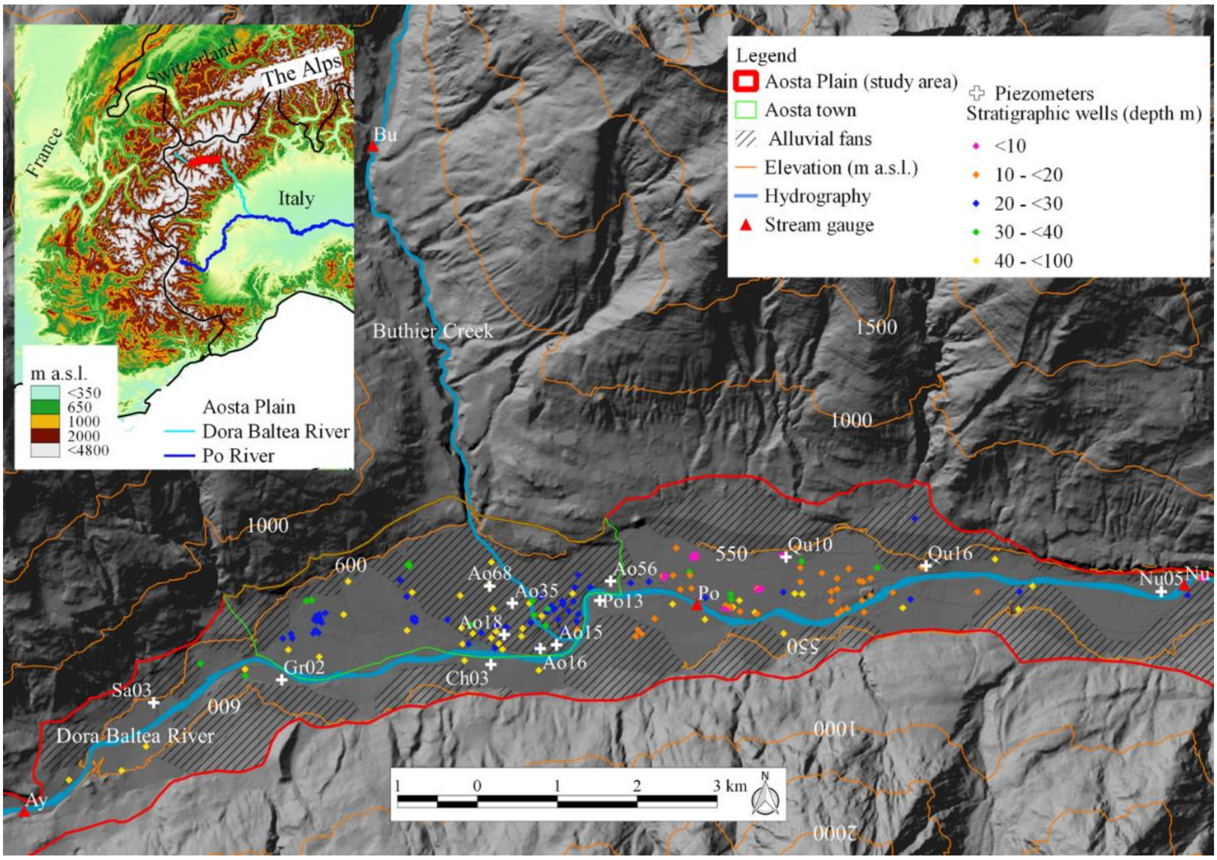

Fig. 1 - The surface water network of the Aosta Plain with locations of available hydrometric stations, piezometers for the monitoring of water-table elevation, and stratigraphic wells.

Temperature and precipitation, measured at various monitoring stations in the Aosta Valley, were analyzed to obtain the average monthly values related to different elevation zones of the region: north-west (2,336 m a.s.l.), north-east (1,979 m a.s.l.), South (1,951 m a.s.l.) and the Aosta Plain (581 m a.s.l.) (Fig. 2). Although the study area is limited to the Aosta Plain, the precipitation in the surrounding catchment areas is also of interest because it falls mostly on impermeable upland surface and then circulates to the plain as infiltration through alluvial debris and fans at the edge of the valley or as spring flow. The measurements reflect climatic conditions at different elevations; the maximum temperatures are measured in the Aosta Plain (annual average: 12.8°C), the minimum ones in the west area (annual average: 1.7°C). The minimum monthly temperature is in January or February, the maximum in August.

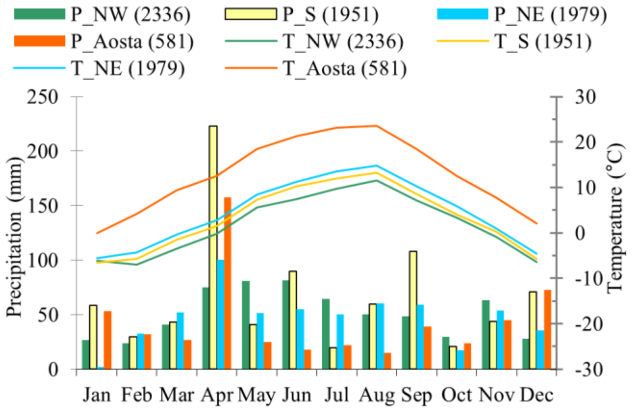

Fig. 2 - Average monthly temperature (C°) and precipitation in different sectors of the Aosta Valley Region. Number in parentheses is the topographic elevation (m a.s.l.) of the station

The maximum precipitation is generally recorded in April, although in the north-west watershed the wet period extends from April to June. The minimum precipitation is usually in October in the South watershed, in January in the north-east and north-west watersheds and in August in the Aosta Plain. Except for the plain area, the precipitation is in the form of snow from November until March, and the snow melt occurs from March until June.

Conceptual model

Hydrogeological system

The Aosta Plain is underlain by a series of fluvioglacial, lacustrine, alluvial and fan sediments, Quaternary in age, which in turn lay on a deep crystalline basement eroded by the Balteo Glacier. The aquifer is bounded to the north and south by the crystalline bedrock of the Alps (PIAHVA 1992). In this sedimentary basin, a silty-sandy deposit, never completely penetrated by wells, is located at the depth of about 50-90 m (decreasing from west to east) from the land surface and its thickness is estimated to be over 40 m (Pollicini 1994; Triganon et al. 2003; Bonomi et al. 2013, 2015; Rotiroti et al. 2015). This deposit of lacustrine origin is considered to act as a low-permeability basement boundary for the overlying aquifer used for water supply. Furthermore, two recent Electric Resistivity Tomography surveys (ERT) conducted in the towns of Aosta and Pollein during 2013 (unpublished data provided by the Regional Environmental Protection Agency of Aosta Valley (ARPA VdA)) revealed the presence of a deeper sandy-gravel aquifer (of likely glacial origin), not yet exploited, below the lacustrine aquitard. Moreover, the ERT showed that the lacustrine aquitard has some discontinuities (coarse deposits that act as higher permeability windows) that allow the deeper glacial aquifer and the overlaying exploited aquifer to be interconnected.

The exploited shallow aquifer, consisting mainly of heterogeneous alluvial deposits, ranges in thickness from 85 to 90 m in the western part to 50 m in the eastern part where the aquifer is divided into an unconfined (about 20 m thick) and a semi-confined portion (between 25 and 12 m) by a silty layer (Pollicini, 1994; Nicoud et al. 1999; Triganon et al. 2003).

Available hydrological and hydraulic head data

The available discharge data of the stream network between 2008-2014 were provided from the institutional monitoring network of ARPA VdA. The streamflow data were recorded by four hydrometric stations: Aymavilles (Ay - 618 m a.s.l.), Pollein (Po - 545 m a.s.l.), Nus (Nu - 534 m a.s.l.) and Roisan (Bu - 742 m a.s.l.). The first three are related to the Dora Baltea River whereas the Roisan station is related to the Buthier Creek (Fig. 1). Generally, the Dora Baltea River is characterized by two yearly streamflow peaks respectively in June and November (Fig. 3). The first one is greater than the second and represents the snowmelt and high precipitation period of the year, the second arises only from the autumnal rainfall peak. With regard to 2009, in January the average streamflow at Aymavilles (3.77 m^3/s) was higher than the one at Pollein (2.51 m^3/s) which was lower than at Nus (3.06 m^3/s). In June, the peak recorded at Pollein (129.73 m^3/s) hydrometric station was higher than both those at Aymavilles (109.15 m^3/s) and at Nus (100.80 m^3/s). As for the Butheir Creek, it had the same yearly streamflow features of the Dora Baltea, though its discharge has always been much lower than the previous one. For the surface water, the low flow period is usually in winter when the temperatures are low and the precipitation is in the form of snow.

The hydraulic-heads trend analysis was carried out in order to better understand the behavior of the aquifer. Hydraulic head data from the institutional monitoring network of ARPA VdA (Fig. 4) were available from 2000 to 2012. Special attention was given to heads data measured within the modelled area between 2009-2010 (selected period for the groundwater flow model). The hydraulic head (Fig. 4) decreases from about 582 m a.s.l. (Sa03 – upstream area) to 522 m a.s.l. (Nu05 – downstream area), suggesting a principal flow direction from west to east. Hydraulic head data show a seasonal oscillation between the yearly maximum value in summer and the minimum value in March-April. In particular, for the upstream area (Sa03) the oscillation is about 6-7 m and decreases by up to 1 m while moving to the downstream area (Qu16). This sharp reduction is related to a likely draining behavior of the Dora Baltea River on the groundwater which seems to decrease starting from Pollein hydrometric station toward the downstream area (Bonomi et al. 2015).

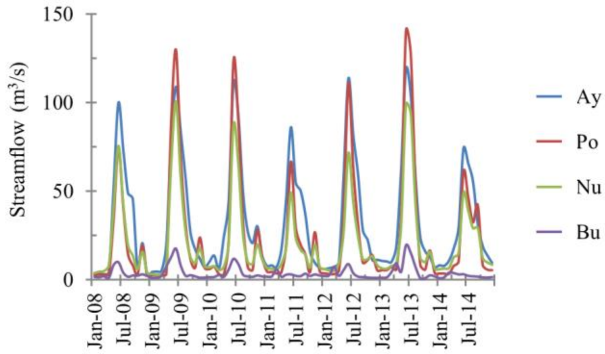

Fig. 3 - Average monthly streamflow (m3/s) of the Dora Baltea River (Ay, Po, Nu) and Buthier Creek (Bu)

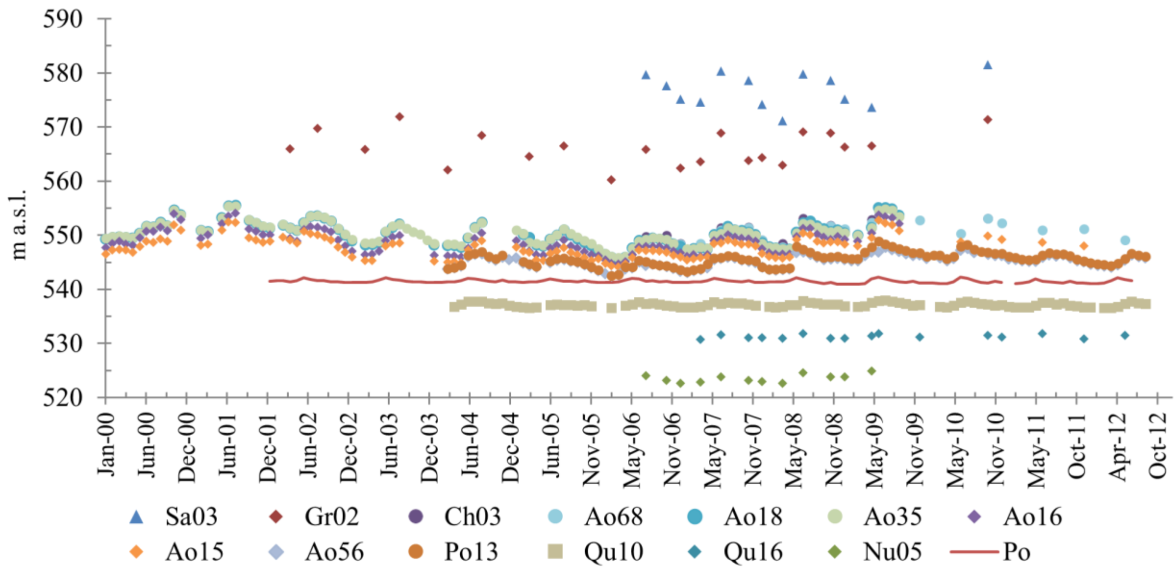

Fig. 4 - Water table elevation (m a.s.l.) measured in monitoring piezometers (see Fig. 1 for locations) and in the Dora Baltea River (Po station) between 2000 and 2012 in the Aosta Plain

Groundwater flow

The water table, built using Ordinary Kriging interpolation of monthly hydraulic heads from piezometers (monitored from ARPA VdA) and from the Po hydrometric station, is represented by the piezometric map in Fig. 5 (January 2009).

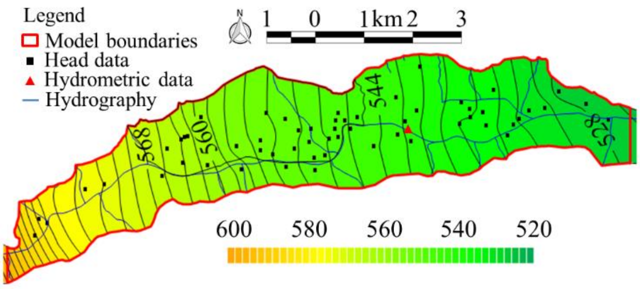

Fig. 5 - Groundwater head (January 2009) with a contour every 2 m, used as the initial condition for the steady-state model. (modified after Bonomi et al. 2013)

As a consequence of the valley shape, the aquifer structure, and the relationships with surface water, the piezometric heads vary from 600 to 526 m a.s.l. from west to east along the valley. The hydraulic gradient decreases downstream: it is 1% in the western, 0.5-0.6% in the middle and 0.3-0.4% in the eastern sector of the area.

As for the relationship between surface water and groundwater, the Dora Baltea River is losing upstream of the Po hydrometric station (PIAHVA 1996; Triganon et al. 2003), but downstream of the Po hydrometric station it becomes gaining with hydraulic connection (PIAHVA 1996; Triganon et al. 2003; Bonomi et al. 2013, 2015).

The water depth decreases longitudinally from west to east and transversely from the valley slopes to the Dora Baltea River, ranging from a maximum of around 20 m and 25 m respectively in the western sector and in the alluvial fan of the Buthier, to a minimum of 10 m and 4 m respectively in eastern sector, near the Dora Baltea River. This distribution restates the relationship between groundwater and the Dora Baltea River which is losing in the western sector while it is gaining in the eastern sector, in particular from the Po hydrometric station.

With respect to the temporal groundwater oscillations, the difference between the hydraulic head of July and January 2009 shows that in the western area the combined effect of the narrow valley, snowmelt and probable recharge from the Dora Baltea River causes water-level oscillations up to 6-8 meters, while towards the widening of the valley, lower oscillations occur. Finally, in the eastern part, the river drainage reduces groundwater head fluctuations to several meters.

Well pumping

The Aosta Plain aquifer is subjected to intense groundwater exploitation serving both drinking and industrial supplies. Local industries are served by 19 wells located in the central and in the eastern part of the Aosta Plain whereas the drinking water supply comprises 8 wells located in the western part of the plain (Fig. 6a). Therefore, the total number of operating wells in the area is 27. Other wells for domestic supply exist in the study area, however, their smaller discharges are negligible for the purposes of the present work.

Data on groundwater abstraction from these 27 wells were provided by ARPA VdA. These data concern the monthly average well discharge (m^3/hour) and the well working time (hours) for the period 2009-2010. The total volume of groundwater pumped was 19,656,447 m^3 in 2009 (82.87% for industrial and 17.13% for drinking uses) and 2,2024,240 m^3 in 2010 (81.35% for industrial and 18.65% for drinking uses). From January to August 2009 the total well discharge decreases from 63,000 to 44,000 m^3/d. Between September and December 2009 a peak was recorded in October (i.e. 69,000 m^3/d) due to industrial needs. Concerning the 2010, the well discharge gradually rose from January to July, then it fell in August representing the annual minimum (49,000 m^3/d). From September to December 2010, the discharge was quite stable around 60,000 m^3/d.

Numerical model

Previous models

Although the Aosta Plain aquifer was already modelled by three previous works (Triganon et al. 2003; Bonomi et al. 2013, 2015), some key aspects concerning groundwater/surface-water interactions remained unclear and required the development of a new improved model. A brief description of these earlier models (and their limitations) is given in the following.

The first model presented by Triganon et al. (2003) took into account the shallower part (up to 90 m) of the Quaternary sediments subdividing it into two layers. Only the Dora Baltea River was simulated using the RIV package, hence without considering its discharge. The hydraulic conductivity was discretized in four isotropic zones of piecewise constancy with the same distribution between layers. This steady state model provided a preliminary analysis on the effects of the surface water level on both the water table elevation and the water exchanged between the main river and groundwater. The coarse refinement of the grid and the hydraulic conductivity coupled to the use of the RIV package led to rough estimates for results, in particular, concerning the amount of exchanged water between the river and aquifer.

Bonomi et al. (2013) presented a steady state model, which considered the whole hydrographic network of the Aosta Plain simulated by the SFR2 Package and MODFLOW2000. That work focused on the definition of a preliminary conceptual model of the aquifer in order to improve the general knowledge of the system. However, the use of a steady state condition prevented the understanding of the temporal variations on groundwater/surface-water interactions.

Bonomi et al. 2015 improved their previous work implementing a transient model based on monthly recharge values with the aim of simulating the seasonal oscillation of the water table, however no evaluations of the water budget and exchanged fluxes were done.

In order to overcome the limitations of the above-mentioned previous models, the present work implements the following new aspects: (1) a new reconstruction of the system geometry that incorporates the deeper glacial aquifer which is likely interconnected with the shallower units as evidenced by new available data (i.e. ERT surveys and new well logs, see section 2.2.1); (2) an improved three-dimensional reconstruction of the hydraulic conductivity distribution (see the Electronic Supplementary Material - ESM for details) in order to include the new available well logs; (3) an automatic calibration, using PEST, for estimation of model parameters.
Nevertheless, the detailed calculation of monthly recharge inputs made by Bonomi et al. (2015) is retained in the present work. These recharge values were calculated as the water average surplus obtained by the Thornthwaite-Mather's hydrological balance model starting from the average monthly precipitation and temperature data (available only for 2009 and 2010 and calculated for the different regional watersheds; Fig. 2).

Hydraulic conductivity reconstruction

In order to reconstruct the spatial distribution of hydraulic conductivity, the TANGRAM© database was used (Tangram, 2016; Bonomi et al. 2014). This database is meant to manage administrative, borehole construction, stratigraphic and piezometric information. TANGRAM© has an internal coding system that allows the standardization of stratigraphic information and the extraction of stratigraphic data in terms of hydraulic conductivity (k), according to depth, measured at the meter scale in the present work. The hydraulic conductivity values of 176 stratigraphic logs were extracted from TANGRAM© in order to obtain a XYZk point dataset, where X and Y are coordinates in the UTM system, Z is the elevation (m a.s.l.) and kis the hydraulic conductivity value (in terms of ln(k)). The values of hydraulic parameters are defined in relation to textural percentages (Bonomi et al. 2002; Bonomi et al. 2009), by means of a conductivity data conversion table integrated into the TANGRAM© database. The distribution of hydraulic conductivity was assumed to be lognormal (Martin and Frind 1998) and a well-known method (Dagan and Lessoff 2007; Dagan 2012) for calculating the weighted standard mean (Sanchez-Vila et al. 1995) of hydraulic conductivity values attributed to the individual lithologies was followed (ranging from 436 m/d for gravel to 0.864 m/d for silty-clay; for more details on the interpolation see the ESM).

For this study, the hydraulic conductivity values assigned to the conversion table in TANGRAM© were previously calibrated by trial and error on the basis of nine pumping tests reported in literature (Pollicini 1994; De Luca et. al 2004). The calibration was focused on the minimization of the difference between the ln(k) value calculated by TANGRAM© and the ln(k) value from the literature. The coded lithologs were imported into a 3D grid and interpolated by geostatistical approach in GOCAD®. The GOCAD® code (Geological Object Computer Aided Design, Paradigm 2008) was used to build the computational grid, then apply the geostatistic technique of Ordinary Kriging, based on the assumption of stationary spatial conditions with respect to the statistical distribution of the subsurface stratigraphic data. For more details on the interpolation see the Interpolation Grid section of the ESM.

Model design

This work is the evolution of specific existing models (Bonomi et al. 2013, 2015). Indeed, data about hydrogeological balance (e.g. recharge, pumping rate, river parameters) derive from these previous works. They have been integrated with new information allowing researchers to improve the knowledge of the investigated aquifer.

The model grid has 3,183,300 cells divided in 243 rows and 655 columns with a uniform cell spacing of 20x20 m, covering an area of ~60 km^2 (active cell ~25 km^2). The vertical discretization of the grid reflects the stratigraphic grid used for the interpolation of the hydrogeological parameters. It consists in twenty layers: eighteen of them have a constant thickness, whereas two (second and third layers) are variable (Min 0.8 m; 25th percentile 5.6 m; median 10.4 m; 75th percentile 20.2 m; Max 72.8 m). The first sixteen layers were used to model the exploited aquifer, whereas the last four layers (90 m thick) were used to consider the silty layer (lacustrine aquitard of the main shallow aquifer; see section 2.2.1) and the underlying coarse (gravelly-sand) deposits recorded by ERT. The refinement of the vertical spacing helps to capture hydrogeologic trends and allows the model to closely match the intervals over which pumping wells are screened, thereby increasing the accuracy of the model in simulating withdrawals. Furthermore, the low thickness of the upper layers has allowed an accurate positioning of the riverbed, improving the simulation of the rivers and groundwater interaction.

The complex three-dimensional reconstruction of hydraulic conductivity (Fig. S1 of the ESM) was subsequently discretized in ten zones of piecewise constancy by means of the analysis of the frequency distribution of the obtained hydraulic conductivity. As for the last four layers, two additional zones were defined: in the central part was assigned a low value (0.0864 m/d) in order to reproduce the silty-clay lacustrine layer, whereas at the edge a high value (69.12 m/d), typical of the sandy deposit, was assigned. The groundwater flow equation of a transient model is complicated by another term representing the aquifer storage capability (i.e. specific storage (Ss) and a specific yield (Sy)). As for the storage, the discretization in zones was obtained from the hydraulic conductivity distribution, whereas the values were selected from literature. In particular, the assigned values on each zone varied between 0.05 and 0.28 for Sy, and between $5x10^{-6}$ and $1.5x10^{-4}$ for Ss (Domenico and Mifflin 1965). The obtained conductivity/porosity zones and their values became the basis for the flow model.

The used code was MODFLOW 2005 (Harbaugh 2005), visualized through the GroundwaterVistas6 interface (Rumbaugh and Rumbaugh 2004).
The model was solved both in steady-state and transient condition with GMG package and considering the rewetting capability. The steady-state configuration was referred to January 2009 in order to reproduce an average condition of the aquifer between 2000 and 2012 (Fig. 4). The transient analysis was limited to a two-year period (2009-2010) using 24 stress periods (one per month). This approach allowed both evaluation of the non-steady-state model response to variable stresses (Taviani and Henriksen 2015) and evaluation of how the change of the water balance during seasons takes into account the storage component. The choice of the selected simulated period was mainly related to the availability of measured data on well abstractions (see section 2.24.). This is a key aspect since the main goal of this work is to understand the effects of well pumping on the relationship between groundwater and surface water. The use of measured discharges rather than a speculative estimation of their values is preferred since it decreases the uncertainty and increases the accuracy of model results.
The streamflow data of the Dora Baltea River and Buthier Creek in addition to the piezometric and precipitation data referred to 2009-2010 were used both in the steady state model (January 2009) and in the transient one (2009-2010).
In order to evaluate the impact of wells on both rivers and groundwater, simulations with different configurations of the pumping were conducted (Feinstein et al. 2010; Barlow and Leake 2012). The transient solution with 27 active wells (baseline scenario) was compared with two new scenarios. Each new scenario differs from the baseline scenario in the discharge value of only one well: scenario A, which aims to evaluate the effects of well pumping in the upstream area where the Dora Baltea River is losing, considers an increase of 1,000 m^3/d for the discharge of the well W_US (see location in Fig. 9); scenario B, concerning the effects of pumping in the downstream area where the Dora Baltea River is draining, considers an increase of 1,000 m^3/d for the discharge of the well W_DS (see location in Fig. 9). Results of the different scenarios where compared through the analysis of the MODFLOW mass balance output file (i.e. *.lst file).

Boundary hydraulic conditions

The boundary conditions were defined on the basis of the hydrogeological configuration of the Aosta Plain and the piezometric trend of the period 2009-2010. The conditions imposed are: 1) No Flow, Neumann-type boundary conditions, at the northern and southern edges of the plain, at the boundary between fan deposits and the slope. In depth, the limit to no-flow defines the geological shape of the valley, cut in the western part and progressively widening towards the east (Bonomi et al. 2014). 2) General Head Boundary (Cauchy-type boundary conditions), at the western and eastern edges of the model, with the aim to simulate groundwater flow into and out of the valley. GHBs have been reconstructed, one for each time step. Their position derived from piezometric maps related to January and July 2009.The assigned head values to each time step were taken from well piezometric data measured from 2009 to 2010. 3) Stream (Cauchy-type boundary conditions), to match the hydrographic network and to simulate the interactions between the surface and groundwater systems. Considering the importance of groundwater/surface-water exchange to the study overall, more details about this boundary condition are discussed in the next paragraph.

Hydrographic system modeling

The hydrographic network was simulated using SFR2. This package routes stream flow along the hydrographic network and calculates the exchange between the surface and groundwater systems. Moreover, it allows researchers to simulate the induced water flow from the river to the aquifer by means of the wells pumping up to the maximum discharge available into river, after which the cells become dry. The SFR2 selected option allows stream stage to be calculated based on specified overland flow rates at upstream locations, the calculated groundwater exchange for each model cell occupied by a stream, Manning's equation relating channel roughness to streamflow, and a channel geometry assumed to be rectangular.

An outline of the hydrographic network in a series of reaches and segments, ranked in a strict sequence according to tributary order, allows the modelling of complex hydrographic networks. In particular, a reach corresponds to a single cell of the model grid, while a segment is made of one or more reaches with characteristics similar to one another (Prudic 2004). A sequence of 32 segments (1,908 reaches) represents the hydrographic network of the study area, each segment corresponding to a tributary of the Dora Baltea or to a section of the Dora Baltea between two confluence points (Fig. 6).

For each reach the following information was specified: stage of stream, streambed elevation, width of stream, length of stream, thickness of streambed, streambed hydraulic conductivity, streambed slope, streambed roughness, flow entering segment (only for the boundary segments).

