The anomalous La Rossa groundwater of the Val d'Agri oil field (southern Italy)

Albina Colella[1] **and Franco Ortolani**[2]

[1] Dipartimento di Scienze, Università della Basilicata, Potenza, Italy. email: *albina.colella@unibas.it*
[2] Università Federico II di Napoli, Italy, retired. email: *fortolan@unina.it*

Abstract

A massive injection of wastewater associated to the production of the Val d'Agri oil field (southern Italy) started since 2 June 2006 in the Costa Molina 2 well, through pumping in the underground of an area subject to an high seismic hazard. In 2011 two anomalous pools of turbid, warm and saline groundwater suddenly appeared on agricultural soils of Contrada La Rossa (Montemurro), at a distance of ~ 2.3 km from the injection well.

Site surveys were conducted in order to investigate properties and source of La Rossa murky groundwater, by combining data of previous water analyses with the new ones, field mapping, hydrogeological observations and recently published data on the seismotectonic framework of the area and wastewater induced microseismicity.

The results of this investigation: 1) confirm the similarities of La Rossa groundwater with the general properties of oil wastewater from many basins in the world and from Val d'Agri; 2) document the mixing of La Rossa toxic groundwater with meteoric groundwater; 3) indicate that injected wastewater may have reached the surface in Contrada La Rossa after migration for several kilometers in the underground, according to data of Improta *et al.* (2015), that document the presence of faults with high-permeability fractured zones just below the Costa Molina 2 well and microseismicity induced by wastewater injection; 4) reconstruct the Quaternary tectonic structure of the Costa Molina 2 area, identifying a morphostructure controlled by normal faults oriented NNE-SSW dipping ESE and NNW-SSE dipping WSW, where induced microseismicity appears to be concentrated.

1. Introduction

One of the most common methods for oil and gas produced water (wastewater) disposal is the underground injection in permeable rock formations below drinking water sources. Until recently scientists and companies have assumed that the risks posed by all this dumping are minimal, since deep rocks beneath the surface would safely entomb the oil and gas produced water. However USA hydrogeologists and USEPA technical experts are quite concerned on the effects of high pressure injection that can cause, among others, man-made fractures that allow wastewater to flow more freely in the underground, and pollution of most groundwater (Lustgarten, 2012).

In several areas of United States injection wells have repeatedly leaked, sending dangerous chemicals and waste to the surface or contaminating shallow aquifers that store the drinking water resource. In 2010 contaminants from an injection well bubbled up in a Los Angeles dog park; similar fountains of oil and gas wastewater have appeared in Oklahoma and Louisiana. More than 220,000 well inspections found that structural failures inside injection wells of USA are routine. From late 2007 to late 2010 one well integrity violation was issued for every six deep injection wells examined. More than 7,000 wells showed signs that their walls were leaking (Lustgarten, 2012).

The increase of hazard, due to a substantial greater industry interest of drilling in fragile ecosystems and in production and disposal of large amounts of wastewater, is becoming a matter of compelling debate. The most significant environmental effects are the degradation of soils, ground and surface water, ecosystems by suspended and dissolved hydrocarbons and radioactive and saline produced waters (Otton, 2006).

In 2011 two pools of murky and saline groundwater, never described in Southern Apennines, suddenly appeared on agricultural soils of the Val d'Agri oil field (Basilicata), at 2.3 km from the Costa Molina 2 (CM2 hereinafter) injection well (Colella, 2014), where the 2 June 2006 an oil company officially had begun pumping oil produced water at a depth of ~ 3,000 m below sea level. This groundwater gurgled in a bucolic farm field of Contrada (Cd.) La Rossa, near Montemurro, the Val d'Agri village devastated by the M7 earthquake of 1857 with 3,000-4,000 victims. Special concern raised immediately in this agricultural land.

A first monitoring of La Rossa anomalous groundwater showed that its physico-chemical properties had several similarities to oil produced water: elevated values of total dissolved solids, electrical conductivity, hydrocarbons, phenols, sodium, salts, manganese, barium, lead, ecc., compared to the average composition of the principal Val d'Agri springs, were found (Colella, 2014). On the basis of the concerns raised by such preliminary results, the geological study continued between 2015 and 2016, compatibly with the lack of funds, and new physico-chemical analyses, hydrogeological observations and fieldmapping were realized, taking into account also new seismological data on the CM2 area from Stabile *et al*. (2014) and Improta *et al*. (2015).

