Multi-scenario numerical modeling applied to groundwater contamination: the Popoli Gorges complex aquifer case study (Central Italy)

Modellazione numerica multi-scenario applicata alla contaminazione delle acque sotterranee: il caso dell’acquifero complesso delle Gole di Popoli (Italia centrale)

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Abstract: In this research, a multi-scenario numerical modeling was implemented to assess the effects of changes to abstraction patterns in the Sant’Angelo well-field (central Italy) and their implications on the aquifer hydrodynamic and the advective transport of contaminants. Once implemented and calibrated the steady-state numerical model by means of MODFLOW-2005, the well-field turning off scenario was modelled. In addition, the numerical results were analyzed by means of the post-processors ZONEBUDGET and MODPATH, to assess respectively the contribution of each hydrogeological feature to the total budget and the advective transport of contaminant particles. Comparing the two steady-state numerical models and the relative particle tracking analyses, the well-field turning off, although no longer acting as a hydraulic barrier, increased the residence time of contaminant particles and limited their mobility in the aquifer. Furthermore, the general decrease in groundwater abstractions also caused a higher increase in river flow, favoring contaminants’ dilution in surface water.

Introduction

The numerical modeling is widely applied to groundwater management issue which span from assessment of environmental sustainability from abstraction, pumping performance and groundwater storage and recharge (Ayvaz and Karahan 2008; Shammas 2008; Rossetto et al. 2018; Stefania et al. 2018).

Other applications of numerical modelling include the validation of conceptual models for a given hydrogeological context (Rojas et al. 2008; La Vigna et al. 2014; Caschetto et al. 2016; Viaroli et al. 2018a), which improves the understanding of the aquifer system.

Numerical modelling of contaminant fate and transport in groundwater is not of least importance (Greskowiak et al. 2006; Mastrocicco et al. 2012; Refsgaard et al. 2012). Such studies aim to study the evolution of groundwater contamination in the subsurface and support the planning of remedial actions as well as assessing the success of such interventions.

The transport of contaminants in aquifers is widely covered in literature (Freeze and Cherry 1979; Beretta 1992; Fetter 2000; Appelo and Postma 2005) and is connected to several hydrodynamic and hydrogeochemical factors. Most of the factors affecting the movement of contaminants in groundwater tend to slow the downstream movement of the contaminant except for advection, which is directly related to...
the aquifer velocity. Advective transport is clearly related to changes in the hydrodynamics of the aquifer which, in turn, are influenced by changes in the abstraction patterns.

The main objective of this study is to assess the effects of changes to abstraction patterns, which occurred between 2007 and 2008, to the advective transport of groundwater contaminants within an aquifer contaminated with organochlorates. The validation of the hydrogeological conceptual model was also a critical objective of the study. A simplified approach was adopted: two scenarios with different boundary conditions (steady-state models) were compared. The simplified approach provides important indications on the contamination spread in the aquifer, mainly because the advective transport influences the downstream movement of a contaminant. Therefore, considerations made in this study can be extended to other cases of groundwater contamination.

**Study area**

The study area coincides with the Popoli Gorges (PG) at the confluence between the Pescara River and the Tirino River (Central-Eastern Apennines; Fig. 1). There is a significant anthropogenic influence in the area given its strategic location. Critical traffic routes, a hydroelectric plant, a well field (i.e. the Sant’Angelo well field, SAWF) and a chemical industrial site (i.e. the Bussi Officine site, BOS), now no longer active, are all located in the area. Industrial wastes from the latter chemical industrial site were buried near the Pescara River and have now contaminated the groundwater in the area (Di Molfetta & Fracassi 2008; Filippini et al. 2018). Due to this contamination, the well field (approximately 300 l/s; Rusi 2007) was turned off in 2008 and the PG were declared a Site of National Interest (SNI).