Streambed roughness was imposed at 0.05 (-), intended to represent river beds with pebbles and some rocks (Barnes 1967). Streambed slope was calculated between adjacent cells, as a function of the inclination of the streambed. The values obtained for the Dora Baltea River are between 0.1% and 1.5%, but for the tributaries the slope can be as high as 40%.

An inflow (Q) to the segments at the model upstream boundaries was applied to the first cell of each segment and for each stress period, to allow the simulation of flow rate propagation in the river (Prudic 2004). The estimated average monthly flow values referred to 2009 and 2010 were assigned to the first reach of SFR2 related to the Dora Baltea River (Aymavilles hydrometric station, estimated net of diversion) and the Buthier Creek, whereas for the remaining streams it was estimated on the basis of information gathered and occasional ARPA VdA measurements.

Model recharge and discharge

As remarked by Bonomi et al. (2015), the recharge of the studied aquifer is closely related to the snowmelt (occurring from April to July) which, in turn, is related to both the quantity of snow occurring in winter and the increase of the temperature during following seasons. The recharge was imposed through 4 zones and using monthly time steps (Bonomi et al 2015). The minimum imposed value was 0.099 mm per month in the central part of the plain in January 2010, whereas the maximum value was 2292.14 mm per month per day in the southern-west of the plain in May 2009. Another important stress and element of the hydrologic budget is well withdrawal. Measured monthly well withdrawals were assigned to the 27 operating wells (see section 2.2.4) depending on their own flow rate, ranging between 0.26 and 18,000 m^3/d. The screen lengths and depths were inserted for each well, and they are distributed between 20 m and 80 m in depth.

Calibration and Target

Both hydraulic head target and flux target were used to calibrate the model. The head targets were compiled from the piezometric monitoring network of ARPA VdA (Fig. 1) on a monthly basis or quarterly data. It was considered inappropriate to define an allowable error in the head target comparison values (Sonnenborg et al. 2003) both because the data are the actual monthly measurements (not derived from the mean of data referred to longer periods) and because it is considered reliable (ARPA VdA monitoring). Local errors might still be related to piezometric measurements influenced by the pumping of the surrounding wells. The number of hydraulic head observations was 25 for the steady-state condition and 348 for transient simulation heterogeneously distributed among 37 head target.

The flux target (ARPA VdA monitoring) is located in the central area of the model (Po hydrometric station - Fig. 1). The flux target reported 24 values defined as the monthly average of the daily streamflow recorded by Po hydrometric station between 2009 and 2010. All targets are shown in Fig. S3 of the ESM.

The model calibration was done on the steady state model using PEST (Doherty 2008, Doherty and Hunt 2010). A preliminary sensitivity analysis on hydraulic parameters (kx=kv, kz=kx/10) and SFR2 conductance was performed on the steady-state model. All of those most sensitive parameters (>1%) were selected for the calibration process (Hill 1998). A reasonable upper and lower bound was applied to the initial value of each selected parameter (±50% of the starting value for k and 0.0001 to 5 (m/d) for the stream bed conductivity). The obtained calibrated model was employed as a starting condition for the transient model. To improve the performance of the transient model and to better reproduces the strong oscillation of the water table, a second calibration was carried out by PEST. A new sensitivity analysis on storage values (Ss and Sy) and hydraulic conductivity (kx=ky) was done (Fig. S4 of the ESM). Parameters with sensitivity more than 1% of the greatest value of the composite sensitivity were calibrated applying reasonable upper and lower bounds (Table 1).

Table 1 – Applied bounds and final values of the selected parameters (k - m/d, ss - 1/m) by sensitivity analysis

		initial	lower	upper	final
kx_2	gravel	571	143	1000	517.943
kx_3	sandy gravel	127	32	222	197.34
kx_4	sand (semi_conf Po)	100	25	175	162.65
kx_7	sandy gravel (fan)	164	41	289	253.25
kx_11	sand (unexp_acq)	69	17	121	101.11
kx_12	silty clay (deep aquitard)	42	11	74	37.04
Ss_1	silty clay (deep aquitard)	$5x10^{-4}$	$2.5x10^{-4}$	$7.5x10^{-4}$	$6.03x10^{-4}$
Sy_3	sandy gravel	0.2	0.01	0.28	0.17

III. Results and Discussion

Steady state simulation (January 2009)

The choice of January is connected to the flow rate of the surface system, which is representative of the low-flow period (Feinstein et al. 2010); in fact as shown before, this is the month when the water table is lowest and the runoff from stormflow is largely absent. Furthermore, January 2009 represents an average condition of the aquifer during the last decade.

Fig. S5 of the ESM shows the distribution of the calibrated value of the hydraulic conductivity within layer 4. The values of this parameter are in agreement with previous studies on the Aosta Plain (Triganon et al. 2003; Bonomi et al. 2013, 2015; Stefania et al. 2015) ranging between 0.0864 m/d to 572 m/d.

The Dora Baltea River conductance was calibrated starting from a hydraulic conductivity of 1 m/d. As a result of the calibration, it changes among 0.15 m/d in the western part to 0.01 m/d in the central part and it increases to 4 m/d in the eastern part (Hatch et al. 2010) (Fig. 6 a).

The simulated head, which takes into account the wells pumping and the exchange between rivers and groundwater, produced the piezometric configuration shown in Fig. S3 of the ESM. It represents, with spacing of 1 m, a variation of head from 580 m a.s.l. in the west to 526 m a.s.l. in the east, and a flow direction west-east. It closely reproduces the variations of the gradient, which increases from the west towards the Aosta Plain, decreases near the areas with high hydraulic conductivity around the fan of the Buthier and increases again towards the downstream sector.

The solution has the following statistics: the residuals ranged from -0.96 m to +0.94 m, with a Residual Mean of -0.02 m, Absolut Residual Mean of 0.40 m, and a Scaled Root Mean Square value of 1%, and the sum of square residuals (the square root of the average of the squared error, Anderson and Woessner 1992) was 5.63.

The simulated flux at the Po hydrometric station (2.76 m^3/s) appears in good agreement with the observed one (2.55 m^3/s), considering the observed Dora Baltea River discharge and all of the factors that cause it, among which: 1) the diversion near Aymavilles hydrometric station, 2) tributaries discharge contribution, 3) exchange between surface water and groundwater.

With regard to the mass balance (which has an error less than 0.001%), approximately 21,521 m^3/d are conveyed into the model due to the recharge contribution, and about 62,849 m^3/d exit due to 27 wells. In the present configuration, the surface water system recharges the aquifer at a rate of 132,534 m^3/d (IN from stream to aquifer), and drains the aquifer at a rate of about 90,130 m^3/d after the Po hydrometric station (OUT to the stream).

In the central area of the Aosta Plain, around the fan of the Buthier, the simulated head shows values higher and lower than the observations (Fig. S3 of the ESM). These discrepancies may be associated to different aspects: a) an in-depth analysis is necessary for a better description of heterogeneities distribution which

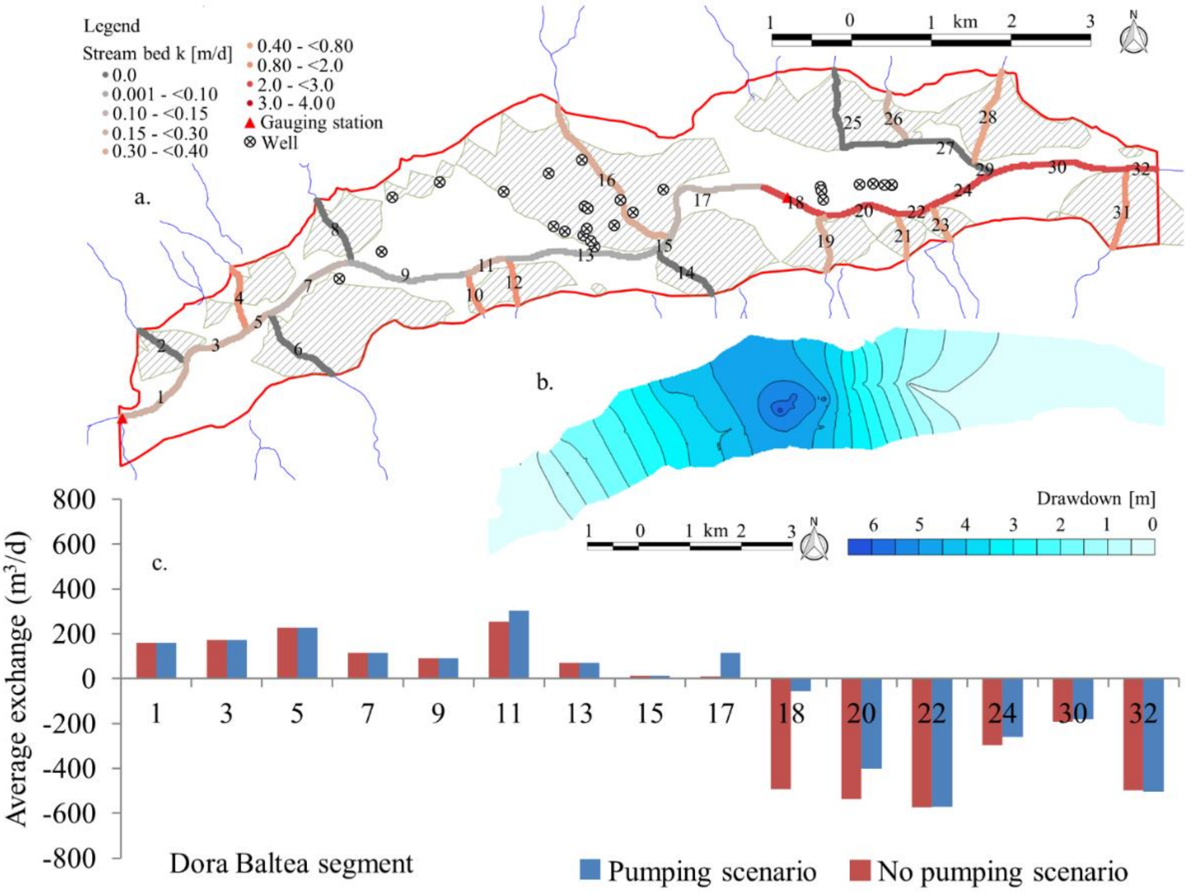

Fig. 6 – (a) Segment numbers and streambed hydraulic conductivity values (m/d) of the Dora Baltea River and its tributaries, and locations of pumping wells. (b) The difference in drawdown between pumping and no pumping scenarios (m). (c) Average monthly exchange between the Dora Baltea River and the surrounding aquifer for each segment (m³/d); blue bars represent the pumping scenario and red bars represent the no-pumping scenario.

regulate groundwater flow on a local scale, b) the attribution of monthly average pumping rate values in the model, whereas the real hourly flow rate might have influenced the measured water levels, generating noise in the targets which is not reproducible by the simulation, c) the real head target values represent monthly average levels and they may not be perfectly correlated with monthly pumping. In the eastern part, the simulated head suffers from an overestimation. This result suggests that as to the downstream area, probably, further geological investigations should be considered, to correctly understand how the water leaves the modelled area through the narrowing of the valley edges. In order to evaluate the impact of well pumping on the water table and stream depletion, a simulation without pumping was done, then it was compared with the calibrated solution. The simulation without pumping shows a considerable rise of the water table especially in the central part of the area where the wells' withdrawal is bigger. In this area, beneath of the Aosta town, the water table was pushed down more than 5 m due to well pumping (Fig. 6b). Table 2 shows the changes induced by pumping on water balance. Overall, the pumping limits the amount of the water gained by the Dora Baltea River (~34,400 m^3/d) and increases its leakage (~16,300 m^3/d). This result highlights that surface water is an important part of the hydraulic budget of the Aosta Plain. The groundwater/surface-water exchanges (average flux m^3/d) along the Dora Baltea River are shown graphically to emphasize their spatial variability for both pumping and no pumping scenarios (Fig. 6). The drawdown induced by the wells' withdrawal not only affects the shape of the water table, in fact, it also induces changes on the surface/groundwater exchange flux with a slight increase of the stream leakage by segment 11 and about one order of magnitude from the segment 17. Segment 18 shows the greatest variation with a sharp decrease of the water drainage (e.g. from 490 to 21 m^3/d) as a result of the groundwater depletion. Also segments 20, 22 and 24 decrease their drainage flux, however, less than the previous one. The largest difference of water exchange recorded in segment 18 is related to the downstream moving of the transition point from losing to gaining behaviour of Dora Baltea River. This transition point is located within segment 18 in both scenarios, however, its movement downstream in the pumping scenario, due to water-table lowering, leads to a decrease of the water drained by the river. In the central area (close to segment 13 and 15), the water-table elevation never exceeds the riverbed elevation thus preventing any variation of water exchange between the river and aquifer.

Table 2 – Water balance (m^3/d) for the pumping and no-pumping scenarios.

	Pumping (P)		No Pumping (NP)		Pumping vs No Pamping	
Terms of the water balance	IN	OUT	IN	OUT	IN_P-IN_NP	OUT_NP-OUT_P
General Head Boundary	30282	31356	19579	32759	10703	1403
Recharge	21521		21524			
Well withdrawal		62849				
Dora Baltea River	82231	90130	66017	124544	16213	34414
Tributaries	50304		50185		119	
Total	184337	184335	157305	157303	27035	35817

The well pumping has no influence on the tributary streams (Table 2) because a) the great unsaturated thickness (around 30 m on average and up to 96 m) beneath tributary streams prevents any direct interaction between the tributary water and groundwater; b) the greater slope of the riverbed up to 0.45% (Bonomi et al. 2013) increases the water flowing velocity while, on the other hand, decreasing the possibility of its infiltration toward groundwater; c) the available discharges of the tributary streams are about two orders of magnitude lower than the main river. Furthermore, some of the tributary streams (i.e. segments 2-6-8-14-25-27-29) have an impermeable riverbed that prevents any water exchanges.

Transient simulation (January 2009 - December 2010)

Models with two different sets of hydraulic parameters were compared (Fig. 7). The new set of parameters obtained by the second analysis of sensitivity (Fig. S4 of the ESM) and subsequent recalibration (Table 1), as defined in Section '*Calibration and target*', better reproduces the hydraulic head trend both upstream and downstream of Aosta town (Fig. 7). The spatial and temporal behavior of residuals between observed and simulated values highlights that the first solution with respect to the recalibrated solution, overestimates the hydraulic head, especially during the low flow periods, inducing a water accumulation in the downstream area.

The analysis of sensitivity has shown that the water accumulation was dependent on both storage and conductivity parameters. Another important aspect was that the newest calibrated values remained consistent with those that were initially derived from the TANGRAM database (see section 2.3.2), however a slight increase of the values (except to sy_3) was observed. With regard to the reconstruction of the streamflow of the Dora Baltea River, the modelled discharge (Fig. 7) compared with the measured data was in good agreement, even if it has not correctly reproduced the fall in discharge peaks. However, the modelled streamflow seems to be acceptable taking into account that the discharge of tributaries has been estimated and the hydraulic conductivity is a challenging parameter to be estimated (Hatch et al. 2010).

Comparing the simulated water table with the bottom elevation of the Dora Baltea River, it becomes clear how the piezometric oscillation affects the Aosta Plain aquifer during the seasons and how it changes their relationship along the investigated area (Fig. S6 of the ESM). Upstream of Aosta town, the distance between the water table beneath the streambed and the stream bottom decreases steeply, with occasionally sharp reduction dependent on streambed jumps.

Close to Aosta town, the water table falls, probably due to the wells' withdrawal with a variable magnitude which changes seasonally. Another important outcome is that some of the Dora Baltea reaches located upstream of Aosta town change from losing to gaining and vice-versa. In fact, upstream of Aosta (between 5.5 and 7.2 km) during the summer of 2009, when the water table was the highest, it was above the streambed, whereas close to Aosta, this relation was reversed by pumping, making the Dora Baltea River losing.

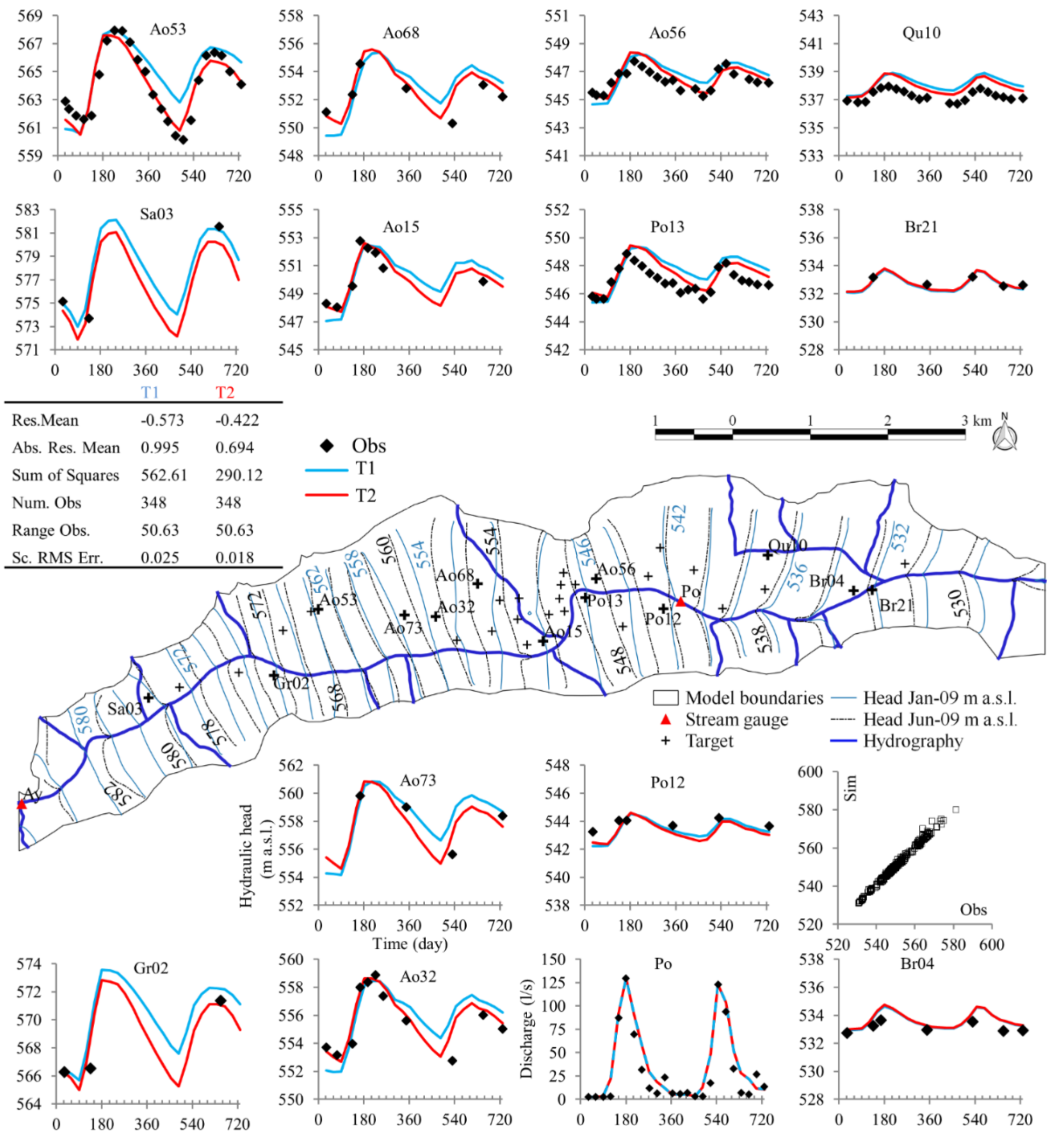

Fig. 7 - Simulated head (m a.s.l.) and flux (m3/s) referred to two transient solutions. Blue line (T1): solution with the model parameters from the steady state model; Red line (T2): solution with the second set of parameters from the calibrated transient model.

This behavior is reasonable because during June 2009 the well pumping was lower and the recharge was higher inducing a great rise of the water table. Downstream of Aosta town, the Dora Baltea River becomes draining; moreover the reach where the river changes its behavior is moved upstream by about 1 km, compared to June 2010. The water budget of the Aosta Plain aquifer was obtained from the transient simulation (Fig. 8): it is characterized by two peaks of inflow due to recharge during the spring 2009-2010.

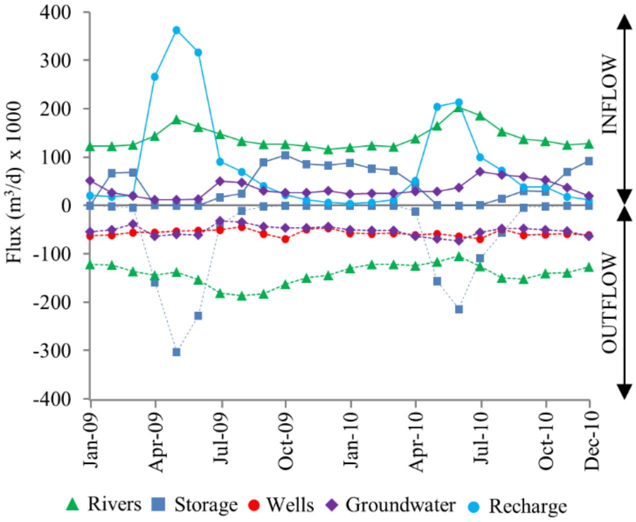

Fig. 8 - Water budget of the transient solution. Negative values (dashed line) represent water leaving the aquifer, whereas positive values (continous line) represent water entering the aquifer.

The hydrography network is both an inflow and an outflow: the latter increases when the water table is higher (summer), confirming that the water table oscillation is reduced by the river drainage especially in the downstream area. The greater river inflow occurs during the periods of most infiltration, confirming that snowmelt plays a key role in the recharge of the groundwater system. As for the storage, it appears an important element of the groundwater budget because it acts as a tank. In fact, the aquifer is recharged during the water-available periods (SINK element) and becomes a source of water during the low flow period, typically in winter. In October 2009 there is the highest well withdrawal (about 69,000 m3/d) which induced the most important outlet from the storage. These results have highlighted that the Aosta Plain aquifer storage capability is a key aspect of the groundwater system which together with recharge and surface water seepage/drainage, contributes to the complex dynamics that occur on the studied aquifer, allowing fluctuations of the water table more than 5 m in amplitude.

Impact of wells on the groundwater and river budget

The first important feature which emerges and confirms the goodness of the obtained groundwater model is that it is able to give back the imposed increase on the well discharge without producing mass balance errors. The obtained results highlight two different behaviors of the aquifer: in downstream area (i.e. Scenario B) the

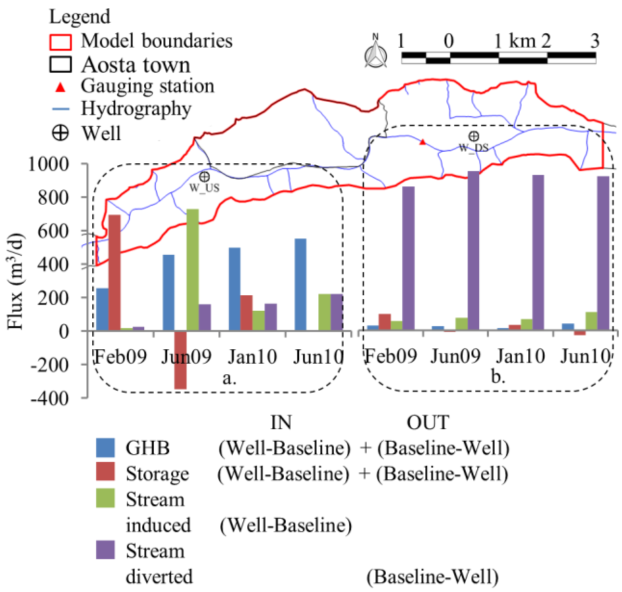

Fig. 9 - Well-pumping impact on the groundwater and surface water balance. W_US: well located in the upstream area; W_DS: well located in the downstream area. The legend shows the formulas used for the calculation of the flux variations induced by well pumping (i.e. W_US and W_DS), between the reference solution (baseline scenario) and (a) scenario A and (b) scenario B.

water to the well comes mainly from the river, whereas for the upstream area (i.e. Scenario A) different elements of the water budget actively contribute to the well discharge. In particular, as for the well in the downstream area (W_DS in Fig. 9b), about 80% of the extracted water, for each considered period, would have reached the river (stream diverted) adding itself to the baseflow component of the river flow, but it is instead pumped out by the well. The fact that the impact of W_DS well on the budget is constant over time strengthens the hypothesis that, in the downstream area, the river is hydraulically connected with the aquifer and it acts on the water table, regulating its seasonal oscillations and the exchanged fluxes. As for the well in the upstream area (W_US in well (Fig. 9a), the pumped water comes from different budget items (i.e. aquifer storage, river, upstream groundwater inflow simulated by the GHB). In particular, the contributions of the storage and the river (e.g. stream induced = water induced through the riverbed) change over time as a function of the hydraulic condition of the aquifer and river. In fact, when the water table is the lowest (e.g. February 2009) then the well pumping is not able to abstract water from the river because the flow through the unsaturated zone is likely low, consequently the water is mainly produced from the storage (Sanz et al. 2011). Instead, when the water table is higher (e.g. June 2009), then the well water is mainly from the river (stream induced). For the two other periods referred to W_US, the well impact on the water balance is similar between the lower and higher period because the water table elevation changes less than the previous periods (Fig. S6 of the ESM). Nevertheless, for the higher period (i.e. June 2010), the amount of induced water from the river is more than the amount induced during the lower period (i.e. January 2010), confirming that the water table oscillation plays a key role in the water exchanges between the groundwater and surface water.

IV. Conclusion

This work dealt with the modelling of an Alpine valley aquifer in the Aosta Valley Region, assessing the water exchanges occurring between the main regional river (i.e. Dora Baltea River) and the underlying shallow aquifer. After having defined the conceptual model of the system and reconstructed the distribution of the hydraulic parameters, a steady state model was calibrated on the low flow period and an evaluation of the pumping from the whole well system was performed. The steady state model was used to initialize a two-year transient model by which both the water table oscillation during the seasons and the impact of the pumping on the groundwater/surface water budget were evaluated. This work has improved the understanding of the Aosta Plain aquifer, in particular:

I. the reconstruction of the hydraulic parameters shows an aquifer mainly characterized by a gravelly and sandy deposit with a local silty-clay layer especially in the downstream area;

II. the main recharge of the aquifer derives from the slope region, and only secondarily from infiltration on the plain. The obtained recharge rate is typically highest during the summer as a result of high precipitation and snow melt. This explains the wide range of water table oscillation which affects the studied aquifer;

III. the calibration phase, using head and flux targets, has demonstrated the importance of the three-dimensional reconstruction of the system heterogeneity for the model response; moreover the calibration analysis suggested that the modification of the streambed conductivity and also a few other hydraulic parameters, especially Sy and Ss, have turned out to be influential parameters to achieving a good fit on targets;

IV. the model highlighted that from west to east of the valley, the Dora Baltea River changes its relation with the aquifer, acting as a source of water in the upstream area and as a sink in the downstream area. The analysis on the whole well pumping system determined that it limits the amount of the water-gaining by the main river (~34,400 m^3/d) and increases its leakage (~16,300 m^3/d). The seasonal changes in the water table elevation play a key role in the relationship between the river and the underlying aquifer. Furthermore, it is evident that the rising of the water table, typically in summer, is a consequence of the recharge (in the form of infiltration) which during its higher discharge months is linked to snowmelt. Another key aspect is related to the storage parameters, that allow either to retain or to release the water as a function of the stress (natural and anthropogenic) to which the aquifer is subject;

V. in the downstream area, the water table is always above the riverbed surface, meaning that the river is a sink for the aquifer. In this area, about 80% of the water pumped by the selected well comes from the base flow component of the river discharge, during the whole simulated period. In the upstream area, the water table is always beneath the riverbed; however, during only one of the two simulated high flow periods, along a river segment (1.5 km length), the water table overcomes the riverbed by 0.5 m. In this area the contribution of the well pumping components of the water budget changes as a function of the hydraulic conditions of the aquifer, however the stream depletion is always less than the depletion with respect the downstream area.

