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Hydrogeological problems for the rehabilitation and re-utilisation of the water resources of the mining area of Gavorrano (Italy)

C. A. Garzonio · A. M. G. Affuso

Abstract The paper describes the hydrogeological problems linked to the rehabilitation and re-utilisation of the water resources of the mining area of Gavorrano (Tuscany, Italy). It shows how the geological settings of the area control the water quality, chemistry and discharge. The results of the studies and the recent situations concerning circulation, quality and discharge of the mine water are reported, with particular reference to the effects of the controlled water rebound and the complex measures necessary for the dewatering stoppage. Water rebound is analysed on the basis of available historical and recent data for its hydrodynamic influence and the consequences on water resources restoration. Different uses and possible actions are proposed, taking into account thermal, chemical and discharge characteristics as well as local planning objectives.

Keywords Mine · Groundwater · Rehabilitation · Mine water re-utilisation · Italy

Introduction

Over the last few decades mining activity has decreased progressively in Italy, as in many other countries. The decommissioning of a mine triggers a series of problems

regarding social safety, health and the economy. Therefore, the closure of a mine is regarded as an environmental threat and an economic problem. Mine water drainage is a problem during mining but also after mining activities has completely ceased. When a mine is abandoned and dewatering by pumping is discontinued, the water level rebound and groundwater reoccupies geological formations in an attempt to re-establish an old water circulation system. Nevertheless, mining acts as a drainage and percolation system, so that the water can rarely return to its original conditions and circulation path. Water level recovery after exploitation causes different problems for the stability of underground openings, but in particular for the environment and the reconstitution of groundwater resources. Acid mine drainage is one of the most common consequences associated with mining operations and with the oxidation of sulphide minerals (e.g. pyrite) during exposure to air and water (Banks and others 1996; Bell and Bullock 1996; Crosta and Garzonio 1998a). This exposure can occur in a mine or in spoils or mineral stockpiles. If no acid drainage is produced, the presence of toxic elements, metal or salts could exclude the uncontrolled discharge of these waters and their use for different purposes. At the same time, the recovery and re-utilisation of mine drainage waters show some very interesting aspects, especially where increased water resources are required because of increasing demand.

The case history described in the paper deals with the decommissioning of the Gavorrano mine located in the Colline Metallifere mining district (southern Tuscany). The Gavorrano mine was one of the largest pyrite mines in Europe throughout the last century. Production ceased in 1981 and since then the mine has been under maintenance. The company is trying to give up its mining concession by adopting the safety measures required by the Bureau of Mines for the decommissioning. A multipurpose study was set up in 1995 to evaluate the possibilities of creating a natural reserve and mining park by recovering the mining area and all its historical mining structures. The environmental rehabilitation of the area includes quarries (with trekking and rock-climbing tracks and the construction of an open-air theatre), tailing ponds, the reforesting and stabilisation of spoil dump areas, and the restoration of significant, old mining structures. A major aspect of the

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rehabilitation involves the evaluation of the stability of slopes and underground openings as well as that of the pollution deriving from acid mine drainage resulting from the mining activity and the recovery of water resources. In particular, the paper describes the dewatering operations, and the recent effects of the water level rebound and the evaluation of the groundwater volume storable within the mine under safe conditions. The water drainage problem was analysed starting from the hydrogeological scheme of the area, through historical data concerning water springs and water level recovery, and moving on to hydrochemical data. The analysis of this case history, like the ones in the literature (Civita and others 1983, 1994; Banks and others 1996), shows the importance of groundwater level monitoring during and after mining activity in estimating rebound potential, and the need to keep records of water hydrochemistry throughout the mining activity to assess the potential for acid generation on closure. With respect to previous studies (Crosta and Garzonio 1998b; Garzonio 2000), the paper reports the results of a deep sounding and the construction of a new pumping point in the depth of the Rigoloccio mine, by drilling the base of an ancient shaft. A series of samplings was performed over the last few years to complete the dataset already available and to allow highlighting of the evolution of the water condition. The present research is financed by the local council, the objective being to obtain European financing to carry out the rehabilitation project.

Geological and hydrogeological outlines

Gavorrano is in south-western Tuscany, in the Metalliferous Hills (Colline Metallifere), 150 km south of Florence and a few kilometres from the sea. The area is character-

ised by rapid topographic changes passing from a very flat plain (Follonica gulf, Pecora River valley) up to rocky hills with a maximum elevation of about 500 m a.s.l.