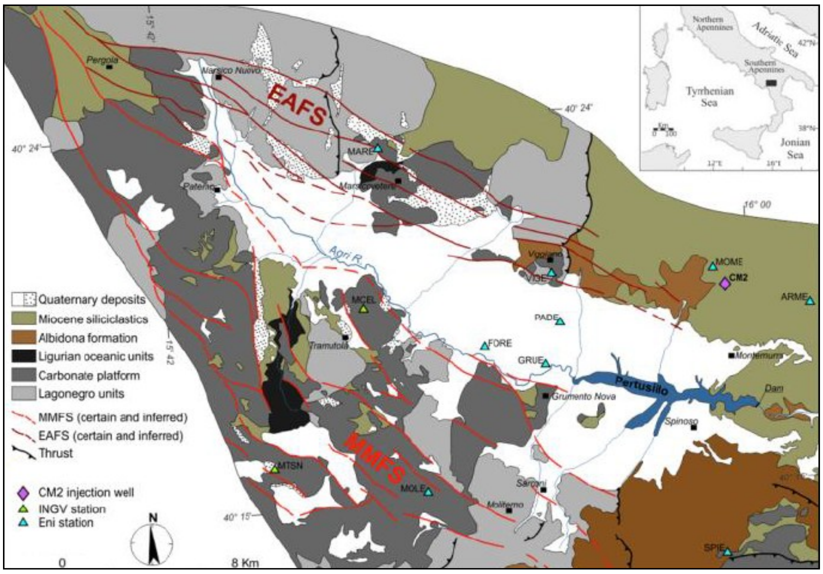
2. The Val d'Agri Oil Field

The Val d’Agri (Fig. 1) is a NW-elongated Quaternary extensional basin (Lazzari and Lentini, 1991; Morandi and Ceragioli, 2002; Colella *et al.,* 2004), located in the axial part of Southern Apennines (Basilicata, southern Italy), bounded by the EAFS and MMFS oppositely-dipping normal fault systems (Cello *et al.,* 2003; Maschio *et al.,* 2005; Improta *et al.,* 2010) and filled by fluvio-lacustrine sediments. The pre-Quaternary bedrock includes Mesozoic to Cenozoic terrains with allochthonous units emplaced onto the shallow-water limestones of the Apulian Platform, overlying Pliocene foreland rocks.

The Val d'Agri hosts the largest exploited oil field of western onshore Europe. The reservoir occurs in anticlines of the fractured low-porosity and carsified limestones of the Apulian Platform (Trice, 1999), drilled at 2 to 3 km depth below sea level and sealed by flysch and mélange sequences, for a total extension of 320 km^2. The 660.15 km^2 large Val d'Agri oil concession actually hosts 37 wells (22 in production; UNMIG, 2016) located mainly in the NE margin of the valley, the Centro Olio Val d’Agri (COVA hereinafter) facility and the CM2 injection well (Fig. 2). The COVA is a desulfurization treatment plant that separates crude oil, gas and produced waters coming from producing wells, removes sulfur from hydrocarbons, realizes the treatment of produced water and sends it by pipelines to the CM2 well for injection (Figg. 3, 4).

Oil production started in the nineties and oil produced water has been injected through the CM2 well into an unproductive area of the carbonate reservoir. The well is placed in the Val d'Agri eastern margin, ~ 4.8 km from the Pertusillo freshwater reservoir and ~ 3 km from Montemurro. The well-head is located at 1,045 m above sea level, the well length is about 4,117 m, the capacity is about 3,200 m^3/day and the well-head pressure reaches maximum values of 13–14MPa.

The Val d'Agri hosts also abundant ground and superficial water, with 23 water-courses, about 650 springs (Civita *et al.*, 2003; Colella and Agrifluid Group, 2003) and the Marsico Nuovo and Pertusillo freshwater reservoirs (Figg. 3, 4). The latter, located ~ 1.8 km SE of COVA, provides water intended for human use to Basilicata and Puglia regions.