In conclusion, the upstream area is a better location for a new well to be drilled, because pumping will affect the river discharge less than in the downstream area.

The present work showed that the use of SFR2 Package may be extended to a particular hydrogeological context (i.e. Alpine valley aquifers) where complex relationships between the river and groundwater could change over space and time due to natural factors (e.g. recharge) and/or human activities (e.g. well pumping). The methodology presented here allows researchers to evaluate the impact of the well pumping on the whole system in terms of both the water table lowering and depletion of exchanged water between the river and aquifer. Furthermore, it is able to assess the origin of the water pumped by wells.

This work can provide to decision-makers and stakeholders a useful tool to understand, manage and quantify the aquifer and the streamflow depletion, not as separate entities, but by considering them as an integrated system. Furthermore, it could be used to simulate the transport of dissolved pollutions, evaluating their impact both on groundwater and surface water (Bonomi et al. 2015; Stefania et al. 2015; Rotiroti et al. 2015).

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Electronic supplementary material: Modeling groundwater/surface-water interactions in an Alpine valley (the Aosta Plain, NW Italy): the effect of groundwater abstraction on surface-water resources

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Interpolation grid

The geometry of the subsurface bodies was reconstructed as a basis for the model grid that reflects the depositional processes responsible for the observed geologic facies. The grid covers an area of ~60 km^2 and it is delimited by two boundary surfaces, the DTM (Digital Terrain Model) and a planar surface, properly constructed.

In particular, the DTM, sized 5x5 m, is derived from Laser Scanner measurements (Aosta Valley Region), whereas the bottom surface was defined in order to have an elevation lower than the minimum elevation reached by available stratigraphy data (440 m a.s.l) and able to contain the silty-clay deeper lacustrine layer plus the shallow part of the unexploited aquifer that emerged from ETR surveys. The deeper surface of the grid has a sub-horizontal trend with elevations ranging between 354 m a.s.l. in the eastern part and 422 m a.s.l. in the western part.

The grid derived from the union of four different sub-grids, each of which follows the logic to contain the different depositional events. At the same it was attempted to have a grid as regular as possible in the saturated zone of the aquifer, in order to more easily solve the flow model.

The first grid contained the river network and it consisted of only one layer, with top parallel to the DTM and with a thickness of 5 m. The second grid, divided into two layers, contained the unsaturated zone and it has allowed researchers to linearize the large changes in elevation related to alluvial fans at the edges of the valley. The layers of this sub-grid have a variable thickness: smaller on the central part of the valley and greater at its edges. The top of this sub-grid corresponds to the bottom of the first sub-grid, whereas its bottom was derived from a polynomial surface obtained by interpolating

heads data relative to January 2009 (average condition of aquifer). The third sub-grid consists of thirteen layers, each with a constant thickness of 5 m. This sub-grid represents the saturated zone and it allowed researchers to correctly highlight both heterogeneity and the two main depositional events which characterize the aquifer of the Aosta Plain. As defined, the bottom of this grid allows researchers to contain the upper part of the deep lacustrine silts, which is considered as the bottom of the exploited aquifer, but never completely drilled (Pollicini 1994; PIAHVA 1992; Novel 1995, Bonomi et al. 2013). The fourth sub-grid (90-m thick) was discretized into four layers and represents the deeper silty-clay lacustrine layer plus the upper part of the unexploited aquifer, in agreement with ERT surveys. The last sub-grid was not used by hydraulic conductivity interpolation.
The subsequent geostatistical interpolation with Ordinary Kriging and the interpolation with GOCAD©, assigned calculated values to individual cells of the model, reproducing both the lateral and vertical heterogeneity. The variogram was reconstructed for hydraulic conductivity in all directions using the exponential model, which best interpolates data without trends (Armstrong 1998). The calculated hydraulic conductivity values (Fig. S1) were between 0.864 and 436 m/d. The distribution of the hydraulic parameters appears consistent with the structure of the studied aquifer, displaying its heterogeneity. A high conductivity value was observed, which predominates in particular in correspondence with the fans in the middle part of the study area. Toward the east there is a decrease of hydraulic conductivity, which marks the separation, by means of a silty-sandy aquitard, of the gravelly-sandy unconfined surface aquifer from a deeper and sandy-gravelly semiconfined one, especially in the north-east edge of the plain. The thickness of the studied aquifer (shallow aquifer), decreases from west to east from 90 m to about 50 m. The relative absence of deeper stratigraphic logs (Fig. 1), especially in the western part of the plain, has prevented the ability to reproduce the silty-clay lacustrine aquitard even if literature and ERT surveys are in agreement on the assumption of its presence. In the eastern part, the few available deep logs have been interpolated, displaying the top of the silty-clay aquitard, which is characterized by a discontinuous pattern. Except for the lowest value, the aquifer values appear consistent with those used in a previous flow model (Triganon et al. 2003), which are based on a few .
direct measurements available in the area and range from 8.64 to 436 m/d (being the highest values for the alluvial fan and the neighboring downstream zone). The range results are larger than previous investigators because all subsurface systems were considered, where high- and low-permeability parts exist. The approach followed in the present work did not allow researchers to directly assess values of hydraulic conductivity for remote areas lacking stratigraphic data, including so-called side fans, shallow zones at the top of the major fans or the deeper unexploited aquifer. Values for these areas have been estimated as part of the model calibration process.

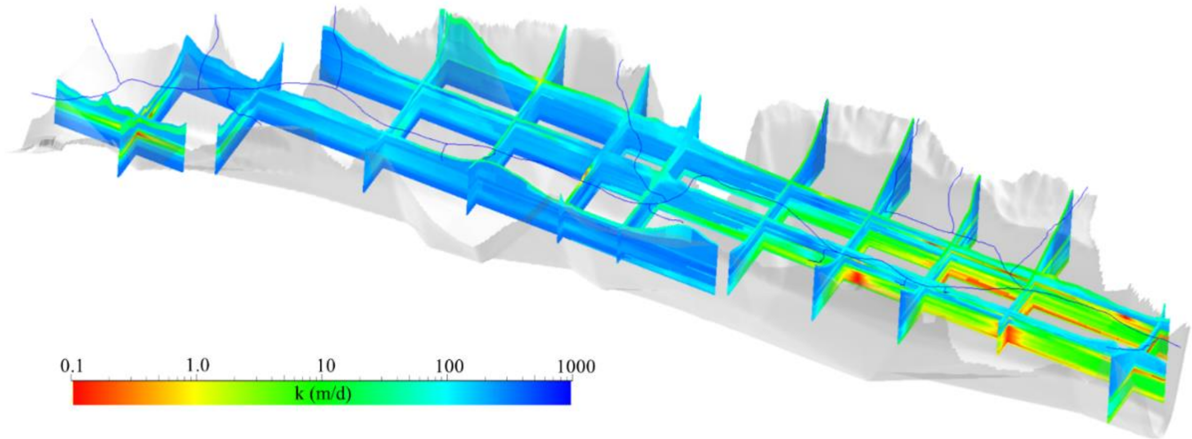

Fig. S1 - Three-dimensional distribution of hydraulic conductivity (m/d)

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Figures

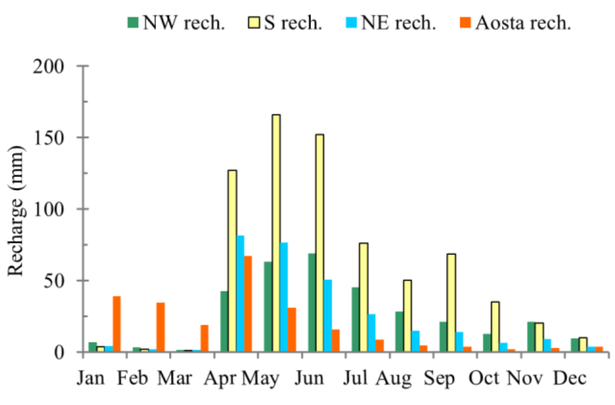

Fig. S2 - Monthly recharge calculation (mm) in different sector of the Aosta Valley Region

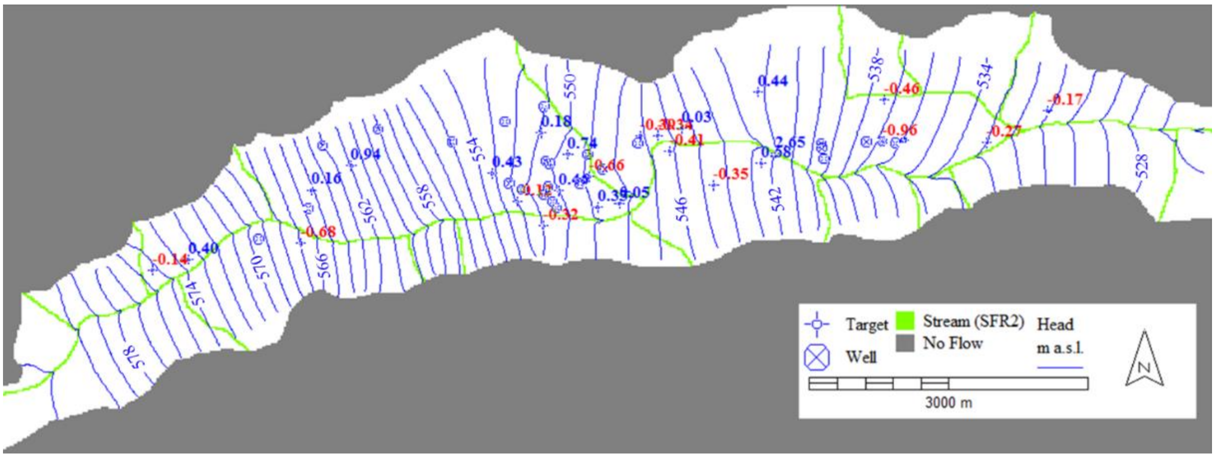

Fig. S3 - Simulated head 2009 for the steady state solution (January 2009) (m a.s.l.)

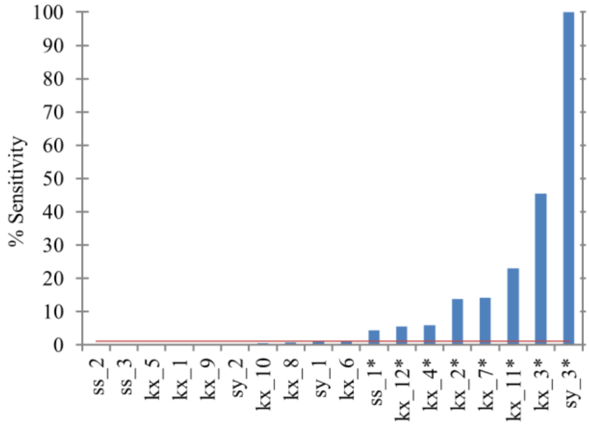

Fig. S4 - Sensitivity analysis before the second calibration. The red line represents the minimum bound of sensitivity used for parameters selection

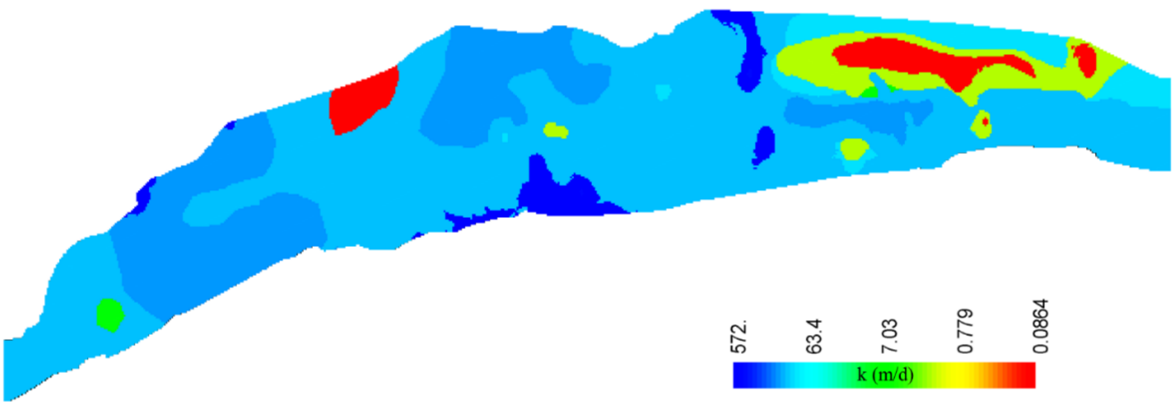

Fig. S5 - Distribution of calibrated hydraulic conductivity values for steady state solution (m/d) - layer 4th

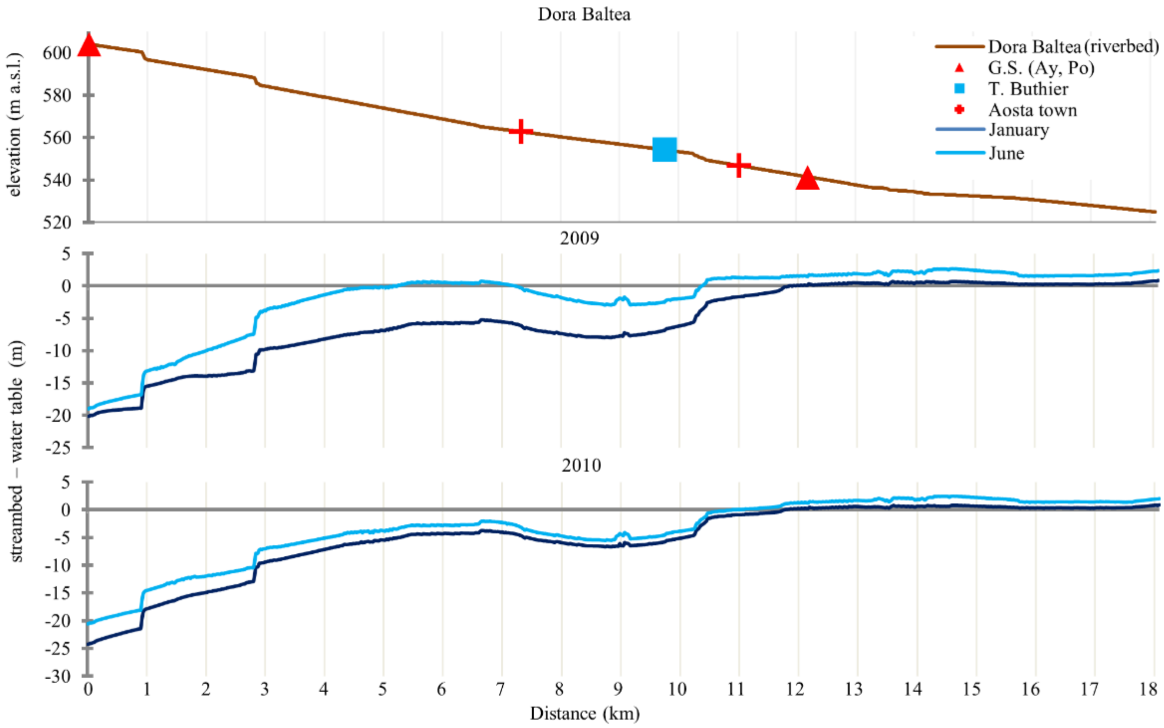

Fig. S6 - Comparison between groundwater head elevation and streambed elevation (m) during January and June 2009 and 2010

5.2. The hydrochemical database TANGCHIM, a tool to manage groundwater quality data: the case study of a leachate plume from a dumping area

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Abstract

Hydrochemical data from groundwater monitoring produce large dataset that require to be properly handled in order to provide well-structured data. This work presents a preliminary conceptual model of a groundwater pollution from a dumping area using the hydrochemical database TANGCHIM as a supporting tool.

TANGCHIM is an on-line database able to store, compute, display and share hydrochemical data from groundwater. TANGCHIM is linked to the hydrogeological wells database TANGRAM, forming an integrated platform able to manage all data referred to wells water.

Results of both statistical and spatial analysis of hydrochemical data referred to a dumping area showed that groundwater is affected by a leachate plume contamination that likely comes from a closed-old landfill built before environmental regulation. This landfill is located upstream to a currently used-new landfill preventing a proper monitoring of the groundwater contamination in the area.

I. Introduction

Hydrochemical data (e.g. concentration of pollutant, isotopes) have a key role in hydrogeological studies. Previous works showed that the reconstruction of the aquifer structure (Dagan & Lessoff, 2007; Bonomi, 2009), the comprehension of groundwater flow dynamics (i.e. groundwater/surface water interaction) (Angelone et al., 2009; Folch et al., 2011; Menciò et al., 2014; Colombani et al., 2016) as well as groundwater contamination by both human (Bonomi et al., 2015) and natural activities (Guffanti et al., 2010; Rotiroti et al., 2014; 2017; Ducci et al., 2016; Dalla Libera et al., 2017) cannot be dealt without a joint analysis of the hydrochemical and hydrogeological data.
The European Water Framework Directive (WFD) (European Community, 2000; European Union, 2006) required to reach a good status for both quality and quantity of the water resource. In particular, as regards to the groundwater, it is necessary to: (1) ensure the gradual reduction of existing contamination; (2) prevent further deterioration of the groundwater and (3) ensure sufficient supply of the resource. To achieve the WFD aims, it is important to begin with the definition of the conceptual model of the aquifer. This allows to design and plan proper monitoring networks and field surveys frequency, with the aim of obtaining new and more representative data to assess groundwater status and plan remedial actions. Historical data are always required in order to design a proper conceptual model of an aquifer. However, these data are often difficult to obtain and share because they are managed by different public or private operators that store data in different formats and on different information supports. Furthermore, new data are progressively added to the existing ones by new wells drilling (e.g. pumping test in the existing or new drilled well, stratigraphic logs) and groundwater field surveys (e.g. groundwater depth, hydrochemical data), inducing a process that, if not properly managed, it could lead to redundancy as far to leak of data.
Nowadays, database able to store hydrogeological and hydrochemical data already exist, but they manage data referred to a specific project or specific area. Moreover, they are designed as a “tank” of data without provide any support to data analysis and without promoting data sharing.
The above considerations highlight the importance to design platforms able to store, manage, compute, link, display and share both hydrogeological and hydrochemical data which could be from different geographical contexts or projects.
The first release of TANGCHIM was in 1999 (Cavallin et al., 1999). In this work the new version of TANGCHIM database is presented. This is now an available online hydrochemical database (http://www.tangchim.samit.unimib.it/) joined to the existing hydrogeological database TANGRAM (http://www.tangram.samit.unimib.it/) (Bonomi et al., 2001; 2014; 2015). The TANGCHIM idea arises from the necessity to provide an on-line platform able to: (1) easily manage hydrochemical time series keeping the connection with the hydrogeological data; (2) manage data derived from different geographical contexts, authorities, projects or private companies; (3) provide

an easy access to the data without losing data confidentiality; (4) provide database access by using whatever devices that support an internet connection (e.g. personal computer, tablet, smartphone). TANGCHIM is able to store, display, and process the hydrochemical data related to water wells already stored in TANGRAM. Currently, TANGCHIM stores more than 115000 hydrochemical data referred to about 430 chemical compounds, that can be modified or added by the user. It also manages synonyms of chemical compounds to avoid data duplication by providing well-structured data. Data export can be performed through queries based on: (1) temporal period, (2) location, (3) chemical compounds and (4) well name. Moreover, TANGCHIM computes simple statistical reports (i.e. descriptive statistics), boxplot and concentration time-series graph. The coupled use of TANGCHIM and TANGRAM allows a better understanding of the results of groundwater monitoring.

Furthermore, the ability of TANGCHIM to manage wide dataset and provide well-structured data makes it useful to support the application of different tools (Rotiroti et al., 2015; Ducci et al., 2016; Dalla Libera et al., 2017) designed for the derivation of the Natural Background Levels (NBLs).

In this paper, the potentiality of the TANGCHIM database are showed through the analysis of the hydrochemical and hydrogeological data coming from the monitoring of groundwater pollution related to a dumping area located in an Alpine fluvial valley (NW Italy). In this area an old landfill located close and upstream to a legal and currently used landfill prevents a proper monitoring of groundwater.

II. Materials and Methods

TANGCHIM database

The development of the TANGCHIM database followed four main steps: design, achievement, pre-processing of the hydrochemical dataset and implementation of the database.

The TANGCHIM database was developed by using HTML, ASP.net, SQL and JavaScript programming languages. It followed a classical RDBMS (Relational Database Management System) (Codd, 1969; 1970) approach. In particular, entity relationship (Chen, 1976), enhanced entity relationship (Teorey et al., 1986), data normalization (Codd, 1971) and queries (Zloof, 1977) were set up. TANGCHIM is composed of tables (relations) each of which connected with one or more tables by means of relational operators which allow to manipulate data in tabular form.

Fig. 1 shows in a schematic way the main tables and the relations existing within TANGCHIM. The hydrochemical and hydrogeological data connection is made by joining TANGRAM and TANGCHIM databases. In particular, the well code both used in TANGCHIM and TANGRAM, allows this relationship. The structure of TANGCHIM database (fig. 1) mainly consists of: (1) a chemical compound table (CC); (2) a synonymous table (SN); (3) hydrochemical dataset tables (HD); (4) a metadata section. The chemical compound table was composed of the name of chemical compounds, an internal identification code number (i.e. compound_ID) assigned for each compound, a chemical classification for each compound (based on three sublevel) previously compiled from existing chemical online databases (GESTIS, 2016; Kim et al., 2016), the CAS-NUMBER of the compounds and other attributes to define if compounds have or not law regulation limit for groundwater. Now TANGCHIM stores more 433 compounds subdivided in 5 groups: Inorganic (85 chemical compounds), Organic (328 chemical compounds), Chemical-Physical (4 parameters), Microbiological (4 parameters) and Others (14 compounds). The name of the compound coupled with the identification code number (i.e. compound_ID) uniquely identifies a chemical compound within TANGCHIM. The synonymous table was designed in order to provide well-structured data and to avoid synonymous troubles about chemical compounds name. In particular, the same compound_ID was assigned to each synonymous of a specific chemical compound listed into the hydrochemical dataset tables stored into the database. TANGCHIM was designed to handle data from different sources (e.g. local authorities, research projects or private projects) by assigning to each of them a different hydrochemical dataset table (HD). These tables must contain at least: well name, well code (from TANGRAM), chemical compound names, concentration of the chemical compounds, unit of measurement and any other useful information. TANGCHIM also stores information related to the source and the provider of data (metadata table).

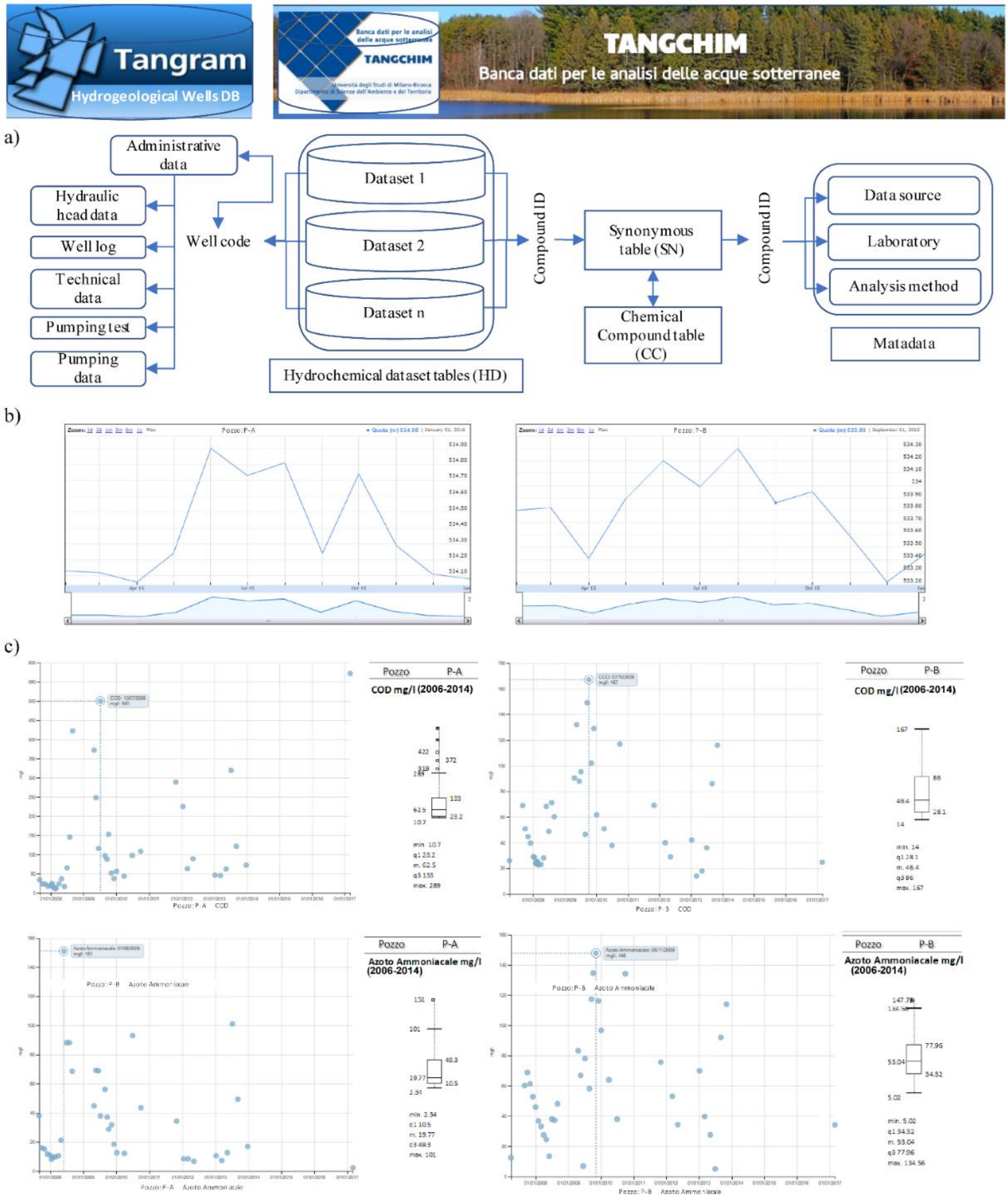

Fig. 2 – (a) Simplified structure of TANGCHIM hydrochemical database and the connection with TANGRAM hydrogeological database. (b) Water table elevation (m a.s.l.) measured in P-A and P-B (see Fig. 2b for locations) piezometers displayed by TANGRAM. (c) Concentration time series graphs, box-plot and simple statistical report for P-A and P-B piezometers referred to COD and NH_4-N displayed in TANGCHIM.