(Mt. Calvo). The Mt. Calvo ridge is just above the village of Gavorrano and it is linked to the lower relief of the Finoria hill. The area is characterised by NNW–SSE-elongated post-orogenic basins developed over an antecedent extensional horst and graben structure consequent to the Tyrrhenian sea opening. Intrusive bodies, with decreasing age from west (7–8 Ma) to east (4 Ma), are typical of this tectonic province, and their emplacement was followed by their greater extension. The activity of the province is attested by important geothermal fields (Larderello, Amiata) within a major mining district (Campiglia, the island of Elba, Amiata). The sedimentary sequence and a Pliocene (4.9 ± 0.15 Ma) quartz monzonitic intrusion are shown in the geological/hydrogeological map (Fig. 1). The intrusion, with successive micro-granitic dikes prevalently oriented N–S, NE–SW and NW–SE, is weathered at the surface and it is frequently bounded by a thick zone of loose, soil-like material (“Renone”). This weathering and alteration disappear along the mining drifts but the “Renone” has often been found along the tectonic contact. The intrusive body is limited by two normal faults (Fig. 2) to the eastern (45° dip) and western sides (60° dip). Minor faults are to the north of the intrusion (Rigoloccio), and to the west of Mt. Calvo, putting the stratigraphic series in contact. The geomechanical characterisation of the area was based mainly on a series of geomechanical field surveys (Crosta and Garzonio 1998a). These field surveys were carried out within the main geological formations, at the surface and in underground excavations (mine of Gavorrano).

The aim was to characterise the rock masses for a general evaluation of their mechanical properties; to assess slope stability and the distribution and persistence of joint planes (Fig. 3), and to assess hydraulic conductivity. The fieldwork highlighted the persistence and the frequency of

Fig. 1
Geological and hydrogeological map

Fig. 2
Schematic geological section

two sub-vertical extensional discontinuity systems. The dominant sets were parallel and normal to the axis of the intrusive body and of its main flow structures (lineations). Secondary sub-vertical faults with the same trend were observed at different sites with the same trend, sub-parallel to the faults limiting the intrusive body. A NNW–SSE and ENE–WSW discontinuity direction characterises the rock mass. The former set is predominant, with the exception of the central part of the intrusive body where normal or cross joints are more frequent. These discontinuities, often accompanied by dike intrusions with pyrite mineralisation, are characterised by changes in the dip angle due to their normal trend with respect to the flow lineations. This situation of highly jointed rock mass, together with the superficial condition of crushed, poorly interlocked materials (RMR 20–30), leads to intensive and deep weathering processes, particularly in correspondence with the faults, where the de-cohesion phenomena of the quartz–monzonite due to the fluid circulation reach a thickness of 50 m along the dip plane in the depth. The hydrogeological system in the Gavorrano area is complicated by the presence of three sub-systems: a superficial alluvial system, a karstic system and a deep

hydrothermal system. The first system consisted of a small, multilayered aquifer in the area around the sub-inclined plane of the alluvial and debris plane of the large village of Bagni di Gavorrano (Fig. 4). Waters from the last two systems have been forcefully mixed by the mining activity. In fact, 500 m of production levels was excavated in over a century of mining. The pre-existing groundwater circulation, with springs placed at a maximum height of 180 m a.s.l., was depressed up to –250 m b.s.l. when old thermal springs (Bagni di Gavorrano, Terre Rosse) were drained through the underground drift system. Hot water springs (up to 47 °C) were found during mining, both at particular sites and diffused in specific ore bodies (Rigoloccio). The permeability classes (Fig. 1) were attributed by considering the lithology, the degree of fracturing, the degree of weathering and alteration, and the presence of karstic structures, as observable at the surface and within mine drifts. Alluvial deposits have been separated from the other materials, because of their characteristics and their natural northward groundwater flow direction. Karstic features and degree of fracturing were determining factors in distinguishing carbonate rocks. Because of their very low permeability, flysch and shales

Fig. 3
Stereoplots of main discontinuities of the rocky masses

Fig. 4

Gavorrano mine area with location of main historical sites

act as a permeability threshold which controls the location of the main springs around the carbonate massif. Intrusive rocks are characterised by a relatively low permeability because of superficial weathering and the low fracture density. A groundwater balance was performed by attributing different coefficients of potential infiltration to the different lithotypes and by computing the contributing areas for each lithotype. In particular, the potential infiltration coefficient for the carbonate rocks was estimated within the range of 8.7 to 10.1 s km⁻², as a function of the increase in fracturing and karst conduits. Varying values of the coefficient can be attributed to the quartz-monzonite changing with the degree of fracturing and weathering. Some in-situ tests were recently carried out to evaluate the real infiltration in the carbonate outcrops (Massiccio limestone), in different attitude, and in the intrusive body. With regards to this aspect, some data can also be inferred from the water level rebound analysis which up to now has only been carried out on the granite mine.