Geologically, the area is characterized by a deeply incised riverine valley, which has cut through the Morrone limestone massif. The valley was subsequently filled with quaternary heterogeneous continental deposits (Massoli-Novelli et al. 1998; Conese et al 2001; ISPRA 2006a, 2006b). The Morrone massif is a limestone structure (Triassic-Miocene), mainly limestone or grain supported facies, that overlies more recent clayey-marly formations due to a NW-SE thrust (Conese et al. 2001; ISPRA 2006a, 2006b). Distensive tectonic structures are also present with a NW-SE trend. These structures run below the continental deposits in the PG and disarticulate the limestone massif.

The quaternary continental deposits have a thickness that varies between 65-100 m. These lithologies are variable in nature, depending on the depositional environment (Di Curzio et al. 2016; Vessia and Di Curzio 2018). Specifically, coarse head deposits (i.e. breccias, locally cemented) have been identified. These are associated with the erosion of the limestone massifs in the area and lie on the limestone and clayey-marly bedrock formations. Different travertine facies are found lying over the head deposits. These vary from solid concretions of travertine with cavities to travertine sands. In the western areas, the travertine deposits are incised and infilled with silty-sandy lacustrine deposits and peat, which are locally more clayey. Alluvial deposits are present with discontinuity at the surface across the whole study area. Each geological body present in PG represents a hydrogeological complex of the corresponding aquifer.

Previous studies (Boni et al. 1986; Massoli-Novelli et al. 1998; Conese et al. 2001; Rusi, 2007; Petitta et al. 2018) have identified that groundwater circulation occurs mainly in the continental deposits. The recharge to these...
continental deposits is primarily from the limestone massif and subsequently from rainfall recharge. Surface water-groundwater interactions are known to occur between the Pescara River and the aquifer (Chiaudani et al. 2017). In fact, strong flow increases are observed near SAWF (Fig. 1). This increase in flows has been estimated to be between 0.6 and 1 m³/s (Boni et al. 1986; Massoli-Novelli et al. 1998; Conese et al. 2001; Rusi 2007). Periodic monitoring of groundwater levels in the area of confluence between Pescara River and the Tirino River (Di Curzio et al. 2014) has identified that changes in groundwater levels correlate with changes in river levels, especially during high flow events.

Dataset

The geometries of the geological bodies that constitute the aquifer were identified through the detailed hydrogeological characterization discussed in Di Curzio et al (2014). This represents the starting point for implementing the numerical model. 32 hydrogeological cross-sections (Fig. 1) were developed utilizing available geological surveys (i.e. borehole logging) and geophysical surveys (i.e. geoelectrical surveys). These were undertaken by Autostrade S.p.A. during the construction of the Pescara-Roma motorway and by ACA S.p.A. for the development of the SAWF. Surveys from ARTA (“Agenzia Regionale per la Tutela dell’Ambiente”; the Regional Environmental Protection Agency) of Abruzzo Region for groundwater monitoring, following the identification of contamination, were also sourced. Survey results from all those companies that have had their activities in the industrial area were also used for the development of the hydrogeological sections.

Groundwater level data used for model calibration purposes were from the monitoring undertaken during the summer of 2007 (Rusi 2007; Di Molfetta and Fracassi 2008). Data from the “Popoli” rain gauge and the “Pescara at Maraone” hydro-metric station, located just upstream of the study area, were used to derive respectively the recharge data (model input) and relationships for surface water-groundwater interaction.

Spring discharges available from literature (Boni et al. 1986; Massoli-Novelli et al. 1998; Conese et al. 2001) were used for the water balance outputs. Abstraction data from the SAWF and from the hydraulic barriers developed in the industrial areas were also used as outputs (Rusi 2007; Di Molfetta and Fracassi 2008).

Topography (e.g. stream bed elevation) was implemented in the model using DTM LiDAR 1x1 m data for the Abruzzo Region, provided by the Ministero dell’Ambiente e della Tutela del Territorio e del Mare (MATTM) and distributed under Creative Commons licence.

From the conceptual model to the numerical model (methods)

Steady-state simulations were undertaken to refine the hydrogeological characteristics of the area and to validate the conceptual model. Boundary conditions were subsequently changed to assess the effects of the SAWF turning off.