In order to guarantee normalization, consistence and integrity of the database, the updating or the adding of new data regarding the chemical compound table (CC) and synonymous table (SN) must be carried out by the database Manager. A specific section of the TANGCHIM on-line interface allows the authorized users to upload new data for existing hydrochemical dataset by using a spread sheet file format (e.g. *.xls, *.csv).

Data export and data analysis are allowed by a query section based on: (1) single chemical compound, (2) homogeneous groups of chemical compounds or (3) all chemical compounds. This query can be applied to: (1) all existing wells, (2) wells in a specific area, or (3) a single well. Each query can be referred to different periods of time: a single year or a specified time period.

TANGCHIM can display concentration time series, box-plot and compute simple statistical report (i.e. minimum value, first quartile, median, third quartile, maximum value and all data used to the graph) for each well and for a selected chemical compound (fig. 1c). In order to do that, a numerical format of the data is always required. However, concentrations could be below the method or instrumental detection limit (“<DL”), in that instance, a simple internal script converts the “<DL” in “DL” considering this value for both graphs and statistical reports.

Case study

Study area

The study area is located in an Alpine fluvial valley (NW Italy) where lacustrine, alluvial and fan deposits (Quaternary in age) filled an Alpine valley eroded by previous glacial activity. In this valley, a gravelly mono-layer unconfined aquifer with a local subdivision into an unconfined shallow aquifer and a semiconfined aquifer occurs due to a discontinuous silty layer. Groundwater mainly flows from West to East with some local perturbations due to wells withdrawal and surface water drainage.

The study area consists of a dumping area composed of two main landfills: a legal landfill (more recent and currently used) and an old illegal landfill (currently closed) plus other smallest waste deposits of which the locations are unknown. The old landfill and the waste deposits located in the area are related to the historical usage of the area (before environmental regulations) as an uncontrolled disposal area of waste.

Downstream to the new landfill the main regional river flows from SW to NE. The legal landfill was used as point of collection of municipal solid waste and sludge of wastewater treatment plants, whereas both the illegal landfill and the other smallest deposits were filled with inert, plastic and urban wastes of different and unknown composition. Only the legal landfill has an impermeable surface (a clay layer) 1 m thick. An important aspect to consider is that the old landfill is located close and upstream to the legal landfill (fig. 2), preventing a proper groundwater monitoring downstream the currently used landfill.

Hydrogeological and hydrochemical data

The dumping area is monitored by more than 39 piezometers (about 15 m deep) located around the two main landfills (fig. 2). The available data were: 14 well logs, hydraulic head data from 2012 to 2015 and hydrochemical data from 2006 to 2014.

The hydraulic head data were analysed in order to identify the groundwater flow direction and seasonal water table oscillations (fig. 1b). A piezometric map referred to March 2014 was built by using Ordinary Kriging interpolation (fig. 2).

The present study used the data referred to the landfill site provided by the local regional environmental protection agency.
The available hydrochemical data (a total of 6695) were: Dissolved Oxygen (O_2) from 2012 to 2013; Chemical oxygen demand (COD) and Ammonium nitrogen (NH_4-N) from 2006 to 2014; Electrical conductivity (EC) from 2012 and 2014; Iron (Fe), Manganese (Mn) and Arsenic (As) from not filtered samples were from 2006 to 2010 while those from filtered samples were from 2011 to 2014 (table 1). The latter samples were filtered in the field through cellulose acetate membrane with a pore size of 0.45 µm.

All available data were pre-processed and stored in TANGCHIM database. The IBM SPSS® software was used to perform the statistical analysis. In particular, the correlation matrix was calculated on the available data (without considers filtered As because data were available for only 14 piezometers) in order to evaluate if some relations exist within the hydrochemical data.

The statistical analysis was combined with the median maps (performed by GIS software) of the hydrochemical data and the hydrogeological data (e.g. piezometric map) in order to understand the role of each landfill and the unknown waste deposits on the groundwater contamination located beneath the dumping area.

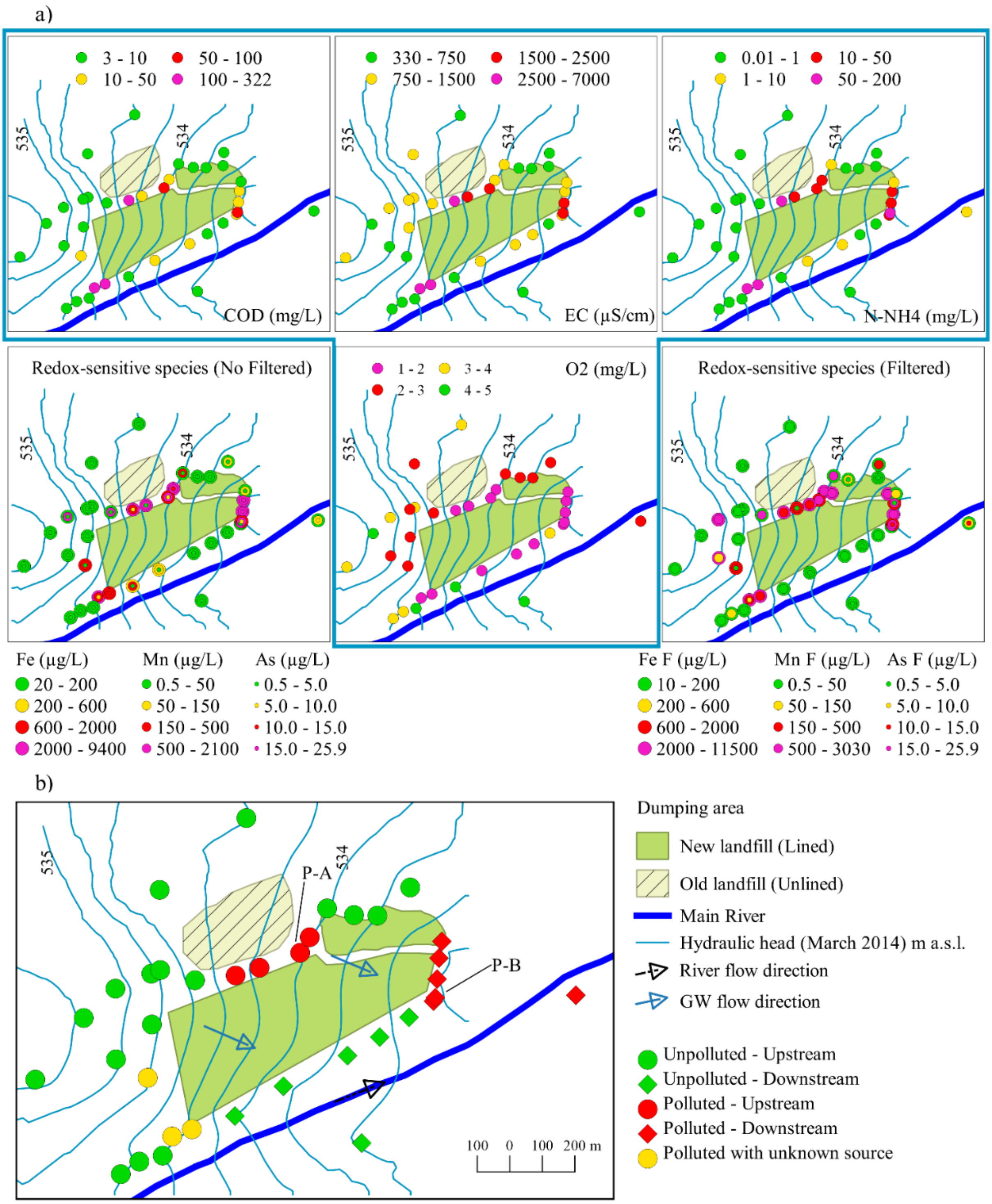

Fig. 2 – (a) Median maps of available data: COD (mg/L), EC (µS/cm), NH_4-N (mg/L), O_2 (mg/L), redox-sensitive species (Fe, Mn, As). The last three compounds are both filtered and no filtered. (b) Location of P-A and P-B piezometers and piezometers groups

Table 1 - Hydrochemical and hydrogeological available data from the dumping area.

Sampling points							
Piezometers	39	Well-logs	15	Piezometers depth			~15m
Hydrogeological data							
	Data availability	n. of data	n. of piezometers	Mean	Min	Max	Dev. Std.
Hydraulic head (m a.s.l.)	2012-2014	731	36	534.34	530.79	536.23	0.71
Hydrochemical data							
	Data availability	n. of data	n. of piezometers	Mean	Min	Max	Dev. Std.
EC (μS/cm)	2012;2014	224	37	1439	159	20700	2398
COD (mg/L)	2006-2014	1470	37	60.81	0.5	3810	275.55
NH_4-N (mg/L)	2006-2014	1470	36	38.26	0.003	12246	346.22
O_2 (mg/L)	2012-2013	322	36	2.71	0.05	7.34	1.48
Fe (μg/L)	2006-2010	633	36	1291.18	5.91	24000	2929.13
Mn (μg/L)	2006-2010	633	36	395.95	0.25	4170	668.31
As (μg/L)	2006-2010	323	36	5.19	0.21	100	11.04
Fe Filterd (μg/L)	2011-2014	200	39	1216.29	0.05	24500	3217.51
Mn Filtered (μg/L)	2011-2014	200	39	245.05	0.19	3980	473.03
As Filtered (μg/L)	2011-2014	150	14	3.95	0.18	64.02	7.13

III. Results and Discussion

The available 14 well logs (stored in TANGRAM database) up to 15 m deep showed that gravelly-sandy as well as gravelly-silty deposits are common in the subsoil beneath the dumping area. The piezometric data showed that the water table depth ranges from 0.8 to 9.9 m with seasonal fluctuations up to about 2 m. Groundwater table oscillations were similar during the years due to the drainage effect of the river that flows close and downstream of the dumping area (fig. 2).

Fig. 1c shows an example of the graphical output achievable by TANGCHIM on-line interface. The graphs are referred to hydrochemical data from two piezometers of the monitoring network of the dumping area (i.e. P-A and P-B). In particular, concentration time series and boxplot for COD and NH_4-N (i.e. *Azoto Ammoniacale* in the fig. 1c) were displayed. The P-A piezometer is located downstream of the old landfill, whereas P-B is downstream of the new one and along the same groundwater flow direction of the P-A (fig. 2b). The hydraulic head data for P-A and P-B showed that the water table is low during winter season and high during summer (fig. 1b). Both piezometers recorded the highest concentrations of both compounds during the low flow period that occurs in winter season. (fig. 2b-c).

Table 1 shows the statistical summary of the available data. All hydrochemical compounds have a wide range of variation highlighting that groundwater contamination is characterized by a wide range of concentration at local scale within the studied site.

The correlation matrix (table 2) shows high-positive correlation between EC, COD, NH_4-N and As. In particular, the correlation index is 0.793 for COD and NH_4-N and 0.985 between EC and COD. Furthermore, the correlation index between As and Fe is positive and quite high (i.e. 0.674). A positive correlation index (~ 0.8) between filtered and not filtered Fe and Mn was also remarked. As regards to O_2 the correlation index is always low (absolute value) and negative (i.e. less than -0.483). Median maps of COD, EC, COD, NH_4-N, O_2 were reported in fig. 2a. Furthermore, fig. 2a shows redox-sensitive species (i.e. Fe, Mn, As) as overlapped layers in two maps for filtered and no filtered samples. Concerning the EC, 30 piezometers had median values lower than 1500 µS/cm, whereas 7 piezometers were up to 7000 µS/cm. The highest values were located between the old and new landfill as well as downstream of the latter. Two piezometers in the south-west side of the landfill showed high values of EC (i.e. >1500 µS/cm).

Although the COD is generally used to quantify the amount of organic matter in water, its content is also affected by other reduced species like Fe, Mn or H_2S that can significantly contribute to it. For this reason, COD is usually used as tracer for leachate plume in groundwater (Fatta et al., 1999; Mor et al., 2006; Clarke et al., 2015). In this area COD showed the same concentration pattern of the EC with median values ranged between 3 to 322 mg/L. Five piezometers had COD median values more than 50 mg/L, between these, two are located between the old and the new landfill, one is along the same groundwater flow direction of the previous ones but downstream of the new landfill and two are on the south-west edge of the new landfill.

*Table 1 - Pearson correlation matrix for available data from groundwater around dumping area. F is referred to filtered sample. **Correlation is significant at the 0.01 level, *Correlation is significant at the 0.005 level*

	O_2	EC	COD	NH_4-N	As	Fe	Fe F	Mn	Mn F
O_2	1								
EC	-0,335*	1							
COD	-0.248	0,985**	1						
NH_4-N	-0,370*	0,806**	0,793**	1					
As	-0,464**	0,663**	0,666**	0,597**	1				
Fe	-0,428*	0,502**	0,490**	0,527**	0,674**	1			
Fe F	-0,401*	0,351*	0,335*	0,394*	0,494**	0,807**	1		
Mn	-0,483**	0.105	0.035	0.104	0.312	0.323	0.224	1	
Mn F	-0,428*	0.053	-0.010	0.068	0.112	0.163	0.190	0,765**	1

The median values of the NH_4-N ranges between 0.01 to 153 mg/L. In particular, 22 piezometers were below 1 mg/L, 5 piezometers were between 1 and 10 mg/L, while the remaining ones reached 153 mg/L. The redox sensitive species (i.e. Fe, Mn) were always present in all piezometers, both no filtered and filtered, whereas the filtered As was measured on 14 piezometers. As regards to the Fe, median values ranged from 20 to 9400 µg/L for the no filtered samples and from 10 to 11500 µg/L for the filtered samples. In particular, 24 piezometers had median values lower than the Italian regulatory limits (200 µg/L) for both no filtered and filtered samples.

The median values of Mn were more frequently higher than the regulatory limit (50 µg/L) with respect to the Fe medians. As for no filtered Mn samples, 17 values of median were lower than 50 µg/L (regulatory limit), 10 piezometers were lower than 500 µg/L and 9 piezometers were between 500 to 2100 µg/L. Concerning the filtered Mn samples, 16 median value were lower than 50 µg/L, 12 were between 50 and 500 µg/L and 9 were between 500 to 3030 µg/L.

The regulatory limits' exceeding values for Fe and Mn were detected: 1) between the old and the new landfill, 2) from piezometers located on the east side of the new landfill and 3) upstream of the new landfill (south-west side).

As regard the available As median values (not filtered), 32 points of sampling were lower than the regulatory limits (10 µg/L), while 4 ranged between 10 to 25.9 µg/L. In the same manner, the As filtered samples showed only 2 of 14 median values with trespassing regulatory limits (10 µg/L). Except for the piezometer located in the upstream side of the new landfill, the exceedance of the As regulatory limits were located between the old and the new landfill and downstream to the new landfill along the same flow direction.

The high correlation between EC, COD and NH_4-N suggests that the groundwater pollution is induced by organic matter infiltration likely coming from the landfill. The organic matter induces the decrease of the dissolved oxygen (which is always negatively correlated with other parameters) explaining the high concentrations of Fe, Mn and As that affect groundwater beneath the dumping area (Fatta et al., 1999; Christensen et al., 2000; 2001; Mor et al., 2006).

The positive correlation between As, COD, NH_4-N and EC provides further supports to the hypothesis that the high concentrations of the redox-sensitive species are induced by the infiltration of organic matter from the waste deposits that have been placed in the dumping area. On this basis, the available hydrochemical compounds could be clustered into two main groups: the leachate plume indicators (composed by EC, COD and NH_4-N) and the redox-sensitive species indicators (composed by Fe, Mn, As, filtered Fe, filtered Mn).

The spatial distribution of the median maps suggests that the highest concentrations of the previous two groups of compounds (i.e. a leachate plume indicators and a redox-sensitive species indicators) are mainly located between the old landfill and the new landfill. However, high concentrations are also found in five piezometers located close and downstream of the new landfill (fig. 2b - diamond symbol). This group of piezometers is likely affected by leaks of leachate that comes from to the old landfill built without a bottom impermeable surface before environmental regulation. The median maps also show that three piezometers located upstream to the new landfill (West side) are polluted mostly by COD, Fe, Mn (filtered and not filtered). This contamination could be related to previous uses of the dumping area as an uncontrolled disposal of waste.

On this basis and taking into account both groundwater flow direction and median maps of the available hydrochemical data, the piezometers around the dumping area were grouped in: (1) Unpolluted - located upstream and downstream of the new landfill; (2) Polluted - located downstream of the old landfill and downstream of the new one, along the same flow direction and (3) Polluted with unknown source - located upstream of the new landfill; this pollution could be related to waste deposits with unknown location or leaks from the new landfill and/or their related sub-services (fig. 2).

IV. Conclusions

This work presents a preliminary characterization of a groundwater pollution from a dumping area using the new online hydrochemical database TANGCHIM as supporting tool.

TANGCHIM addresses the need to provide an integrated platform able to manage, analyze and share all available data (i.e. hydrogeological and hydrochemical) referred to wells and groundwater by the connection with the TANGRAM hydrogeological database.

Results of the groundwater quality monitoring in the study area (NW Italy) showed reducing conditions with low dissolved O_2 and high EC, COD, NH_4-N, Fe, Mn and As that are typically found in leachate groundwater plume. The analysis of both hydrochemical and hydrodynamic data suggested that the plume is mainly sourced from the old landfill and, likely, from other unknown waste deposits located into the dumping area.

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5.3. Determination of trigger levels for groundwater quality in landfills located in historically human-impacted areas

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Abstract

Landfills are one of the most recurrent sources of groundwater contamination worldwide. In order to limit their impacts on groundwater resources, current environmental regulations impose the adoption of proper measures for the protection of groundwater quality. For instance, in the EU member countries the calculation of trigger levels for identifying significant adverse environmental effects on groundwater generated by landfills is required by the Landfill Directive 99/31/EC. Although the derivation of trigger levels could be relatively easy when groundwater quality data prior to the construction of a landfill are available, it becomes challenging when these data are missing and landfills are located in areas that are already impacted by historical contamination.

This work presents a methodology for calculating trigger levels for groundwater quality in landfills located in areas where historical contaminations have deteriorated groundwater quality prior to their construction. This method is based on multivariate statistical analysis and involves 4 steps: a) implementation of the conceptual model, b) landfill monitoring data collection, c) hydrochemical data clustering and d) calculation of the trigger levels.

The proposed methodology was applied on a case study in northern Italy, where a currently used lined landfill is located downstream of an old unlined landfill and others old unmapped waste deposits. The developed conceptual model stated that groundwater quality deterioration observed downstream of the lined landfill is due to a degrading leachate plume fed by the upgradient unlined landfill. The methodology led to the determination of two trigger levels for COD and NH_4-N, the former for a zone representing the background hydrochemistry (28 and 9 mg/L for COD and NH_4-N, respectively), the latter for the zone impacted by the degrading leachate plume from the upgradient unlined landfill (89 and 83 mg/L for COD and NH_4-N, respectively).

I. Introduction

Groundwater often constitutes the main fresh water reservoir which is widely used for drinking, domestic, irrigation and industrial purposes. Its protection is important to ensure the fulfillment of human needs and, at the same time, to preserve its environmental values. In many countries worldwide, current national and supranational regulations try to protect groundwater resources in this perspective. For instance, the EU Water Framework Directive (EC 2000) and Groundwater Directive (EC 2006) aim to ensure a sustainable use of groundwater resources and to guarantee a good status of groundwater ecosystems by establishing specific measures to prevent pollution and quality deterioration.

One of the most relevant source of groundwater contamination around the world is constituted by landfills (Bjerg et al. 1995; Christensen et al. 1998, 2000, 2001; Han et al. 2016; Kjeldsen 1993; Looser et al. 1999; MacFarlane et al. 1983; Rapti-Caputo and Vaccaro 2006, Talalaj 2014). Both unlined and lined landfills can impact groundwater by hazardous chemicals: the former due to direct leaks of leachate, the latter due to the failure of the liners (Han et al. 2014, 2016; Reyes-López et al. 2008). The EU Landfill Directive (EC 1999) aims to prevent or reduce the negative effects of landfills on soils, surface water and groundwater. It establishes a list of requirements for a proper groundwater monitoring network in landfill sites, addressing the identification of sampling points, sampling frequency and parameters to be analyzed. Furthermore, it specifically imposes the definition of trigger levels for identifying significant adverse environmental effects on groundwater generated by the landfill. The trigger levels must be determined taking into account the specific hydrogeological and hydrochemical features of the site where the landfill is located. When a trigger level is reached and confirmed by repeating samplings, the landfill contingency plan and remediation actions should be adopted. The determination of trigger levels in landfills follows other research efforts aimed at providing groundwater quality threshold values for the management and protection of water resources, such as natural background levels and threshold values (Dalla Libera et al. 2017; Ducci et al. 2016; Hinsby et al. 2008; Rotiroti et al. 2015b) or environmental quality standards (Valsecchi et al. 2017).

The EU Landfill Directive does not specify how to calculate the trigger levels, however for newly constructed landfills, they could be easily derived from groundwater quality data of the area before the filling operations, if available. Conversely, the derivation of trigger levels becomes challenging when groundwater quality data prior to the construction of the landfill are missing and in the case of historically human-impacted areas, such as many urban environments (e.g. brownfield sites). Here, the baseline groundwater chemistry could be the product of existing and different (in space and time) anthropogenic influences on groundwater quality instead of natural processes. Therefore in these cases, high concentrations of pollution indicators measured downstream of a landfill could be the effect of historical groundwater pollution rather than leachate spills from the landfill itself and distinguishing between them is a key aspect.

The aim of this work is to present a methodology for determining trigger levels for groundwater quality in landfills located in areas where historical contaminations have already deteriorated groundwater quality and when groundwater quality data of the area before landfill construction are missing. The purpose is not only to meet the requirements of the EU Landfill Directive but also, in general, to provide a tool of wider and worldwide applicability for distinguishing between background existing contaminations and any contamination coming from a landfill, in order to better support landfill management and groundwater resources protection.

This methodology is based on multivariate statistical analysis of data measured from the existing network of wells/piezometers for monitoring the groundwater quality nearby the landfill. Several studies suggested the use of data-driven procedure in order to identify groups of well with similar hydrochemical features (Cloutier et al. 2008; Singh et al. 2005). Cloutier et al. (2008) and Devic et al. (2014) successfully applied hierarchical clustering methods for the evaluation, interpretation and grouping of groundwater quality data since multivariate statistics are independent and quantitative methods. In particular, Güler et al. (2002) compared the performance of graphical and statistical methods for classifying water samples: the most efficient result was achieved by statistical clustering techniques, demonstrating that graphical techniques have limitations compared to multivariate statistics in the case of large data sets.

The presented methodology is applied to a case study in northern Italy. Here, a more recently constructed and currently used landfill is located in an area that was used in the past decades (before the implementation of environmental regulations) as an unregulated disposal site (no other possible historical contaminations of a different type affected the area). Therefore, the correct identification of the proper source of groundwater pollution that lowered the groundwater quality in the area (i.e. the more recent landfill or the older unregulated waste deposits) is challenging and requires specific tools of investigation and analysis.

II. Materials and Methods

Study area

The area under examination is located in an Alpine region in northern Italy. The study area corresponds to a dumping area (Fig. 1) that covers about 0.55 km² and hosts: a) a lined landfill constructed in the 1989 and currently used b) an old unlined landfill closed in the 90's and c) other old smallest waste deposits whose the correct number and locations are unknown. The lined landfill is filled with municipal solid waste and sludge of wastewater treatment plants. It covers an area of ~6 ha in which ~1,800,000 t of waste are stored. The annual quantity of stored waste is about 70,000 t. The liner is formed by a 1 m thick impermeable clay layer. The old unlined landfill and the other smallest deposits were filled with inert, plastic and urban wastes of different and unknown composition. This was done during the 60-80's, before the implementation of environmental regulations. In the 90's, the unlined landfill was capped with a clay layer in order to prevent rain infiltration.

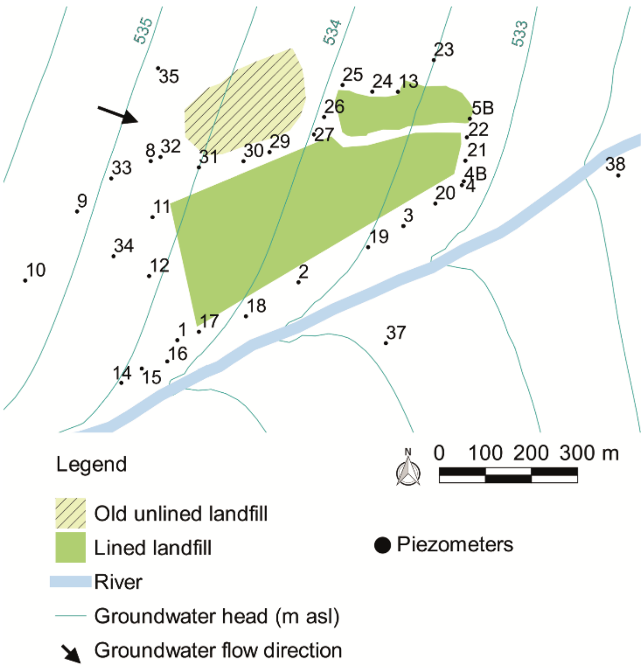

Fig. 1. Location of landfills and monitoring points and contour map of groundwater heads in the study area.