Average annual rainfall in the area ranges between 750 and 800 mm year⁻¹, with an average evapo-transpiration of 430 mm year⁻¹ and a rainy season lasting from October to February, with the maximum average monthly rainfall in November (120 mm) and very low precipitation in summer (20 mm in July). From these data, the calculated evapo-transpiration and a series of infiltration coefficients, it emerges that 1.2 Mm³ of water forms the annual groundwater recharge.

However, it must be stressed that rock mass properties, in particular hydraulic conductivity, have been strongly and permanently influenced by mining and subsequently induced processes (e.g. tunnel presence, the increase in the fracturing degree, and the enlargement of existing fractures by acid water circulation and water level lowering which increased karst solution in places). In fact, tunnels and drifts form a drainage network characterised by voids and refilled spaces.

Finally, as far as water discharge and the hydrogeological modelling related to resource re-utilisation are concerned, some exceptional climatic events were of particular interest—August 1997, and January 1997 and 2001 (with precipitation of 180, 210, 260 mm respectively).

Water discharge

Groundwater level recovery is typical of the closure of mines. It is a common process which can give important information for understanding the effects, starting from the data recorded during the water level lowering and some occasional or accidental water rising. The control of groundwater rebound, in progress at the Gavorrano mine since August 1995, is regulated by submersible pumping systems. These systems consist of two pumping points immersed in the Impero shaft and the Roma shaft respectively (Fig. 5). Subsequently a new pumping point (Rigoloccio shaft 3) was realized (in 2000). They are adopted to avoid too fast a rising in the groundwater level, which could induce turbulent flow and internal erosion of the backfilling, excessive hydraulic gradients and groundwater re-emergence at the surface within inhabited areas (Bagli di Gavorrano). Furthermore, the controlling of the rebound allows the evaluation of the volume of water storable within the mine void system, as well as the changes in the chemical composition of drainage waters. A deep borehole was recently drilled to increase the monitoring system of the water levels (where the piezometers are too near the surface; (Figs. 4, 5), and to identify the lithological and mechanical characteristics of the terrains near the Bagli di Gavorrano village. Furthermore, because of the almost constant temperature of the pumped water, it can be assumed that the hot water discharge increases with the fresh karstic water discharge during wet periods, maintaining an almost constant ratio between the two. Geophysical and geomechanical soundings were carried out to identify the geometry of the aquifer above the built-up area of Bagli di Gavorrano, above all to assess the hazards. The results of the mechanical soundings (S. Guglielmo borehole), for a depth of over 250 m and which went through a debris and “Renone” cover (granite alteration) for less than 30 m, then a crystalline calcareous level and finally the cavernous limestone, are in contrast with previous geostructural analyses and the geophysical results. In other words, the cavernous limestone is less permeable than elsewhere, with few and closed fissures, few cavities, even though scarce in gypsum levels. However, the possibility of local and important fractures or

NW

SE

Fig. 5

Schematic section of the mine with water pumping systems and sampling points

small faults is not to be excluded. More information will be collected by geoelectric or by new soundings to set up a monitoring system. For all these reasons too, before carrying out further drillings it was decided to reopen a shaft near Rigoloccio to reach the tunnel (up to -200 m b.s.l.), which connected the Rigoloccio mine with the Gavorrano one (Roma shaft), and then intercept the waters, analyse them and install a new pumping system. An initial analysis has shown that this operation could produce good results, not only for the control and the safety of the water rising operations, but also for the separation, albeit not total, of the hot and cold waters infiltrated in Mt. Calvo.

The passage of the Second World War front between 1944 and 1945 caused a forced water level rising and, together with data collected since 1995, these are the only ones available for the mine. Figure 6 shows the water level

rising which is correlated to the pump discharge needed to maintain a prefixed water level during each flooding step since 1995.