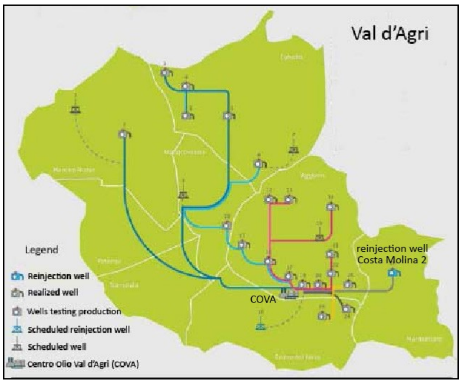


Fig. 1, left - Schematic geological map of the Val d'Agri basin (from Stabile *et al.*, 2014), showing the EAFS and MMFS fault systems, and the location of CM2 injection well.

Fig. 2, right - Val d'Agri oil wells, CM2 injection well, COVA and pipelines (mod. from ENI, 2014).

3. Site Sampling and Analysis

The La Rossa pools of water occur at ~ 967 m above sea level where the rocks of the Gorgoglione Flysch crop out, at ~ 2.3 km to the ENE of the CM2 injection well and at ~ 2.06 km to the SE of the CM3 abandoned well (Fig. 5). The latter, drilled in 1987 for a depth of ~ 4,364 m, is located at 1,255 m above sea level (Osservatorio Val d'Agri). CM3 has been closed in 1988; in July 2016 the well area has been fenced off by the oil company and will be subject to monitoring (Figg. 5, 6).

The two La Rossa pools of water, named S2, S3 (S2,3 hereinafter), are ~ 3.5 m apart and their flow path converges downslope (Figg. 7a-d). The initial sampling trips conducted between 2013 and 2014 showed the physico-chemical anomalies of La Rossa waters and the impacts on soils, requiring additional investigations. To further study water composition, to provide a better understanding of the lithological, hydrogeological and structural characteristics of the area, between 2015 and 2016 additional water samples were collected and fieldwork and ground excavation were realized with the authorization of the owner of the land.

La Rossa S2,3 waters were sampled periodically and simultaneously seven times between June 2013 and May 2016. For comparison, water analyses were extended to other four Val d'Agri springs, S1, S4, S5 (S1,4,5 hereinafter) adjacent to La Rossa waters (Figg. 5, 7a) and Tr near the Tramutola village, in the central Val d'Agri, where crude oil naturally flows out with groundwater. The results were compared with

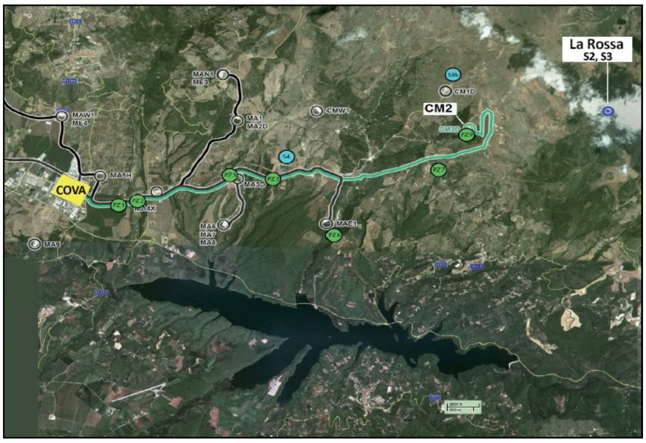


Fig. 3, left - Location of the anomalous La Rossa S2, S3 pools of water, the CM2 injection well, the produced water pipeline and the COVA treatment plant (modified from ENI, 2015).

Fig. 4, right - Photo of the CM2 injection well and the Pertusillo freshwater reservoir.