The aquifer beneath the dumping area is composed of alluvial sediments of medium and coarse textures (i.e. sands and gravels) and is unconfined. The bottom of this aquifer is placed at 25-30 m bgl where a silty layer with an average thickness of about 5 m is found. Groundwater table beneath the dumping area has an average depth of 4.5 m bgl with seasonal fluctuations in the range of 1.5-2

m. Groundwater mainly flows from NW to SE, controlled by the gaining behaviour of the river that flows along the southern border of the lined landfill (Stefania et al., 2018). The local hydraulic gradient is between 0.4 and 0.3% (Bonomi et al. 2015)

Available data

The data used in this study are the results of the hydrochemical monitoring performed on the monitoring network of the lined landfill (36 piezometers with an average depth of 15 m bgl; Fig. 1) during the period 2006-2010. No data on groundwater quality before the construction of the lined landfill are available. The available data were provided by local Authorities. The monitoring points were averagely sampled every two months. The total number of samples is 1,004. The monitored parameters were chemical oxygen demand (COD), ammonium-nitrogen (NH_4-N), nitrate-nitrogen (NO_3-N), nitrite-nitrogen (NO_2-N), total phosphorus (P-tot), SO_4, F, As, Cr, Fe, Mn, Ni, Pb, and Cu. Sampling operations and laboratory analysis were done using standard methods by technicians of the company that manages the lined landfill. The piezometers were purged of 3 well volumes before samples collection. The COD was analyzed by titration method, the NH_4-N was determined by the indophenol blue spectrophotometric method and the NO_2-N was analyzed by the Griess regent spectrophotometric method. The NO_3-N, SO_4 and F were analyzed by ion chromatography whereas metals and P-tot were determined by inductively coupled plasma mass spectrometry. The method detection limits (MDLs) varied within the considered period of analysis, the maximum and minimum MDLs were 50-2.5 mg/L for COD, 0.08-0.03 mg/L for NH_4-N, 0.1-0.014 mg/L for NO_3-N, 30-1.5 µg/L for NO_2-N, 60 µg/L for P-tot, 0.1 mg/L for SO_4, 123-50 µg/L for F, 1 µg/L for As and Cr, 20 µg/L for Fe, 20-0.5 µg/L for Mn, 50-0.5 µg/L for Pb and 10-1 µg/L for Cu and Ni.

Determination of trigger levels

The proposed methodology for determining the trigger levels for groundwater quality in a landfill involves 4 steps: a) implementation of the conceptual model, b) landfill monitoring data collection, c) hydrochemical data clustering and d) calculation of the trigger levels.

The elaboration of a proper conceptual model of the area, in terms of hydrogeological and hydrochemical features and anthropogenic pressures, is a key aspect since the determination of trigger levels should be based on specific information on the landfill site (EC 1999). The implementation of the conceptual model requires the collection of existing information and data on the hydrogeology (e.g. thickness and type of aquifer, groundwater table depth, groundwater flow direction, etc.) hydrochemistry (e.g. baseline hydrochemistry) and anthropogenic impacts on the area (e.g. past and current utilization of the nearby areas and pollution events).

Data measured through the existing monitoring network of piezometers in a landfill, that is required by the EU Landfill Directive (EC 1999), form the initial dataset for the proposed calculation of trigger levels. This is a cost-effective choice since, in this way, the methodology is based on existing data and no new costly specific monitoring is required.

The initial dataset is then processed through a cluster analysis in order to identify groups of monitoring points having similar hydrochemical features. This operation allows the creations of sub-datasets on which the calculation of the trigger levels will be based. The data clustering aims at identifying different types of groundwater in the landfill area. Each type of groundwater should be explained by the conceptual model. Moreover, results of the cluster analysis could help to improve the conceptual model itself. The resulting groundwater clusters are then classified in suitable or not suitable for the determination of trigger levels. This classification should be based on the conceptual model, however, general remarks on the choice of suitable or not suitable clusters could be: a) if it is known from previous studies that a leachate spill/leak is occurring from the landfill under analysis, then the downstream piezometers affected by this contamination should be considered as not suitable, since in this condition the trigger level is already exceeded, and so, it is not identifiable by the same data; b) all clusters that have some points located downstream of the landfill and are unaffected by contamination attributable to the landfill itself should be considered as suitable. Only within the suitable clusters, the trigger levels are determined. The final identification of the trigger levels involves a) the choice of representative parameters and b) the calculation of the trigger value. More specifically, the derivation of the trigger levels involves the following procedure:

1. Pre-processing of the initial dataset. This consists in the a) management of censored data (i.e. concentrations below the MDL) and b) calculation of mean values for the time series of each monitoring point. Both operations should be applied for each chemical species contained in the dataset. Concerning the censored data management, the simple substitution method, that involves the substitution of concentrations below the MDL with a value of MDL/2, is recommended only when the percentage of censored values is below 20%, or more (i.e. up to ~50%) if the dataset is large (i.e. number of samples greater than 20), highly skewed (geometric standard deviation greater than 3) and has more than one MDL (Hewett and Ganser 2007; Hornung and Reed 1990). If this percentage is greater than 20% (or 50% under the above mentioned conditions) the log-probit regression (LPR) or maximum likelihood estimation (MLE) methods are recommended (Hewett and Ganser 2007). When the percentage of censored data is greater than 80% for a certain chemical species, it is recommended to exclude this species from the trigger level derivation process. Concerning the calculation of mean values for each monitoring point, this is done to ensure an equal contribution of all

sampling points to successive elaborations, in particular, to obtain a proper input dataset for the cluster analysis avoiding missing data. Moreover, this operation is consistent with methodologies for the calculation of other groundwater threshold values, such as natural background levels (Muller et al. 2006; Rotiroti et al. 2015a). The calculation of the mean, instead of the median, values is preferred since it is more sensitive to extreme concentrations that represent contaminations.

2. Cluster analysis on the pre-processed dataset. The Ward method (Ward 1963) is recommended for performing the cluster analysis. This method consists in a hierarchical clustering aimed at identifying mutually exclusive subset, each of which has elements that are maximally similar. The main advantage of hierarchical methods is that they do not require any prior knowledge of the number of clusters, as opposite to non-hierarchical methods (Sharma 1996). The Euclidean distance is recommended as distance measure, as suggested by Cloutier et al. (2008) for the proper application of the Ward method. Before performing the cluster analysis, data should be standardized to zero mean and standard deviation equal to one. By doing that, each variable is equally considered in the statistical analyses, in order to avoid that the Euclidean distances will be heavily influenced by the variables with a wider range of values (Judd 1980).

3. Identification of suitable clusters. On the basis of the conceptual model of the study area (see above for more details), some clusters of monitoring points resulting from the cluster analysis are selected to be the base for the successive calculation of the trigger levels.

4. Selection of chemical parameters for the trigger level. A parameter, or a group of parameters, indicative of a possible contamination from the landfill under analysis is chosen. This choice should be based on the type of waste stored in the landfill and/or leachate composition, the results of the cluster analysis and the conceptual model.

5. Data preparation for the calculation of trigger levels. For each selected chemical parameter (see the previous point) and for each cluster classified as suitable, the whole time series of all the monitoring points forming a cluster are put together to form a new dataset that will be used for the trigger level calculation. For example, if two parameters were selected (e.g. COD and BOD) and two clusters were classified as suitable, with the first cluster having 4 monitoring points with 20 samples each and the second cluster

having 7 monitoring points with 18 samples each, four datasets are obtained: two datasets for the first cluster (one for COD and the other for BOD) formed by 80 samples each and two datasets for the second cluster with 126 samples each. For each of these datasets, an analysis for the identification and deletion of outliers (Hawkins 1980) should be done before calculating the trigger levels.

6. Final calculation of the trigger value. For each prepared dataset (see the previous point), the trigger level is calculated using statistical indicators such as the 90th percentile, 95th percentile, etc.

Concerning the presented case study, the used dataset is described in Sect. 2.2. The simple substitution method was used during the management of censored data. The pre-processing led to the creation of an input dataset for the cluster analysis formed by 36 samples and 14 variables. The 95th percentile was used for the estimation of the trigger values (ISPRA 2017).

III. Results and Discussion

Conceptual model

The hydrogeological information on the study area (Sect. 2.1; Fig. 1) indicates that the old unlined landfill is located upstream of the lined landfill, therefore it constitutes a potential source of groundwater contamination that could mask any leachate spills from the lined landfill. An overview of groundwater quality in the dumping area can be evinced from Fig. 2 that shows the mean values of COD and NH_4-N in the monitoring network. These parameters can be considered as indicative of contamination sourced by municipal solid waste landfills (Laner et al., 2012). The maps in Fig. 2 show that groundwater quality is deteriorated in the northern part of the area, more specifically, in the following two zones that are aligned along the same groundwater flow path: a) the zone upstream of the lined landfill and downstream of the old unlined landfill and b) the zone downstream of the lined landfill. Although for the former the observed deterioration of groundwater quality can be reasonably attributable to the old unlined landfill, for the latter different hypotheses can be taken into consideration.

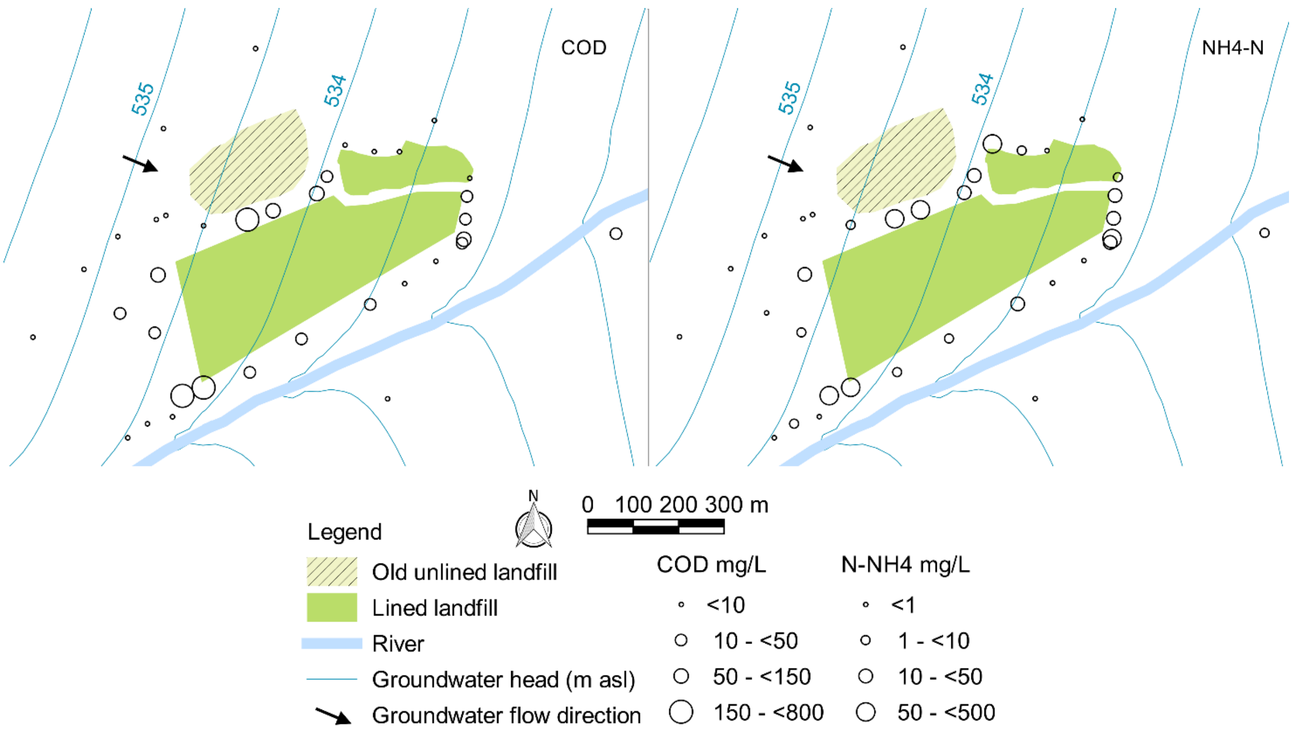

Fig. 2. Maps of mean values of (a) COD and (b) NH_4-N in the study area.

Indeed, this low groundwater quality could be attributable to a) the sole unlined landfill, so the higher values of COD and NH_4-N downstream of the lined landfill would be the effect of their transport along the groundwater flow path or b) to concomitant leachate spills from both the older unlined and lined landfills. The interpretation of the results of the cluster analysis (Sect. 3.2) helped in elucidating this issue.

Moreover, the maps in Fig. 2 show a deterioration of groundwater quality in the zone upstream of the south-western corner of the lined landfill. This could be attributable to the presence of an unmapped old waste deposit (see Sect. 2.1).

Hydrochemical data clustering

Results of the cluster analysis are shown by the dendrogram in Fig. 3. Three main clusters (C1, C2 and C3) were identified. Location of monitoring points and centroids for each cluster are shown in Fig. 4. Table 1 reports the mean values of the considered variables for each cluster. The analysis of centroids shows that C1 has higher values of most of the measured parameters, in particular, COD, NH_4-N, P-tot, Cr and Ni are the highest and characterize this cluster. The first three parameters are commonly used as indicators for organic leachate spills from municipal solid waste landfills (Albaiges et al., 1986; Mor et al., 2006) . Moreover, NH_4-N concentration is generally higher near the source of a leachate contamination and decreases downgradient (Bjerg et al. 1995). On this basis, it can be assumed that monitoring points falling into C1 are likely located near the sources of a leachate contamination. Fig. 4 shows that these monitoring points are all located upstream of the lined landfill, therefore it can be reasonably speculated that the sources of the leachate contamination in the study area are the old unlined landfill in the northern zone and some old unmapped waste deposits in the south-western zone. The cluster C2 has the highest concentration of Mn and is characterized also by higher values of Fe, As and F. High concentrations of Mn and Fe are typically found in leachate plumes, more specifically, the peaks of their concentrations are generally found hundreds of meters downstream of the leachate sources, according to the redox zonation of leachate plumes (Bjerg et al. 1995; Christensen et al. 2000; Lyngkilde and Christensen 1992). The higher concentration of As can be also related to Mn and Fe *via* the reductive dissolution of Fe and Mn oxides, a process typically found in natural systems (Fendorf et al. 2010; Ravenscroft et al. 2009; Rotiroti et al. 2017) but that can be also triggered by contaminant plumes of organic compounds (Burgess and Pinto 2005; Rotiroti et al. 2014). Since the points downstream of the lined landfill fall into C2, it can be assumed that the cause of the groundwater quality deterioration downstream of the lined landfill is not attributable to the lined landfill itself but it is likely related to the chemical evolution along groundwater flow paths of the leachate plume sourced from the old unlined landfill. Finally, the cluster C3 has lower values for all measured parameters, so that it can be considered as representative of the baseline hydrochemistry of the area.

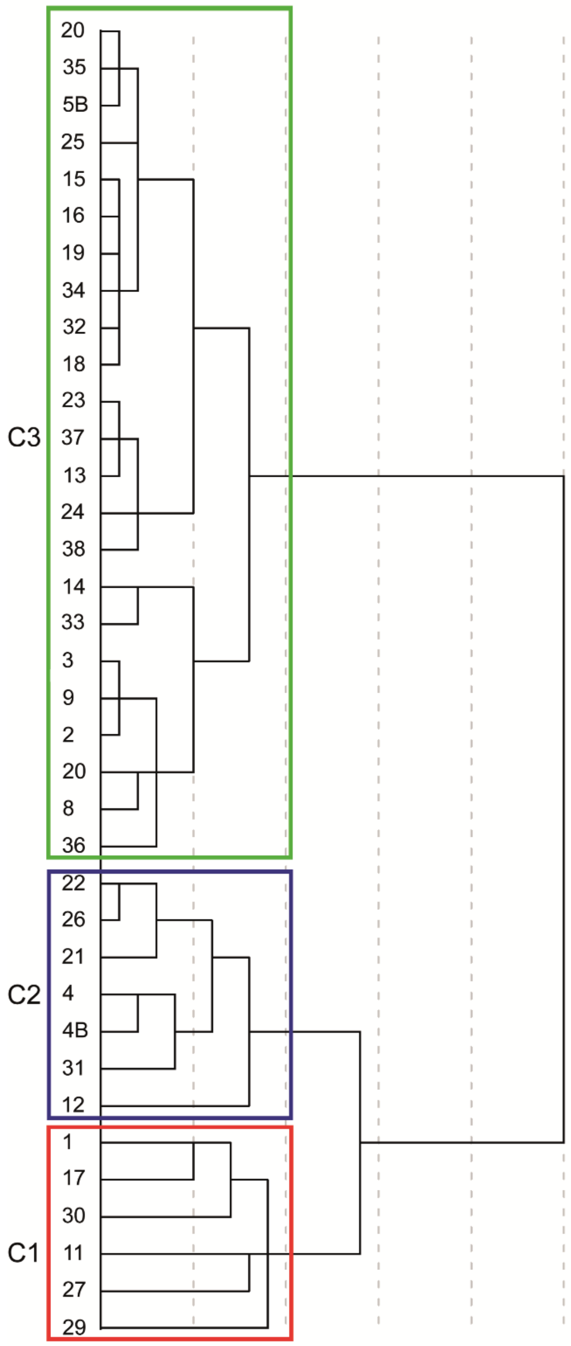

Fig. 3. Dendrogram of the cluster analysis showing the three identified clusters (C1, C2 and C3); labels are monitoring points IDs.

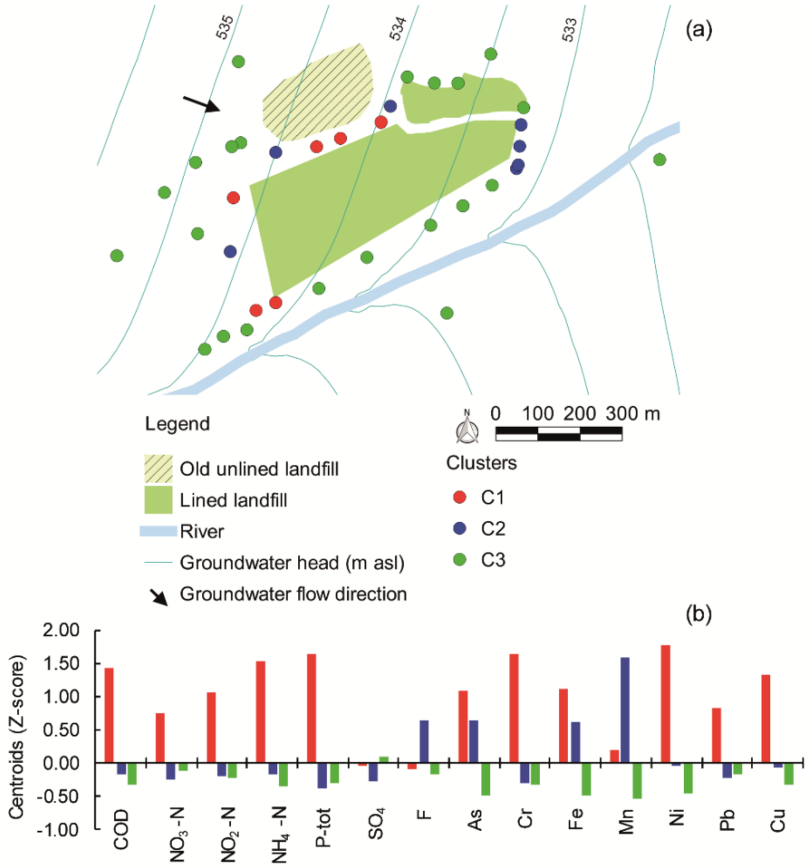

Fig. 4. (a) Location of monitoring points and (b) histogram of centroids for the three identified clusters (C1, C2 and C3).

Table 1. Mean values of measured parameters for each cluster.

		Cluster C1	Cluster C2	Cluster C3	Regulatory Reference*
COD	mg/L	240.2	28.3	9.0	-
NO_3-N	mg/L	5.76	1.92	2.44	11.30
NO_2-N	mg/L	1.26	0.09	0.07	0.15
NH_4-N	mg/L	175.05	23.32	5.99	0.39
P-tot	µg/L	461.6	43.0	59.6	-
SO_4	mg/L	91.8	85.3	95.7	250
F	µg/L	334.5	1238.3	235.6	1500
As	µg/L	12.7	9.5	1.5	10
Cr	µg/L	50.2	3.1	2.3	50
Fe	µg/L	3581.0	2497.4	157.3	200
Mn	µg/L	510.9	1239.3	117.7	50
Ni	µg/L	60.1	15.4	3.8	20
Pb	µg/L	4.5	1.5	1.7	10
Cu	µg/L	17.1	5.5	3.2	1000

*D. Lgs. 30/09 and D. Lgs. 152/06

Trigger levels

Once implemented the conceptual model and performed the data clustering that, in turn, helped to improve the conceptual model itself, the classification of clusters in suitable or not suitable for the calculation of trigger levels can be done. Since the monitoring points downstream of the lined landfill fall within clusters C2 and C3 and leachate spills are presumably absent from the lined landfill, the clusters C2 and C3 were classified as suitable for the calculation of trigger levels. Conversely, the cluster C1 was considered as not suitable since it groups monitoring points that are all located upstream of the lined landfill, moreover, they are affected by a type of contamination that is constrained to the zone upstream of the lined landfill.

Considering that the type of waste stored in the lined landfill is municipal solid waste, the choice of the parameters on which the trigger levels should be calculated fell on COD and NH_4-N. This choice is justified by the fact that these parameters a) are commonly used to identify leachate spills and b) can help to identify possible future leachate spills from the lined landfill also in the zone already influenced by the degrading leachate plume sourced from the old unlined landfill, since here the existing groundwater quality problems are constrained to Mn, Fe and As.

Table 2 reports the calculated trigger levels for COD and NH_4-N on clusters C2 and C3, together with statistical parameter of the datasets used to calculate them. Trigger levels C2 regard the zone affected by the degrading leachate plume fed by the old unlined landfill whereas trigger levels C3 refer to the zone with background hydrochemistry. Concerning COD, both trigger levels C2 (89 mg/L) and C3 (28 mg/L) resulted below some Italian environmental standards, such as the limit of 160 mg/L for the discharge of treated water into surface water bodies (D. Lgs. 152/06), so highlighting that the zones represented by clusters C2 and C3 are currently unaffected by COD. Conversely, trigger levels for NH_4-N (C2 = 83 mg/L and C3 = 9 mg/L) are largely above the regulatory limit of 0.39 mg/L (i.e. 0.5 mg/L of NH_4). This high value for C2 confirms that the degrading leachate plume from the old unlined landfill affects, in terms of NH_4-N, also the zone downstream of the lined landfill. The high value for C3 (although much lower than C2), that represents the baseline hydrochemistry of the area, is related to some sporadic high concentrations of NH_4-N that are likely due to some small variations in the groundwater flow system, leading to occasional inclusion of some C3 piezometers into the existing leachate plume. This can be also seen from the distribution of the data used to derive the trigger level C3, that is heavily tailed, as shown by statistical parameters of Tab. 2.

Table 2. Trigger levels and statistical parameters of the datasets used to calculate them.

	Cluster	n piezometer	n samples	Mean	Min	25th percentile	Median	75th percentile	Max	Trigger Level (95th percentile)
COD (mg/L)	C2	7	201	27.8	0.5	8.3	19.2	34.1	167	89
	C3	23	625	7.5	0.5	3	3.3	7.8	107	28
NH_4 -N (mg/L)	C2	7	198	22.52	0.01	2.08	12.95	26.03	234	83
	C3	23	624	2.54	0.004	0.02	0.06	0.78	197.37	9

In summary, as for the future management of the considered landfill, trigger level C2 should be adopted for the monitoring of the 4 piezometers downstream of the lined landfill and impacted by the degrading leachate plume sourced from the upgradient unlined landfill, whereas trigger level C3 should be considered for the 6 piezometers downstream the lined landfill representing the baseline hydrochemistry.

IV. Conclusions

This paper presented a methodology for calculating trigger levels for groundwater quality in landfills, focusing on the case of historically human-impacted areas where there are no data of groundwater quality prior to the construction of the landfill. The methodology was applied to a landfill in northern Italy that was build in an already contaminated area. More specifically, the study area was impacted by an old unlined landfill and some old unregulated and unmapped waste deposits.

The performed hydrochemical data clustering, that constitutes the core of the proposed methodology for calculating the trigger levels, had also proved to be a key tool for the improvement of the conceptual model of the area. Indeed, it helped identifying the likely sources of contamination in the study area, in particular, the cluster analysis revealed that the deterioration of groundwater quality observed downstream of the lined landfill is due to a degrading leachate plume sourced by the upgradient unlined landfill rather than a presumable leachate spill from the lined landfill itself.

A point of strength of this methodology is that it combines data-driven methods (cluster analysis) with the soft data (conceptual model) on hydrogeology and human uses of the study area, so leading to the calculation of more reliable and usable trigger levels.

The proposed methodology has a potential wide and worldwide applicability since a) landfills are frequently located in urban and/or industrial areas that can be already impacted by historical contaminations and b) the use of existing data from the landfill groundwater monitoring network makes this method simpler and cost-effective since no new costly specific monitoring is required.

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

Keywords: Waste management, MSW, Groundwater quality classification, Landfill leachate, Water quality, Environmental tracers

Manuscript in preparation, to be submitted

Abstract

The identification of groundwater pollution sources is a challenging issue, especially in the case of multiple-source pollution. It is of fundamental importance in order to properly remediate a polluted site and to improve groundwater quality.

This work concerns the identification of pollution sources for groundwater in a landfill site, using artificial sweeteners as chemical tracers, supported by multivariate statistical analysis of hydrochemical data and by a quantitative analysis of the groundwater flow system through particle tracking and transport modeling. The study area is located in northern Italy that 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 sweetener concentrations together with results of multivariate statistical analysis of hydrochemical data, particle tracking, and a chloride transport model suggest 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 leaking from the older unlined landfill that seems to affect also an area downstream of the lined landfill. Direct leachate leaks from the lined landfill seem unlikely, although they cannot definitely be excluded.

I. Introduction

During the last decades, the industrialization process 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 of leachate 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 through soil into groundwater (Reyes-López et al., 2008). Nowadays, to better protect environmental resources, many countries (e.g. member states of EU) imposed 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 the time inducing a groundwater quality depletion (Lee et al., 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), and stable isotopes (Castañeda et al., 2012; Nigro et al., 2017), 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 groundwater pollution sources identification is a complex and critical issue. For instance, in most urban environments, new lined landfills were built in areas already covered by older unlined landfills, making the proper identification and attribution of pollution sources challenging. An inadequate knowledge on pollution sources affecting a site would lead to inefficient remediation strategies or complex legal disputes. Therefore, the estimation of groundwater pollution sources, including their numbers, locations, and dynamics, plays a key role for the management and remediation of polluted sites (Ayvaz, 2010). Various techniques and methods for identifing groundwater pollution sources are reported in literature, based on multivariate statistical analysis (Tariq et al., 2008), isotopic analysis (Alberti, 2017; Grimmeisen et al., 2017), and transport modeling (Ayvaz, 2010).

A recent work by Roy et al. (2014) showed that artificial sweeteners can be used to trace leachate pollution from municipal solid waste (MSW) landfills, so they could 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 and is a soil metabolite of some 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. Using different types of artificial sweeteners that entered the market in different years, leachate plumes originating from landfills with different age may be distinguished. 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., 2017, and unpublished results) showed that the old unlined landfill likely affects groundwater quality, however, other unknown sources have to be considered as well, so their proper identification is needed to address remediation strategies.