Data for the 1944–1945 forced rising are available for the main mining centres of that time (Rigoloccio, Boccheggiano-Gavorrano and Valmaggiore from N to S). These data suggest a power-law trend for the groundwater level rise with decreasing rate and with the general form:

$$\Delta H = -(H_t + H_0) * \exp^{(-a * \Delta t)} + (H_t + H_0) \quad (1)$$

where H_t and H_0 are the initial and final groundwater level elevations, and Δt is the elapsed time. In fact, the rising rates at Boccheggiano-Gavorrano and Valmaggiore are quite similar while at the Rigoloccio the rate was lower (Crosta and Garzonio 2000). The recent records were compared with the old ones by putting each of the 10 rising steps (from -197 to -143 m b.s.l.) in sequence, without considering the steady-level intervals. It must be stressed that the mines were separated during the 1944–

Fig. 6

Groundwater level rising during each controlled flooding step of the 1995–1999 period. Also plotted are the curves (shaded lines) calculated by using the suggested power-law function for different values of the maximum groundwater level increase

Fig. 7
Pump discharge decrease after the maximum peak as measured during the 1997 and 1998 recession events

1945 period, and have only been linked since 1969. By putting the data for each of the 11 steps used for the controlled groundwater level rising in a sequence and fitting them with the above-mentioned equation, it was possible to determine the expected maximum groundwater level (+186 m a.s.l.) and the time to reach it through a continuous, uncontrolled rising (almost four years). By plotting the groundwater level recovery for the 1944–1945 and the 1995–1999 periods, it was possible to observe the non-linearity of the process. In particular, the rising is slower at the beginning and faster in the final step. This can be attributed to the change in the fracturing degree of the rock mass, the opening of the main joint sets, and the possible decrease in volume of the voids and of the main aquifer area.

Since 1995 the pump discharge has remained almost constant at 65 l s^{-1} , with the exception of three periods of heavy rainfall with discharge until 110 l s^{-1} . This allowed the storage of about $300 \times 10^3 \text{ m}^3$ of water, excluding the initial, uncontrolled water level rising between -236 and -197 m b.s.l. Using the data recorded during the two phases (1997, 1998) of increased discharge, it was possible to perform a recession analysis (Fig. 7) which gives a good insight into the aquifer structure.

Starting from these data and the recession analysis, confirmation of the previous results concerning the groundwater balance was obtained. In fact, according to the recession analysis, the average water resources which are renewed yearly amount to 2.2 Mm^3 or 66 l s^{-1} . These values are quite comparable with the average yearly pump discharge (65 l s^{-1} or 2.08 Mm^3). Finally, by comparing these data with the ones obtained by the effective infiltration analysis (1.1 Mm^3), it emerges that almost 1 Mm^3 of hot water flows regularly from the deep circulation system into the mine every year. The residual volume of the hollows produced during the whole mining activity has been estimated by Sammarco (1993) at about 3.6 Mm^3 . Furthermore, because of the almost constant temperature of the pumped water, it can be assumed that the hot water

discharge increases together with the fresh karstic water discharge during wet periods, maintaining an almost constant ratio between the two (when the discharge increases, a steady value in the temperature can be observed).

Chemical analyses of the waters

A further series of samplings was performed over the last four years to complete the dataset already available. In particular in 2001, some new water sampling campaigns were carried out to verify the possibility of a variation in the chemistry of the pumped water, after the setting up of the new pumping system in Rigoloccio shaft 3.

The sampling points at the ground surface (wells and springs) and within the mine are shown in Figs. 4 and 5 respectively, together with the ore-body limits (Boccheggiano ore body; Figs. 8, 9) and the carbonate/intrusive rock contact.

Data from superficial sampling points are given mainly for a general water classification and for a comparison between superficial thermal springs (Bagni di Gavorrano) and deep hot waters. More attention is actually paid to the 30 samples taken from the mine (Fig. 5), because of their importance for the understanding of the main aquifer hydrodynamics, the hydrochemical composition of the waters, and their possible changes with the proceeding of water rising and the consequent mixing. The data must be read with care when referring to the $+70 \text{ m}$ elevation (a.s.l.) samples, because these values refer to the mine drainage waters sampled at the exit of the drainage tunnel (almost 1.5 km long and excavated in flyschoid rocks). At a regional scale it was observed that sulphate waters commonly spring from the Cavernoso limestone and from the intrusive rocks. Calcium bicarbonate waters are mainly associated with carbonate formations and shallow depths and are considered the less-mature water class. Seawater influence is absent, with the exception of very few points where wells probably intercepted small remnants of old, entrapped seawater (Avio and others 1995).