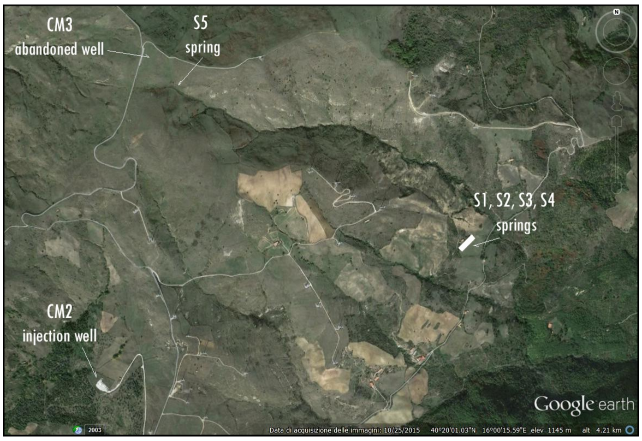
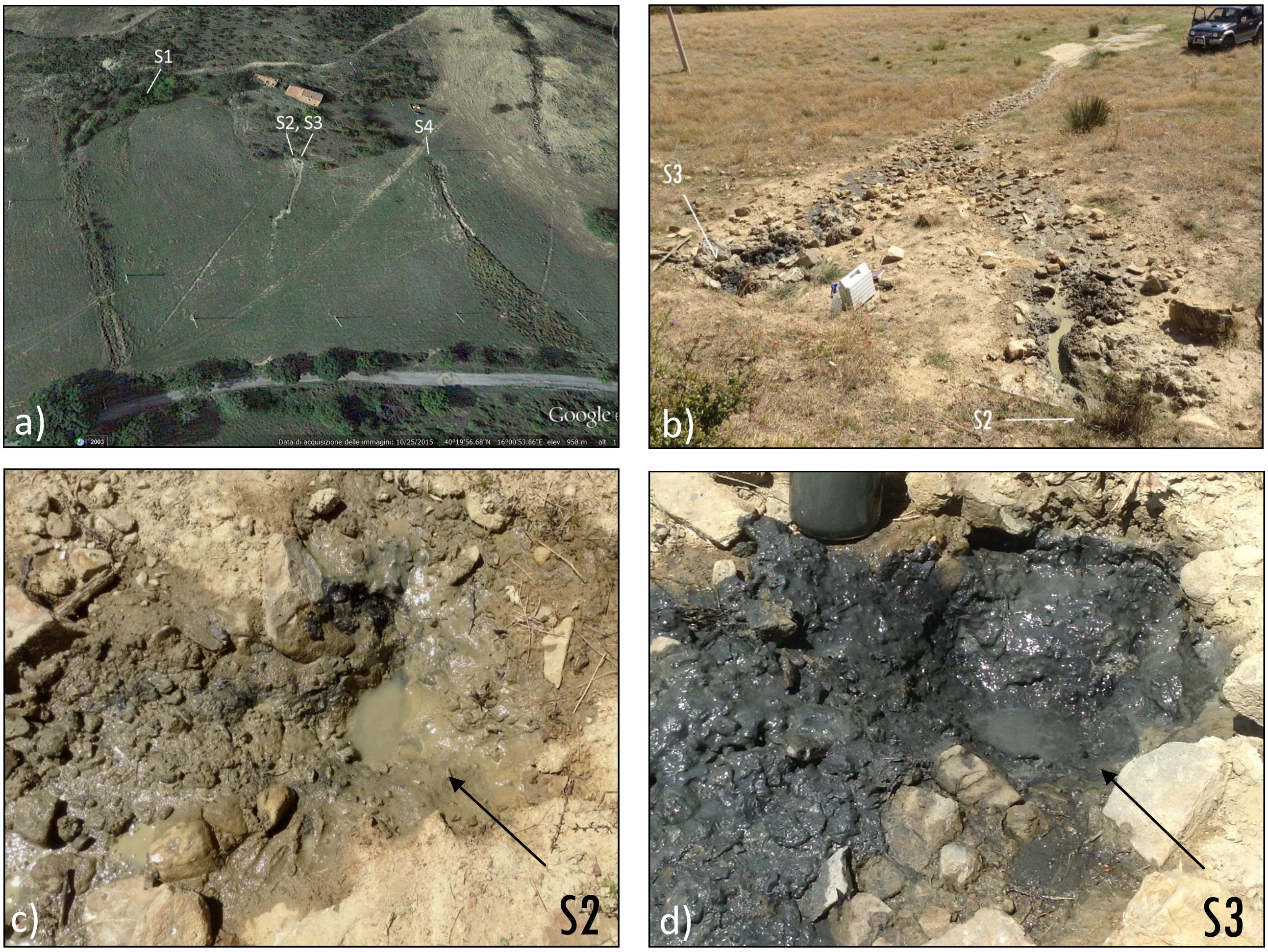


Fig. 5, left - Location of the S1 to S5 springs, the CM3 abandoned well and the CM2 injection well, in the area of Montemurro. Courtesy of Google Earth.
Fig. 6 - right. Location of the CM3 abandoned well. It was closed in 1988 and in July 2016 has been fenced off for monitoring.