The main aim of this work was to identify the sources of leachate pollution affecting the study area using artificial sweeteners as tracers, supported by multivariate statistical analysis of hydrochemical data and transport modeling. Another related aim of the work is to evaluate and confirm the potential of the use of artificial sweeteners to trace leachate plumes (Roy et al., 2014). This involved: a) an initial groundwater quality classification, made by cluster analysis of hydrochemical data; b) the pollution sources identification, done by the interpretation of measured artificial sweeteners concentrations, factor analysis of hydrochemical data, particle tracking, and transport modeling; c) recommendations for improving the groundwater quality at the study area.

II. Materials and methods

Study area

The study area is located in an Alpine valley, in northern Italy, more precisely, in an alluvial plain at the valley floor. This plain has a length of ~13 km from west to east and its average width is ~2 km. It hosts 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.

The thickness of the unconfined aquifer ranges from 50 to 90 m. It is limited at the bottom by a lacustrine silty layer which 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 of thickness in the eastern part of the plain, that subdivides the main aquifer in an unconfined (~20 m thick) and a semiconfined (between 12 and 25 m in thickness) part (Bonomi et al., 2015a; Novel et al., 2013; Triganon et al., 2003). The regional groundwater flow is from west to east following the slope of the valley. The main regional river flows along the plain from west to east changing from losing to gaining along its path (Bonomi et al., 2015b; Stefania et al., 2018).

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 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 municipal solid waste (MSW) landfill was built downstream of the old unlined landfill. The liner system consists at least of a 1 m thick clay layer at the bottom. During the 90's, a capping was placed on top of the unlined landfill in order to prevent rain infiltration to the waste.

The MSW landfill hosts about ~1,800,000 t of waste with an annual amount of 70,000 t of waste stored. The wastes stored in the MSW landfill are domestic waste and sludge of wastewater treatment plants, whereas those in the unlined landfill are inert, plastic and urban wastes of different and unknown composition. The whole landfill area is monitored by 38 piezometers with an average depth of 15 m bgl located around the MSW and unlined landfills.

A leachate collection system serving the MSW landfill is composed of 4 underground tanks (3 x 5 m and unknown depth), 3 leachate wells, and related underground pipes that cross the western and southern sides of the area (Fig. 1). The leachate is then pumped to a wastewater treatment plant (WTP) located in the western part of the dumping area (Fig. 1) that serves ~115,000 equivalent inhabitants.

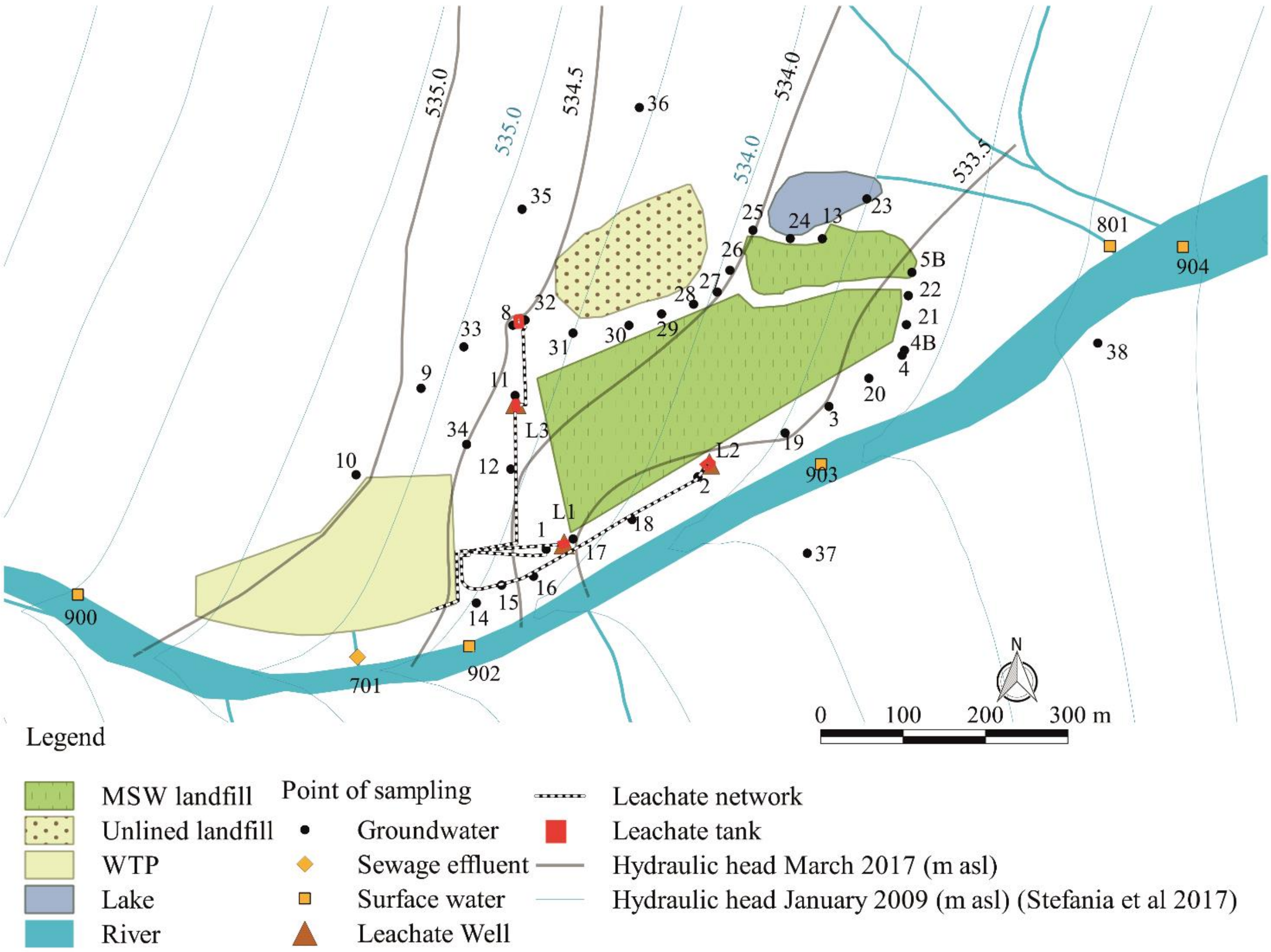

Fig. 1 - Map of the study area showing piezometric maps for January 2009 and March 2017 and locations of landfills, leachate collection system and sampling points (numbers are point IDs). MSW: Municipal Solid Waste, WTP: Wastewater Treatment Plant, L: Leachate Well.

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. 1. 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. The piezometers are 15 m deep and they have a diameter of 10 cm. 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), electrical conductivity (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), chemical oxygen demand (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 S2 in Supplementary Materials 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 regent spectrophotometric method for NO_2^--N (Barnes and Folkard, 1951), and ion chromatography for NO_3^--N (Thermo Scientific™ Dionex™; Leoni et al., 2014). The titration method was used to analyse COD whereas SO_4^{2-} and major ions were measured using the Ion Chromatography (Thermo Scientific™ Dionex™; Leoni et al., 2014).

The 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 method detection limits (DLs) were 2.5 mg/L for COD, 0.03 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, 1.00 μg/L for SUC, 0.40 μg/L for ACE, 0.10 μg/L for CYC, and 0.30 μg/L for and SAC. Results of chemical analyses were stored in the TANGCHIM database (Stefania et al., 2017).

Multivariate statistical analysis

Multivariate statistical analysis was applied on groundwater data involving 13 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-}) and 37 samples. The sample 28 was excluded since only major ions were measured. Concentrations below the DL were substituted with a value of DL/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 higher or equal to 1 were considered as significant factors (Kaiser, 1958).

Particle tracking and transport modeling

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

The transport modeling was done using MT3DMS (Zheng, 2010; Zheng and Wang, 1998). 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 an advective-dispersive transport from the old landfill to downstream of 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 plume length 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 calculated for each piezometer on legacy data (over the 2011-2017 period) provided by local authorities (Table S3 of the Supporting Material). 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. 2018) and b) some variations in the groundwater flow occurred between March 2017 and January 2009 (see Sect. 3.1), so the use of measured Cl^- in March 2007 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, 1998).

A model for simulating a drainage system collecting leachate from the old unlined landfill was also implemented. Details on settings and results are reported in the Supporting Material.

III. Results and Discussion

Groundwater flow

Fig. 1 shows the piezometric map obtained by ordinary kriging interpolation of groundwater levels measured in March 2017. Fig. 1 also reports the simulated piezometric map by Stefania et al. (2018) 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., 2018). 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 (Stefania et al., 2018), therefore it could not account for local factors influencing groundwater flow as, conversely, a detailed groundwater level survey, as that of March 2017, can do. Moreover, some variations in the hydrodynamic conditions may have occurred between January 2009 and March 2017. Anyway, what is well known is that the gaining behavior of the river nearby the landfill is kept throughout the year, also during the early summer when the river has its highest discharge due to snow melting (Stefania et al., 2018).

Groundwater quality classification

Results of CA (Fig. 2) showed that groundwater samples can be grouped into three main clusters, called C1, C2 and C3.

The 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. 2c). The cluster C1 is mainly characterized by high values of COD, K^+, Mg^{2+}, Na^+, Cl^-, P-tot and EC (Fig. 2b) ranging between 172 and 572, 123.6 and 434.1, 40.4 and 81.0, 218.7 and 633.5, 360.0 and 736.1, 0.25 and 1.84 mg/L and 1180 and 6260 μS/cm, respectively. All these parameters, in particular COD and K, are typical indicators of groundwater contamination by landfill leachate (Christensen et al., 2001; Mor et al., 2006; Öman and Junestedt, 2008), therefore their high concentrations reveal that piezometers forming cluster C1 (i.e. 27, 17 and 1) are affected by a severe pollution from the landfill. This leads to assume 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 <DL in piezometer 1 to 455 mg/L in piezometer 27; this may indicate the presence of different types of pollution source within this cluster (see Sect. *Identification of pollution sources* for a more detailed discussion).

Cluster C2 groups piezometers located in three different zones of the landfill site (Fig. 2c): 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 as affected by a moderate leachate pollution. This could be related to some leachate spills/leaks of less magnitude with respect to C1 or to the transport of main leachate plumes (originating close to piezometers forming C1) that evolve their chemical composition along groundwater flow paths.

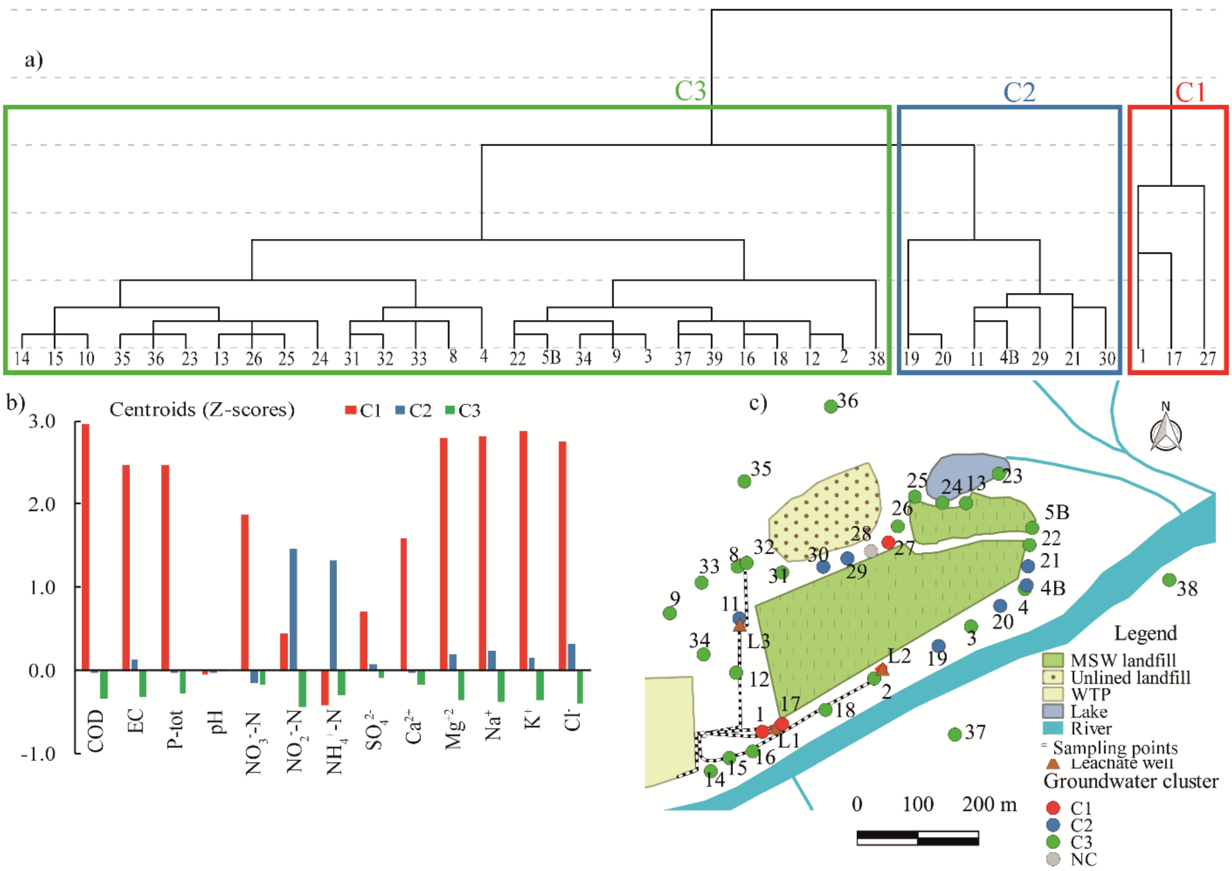

Fig. 2 – Results of cluster analysis of groundwater hydrochemical data. a) Dendrogram showing the obtained three main clusters (C1, C2, and C3); numbers are sampling points ID. b) histogram of centroids for the three identified clusters (C1, C2 and C3). c) Location of groundwater sampling points grouped into the three identified clusters (C1, C2 and C3); NC = not classified.

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. 3 shows the scatter plot of Cl^- *vs* K^+ for groundwater, surface water and sewage effluent samples. The ions Cl^- and K^+ are useful tracers for MSW leachate pollution since they are conservative and typically found with 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 wastes, e.g. paper (Naveen et al., 2017), and Cl^- is contained in domestic salts (Rotiroti et al., 2017). In general, the Cl^- *vs* K^+ plot confirms the groundwater classification resulting from CA. Indeed, samples from C1 were the most polluted, followed by samples from C2 and then by C3 with the lowest values. Within the latter, representing the baseline hydrochemistry, a sub-classification can be seen. Indeed, some points exhibit lower concentrations ($Cl^- < 21$ and $K^+ < 5$ mg/L) attributable to the natural baseline (i.e. piezometers 35-38 located outside of the landfill site) whereas for the other points with higher concentrations, an anthropogenic baseline, accounting for all human activities in the site over the time, can be considered, as for piezometers 8, 31 and 32 that reach Cl^- concentrations around 200 mg/L. However, for these piezometers, a slight influence of the leachate collection system serving the MSW landfill cannot be excluded since they are all located close to an underground leachate tank (Fig. 1). The samples from cluster C1 together with sample 28, that has high Cl^- and K^+ concentrations, but was excluded from the CA (see Sect. 2.3), show a good linear correlation between Cl^- and K^+ ($r^2 = 0.98$).

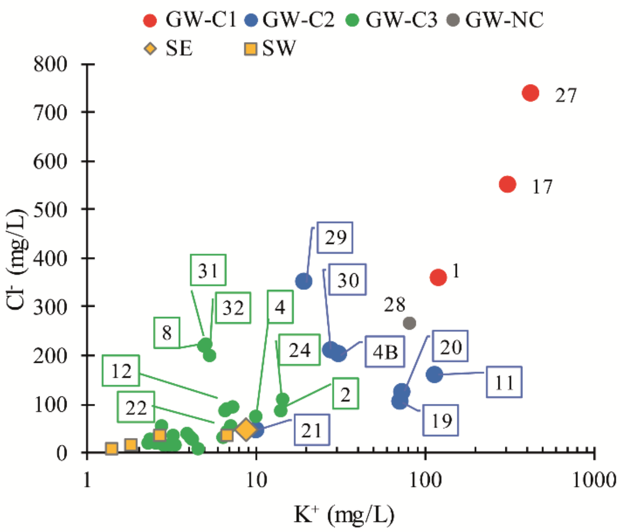

Fig. 3 - Scatter plot of Cl^- vs K^+ for groundwater (GW), surface water (SW) and sewage effluent (SE) samples; numbers are sample IDs; groundwater samples are grouped into the three identified clusters (C1, C2 and C3); NC = not classified.

This leads to the following two considerations: a) sample 28 likely has similar hydrochemical features with respect to the samples forming cluster C1, so it can be considered as part this cluster b) all these four piezometers are affected by the same landfill pollution evidenced by CA results.
Fig. 3 shows that concentrations of Cl^- and K^+ in surface water samples were similar to groundwater samples from cluster C3. This suggests that, at the time of sampling, the main regional river was not affected by the landfill although it gains groundwater crossing the landfill site. This could be due to attenuation (i.e. dilution/dispersion/degradation) occurring along groundwater flow paths and within the river. The highest concentrations of K^+ and Cl^- in surface water were found just downstream of the discharge of treated wastewater from the WTP.

Identification of pollution sources

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

Severely polluted groundwater

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

The FA identified 4 significant factors (FAC1-4) explaining a total cumulative variance of 87.33% (Table S1 of the Supplementary Material). The FAC1 explains 52.44% of the total variance. The original variables that represent FAC1 (i.e. loading value > |0.7|) are NO_3^--N, Ca^{2+}, and SO_4^{2-}. The FAC2 explains 17.69% of the variance and is mainly represented by EC, P-tot, COD, and Cl^-. FAC3 and FAC4 explain 9.20 and 8.01 % and are represented by only $NH4^+$-N and pH, respectively.

Fig. 4 reports the loading and score plots for FAC1 *vs* FAC2 (results for FAC3 and FAC4 are reported in Fig. S2 of the Supplementary Material). Fig. 4a clearly shows that FAC1 and FAC2 are able to separate the samples forming cluster C1 into two sub-groups. This means that two different types of leachate pollution can be identified: piezometer 27 is polluted by leachate having higher NO_3^--N, Ca^{2+} and $SO4^{2-}$ whereas piezometers 1 and 17 are polluted by leachate with higher EC and P-tot (Fig. 4b). Considering the location of these piezometers (Fig. 2c), FAC1 may represent pollution by leachate leaking from the older unlined landfill whereas FAC2 may represent pollution by leachate coming from the leachate collection system of the younger MSW landfill, in particular from the leachate well L1 and/or its related underground tank.

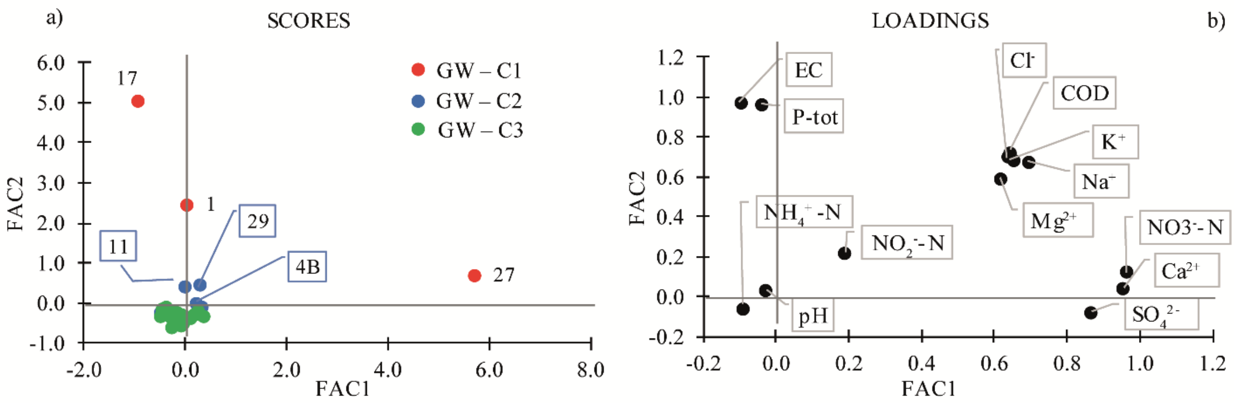

Fig. 4 - Score and loading plots resulting from factor analysis of groundwater hydrochemical data; scores are grouped into the three identified clusters (C1, C2 and C3). a) Score plot of FAC1 vs FAC2; b) Loading plot of FAC1 vs FAC2.

The higher values of NO_3^--N and SO_4^{2}- together with lower COD, that characterize FAC1, seem consistent with leachate coming from an older landfill. Indeed, Lee et al. (2010) reported an increase of SO_4^{2}- and a decrease of COD 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 (from 2 to 12 years), observing a decrease of NH_4^+-N and an increase of NO_3^--N over time. On the other hand, the higher values of COD, EC and P-tot, characterizing FAC2, 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 content of the oxygenated form of nitrogen (NO_3) and sulfur (SO_4^{2-}) (Aziz et al., 2010; Lee et al., 2010; Ziyang et al., 2009).

A confirmation of these assumptions can be also given by the plot of SO_4^{2-} *vs* Cl^- (Fig. 5), that were 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.

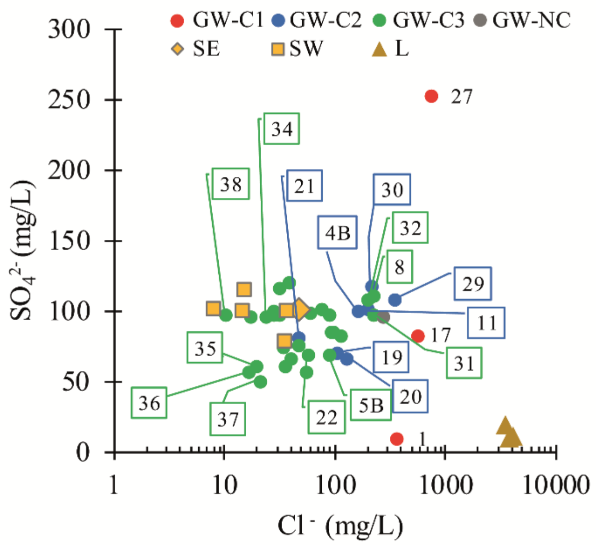

Fig. 5 – Scatter plot of SO_4^{2-} vs Cl^- for groundwater (GW), surface water (SW) sewage effluent (SE) and leachate (L) samples; numbers are sample IDs; groundwater samples are grouped into the three identified clusters (C1, C2 and C3); NC = not classified.

Moderately polluted groundwater

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

Artificial sweeteners

Fig. 6 shows the spatial distribution of measured artificial sweeteners in groundwater and surface water. In general, ACE was the most common artificial sweeteners detected, whereas SUC was the least detected (note the higher DL for SUC). This is consistent with previous studies in other urban environments worldwide (Van Stempvoort et al., 2011)

ACE was measured above the DL in 7 groundwater samples, with maximum concentrations found in those piezometers affected by spills of leachate likely from the leachate collection system (Sect. 3.3.1), that are piezometers 1 (9.69 µg/L) and 17 (5.15 µg/L). ACE was also able to trace the other significant leachate spill in the area (i.e. the leachate spill from the older unlined landfill) indeed, relevant concentrations were measured in piezometers 27 (4.55 µg/L) and 28 (0.68 µg/L). Within the piezometers classified as moderately polluted, ACE was detected in piezometer 11 (0.82 µg/L), close to leachate well L3, and in piezometers 19 and 20 (1.71 and 1.51 µg/L), located downstream of the MSW landfill.

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

The detection of SUC in the leachate sample L3 (0.15 μg/L) indicates that this sweetener can be used to trace pollution in groundwater by leachate from more recent landfills, as the case of piezometer 1. Concerning surface waters, SUC, ACE and CYC were detected in the main regional river (3.21, 4.93 and 0.12 μg/L, respectively), but only just downstream of the discharge of treated effluent from the WTP that showed concentrations of 3.43, 7.05, 0.32, and 0.53 μg/L for SUC, ACE, CYC, and SAC, respectively. Therefore, the concentrations measured in the river seem to be related to the discharge of the WTP rather than the gaining of polluted groundwater from the landfill site.

All these results lead to the following main considerations: a) the four artificial sweeteners allowed to trace pollution likely originating from the leachate collection system serving the MSW landfill and affecting piezometers 1 and 17; b) the detection of SUC (the most recently marketed sweetener) only in piezometer 1 confirms that this point is affected by younger leachate; c) the absence of SUC in piezometer 27 sustains the assumption that this point is affected by leachate from the older landfill that is likely free from this more recently marketed sweetener; d) SAC was the only sweetener detected in the eastern part of the area, so it may indicate some older anthropogenic influences related to the old unlined landfill; e) ACE gave more comprehensive information than the other sweeteners, indeed, it was able to trace the two main leachate spills/leaks (from the leachate well L1 and from the unlined landfill) and identify some of the piezometers classified as moderately polluted (i.e. piezometers 11, 19 and 20); 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 pollution classified as moderate for 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.