Fig. 8

Dewatering system in the drift –140 m (near the Impero shaft)

The mine water samples can be clearly subdivided into two main groups: “superficial” bicarbonate waters (from levels +240 m a.s.l., +155 m: Mg–Ca, +90 m: Ca–Mg–HCO₃) and deep sulphate waters (Ca–Mg–SO₄, –80 m b.s.l., –110, –140 and –200 m), as suggested by the Piper plot

Fig. 9

Water sampling in the drift of level –110 m

(Fig. 10). This grouping can be done on the basis of the sulphate (from sulphide oxidation and evaporites solution), iron and silica contents, and it is also suggested by the few temperature data, even if more qualitative observations were made. In fact, by fitting the temperature measurements, excluding samples taken at the outlet of the drainage tunnel (1.5 km long), a geothermal gradient of about 75 °C km^{–1} was obtained. This geothermal gradient is in agreement with the data published by Baldi and others (1995) concerning southern Tuscany and indicates, for the marginal areas of the geothermal fields (Larderello, Amiata, Travale, Radicofani), a gradient of no lower than 70 °C km^{–1}.

A water-type subgroup, with peculiar characteristics, is composed of four samples all collected within the intrusion in a relatively localised area (Fig. 9), and characterised by very low pH values and high TDS contents (in Table 1 the sample C2 is reported). The area was characterised by a conspicuous air flow and abundant water presence, with clear and cold waters. The pH values strongly characterise this minor group. All the other sampled waters generally presented values just a little over neutral (7–8). Mine drainage is characterised by an average temperature of 32 °C, a 7 to 8 pH value (Table 1), and it can be classified as a Ca–Mg–SO₄ or a Ca–Mg–SO₄–HCO₃ water, probably as a result of temporal changes and the mixing action caused by pumping. In comparison, the water of the old spring at Bagni di Gavorrano was characterised by constantly higher Na and Cl contents, with a minor SO₄ content. Recently and during the increasing of the discharge, in particular in Rigoloccio shaft 3, higher temperature values and lower pH values (6.6) can be observed.

Re-utilisation project

The flooding of new mine levels, during successive rising steps, is without doubt an important source of instability for water properties (chemical and physical). The reason lies in the fact that rock resaturation and the filling of mining drifts are associated with the washing out of the sulphate-rich and heavy metal-rich pyrite

Fig. 10

Piper plot of the Gavorrano mine deep waters

Table 1
Chemical analyses of the waters (mg l⁻¹)

Site	Date	Sample	Depth	pH	Cond.	Mg	Ca	Fe	Cl	SO ₄	HCO ₃
Bagno di Gavorrano	31 December 1924				134	59.890	328.020		28.480	844	253.000
Valmaggiore	1 April 1993	Eniacqua			1,980	106.000	400.000			1,285	
Dewatering drift	1 July 1995	C	-200	6.88		117.700	280.000		35.400	1,075	36.600
Dewatering drift	1 July 1995	D	70	7.73	2,150	33.500	404.000	0.000	39.400	1,100	131.200
Dewatering drift	1 January 1996	E	-220	8.31	2,130	99.700	471.000	0.082	42.000	1,464	136.000
Ancient shaft at -140	1 May 1996	C2	-140	3.41	3,180	144.000	421.000	3.150	27.410	1,689	0.000
Dewatering drift +70	1 May 1996	L	70	6.83		106.800	467.000		39.030	1,554	109.800
Dewatering drift +70	dic-1997	M2		7.35	3,472	99.671	456.912		35.453	1,417	231.830
Dewatering drift +70	dic-1997	1		7.40	4,021	142.214	450.900		34.035	1,715	
Shaft 3	June 2001	C17		6.30		117.904	382.764		28.362	1,364	195.226
Roma shaft	June 2001	C20		6.25		106.964	420.840		17.727	1,431	219.629
Rigoloccio shaft	June 2001	C19		6.23		115.473	408.816		24.817	1,374	213.528
Impero shaft	1995	M15	-200	7.50	1,530	73.000	207.000	0.013	26.000	791	128.000
Rigoloccio shaft -200	1995	M16	-200	7.20	2,180	86.000	371.000	2.800	55.000	1,348	165.000

oxidation products (Banks and others 1996). Up to now the analyses of the pumped waters have pointed out the constant chemical characteristics. It will be necessary to verify the parameters when the ancient sectors of the mine are flooded. The new data and the discharge from the new pumping system of Rigoloccio shaft 3 highlighted the remarkable quantity of the water resources, in particular the volume of the thermal waters (with temperature of 38–40 °C). All the toxic elements (As, Hg, Pb, Cr, Zn, etc.) were found in traces and the water was almost free of nutrient contamination (nitrate, phosphate, BOD, etc.). Sulphates are well beyond the admissible threshold value, while iron and manganese contents change from sample to sample. The acidity was quite stable, while turbidity changed as a function of time and pumping discharge (the Roma shaft generally shows less-clear waters).