Fi.g 7 - a) Location of the S1 to S4 springs. Courtesy of Google Earth; b) S2, S3 La Rossa anomalous pools of water, whose flow path converges downslope; c) S2 La Rossa pool; d) S3 La Rossa pool.

For each water sample measurements included: total hydrocarbons, phenols, aromatic organic compounds, IPA, COD, TOC, BOD5, TDS (total dissolved solids), SAR (sodium adsorption ratio), sodium, calcium, magnesium, potassium, chlorides, chlorites, sulphates, sulphites, phosphates, nitrates, nitrites, bicarbonates, metals. Surfactants were investigated (and found) only in the last two samples. Temperature, pH, Eh, EC were determined mostly in the field, immediately after the groundwater emergence to the surface. The other parameters were measured by S.C.A. laboratory (Mesagne, Italy). Water samples were all filtered through a 0.45μm membrane and analyzed by the same methods: EPA, APAT CNR IRSA, UNI EN ISO, UNICHIM. Total hydrocarbons were measured using a gas chromatographer equipped with a FID (Flame Ionisation Detector).

4. Results

La Rossa S2,3 groundwaters show different physico-chemical properties compared with S1,4,5, Tr springs, and with the principal VA springs described by Mongelli *et al*. (2003).

The two La Rossa pools of water:

- are turbid due to substances with a colloidal behavior (Fig. 8) and produce white salt crusts on soil and clasts after evaporation (Figg. 9a,b), making soil infertile;
- have a bad smell, gas bubbles and sometimes black organic matter;
- showed a feeble flow (Fig. 7b,c,d), sometimes intermittent at daily intervals, that dramatically increased with a trench excavation (Fig. 8);
- have a slightly different composition that varies in a short time (Figg. 10 to 13);
- have a negative redox potential (Eh) up to -250 mV, versus an average value > +50 mV for the principal VA springs;
- have a temperature of about 23°C, versus an average temperature of 11.2°C for the principal VA springs, and of about 13°C for their adjacent springs;
- are alkaline, with pH up to 9.25, versus an average value of 7.72 for the principal VA springs;
- are rather saline. TDS ranges from 550 to 830 mg/L, versus an average value for the principal VA springs of 311 mg/L, and values ranging 150-434 mg/L for S1,4,5, Tr springs. EC reaches values of 1,576 μS/cm versus an average value for the principal VA springs of 372 μS/cm, and values ranging 298 -875 μS/cm for S1,4,5, Tr springs (Fig. 10);
- show the dominance of sodium cation (up to 441 mg/L), followed by calcium (up to 18.3 mg/L), potassium (up to17.3 mg/L), magnesium (up to 8.54 mg/L). The dominant anions are bicarbonates (up to 1,710 mg/L), sulphates (up to 849 mg/L) and chlorides (up to 105 mg/L), with minor phosphates (up to 5.35 mg/L), as shown in fig. 11;
- have high values of SAR reaching 29.5, versus a maximum value of 0.39 measured in S1,4,5, Tr springs;
- have concentrations of total hydrocarbons up to 625 μg/L, even higher than in the Tramutola spring, where crude oil flows naturally with water (Fig. 12);
- contain up to 67 mg/L of phenols, versus values from < 0.1 to 2.10 mg/L for S1,4,5, Tr springs (Fig. 12);
- have up to 1,970 μg/L of surfactants;
- show concentrations of several metals higher than the average value (av) for principal VA springs and S1,4,5, Tr springs (Fig. 13). The most abundant metals are, in decreasing order: aluminum, up to 15,700 μg/L, versus the av for principal VA springs of 9.30 μg/L; iron, up to 7,107 μg/L, versus the av for principal VA springs of 22.48 μg/L; boron, up to 1,220 μg/L; barium, up to 948 μg/L; manganese, up to 658 μg/L; strontium, up to 533 μg/L; lead, up to 248 μg/L, versus the av for principal VA springs of 1.10 μg/L; zinc, up to 208 μg/L, versus the av for principal VA springs of 5.57 μg/L; copper, up to 42 μg/L, versus the av for principal VA springs of 1.53 μg/L; nickel, up to 25 μg/L; vanadium, up to 22 μg/L;
- aluminum, iron, boron, manganese, nickel, lead, hydrocarbons, phenols, sulphates, sodium exceed the threshold values imposed by the Italian legislation D.Lgs. 152/2006 (Tab.2 All.5 Parte IV) and D.Lgs. 31/2001 for groundwater and drinking water; surfactants exceed the values of the old DPR 236/88;
- are "mixed" waters. During some samplings we observed the emergence of two distinct waters, a turbid and a clear meteoric groundwater, that mixed immediately downflow (Fig. 14a,b).