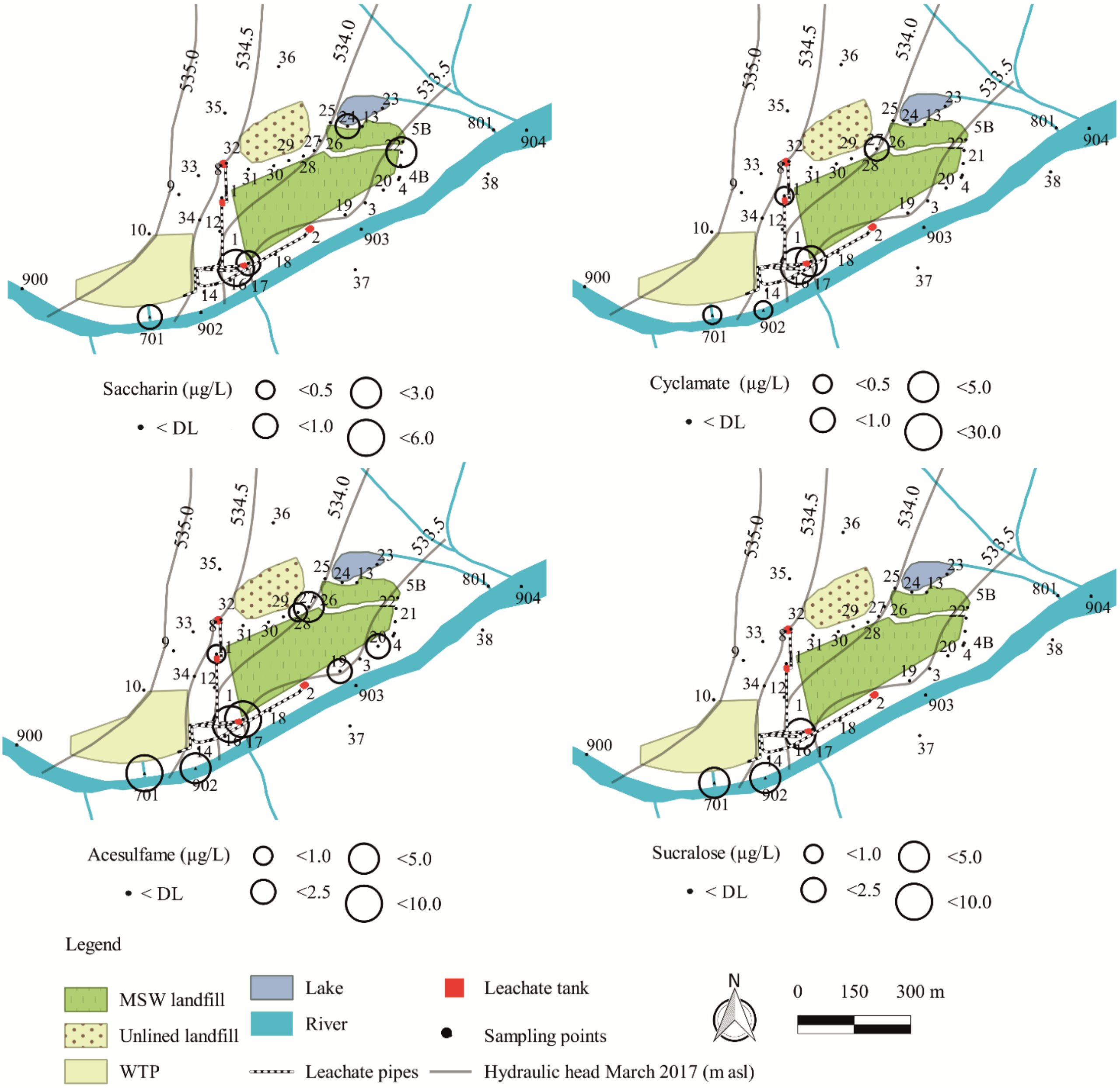

Fig. 6 – Maps of measured artificial sweeteners (March 2017); numbers are sample IDs. a) Saccharine; b) Cyclamate; c) Acesulfame; d) Sucralose.

The distribution of ACE concentrations, with higher values in piezometer 27 and lower values in piezometers 19 and 20, seem to sustain the idea that these piezometers could be affected by a leachate plume sourced from the old unlined landfill. This seems also the case for piezometers 4B and 21, that were classified as moderately polluted too (Sect. 3.2), and are located downstream of the MSW landfill, close to piezometers 19 and 20.

The hypothesis that a leachate plume sourced by the unlined landfill, moving downstream, affects piezometers 4B, 19, 20 and 21 was tested by particle tracking and transport modelling.

Particle tracking

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. 7). The estimated travel time required for groundwater to move from the unlined landfill to these downstream piezometers is ~180 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. 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. 3.2), 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.

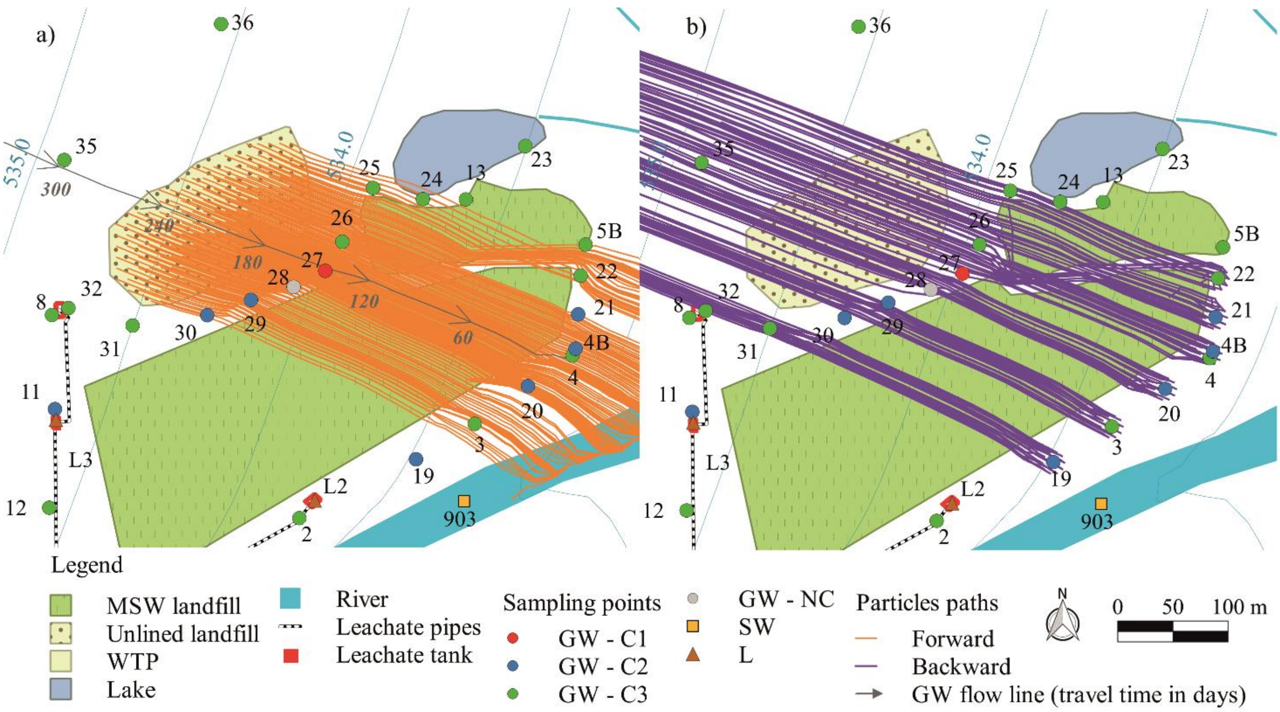

Fig. 7 – Results of particle tracking. a) extension of a hypothetical plume originating from the whole old unlined landfill (forward simulation). The grey line represents the groundwater flow passing through piezometers 27 and 4B, used for the cross-section in Fig. 8. b) origin of groundwater passing through piezometers located downstream of the lined landfill (backward simulation).

Transport modelling

This modelling was aimed at testing if Cl^- concentrations in piezometers downstream of the MSW landfill can be only explained by the advective-dispersive transport of Cl^- sourced upstream of it; if not, leaks from the MSW landfill would be likely. Fig. 8 and Table 1 show the results of this modeling. Fig. 8a depicts results of the sensitivity analysis on longitudinal dispersivity through simulated breakthrough curves of chloride in piezometer 4B. The curve obtained using 1.5 m as α_L fits with the travel time of 160 days estimated by particle tracking, so this value was used for modeling. Fig. 8b shows the map of the simulated Cl^- plume and indicates which piezometers were used as pollution sources and pollution targets (i.e. the piezometers forming cluster C2 located downstream of the MSW landfill). Concerning the latter, the comparison of simulated Cl^- against average measured Cl^- concentrations, that were used in the modeling (see Sect. 2.4 for details), is shown in Table 1. In these target piezometers, the simulated Cl^- concentration resulted in agreement with or lower than the average measured Cl^- concentration. This indicates that the presence of unaccounted additional sources, i.e. leachate leaks from the MSW landfill, seems unlikely. However, piezometer 19 showed a simulated concentration slightly lower than its average measured concentration. This does not allow to definitively exclude leachate spills/leaks from the MSW landfill and leaves the assessment of possible impacts from the MSW landfill an open issue. Moreover, the significantly higher concentrations of NH_4^+-N found in March 2017 in piezometers 19 and 20 (118.0 and 116.0 mg/L, respectively) compared to piezometer 27 (2.34 mg/L) could support this assumption. The $NH4^+$-N values in piezometers 19 and 20 exceed the trigger level for identifying significant adverse environmental effects caused by the MSW landfill that was estimated by Stefania et al. (unpublished results) to be 9 mg/L for this area (calculation based on legacy data from 2006 to 2010), so a 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. Direct leachate spills/leaks from the MSW landfill seem unlikely, although they cannot definitely be excluded, in particular, nearby to piezometer 19.

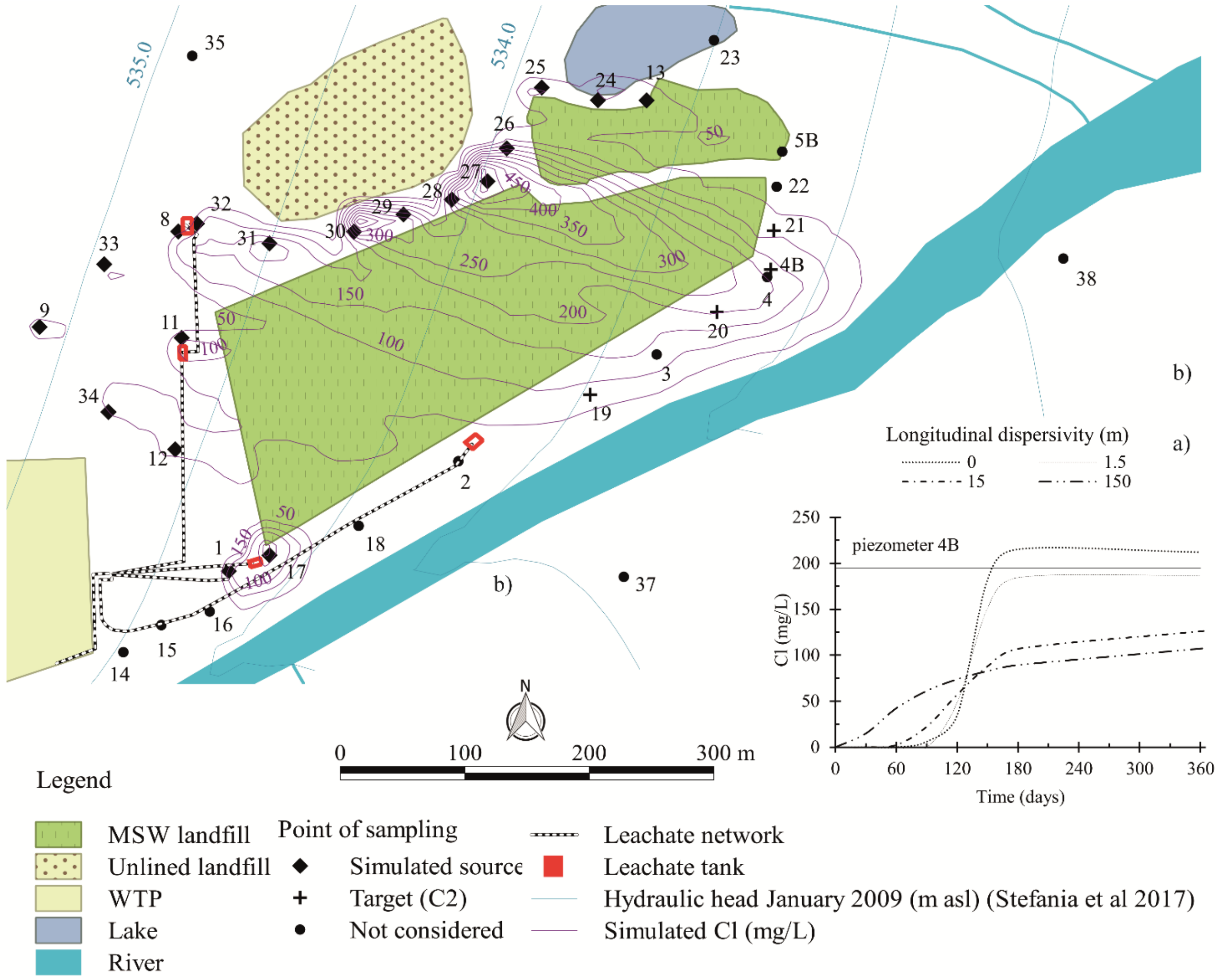

Fig. 8 – Results of the chloride transport model. a) Breakthrough curves of simulated Cl- in piezometer 4B using the different values of longitudinal dispersivity tested in the sensitivity analysis b) Map of the simulated Cl- plume that indicates which piezometers were used as pollution sources and pollution targets.

Table 1 - Comparison of simulated Cl^- (mg/L) against average measured Cl^- (mg/L) concentrations from 2011 to 2017. Targets are referred to piezometers belong to cluster 2.

Piezometer	Average measured (mg/L)	Simulated (mg/L)	Residual (mg/L)	Residual (%)	Discrepancy (%)
4B	195.00	186.87	8.13	4.17	4.26
19	105.49	86.40	19.08	18.09	19.89
20	92.37	202.72	-110.36	-119.48	-74.80
21	76.33	101.57	-25.24	-33.07	-28.38

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 2) the leachate collection system serving the MSW landfill. Therefore, the recommendations are:

- to check the sealing of the leachate collection system in order to identify and repair the spills of leachate;
- 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.

A particle tracking model was used to evaluate the feasibility of a drainage system downstream of the unlined landfill. Results of this model (for more details see the Supplementary Material) showed that an efficient drain could be obtained placing at a depth of 8 m bgl. (i.e. 533.0 m a.s.l) and for a length of 75 m some drainage material (i.e. coarse sand or gravel) with a conductivity of 200-300 m/d and a thickness of 1 m. This system is expected to drain about 2700 m^3/d of polluted groundwater from the unlined landfill. The connection of this drain to the existing WTP could be a reasonable solution since the drained water would increase of only ~6% the actual working discharge of the WTP.

IV. Conclusions

This work presented a detailed identification of pollution sources in groundwater in a landfill site. For each monitored point affected by leachate pollution, the proper source and cause of pollution was assessed. This was done using artificial sweeteners as tracers of leachate pollution, multivariate statistical analysis of hydrochemical data, particle tracking and transport modelling.

Our main findings are:

- artificial sweeteners can be successfully used to trace leachate plume from municipal solid waste landfills, moreover, due to their different marketed years, they are able to give some indications on the age of the leachate; indeed, the presence of SUC indicates that the leachate is sourced from landfill containing recent (after 2000) wastes, whereas its absence may characterize older leachate.
- However, a better understanding of the system under analysis can be given combining the use of artificial sweeteners with other tracers and/or investigative techniques, such as multivariate statistical analysis or transport modelling.
- Within the measured artificial sweeteners, ACE was the most frequently detected, thus it was able to give a more comprehensive description of the pollution.
- 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 can have a broad applicability since they can be reproduced in other polluted landfill sites worldwide.

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Supplementary material

Section S1 (Fig. S1) shows details on the settings and results of the model for simulating a drainage system collecting the unlined landfill plume. Section 2 shows the complete results of FA (Table S1 and Fig. S2). Section 3 shows the hydrochemical data resulting from the field survey of March 2017 (Table S2) and the average concentrations of Cl^- (2011-2017) used to simulate the sources of Cl^- in the transport model (Table S3).

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

Section S1. Settings and results of the model for simulating a drainage system collecting the unlined landfill plume

This section shows the results of particle tracking simulations aimed at designing a drainage system able to capture the leachate plume sourced from the unlined landfill. The simulations were performed using MODPATH (Pollock, 2012). The steady-state regional flow model by Stefania et al. (2017) was used as groundwater flow solution. The drainage system was simulated using the Drain package of MODFLOW (Harbaugh, 2005). The location of the drainage system was fixed on the basis on the limited available space between the unlined and lined landfills (Fig. S1). Starting locations of particles were set within the perimeter of the unlined landfill on the top of the water table. The two main parameters (i.e. drain bottom elevation and drain hydraulic conductivity) that affect the response of a drainage system were tested. In particular, two different values of drain bottom elevation (i.e. 533.5 and 533 m a.s.l.) and four drain hydraulic conductivities (i.e. 100, 200, 300, 400 m/d) were tested in order to check the capability of the drain to catch all particles. Conversely, drain thickness and drain total length were kept constant (i.e. 1 and 75 m, respectively). For both tested values of the drain bottom elevation (i.e. 533.5 and 533.0 m a.s.l.), four simulations were done varying the drain hydraulic conductivity (i.e. 100, 200, 300 and 400 m/d).

The simulated paths of the particles, the particles that overcome the drainage barrier and the overall outflow discharge of the drain are shown in Fig. S1.

As for the drainage system with the bottom elevation of 533.5 m a.s.l. (about 0.5 m below the water table) the increase of the hydraulic conductivity from 100 to 400 m/d induces an increase from 1200 to 1380 m^3/d of the overall groundwater discharge drained. Accordingly, the number of the particles which overcome the drainage system decreases from 8 to 4. Moreover, for a hydraulic conductivity of the drain of 100 to 300 m/d, the estimated plume aerial extent decreases from 51668 to 34986 m^2, whereas there is an increase to 41549 m^2 for the drain hydraulic conductivity of 400 m/d.

Moving the bottom elevation of the drain to 533.0 m a.s.l., all tested values of the drain hydraulic conductivity (i.e. 100, 200, 300 and 400 m/d) are able to prevent that particles overcome the drainage system. As for these last four configurations of the drain: the drained groundwater discharge for all tested values of the hydraulic conductivity is twice as high as for a bottom elevation at 533.5 m a.s.l.. As shown in Fig. S1f, the simulated drained groundwater discharges ranged between 2495 and 2857 m^3/d.

Important considerations arise from the comparison of the different drain settings (see Fig. S1 from a to d):

- The increase of the hydraulic conductivity allows to slightly increase the amount of the contaminated groundwater removed by the drain (Fig. S1f), however, it did not always led to a reduction of the plume extent (Fig. S1d).
- Concerning the drain located at 0.5 m below the water table: although the increase of the hydraulic conductivity from 100 to 300 m/d allows to decrease both the number of the particles able to overcome the drainage barrier and the plume extent, when the hydraulic conductivity was increased up to 400 m/d (Fig. S1d), the drainage system deviated some particles paths toward the north, increasing the plume extent.
- The main parameter that plays a key role in the optimization of the drainage system is the elevation of its bottom. Indeed, lowering the drain bottom down to 1 m below the water table (533.0 m a.s.l.), all particles were captured (Fig. S1e).
- However, an increase of the depth of the bottom of the drain leads, on one hand, to the increase of the costs related to its constructions and, on the other hand, to the increase of the amount of polluted water that has to be treated. On this basis, great attention has to be paid on the selection of the elevation of the drain bottom.
- In the area of the drain system, the discretization of the grid may be increased in order to better define the shape and the exact location of the drain. This improvement of the model may be done before the engineering phase of the remediation system and it could be implemented by using the unstructured grid scheme included into the new versions of MODFLOW such as MODFLOW-USG (Panday et al., 2013) or MODFLOW 6 (Hughes et al., 2017)

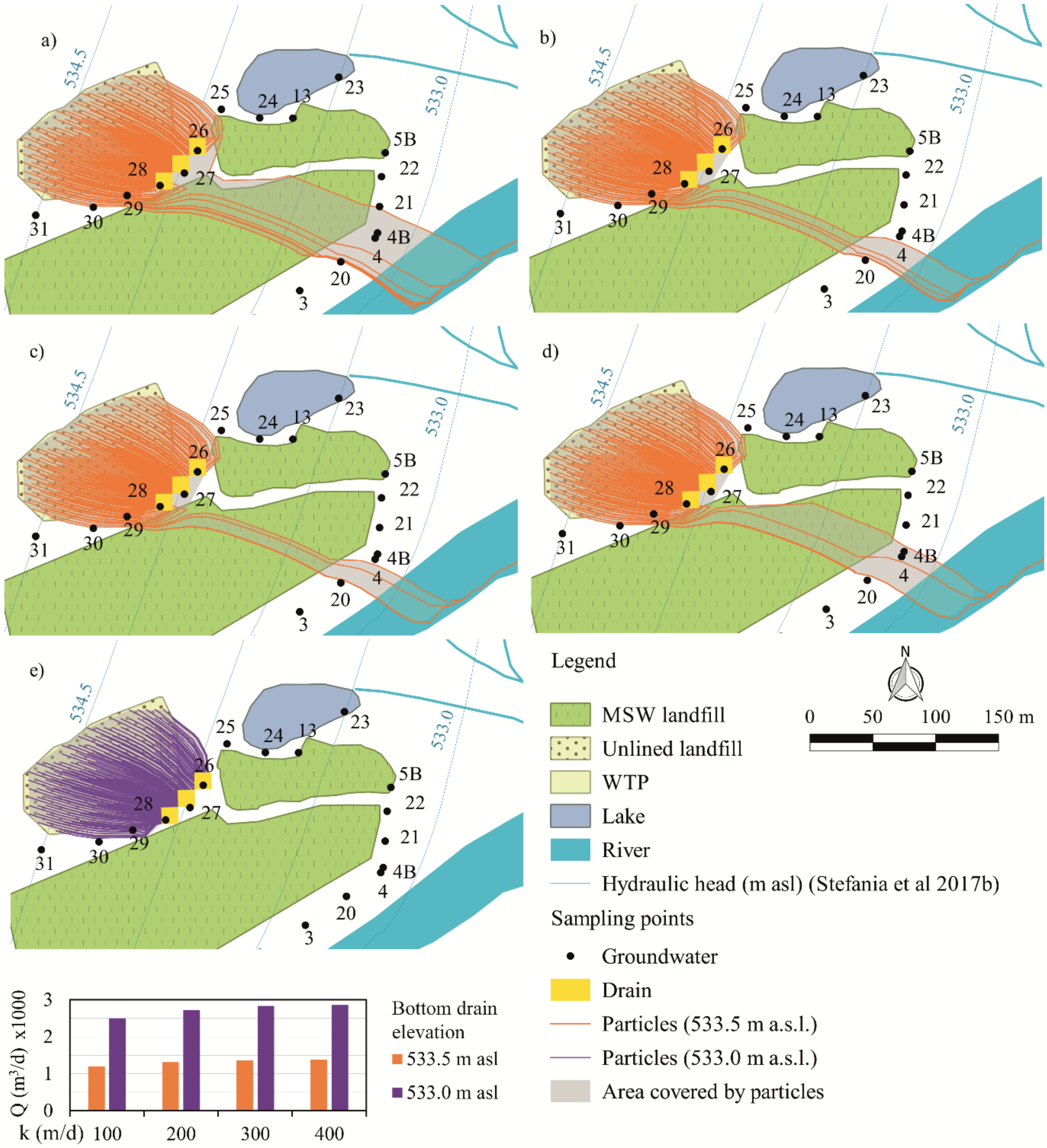

Fig. S1 - Results of different setting of the drainage system. a) Bottom elevation of 533.5 m s.l.m., Hydraulic conductivity 100 m/d. b) Bottom elevation of 533.5 m s.l.m., Hydraulic conductivity 200 m/d. c) Bottom elevation of 533.5 m s.l.m., Hydraulic conductivity 300 m/d. d) Bottom elevation of 533.5 m s.l.m., Hydraulic conductivity 400 m/d. e) Bottom elevation of 533.0 m s.l.m., Hydraulic conductivity from 100 to 400 m/d. f) Drained groundwater discharge: orange bar refers to drain bottom elevation of 533.5 m a.s.l., violet bar refers to drain bottom elevation of 533.0 m a.s.l

Section S2. Results of Factor Analysis

Table S1 - Loadings of variables of significant factors

	Factor (loadings)			
	1	2	3	4
COD	0.64	0.72	0.06	0.04
EC	-0.10	0.98	0.03	-0.03
P-tot	-0.04	0.97	0.03	0.12
pH	-0.03	0.03	-0.04	0.96
NO_3^--N	0.96	0.13	-0.01	-0.03
NO_2^--N	0.19	0.22	0.66	0.19
NH_4^+-N	-0.09	-0.06	0.84	-0.21
SO_4^{2-}	0.87	-0.07	0.09	0.21
Ca^{2+}	0.95	0.04	-0.04	-0.17
Mg^{2+}	0.61	0.59	0.02	-0.07
Na^+	0.69	0.68	0.17	-0.03
K^+	0.65	0.69	0.16	0.01
Cl^-	0.63	0.70	0.17	-0.01
Explaned varance	52.44	17.69	9.20	8.01
Cumulative explained variance	52.44	70.13	79.33	87.33

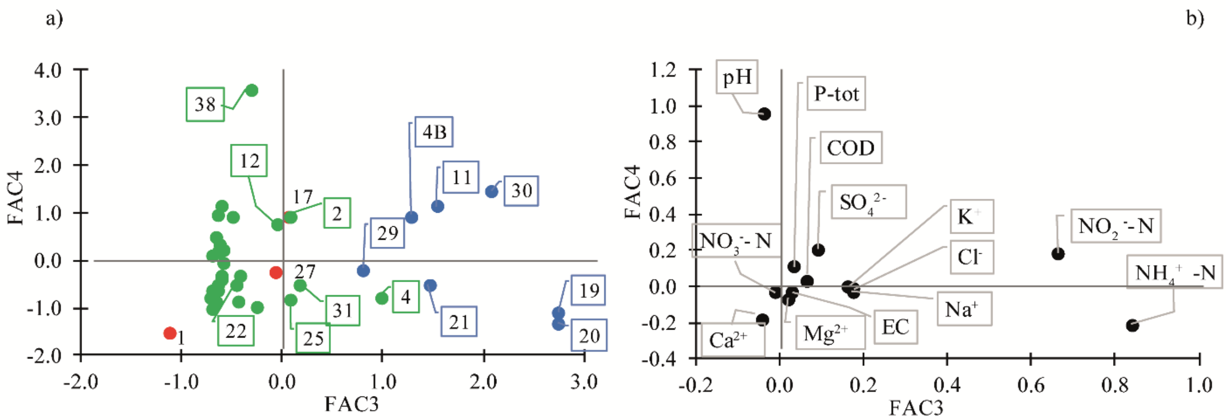

Fig. S2 - Score and loading plots resulting from factor analysis of groundwater hydrochemical data; scores are grouped into the three identified clusters (C1, C2 and C3). a) Score plot of FAC3 vs FAC4; b) Loading plot of FAC3 vs FAC4. See Fig. 4 for score plot and loading plot of FAC1 and FAC2.

Section S3. Additional tables

Table S2 – Hydrochemical data from field survey of March 2017- (-) Not measured. Groundwater (GW), surface water (SW), sewage effluent (SE), Leachate (L) samples.