The numerical model was developed utilizing the MODFLOW-2005 finite difference code (Harbaugh 2005), and the Visual MODFLOW Flex 4.1 graphical user interface. The conceptual model was developed into a numerical model in different phases, as summarized in Fig. 2 for one of the 32 hydrogeological sections.

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The hydrogeological sections developed from Di Curzio et al (2014) were first digitized in vectorial format, then imported and georeferenced within the MOVE Midland Valley software. Subsequently, the tops of the different geological formations were digitized. Some geological bodies have limited thickness and lateral extension from a hydrogeological point of view (e.g. soil). These were included in larger hydrogeological bodies with similar hydrogeological properties. To digitalize the top of the geological bodies, Inverse Distance Weighted (IDW) interpolation was used within MOVE to construct the surfaces, then processed within Visual MODFLOW Flex in order to derive the volumetric extension of the geological bodies (Fig. 3) and the subsequent volumetric gridding of the various model layers (Fig. 2c and 4).

A semi-uniform grid was adopted to obtain a discretization that would be representative of the complex geology of the area. Such a grid allows representing complex geometries like pinch-outs, erosive truncation of geological bodies and general lateral discontinuities and changes in lithologies. The layers that result from such a gridding process have variable thickness that are a function of the hydrogeological units represented in the model. The grid is made of 15 layers with variable thickness (Fig. 2c e 4). Each layer has cells of constant 15x15 m dimensions. Each of them was automatically assigned

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Fig. 3 - 3-D representation of some of the geological bodies present derived from the vectorization of the hydrogeological sections. 1) lacustrine deposits; 2) travertine deposits; 3) head deposits; 4) bedrock.

Fig. 3 - Rappresentazione 3-D di alcuni dei corpi geologici presenti, derivante dalla vettorializzazione delle sezioni idrogeologiche. 1) depositi lacustri; 2) depositi travertinosi; 3) depositi detritici di versante; 4) substrato.

to a specific property zone to permit a more efficient model simulation (Fig. 4).

Hydrogeological parameters were assigned to each property zone (Tab. 1). Specifically, horizontal hydraulic conductivity ($K_x$ and $K_y$), vertical conductivity ($K_z$) and effective porosity ($n_e$) were assigned. These are all necessary with steady-state numerical modelling and particle tracking procedures undertaken with the MODPATH post-processor (Pollock 2012). Initial horizontal hydraulic conductivity values were taken from literature (Rusi 2007, 2014; Gargini et al. 2015) and were optimized during the calibration phase, where horizontal isotropy was chosen ($K_x = K_y$). An anisotropy ratio $K_x/K_z$ equal to 10 was selected for the vertical conductivity, as suggested by Todd and Mays (2005). Effective porosity values ($n_e$) were obtained from Singhal and Gupta (2010).

The boundary conditions (Fig. 5) were set after defining the grid and the hydraulic properties of the various zones, attempting to represent the system as realistically as possible. Each hydrogeological element was simulated using different boundary conditions:

- General Head Boundary (GHB) conditions were adopted using hydraulic head distributions taken from literature (Boni et al. 1986; Massoli-Novelli et al. 1998; Conese et al. 2001; Rusi 2007; Desiderio et al. 2012) and the optimized hydraulic conductivity of corresponding deposits to simulate recharge from the Morrone and Roccatagliata massifs. This boundary condition was used along the boundaries of the active grid, only where the limestone bedrock is present, and both upstream and downstream of the continental deposits.

- River (RIV) boundary conditions, used to simulate river features, that interact with groundwater in different parts of the study area. River sections were divided into various segments to improve the simulation of the surface groundwater interactions. Each segment has different properties, including river hydraulic head, elevation of the streambed, thickness and vertical conductivity of the streambed deposits and width of the river. These river

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**Tab. 1 - List of hydrogeological complex present and their respective property zone of the active grid.** The hydraulic conductivity values ($K_x$, $K_y$, $K_z$) are in m/s; the effective porosity ($n_e$) is dimensionless.