Determining the proposed remediation methods and alternative uses for the mine waters was among the main aims of the Gavorrano project. In particular, today water is often going to become a non-reproducible resource. In fact, in southern Tuscany the anomalous rainfall distribution, and the increasing need due to tourist development and high-quality agricultural activities have made water a strategic resource. Considering the regional and national laws and the European Community code, and taking into account the eventual economic cost and benefit, the following alternative uses could be proposed with a different degree of attainment: drinking or industrial waters, distribution in dual networks for domestic/non-drinkable use; pools and spa waters, pisciculture; irrigation; fire prevention and control; greenhouse and hothouse plants; heating; dilution of polluted water discharges; flocculating agents for sewage or water treatment (Banks and others 1966). The Gavorrano mine could become an important water resource, to be continuously

or intermittently exploited, according to the use and the seasonal requirements by extracting different discharges. It is not yet possible to evaluate the future scenario wherein the water discharges will always be active enough to avoid hazards to the village of Bagni di Gavorrano or only to increase the necessary resources. Mine waters could become drinkable by removing, in order of importance, sulphates, magnesium, calcium, suspended material and relatively small quantities of aluminium, iron, manganese and arsenic. From a cost/benefit analysis, the installation, continuous operation and maintenance of a water treatment plant proved unprofitable with the present water composition. Thus, it is preferable to find a different use, taking into account a possible future change in the water chemistry with the ongoing water rebound. Dual water distribution networks, already functioning in some small and very recent tourist dwellings, could be the best suggestion. Thermal spa waters represent a good solution, and this is supported by a series of data available concerning some spa waters already exploited in Tuscany, and which differ only in the lower iron content. It must be stressed that the new pumping system well intercepts the old drift (level -200 m b.s.l.) of Rigoloccio, where the waters show higher temperatures. Irrigation is a possible use, even if attention must be paid to the soil characteristics and the irrigation technique. Indeed, these waters have already been extensively used for this purpose in the neighbourhood, but relatively high levels of heavy elements and metals have been found in natural soils as well as in some irrigation ditches. Finally, heat exploitation, both in greenhouses or through heat exchangers for houses or public buildings, has been evaluated and it is considered economically profitable. Other interesting uses are for pisciculture, for the production of gypsum products or as a source of lower-quality water for camp sites.

Conclusions

Closed mines are a worldwide environmental problem but in many cases they could represent an important resource. The case history of Gavorrano is associated with water recovery after the termination of pumping operations and the consequent mine water management, which would be characterised by reusing different resources. The study described includes all these aspects and highlights the great importance of continuously monitoring the water level and water chemistry changes during and after the completion of mining operations. It stresses the need to realize new well points with automatic monitoring of the water levels, to perform new geophysical tests when the water rebounds and new chemical and isotopic analyses, pumping separately and contemporaneously in the different systems.

The importance of this monitoring is illustrated, for example, by the rising rates observed at different mining sites (Valmaggione, Gavorrano, Rigoloccio) during the forced World War II pumping arrest. Different rising rates can be related to a different water circulation system and to the maximum depth of excavation (as supported by the 1995–2001 records), which affect the size and geometry of the ideal cone of influence, as well as to the occurrence of intensive rainfall and the effects on the discharge. The pH of the Gavorrano mine waters is almost neutral. This may be due to the content of alkaline minerals within the carbonate rocks in the upper mine levels and the tectonically lowered rock mass near the main faults of the area (thermal water flowing up at the Rigoloccio mine). The neutralization of the naturally acid waters, which derive from iron sulphide oxidation because of their contact with air and water after tunnel excavation, could also be the result of the material used for backfilling excavations (limestone blocks together with clay and cement). The chemical monitoring has pointed out a small trend of decreasing pH values (6.4). The TDS content is high, but the quantities of polluting elements are very low.

The groundwater balance and the discharge rates pumped from the new drilling confirm the volume which could be stored and the important presence of a thermal deep circulation coming from far away. New isotope analyses (^2H and ^{18}O) seem to confirm the residence times recorded in earlier studies (Garzonio 2000). In conclusion, the analyses have highlighted that in the present phase of the water rebound, the proposals of different re-utilisation projects

of the waters are realizable as well as the necessity of setting up a more efficient network of monitoring before the change in elevation of the recovering water table.

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