ID	cluster	type	Data	T °C	pH	EC µS/cm	NO_3-N mg/L	NO_2-N mg/L	NH_4-N mg/L	COD mg/L	P-tot mg/L
1	1	GW	March 2017	12.0	7.10	3710	<0.0089	0.012	0.099	172.0	0.506
17	1	GW	March 2017	13.3	7.60	6260	5.370	0.080	1.420	444.0	1.840
27	1	GW	March 2017	13.8	7.21	1180	455.000	0.073	2.340	572.0	0.250
11	2	GW	March 2017	10.8	7.80	1580	0.875	0.079	54.000	140.0	0.344
19	2	GW	March 2017	14.9	7.06	1000	0.292	0.040	118.000	72.0	0.037
20	2	GW	March 2017	14.7	6.96	868	0.327	0.042	116.000	5.2	0.037
21	2	GW	March 2017	14.2	6.87	861	1.060	0.150	14.100	6.0	<0.0041
29	2	GW	March 2017	15.8	7.20	2140	1.420	0.091	17.500	28.0	0.169
30	2	GW	March 2017	14.6	7.60	1430	4.720	0.202	9.400	23.2	0.020
4B	2	GW	March 2017	13.8	7.70	1620	12.800	0.097	34.200	24.8	0.016
2	3	GW	March 2017	14.0	7.70	901	2.940	0.036	13.600	13.2	0.053
3	3	GW	March 2017	14.5	7.50	926	1.500	0.007	0.035	4.0	<0.0041
8	3	GW	March 2017	12.4	7.40	1440	4.840	0.008	0.141	8.0	<0.0041
9	3	GW	March 2017	12.9	7.40	744	2.320	0.007	1.470	2.8	<0.0041
10	3	GW	March 2017	14.3	6.89	1060	2.380	0.007	0.152	2.0	<0.0041
13	3	GW	March 2017	14.7	6.89	994	0.259	0.040	0.790	7.2	0.005
14	3	GW	March 2017	15.1	7.07	907	1.650	0.007	0.107	2.0	<0.0041
15	3	GW	March 2017	14.5	7.01	861	1.660	0.007	0.116	2.0	<0.0041
16	3	GW	March 2017	12.0	7.80	640	1.840	0.007	0.208	2.0	<0.0041
18	3	GW	March 2017	12.4	7.70	702	2.210	0.016	0.910	2.0	<0.0041
22	3	GW	March 2017	14.5	7.27	916	1.370	0.013	8.000	4.0	<0.0041
23	3	GW	March 2017	15.2	6.94	986	1.930	0.008	0.055	2.0	<0.0041
24	3	GW	March 2017	15.4	7.07	1180	1.440	0.017	0.152	2.8	<0.0041
25	3	GW	March 2017	15.0	6.89	1080	0.773	0.069	0.143	8.0	<0.0041
26	3	GW	March 2017	15.3	6.96	1150	0.883	0.029	0.100	5.2	0.019
31	3	GW	March 2017	15.6	7.21	997	3.400	0.009	30.400	4.0	<0.0041

32	3	GW	March 2017	15.3	7.19	967	3.340	0.007	0.134	3.2	<0.0041
33	3	GW	March 2017	15.4	7.12	869	1.640	0.020	0.216	29.2	0.056
34	3	GW	March 2017	15.9	7.38	1200	2.010	0.007	0.400	2.0	<0.0041
35	3	GW	March 2017	15.3	7.11	866	1.670	0.007	0.086	2.0	<0.0041
36	3	GW	March 2017	14.9	7.06	1100	1.660	0.008	0.031	2.0	<0.0041
37	3	GW	March 2017	9.2	7.80	511	1.960	0.007	0.109	3.2	<0.0041
38	3	GW	March 2017	10.0	8.80	333	0.017	0.010	4.600	2.0	0.018
39	3	GW	March 2017	13.0	7.60	671	2.240	0.007	0.143	2.0	<0.0041
5B	3	GW	March 2017	14.7	7.38	899	1.370	0.011	1.800	4.0	<0.0041
4	4	GW	March 2017	14.7	7.07	869	1.090	0.016	60.000	2.0	<0.0041
12	4	GW	March 2017	11.8	7.60	873	1.050	0.053	0.550	6.0	0.036
28	NC	GW	March 2017	-	-	-	-	-	-	-	-
701		SWE	March 2017	9.5	8.05	715	-	-	-	-	-
801		SW	March 2017	10.6	8.63	573	-	-	-	-	-
900		SW	March 2017	8.1	9.21	406	-	-	-	-	-
902		SW	March 2017	8.3	7.15	629	-	-	-	-	-
903		SW	March 2017	6.3	8.36	474	-	-	-	-	-
904		SW	March 2017	7.7	8.83	419	-	-	-	-	-
L1		L	January 2017	18.0	8.01	36500	<0.18	<0.02	4760.0	6960.0	21.30
L2		L	January 2017	18.0	7.74	34600	<0.18	<0.02	4190.0	8040.0	27.20
L3		L	January 2017	18.0	7.94	39400	<0.18	<0.02	5130.0	8120.0	31.40

ID	cluster	type	Data	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^{+} mg/L	K^{+} mg/L	Cl^{-} mg/L	SO_4^{2-} mg/L	SUC µg/L	ACE µg/L	CYC µg/L	SAC µg/L
1	1	GW	March 2017	153.91	80.95	218.71	123.67	360.00	9.90	3.00	9.69	29.56	5.44
17	1	GW	March 2017	22.17	40.36	444.60	312.30	548.58	83.74	<1.00	5.15	1.05	0.68
27	1	GW	March 2017	451.72	80.70	633.50	434.10	736.10	252.95	<1.00	4.55	0.85	<0.30
11	2	GW	March 2017	108.85	26.71	83.61	116.58	160.50	101.19	<1.00	0.82	0.14	<0.30
19	2	GW	March 2017	64.77	14.87	121.31	72.57	102.97	71.26	<1.00	1.71	<0.10	<0.30
20	2	GW	March 2017	63.54	13.86	116.34	74.50	124.03	66.94	<1.00	1.51	<0.10	<0.30
21	2	GW	March 2017	102.87	11.79	47.31	10.07	46.66	81.20	<1.00	<0.40	<0.10	<0.30
29	2	GW	March 2017	150.53	30.19	190.59	19.75	350.00	109.00	<1.00	<0.40	<0.10	<0.30
30	2	GW	March 2017	112.16	28.90	140.82	27.86	209.14	118.10	<1.00	<0.40	<0.10	<0.30
4B	2	GW	March 2017	116.62	36.77	116.09	31.43	200.00	102.00	<1.00	<0.40	<0.10	<0.30
2	3	GW	March 2017	97.72	16.84	46.86	13.95	89.00	97.50	<1.00	<0.40	<0.10	<0.30
3	3	GW	March 2017	99.45	12.79	66.71	6.70	92.07	86.36	<1.00	<0.40	<0.10	<0.30
8	3	GW	March 2017	135.79	24.88	114.18	4.86	221.47	112.00	<1.00	<0.40	<0.10	<0.30
9	3	GW	March 2017	93.04	12.85	30.98	2.72	59.00	98.87	<1.00	<0.40	<0.10	<0.30
10	3	GW	March 2017	101.43	17.16	47.10	4.14	31.16	116.91	<1.00	<0.40	<0.10	<0.30
13	3	GW	March 2017	77.13	10.11	32.94	8.72	54.85	58.16	<1.00	<0.40	<0.10	<0.30
14	3	GW	March 2017	83.98	13.02	14.89	2.36	27.88	98.53	<1.00	<0.40	<0.10	<0.30
15	3	GW	March 2017	84.19	13.11	15.03	2.31	27.63	100.23	<1.00	<0.40	<0.10	<0.30
16	3	GW	March 2017	85.08	13.06	20.43	2.48	30.93	97.97	<1.00	<0.40	<0.10	<0.30
18	3	GW	March 2017	90.13	13.33	28.36	3.27	17.27	96.10	<1.00	<0.40	<0.10	<0.30
22	3	GW	March 2017	107.35	13.44	50.63	6.95	56.38	70.26	<1.00	<0.40	<0.10	1.28
23	3	GW	March 2017	90.34	9.48	20.01	4.01	35.40	61.06	<1.00	<0.40	<0.10	<0.30
24	3	GW	March 2017	51.98	9.05	34.52	14.24	110.00	82.70	<1.00	<0.40	<0.10	0.50
25	3	GW	March 2017	101.89	12.71	60.37	6.67	46.02	76.84	<1.00	<0.40	<0.10	<0.30
26	3	GW	March 2017	104.37	12.09	55.18	6.35	33.99	74.79	<1.00	<0.40	<0.10	<0.30
31	3	GW	March 2017	129.51	16.58	119.98	4.95	223.69	97.75	<1.00	<0.40	<0.10	<0.30
32	3	GW	March 2017	130.16	16.90	103.34	5.23	200.00	109.00	<1.00	<0.40	<0.10	<0.30
33	3	GW	March 2017	134.44	37.53	38.15	3.17	37.56	120.53	<1.00	<0.40	<0.10	<0.30
34	3	GW	March 2017	82.88	11.68	21.19	2.27	23.43	96.44	<1.00	<0.40	<0.10	<0.30

35	3	GW	March 2017	86.49	8.59	14.53	3.01	19.00	61.40	<1.00	<0.40	<0.10	<0.30
36	3	GW	March 2017	87.32	8.45	14.36	2.80	16.25	56.98	<1.00	<0.40	<0.10	<0.30
37	3	GW	March 2017	57.57	11.15	13.58	2.54	21.00	50.90	<1.00	<0.40	<0.10	<0.30
38	3	GW	March 2017	27.79	10.17	9.52	4.51	10.00	98.60	<1.00	<0.40	<0.10	<0.30
39	3	GW	March 2017	95.66	9.40	21.79	3.92	40.00	66.90	<1.00	<0.40	<0.10	<0.30
5B	3	GW	March 2017	107.72	13.44	50.50	6.55	89.57	69.83	<1.00	<0.40	<0.10	<0.30
4	4	GW	March 2017	101.88	11.72	47.00	9.98	75.89	102.00	<1.00	<0.40	<0.10	<0.30
12	4	GW	March 2017	96.06	16.71	47.06	7.21	96.00	85.40	<1.00	<0.40	<0.10	<0.30
28	NC	GW	March 2017	112.44	40.55	153.75	81.94	266.82	96.76	<1.00	0.63	<0.10	<0.30
701		SWE	March 2017	65.51	12.71	50.83	8.81	46.97	100.79	3.43	7.05	0.32	0.53
801		SW	March 2017	85.73	10.10	18.27	2.72	36.41	78.85	<1.00	<0.40	<0.10	<0.30
900		SW	March 2017	58.72	8.24	10.97	1.42	8.17	100.92	<1.00	<0.40	<0.10	<0.30
902		SW	March 2017	64.81	11.74	39.47	6.81	37.29	100.19	3.21	4.93	0.12	<0.30
903		SW	March 2017	69.72	9.70	12.73	1.81	15.16	114.93	<1.00	<0.40	<0.10	<0.30
904		SW	March 2017	59.83	8.57	12.29	1.83	14.61	99.67	<1.00	<0.40	<0.10	<0.30
L1		L	January 2017	-	-	-	-	3550.00	20.10	-	-	-	-
L2		L	January 2017	-	-	-	-	3790.00	10.20	-	-	-	-
L3		L	January 2017	-	-	-	-	4140.00	11.80	-	-	-	-
L3		L	March 2017	-	-	-	-	-	-	0.15	-	-	-

Table S3 – Assigned values to simulate Cl^- sources. Values are the average of the measured concentrations of Cl^- from 2011 to 2017.

Piezometer	*Average measured* (mg/L)
1	251.37
11	144.25
12	59.18
13	54.85
17	358.29
24	88.56
25	121.01
26	116.50
27	566.55
28	425.41
29	327.13
30	246.35
31	509.07
32	140.95
33	57.13
34	90.22
8	164.74
9	74.65

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6. Conclusions

Groundwater resources are not an isolated system; indeed, they continuously interact with the surface-water bodies. Moreover, these resources are influenced by both natural and human activities that can change their quantitative and qualitative status for example through water withdrawal and contaminants release, respectively. For this reason, the need to design tools able to manage the water resources as an integrated system is growing. However, the implementation of these tools requires skills and times that do not fit the availability of the environmental managers. Therefore, the academic researchers have to gain a key role to provide these tools.

Accordingly, the main aim of this PhD was to apply the academic research on the management of the environment in particular on the groundwater resource. The PhD project was developed in collaboration with the Regional Environmental Protection Agency of the Aosta Valley Region using the Aosta Plain aquifer as a case study. In particular, this work dealt with the development of tools and strategies to support the management of the groundwater resource in order to ensure the preservation of its quantitative and qualitative status over the time.

The studied aquifer represents a particular hydrogeological context in which the interactions between groundwater and surface water as well as the well-pumping have a key role in the hydraulic behaviour of the aquifer. In addition, the hydrogeological setting of these aquifers makes groundwater highly vulnerable to contamination by human activities.

The work addressed three main hydrogeological topics concerning the qualitative and quantitative management of the Aosta Plain aquifer. In particular:

- the first topic regarded the comprehension of the groundwater/surface-water relationships, evaluating the overall effect of well-pumping on the water resources. For this purpose, the numerical groundwater flow model of the Aosta Plain aquifer has been developed aimed to identify and quantify the relationship between groundwater and surface waters and the effect of the well-pumping on the water resources;
- the second topic concerned the management of the groundwater hydrochemical data. This part of the work led to the development of an online hydrochemical database, called TANGCHIM. This database is coupled to an existing hydrogeological database (TANGRAM) to provide an integrated platform able to manage, display and share all available data related to wells and piezometers;
- the third topic considered the analysis of a groundwater pollution induced by the infiltration of leachate from a landfill site located in Aosta Plain. This topic conducted to: 1) the definition of a generalized methodology to support both the definition of the conceptual model of a contaminated site (in this case a landfill) and, at the same time, calculate trigger levels as

suggested to the European Landfill Directive (1999/31 / EC); 2) the identification of the types and the locations of the sources by which the landfill leachate infiltrates into subsoil affecting the groundwater quality, allowing a more efficiently managing of the contaminated site.

Overall, the treated topics led to the following outcomes which have to be considered in order to improve the management of the groundwater resource in the Aosta Plain aquifer.

I. <u>As regards to the groundwater flow model of the Aosta Plain aquifer, the main outcomes raised from the research work are the following:</u>

- the investigated aquifer is mainly composed of gravelly and sandy deposits with local silty-clay layers especially in the eastern sector of the Aosta Plain. The main aquifer lies on a discontinuous silty layer below which an unexploited aquifer contributes to the water availability and hydrogeological behaviour of the aquifer;
- the calibration phase of the model performed by PEST code suggested that the obtained three-dimensional reconstruction of the hydraulic parameters is able to reproduce the main aquifer heterogeneity. Moreover, the riverbed conductivity, Sy and Ss have turned out to be the more influential parameters to achieving a good fit on targets, especially in the transient solution;
- the recharge rate is typically highest during spring and summer seasons as a result of high precipitation and snowmelt. Moreover, the increase of the recharge during these periods allows the sharply rising of the water table elevation in the summer months;
- within the studied area, the relationship between groundwater and surface-water mainly depends on the seasonal water table elevation. Moreover, the Dora Baltea River changes its relationship with the aquifer flowing from west to east of the Aosta Plain. In particular, it acts as a source of water in the western area (upstream) and as a sink in the eastern area (downstream). In the upstream sector of the plain, the water table is always below the riverbed; moving downstream a transition sector was identified; in the downstream sector, the water table is always above the riverbed ensuring a constant gaining behaviour of the main river;
- the aquifer storage retains water during the higher availability water periods, whereas it becomes a source of water during the lower ones. Furthermore, the aquifer storage becomes a source of water for the pumping especially in the upstream area of the Aosta Plain, whereas its contribute become neglected in the downstream area;

- in the eastern sector of the Aosta Plain, where the Dora Baltea River is gaining, the wells pump water that, otherwise, would have flowed into the river. In this light, well-pumping acts as a depleting factor on the surface-water discharge, inducing baseflow depletion. However, the high discharge of the river is able to maintain the minimum flows of the main river in this sector of the plain;
- the western sector of the Aosta Plain is the better location for a new well to be drilled because pumping will affect the river discharge less than in the downstream area.

In conclusion, the obtained groundwater model showed that the use of a more complex boundary condition to simulate surface water (in this case the SFR2 Package), may be extended to a particular hydrogeological context like the Alpine valley aquifers where complex relationships between the river and groundwater could change over space and time due to natural factors (e.g. recharge) and/or human activities (e.g. well pumping). Moreover, the applied methodology allowed to evaluate the impact of the well pumping on the whole system in terms of both the water-table lowering and depletion of exchanged water between the river and aquifer. Furthermore, it is able to assess the origin of the water pumped by wells. However, groundwater model could be improved by a deepen hydrogeological and hydrochemical investigation of the deeper unexploited aquifer.
On the whole, the model provides a useful tool to decision-makers and stakeholders to understand, manage and quantify the aquifer and the streamflow depletion, not as separate entities, but by considering them as an integrated system.

II. <u>Concerning the hydrochemical data management, the main outcomes are:</u>

- data management cover a key role in the groundwater management. Accordingly, data integrity have to be preserved, data duplication have to be avoided, and data sharing have to promote;
- the developed hydrochemical TANGCHIM database addresses the need to manage, analyse and share hydrochemical data referred to groundwater samples. Hydrochemical data stored in TANGCHIM can be queried based on a single or a group of wells and by a single or a group of chemical compounds. Moreover, location and time can also apply to each of previous queries;
- TANGCHIM allows the users not only to store data, but also to analyse stored hydrochemical data by means of concentration time series graphs, box-plot graphs also computing simple statistical reports. These results can be obtained through its online interface accessible by all devices;

- the connection between TANGCHIM and TANGRAM (an existing hydrogeological well database (Bonomi et al., 2014)), allows to understand better the hydrochemical features related to a specific groundwater point of sampling since they provide the possibility to analyse, at the same time, both hydrochemical and hydrogeological data. On the whole, the integrated platform composed by TANGHIM and TANGRAM provides a useful tool especially for the groundwater managers (i.e. Regional Environmental Protection Agencies).

III-1. <u>The analysis of the groundwater pollution induced by the infiltration of leachate from a landfill site located in the Aosta Plain, led to the definition of a methodology to calculate trigger levels for monitoring the groundwater quality in a landfill site:</u>

In particular, the methodology to calculate trigger level involves the following six steps:

1. pre-processing of the initial dataset. This consists in the a) management of censored data and b) calculation of mean values for the time series of each monitoring point. Both operations should be applied for each chemical species contained in the dataset.
2. application of cluster analysis on the pre-processed dataset,
3. on the basis of the conceptual model of the study area, the obtained cluster have to classified in suitable or not suitable for the determination of the trigger level. Only suitable clusters are selected to be the base for the successive calculation of the trigger levels,
4. based on the type of waste stored in the landfill and/or leachate composition, a parameter, or a group of parameters, indicative of a possible contamination from the landfill under analysis is chosen for the trigger level calculation,
5. for each selected chemical parameter and for each suitable cluster, the whole time series of all the monitoring points forming a cluster are put together to form a new dataset that will be used for the trigger level calculation. For each of these datasets, an analysis for the identification and deletion of outliers (Hawkins 1980) should be done before calculating the trigger levels,
6. final calculation of the trigger value using statistical indicators such as the 90th percentile, 95th percentile, etc.

The develop and the followed application of the methodology to calculate trigger on the landfill site located in the Aosta Plain aquifer pointed out that:

- the hydrochemical data analysis performed on historical available data (2006-2010) is able to define the conceptual model of the groundwater pollution. In particular, the poor-quality status of the groundwater observed downstream of the lined landfill is due a degrading leachate plume sourced from the upgradient unlined landfill rather than a presumable leachate spill from the lined landfill itself. Indeed, groundwater is affected by typical contaminants which compose the landfill leachate such as nitrogen compounds, P-tot, COD, redox sensitive species (Fe, Mn and As);

- the application of the methodology to calculate trigger levels led to the determination of two trigger levels for COD and NH_4-N, the first one for a zone representing the background hydrochemistry (28 and 9 mg/L for COD and NH_4-N, respectively), the other one for the zone impacted by the degrading leachate plume from the upgradient unlined landfill (89 and 83 mg/L for COD and NH_4-N, respectively).

In conclusion, the hydrochemical data clustering could be considered a key statistical tool to improve the understanding of the hydrochemical feature of groundwater. In this light, the cluster analysis could allow optimizing groundwater monitoring network. Moreover, the proposed methodology for the quantification of the trigger level combines the use of data-driven methods (cluster analysis) on the historical data with the conceptual model on hydrogeology and human uses of the investigated area leading to the calculation of more reliable and usable trigger levels. The proposed methodology has a potential wide and worldwide applicability since landfills are frequently located in urban and/or industrial areas that can be already impacted by historical contaminations and the use of existing data from the landfill groundwater monitoring network makes this method simpler and cost-effective.

III-2. <u>The sources identification in the landfill site obtained by artificial sweeteners, multivariate statistical analysis, and transport modeling pointed out that:</u>

- hierarchical clustering performed on the hydrochemical groundwater data sampled in March 2017 together with the plot Cl *vs* K confirm the preliminary conceptual model of the landfill site obtained by using historical data. In particular, the piezometers of the landfill monitoring network are representing three different groundwater features: baseline hydrochemistry, severely polluted water by direct leachate infiltration and water lesser polluted by the degradation of the leachate plume. Moreover, surface water samples plot over groundwater samples indicates that the main regional river is not affected by the landfill pollution although it gains groundwater crossing the landfill site. This evidence could be related to the attenuation (i.e. dilution/dispersion/degradation) occurring along groundwater flow paths and within river flow;

- two different types of leachate reached groundwater: an older leachate from the unlined landfill characterized by higher NO_3-N and SO_4^{2-} and a younger leachate from likely spills of leachate from the lined landfill leachate collection system characterized by higher COD, EC and P-tot. The relationship between SO_4^{2-} and Cl^- confirms that the piezometers affected by leachate with different age show different composition in SO_4^{2-}. In particular, more recent landfill produces leachate with low content in SO_4^{2-};

- all considered artificial sweeteners (i.e. saccharin, cyclamate, acesulfame and sucralose) are able to trace landfill leachate infiltration in groundwater. In particular, sucralose (the more recently marketed sweetener) was detected only in piezometer affected by younger leachate. Acesulfame was the most found sweetener and it was able to trace the two main leachate spills affecting groundwater. Indeed, the concentrations detected downstream of the new landfill were always lower than the one found upstream. Accordingly, this evidence strengthens the hypothesis that no lack of leachate is occurring from the lined landfill;
- the transport model shows that the chloride concentrations reported by piezometers downstream of the lined landfill are not affected by leaks of leachate from the lined landfill. This statement is supported by the fact that the upstream simulated concentration is able to explain the concentration recorded downstream. Accordingly, no chloride input comes from the new lined landfill;
- the simulated drainage system could be an efficient system able to capture pollution from the old landfill, allowing a more reliable monitoring of MSW landfill. However, particle tracking simulations showed that during the design phase more attention would have to be paid to the bottom elevation of the drainage system in order to capture all groundwater affected by the old landfill.

In conclusion this work presented a detailed identification of pollution sources in groundwater in a landfill site assessing the proper source and cause of pollution for each piezometers of the landfill monitoring network. Artificial sweeteners can be successfully used to trace leachate plume from municipal solid waste landfills, moreover, they are able to give some indications on the age of the leachate.

A better understanding of a polluted site due to landfill leachate can be given combining the use of artificial sweeteners with other tracers and/or investigative techniques, such as multivariate statistical analysis or transport modelling. A detailed identification of pollution sources for each cluster or sub-group of monitored point leads to suggest effective and specific actions for remediate and improve groundwater quality in a polluted site. Moreover, in the case of multiple managers or owners of the different pollution sources identified, the proposed analysis could help in properly attributing the blame for pollution, on the basis of the polluter-pays principle.

7. Future developments

As a consequence of the topics facing this PhD project, some future research lines could be developed for each of these.
According to the European Directives (2000/60/CE and 2006/118/CE) a recent Italian national guideline (Percopo et al., 2017) suggests an integrated procedure to evaluate the quantitative status of an aquifer. In order to do that, the guideline requires the analysis of the different items of the hydrogeological water balance such as aquifer recharge, groundwater levels, wells withdrawal and surface water discharge. All of these items were an integral part of the developed groundwater flow model of the Aosta Plain. Accordingly, the groundwater flow model will be used to evaluate the quantitative status of the Aosta Plain aquifer.
Moreover, the numerical model could be further evolved in order to develop forecasting scenarios related to climate change that has gained a relative weight on the management of the water resources.

As regard to the hydrochemical TANGCHIM database, starting from the implemented synonymous table, an automatic procedure could be developed due to search and manage synonymous name of the chemical compounds. Another interesting procedure that could be implemented is related to the export of the stored data in a matrix format in order to easily prepare the data for multivariate statistical analysis. Moreover, TANGHIM is now in only Italian language, thus an English version could be developed.
As regard to the management of the landfill site, two main research lines could be developed. The first one could be related to the implementation of a reactive transport model using PHREEQC code (Parkhurst and Appelo, 2013) in order to simulate the fate of the infiltrated organic matter in groundwater by leachate spills from the old landfill. Before modeling, a vertical quantification of the involved redox-sensitive species should be mandatory in order to take into account the likely vertical flows within the wellbore or aquifer. This vertical characterization of the real plume will allow improving the reliability of the model results. The second research line could be related to the use of a different source apportionment methodology such as the Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) typically used for air pollution issues, comparing previous and new results in order to use this methodology also to groundwater pollution issues.

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8. Articles and presentation

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2. Stefania, G., Rotiroti, M., Fumagalli, L., Simonetto, F., Capodaglio, P., Zanotti, C., Bonomi, T. (2017). Modeling groundwater/surface-water interactions in an Alpine valley (the Aosta Plain, NW Italy): the effect of groundwater abstraction on surface-water resources. HYDROGEOLOGY JOURNAL, 26, 147-162. DOI:10.1007/s10040-017-1633-x
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Manuals:

1. Stefania, G.A., Zanotti, C., Rotiroti, M., Fumagalli, L., Bonomi, T. (2017). Determinazione del fondo locale nella falda della piana d'Aosta In *Linee guida per la determinazione dei valori di fondo per i suoli e per le acque sotterranee* – Manuale ISPRA (pp. C98-C104). Roma, Italia.

Articles in preparation

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

Communication to conferences

1. Rotiroti M., Bonomi T., Fumagalli L., McArthur J., Sacchi E., Taviani S., **Stefania G.A.**, Zanotti C., Patelli M., Soler V., Leoni B. (2017). Using Cl/Br ratios and water isotopes to trace aquifer recharge in a highly irrigated area, the Po Plain (N Italy). 44th IAH Congress - Dubrovnik (Oral presentation)

2. **Stefania, G.A.**, Rotiroti, M., Fumagalli, L., & Bonomi, T. (2017). Using the hydrochemical database TANGCHIM to manage groundwater quality data: the case study of a leachate plume from a dumping area. Flowpath 2017, 3rd National Meeting on Hydrogeology, Conference Proceedings, Cagliari, Italy (Poster)
3. Rotiroti, M., Bonomi, T., Fumagalli, L., Zanotti, C., Taviani, S., **Stefania, G.A.**, Patelli M., Nava V., Soler V., Sacchi E., Leoni B. (2017). Hydrochemical characterization of groundwater and surface water supported by multivariate statistical analysis: a case study in the Po plain (in Italy). Flowpath 2017, 3rd National Meeting on Hydrogeology, Conference Proceedings, Cagliari, Italy (Oral presentation)
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