| Hydrogeological complex | Zone | $K_x$=$K_y$ | $K_z$ | $n_e$ |
|-------------------------|------|------------|------|-------|
| Alluvial deposits (near the SAWF) | 1 | $1.0 \times 10^{-4}$ | $1.0 \times 10^{-5}$ | 0.25 |
| Travertine deposits | 2 | $5.0 \times 10^{-3}$ | $5.0 \times 10^{-4}$ | 0.30 |
| Head deposits | 3 | $8.0 \times 10^{-3}$ | $8.0 \times 10^{-4}$ | 0.30 |
| Weathered limestone | 4 | $8.0 \times 10^{-3}$ | $8.0 \times 10^{-4}$ | 0.20 |
| Lacustrine deposits (near the BOS) | 5 | $6.5 \times 10^{-6}$ | $6.5 \times 10^{-7}$ | 0.12 |
| Lacustrine deposits (near the SAWF) | 6 | $3.0 \times 10^{-6}$ | $3.0 \times 10^{-7}$ | 0.12 |
| Alluvial deposits (near the BOS) | 7 | $5.0 \times 10^{-4}$ | $5.0 \times 10^{-5}$ | 0.20 |
features were chosen calibrating the numerical model.

- Well (WEL) boundary conditions were used to simulate abstraction from boreholes and from the hydraulic barriers. The SAWF boreholes, abstracting 300 l/s, and two pump and treat hydraulic barriers, constituted of a total of 13 boreholes (abstraction rates varying between 0.8 l/s and 1.4 l/s) installed in the BOS, were active during the summer 2007 monitoring campaign. This boundary condition was switched off in the second scenario and simulated the SAWF turning off (-300 l/s) following the identification of groundwater contamination. It is important to highlight that the pumping wells in the SAWF have lengths ranging from 32 m up to 63 m. Their filters start at a depth ranging from 6 m to 31 m and reach the bottom in each well. With this set up, the SAWF wells drain groundwater from alluvial deposits, head deposits and fractured limestone. The corresponding layers are variable, although the pumping wells are always located between the 2nd and the 7th layer.

- Recharge (RCH) boundary conditions were used to simulate rainfall recharge. Recharge was initially estimated from the analysis of 1951-2009 rainfall and temperature time-series using the Thornthwaite and Mather (1957) method and with reference to consolidated estimates from literature (Conese et al 2001; Nanni and Rusi 2003; Viaroli et al. 2018b). A constant recharge of 235 mm/y was applied across the entire model area.

The reliability of the calibration, corresponding to the selected combination of parameters and boundary conditions, was validated using specific criteria and statistics (Wels et al. 2012; Anderson et al. 2015):

- the flow paths and the hydraulic gradients must be comparable with the ones observed in field measurements;
- the Mass Balance Error (MBE) must be less than 1%;
- the Normalized Mean Absolute Error (NMAE) must be less than 10%;
- the Normalized Residual Mean (NRM) must be less than 5%;
- the Normalized Root Mean Square Error (NRMSE) must be less than 10%.

**Local water budget**

In order to evaluate the specific contribution of each hydrogeological feature to the total budget of the PG aquifer, inflow and/or outflows from the different boundary conditions were calculated by means of ZONEBUDGET (Harbaugh 1990). This MODFLOW post-processor allows to calculate the water budget in every zone of the model domain.

**Particle tracking**

To evaluate the effects of the SAWF turning off on the advective transport in groundwater, the particle tracking, using MODPATH (Pollock 2012), was performed. The MODPATH post-processor calculates the forward path of each particle and its residence time in the aquifer, starting from hydraulic head and module flux distribution in the numerical domain.

Contamination at the Bussi Officine SN1 is mainly related to industrial waste product burials containing chlorinated solvents (Di Molfetta and Fracassi 2008; Filippini et al 2018), that are DNAPLs (Dense Non-Aqueous Phase Liquids). The industrial wastes dump is characterized by a thickness ranging from about 2 m and up to more than 10 m. During the selected time period (i.e. 2007-2008), it was not physically separated from the host rocks, allowing the leaking of chlorinated solvents into the aquifer. These compounds are characterized by low solubility in water and high tendency to be adsorbed on the solid matrix. Furthermore, they move downward into the aquifer, even in the saturated zone, and accumulate at the bottom, releasing slowly chlorinated solvents in groundwater (Beretta 1992; Fetter 1994; Appelo and Postma 2005). In order to reproduce this behavior, the particle starting points were located vertically under the industrial waste dump.

**Steady-state numerical model**

Below, the results of the numerical model related to summer 2007 monitoring (Scenario 1) are shown, when the SAWF was active. The comparison between simulated and measured hydraulic heads (Fig. 6) and the evaluation statistics (Tab. 2) confirm the hypothesized conceptual model and validate the boundary conditions selected to reproduce every hydrogeological feature of the study area, in
terms of hydraulic conductivity distribution, surface-water-groundwater relationships, recharge from the limestone aquifer, groundwater abstractions, and recharge. However, although statistics are always below the suggested thresholds (Tab. 2), sometimes the simulated hydraulic head differs substantially from the measured one (mean error > 1.5 m; Fig. 6). This difference could be ascribable to: i) the intrinsic variability of hydraulic properties within each geological body, especially for coarse head deposits and travertine facies; ii) the lack of accurate information about main rivers, in terms of geometry of river bottom, thickness and hydraulic conductivity of the hyporheic zone, river level distribution within the study area.

Analyzing the numerical modeling results, the hydraulic head distribution (Fig. 8a) related to Scenario 1 suggests that surface water-groundwater interactions exist near the confluence of Pescara and Tirino Rivers. Surface water leaks about 0.107 m$^3$/s into the aquifer, 0.001 m$^3$/s of which from Pescara River and 0.106 m$^3$/s from Tirino River. These results are consistent with the hypothesized conceptual model. In fact, Tirino River recharges the shallower aquifer layers (i.e. alluvial deposits), present beneath the BOS. Instead, Pescara River appears hydraulically connected to groundwater, but it does not leak water into the aquifer.

The surface water-groundwater relationship is reversed near the SAWF. Here, the hydraulic head distribution suggests that groundwater flows into the Pescara River feeding the increase in river flow reported in literature. Its discharge, calculated in the numerical modeling, is equal to 0.760 m$^3$/s, as previously measured.

The calculated inflow from the Morrone carbonate aquifer is equal to 0.750 m$^3$/s. Nevertheless, this inflow seems to be located mainly near the thrust, where the coexistence of a highly fractured rock mass and a groundwater barrier (no flux) facilitate groundwater discharge into the PG aquifer. This is also confirmed by the modeled hydraulic head distribution in the central part of the study area, where, even though the General Head Boundary (GHB) is present, groundwater does

| Evaluation parameter | Threshold | Calculated value |
|-----------------------|-----------|------------------|
| MBE                   | < 1%      | 0.02%            |
| NMAE                  | < 10%     | 6.47%            |
| NMR                   | < 5%      | 2.33%            |
| NRMSE                 | < 10%     | 7.17%            |

Tab. 2 - Evaluation statistical parameters related to the numerical model, compared with the threshold values (Reilly and Harbaugh 2004; Wels et al. 2012; Anderson et al. 2015).

Fig. 7 - Module flux (in m/s) distribution (b and d) within the cross-sections 10T (a) and 15T (c). Traces of the cross-sections in Fig. 1; vertical exaggeration 2x.
not seem to interact with the carbonate aquifer.

In addition, the groundwater abstraction effect, from the SAWF and the hydraulic barriers in the BOS, is very clear, since it warps the water table.

As expected in such a heterogenous aquifer, the groundwater flow is not homogeneous. Analyzing the module flux distribution (i.e. the specific discharge in each cell; defined as \( v = K \ast i \), where \( K \) is the hydraulic conductivity and \( i \) is the hydraulic gradient) in the cross-sections (Fig. 7), it appears that the module flux is higher within head deposits and weathered bedrock (about \( 9e^{-5} \) m/s, maximum value about \( 1.2e^{-4} \) m/s) than within travertine deposits (about \( 6e^{-5} \) m/s). Lacustrine deposits, instead, show very low module flux values, confirming their role as aquitard. In addition, in Fig. 7d, the very high value (about \( 1.8e^{-4} \) m/s) refers to the increase in river flow.

**Effects of changes to groundwater abstraction pattern**

The SAWF turning off has caused significant changes in the PG aquifer hydrodynamic and in the advective transport, whose effects were assessed by means of the numerical modeling. Starting from Scenario 1, groundwater abstraction from the SAWF was excluded (Scenario 2).

Comparing the hydraulic head distributions obtained from the two simulations, differences between the two scenarios are evident, near the SAWF and the increase in river flow. In Scenario 2, the groundwater flow seems to converge more sharply towards the Pescara River than in the Scenario 1. In fact, the discharge of the increase in river flow for Scenario 2 is equal to 0.93 m\(^3\)/s (about 22% more than in Scenario 1).

The particle tracking results for the two scenarios (Fig. 8 and 9) show significant differences, especially in the central-eastern part of the study area. Starting from the industrial wastes dump, particles move mostly within the head deposits and the weathered bedrock (Fig. 8a, 8b, 9a and 9b). Near the increase in river flow, most of the particles (66.7%) flows into the Pescara River, in both scenarios (Fig. 8c and 9c, Tab. 3). When the SAWF is active (Scenario 1), the remaining part of the particles flows into the pumping wells (24.4%) and, a lesser part (8.9%), downstream in groundwater (Fig. 8c). In Scenario 2, instead, all the remaining particles (33.3%) flow downstream in groundwater (Fig. 9c).

Tab. 4 shows that the SAWF turning off causes an increase in residence times, especially for minimum values (\( t_{\text{min}} = 106 \))...
This effect is clearly related to the substantial groundwater flow decrease (Fig. 10), that takes place as a result of the SAWF turning off. The module flux variation is evident mostly near the SAWF (Fig. 10c and 10d), while it is not significant upstream (Fig. 10a and 10b), near the confluence between the Pescara River and the Tirino River. This suggests that the cone of depression has a relatively small size, although the pumping rate is 300 l/s.

All these differences in hydrodynamic features between the two scenarios have important implications on the advective contaminant transport of the Bussi Officine SNI. In Scenario 1, although the pumping wells of the SAWF act as a hydraulic barrier limiting the contamination spread in groundwater downstream, groundwater abstraction decreases the particle (i.e. contaminants) residence times and facilitate their mobility in the aquifer. On the contrary, in Scenario 2, the decrease in groundwater flow slows down the particle motion in the aquifer, even if the total amount flowing downstream is higher than in Scenario 1. In addition, although the number of particles flowing into the Pescara River is the same in both scenarios (Tab. 3), the higher increase in river flow, caused by the SAWF turning off, favors dilution in surface water, decreasing the contaminants’ concentration represented by the particles.

**Conclusions and future developments**

The hydrogeological modeling results confirmed the great capability of numerical methods in very complex geometry of geological bodies, as in Pupoli Gorges.

Useful information could be obtained about the effect of
the abstraction variations on the aquifer hydrodynamic and the advective contamination transport in groundwater. In fact, the comparison of the two steady-state numerical models and their particle tracking analyses allowed to assess that: 1) the Pescara River is the most important target for the particle that represent in a simplified manner contamination (i.e. only advective transport), regardless of the activity of the well field; 2) the well field, active until 2007, acted as a hydraulic barrier, limiting the contamination spread in groundwater downstream; 3) nevertheless, the cone of depression of the well field decreased the particle (i.e. contaminants) residence times and facilitate their mobility in the aquifer; 4) the well field turning off, although no longer limiting the contamination spread in the aquifer, caused an increase in residence time of particles; 5) the general decrease in groundwater abstractions and their particle tracking analyses allowed to assess that: 1) the abstraction variations on the aquifer hydrodynamic and the advective contamination transport in groundwater.

Even though the implemented numerical modeling provided useful information, further developments could be obtained modeling the effect of the wells’ turning off on the groundwater contamination by means of an advective-reactive-dispersive transport modeling in transient conditions, that is the next step in this research project.
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