The excavation of a trench about 2 m deep showed that: 1) the flow of La Rossa turbid groundwaters, originally feeble (Fig. 7b,c,d), becomes dramatically larger with depth (Fig. 8); 2) groundwaters come out in pressure along a spring line located at 2-3 m below the surface (Fig. 15), at a change of rock type between permeable sandstone and overlying low-permeability mudstone; 3) the latter allows some water to reach the surface forming the S2,3 pools; 4) the pools are not connected and waters have different underground pathways.

Field observations and water analyses indicate some small anomalies in the adjacent S1 and S4 springs, suggesting the spreading of contamination in Cd. La Rossa area.

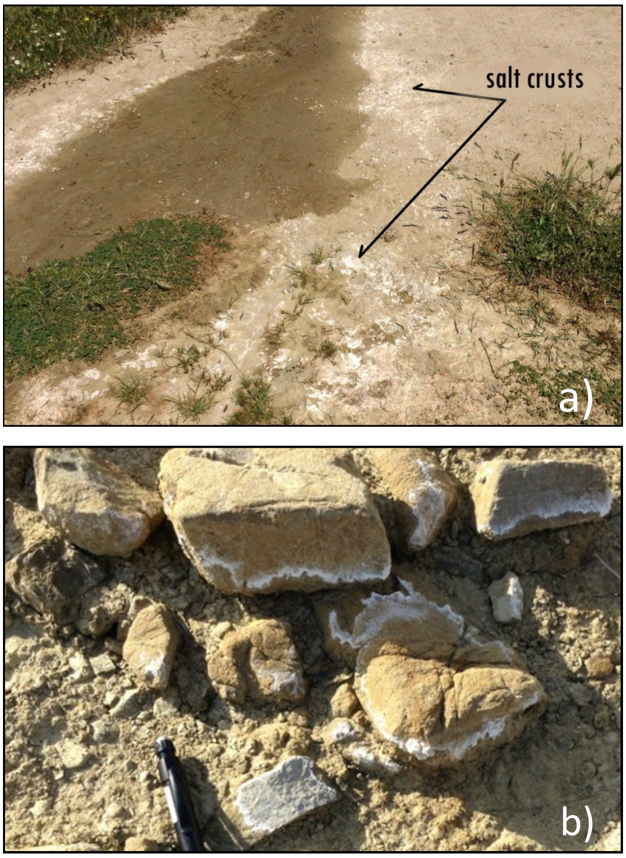


Fig. 8, left -The large flow of La Rossa turbid groundwater after a trench excavation.
Fig. 9, right - White salt crusts on soil (a) and clasts (b) along the flow path of La Rossa S2, S3 groundwaters.

5. Discussion

5.1 Water Quality

The physico-chemical properties of La Rossa S2,3 waters are different from the average composition of the principal VA springs and from the S1,4,5, Tr springs. Such anomalous groundwaters have never been described in Southern Apennines and share many analogies with oil produced water (Colella, 2014). The latter comprises the “formation water", natural water trapped in the underground formations of the reservoir, that becomes "produced water" when is brought to the surface with crude oil and natural gas, mixed with injected water containing production chemicals (Utwik, 1999; Veil *et al*., 2004) and with treatment chemicals.

Produced water is a complex mixture of dissolved and particulate organic and inorganic compounds. Its chemical and physical properties vary widely depending mainly on geological factors, chemical composition of the oil and gas phases in the reservoir, production and treatment chemicals. The major components include dissolved and dispersed oil compounds (i.e. hydrocarbons, phenols), salts, metals, naturally occurring radioactive material (NORM), production chemicals injected into the well and treatment chemicals (i.e. surfactants, caustic soda, ecc), produced solids (sand, silt, proppant, corrosion products, ecc.), scale

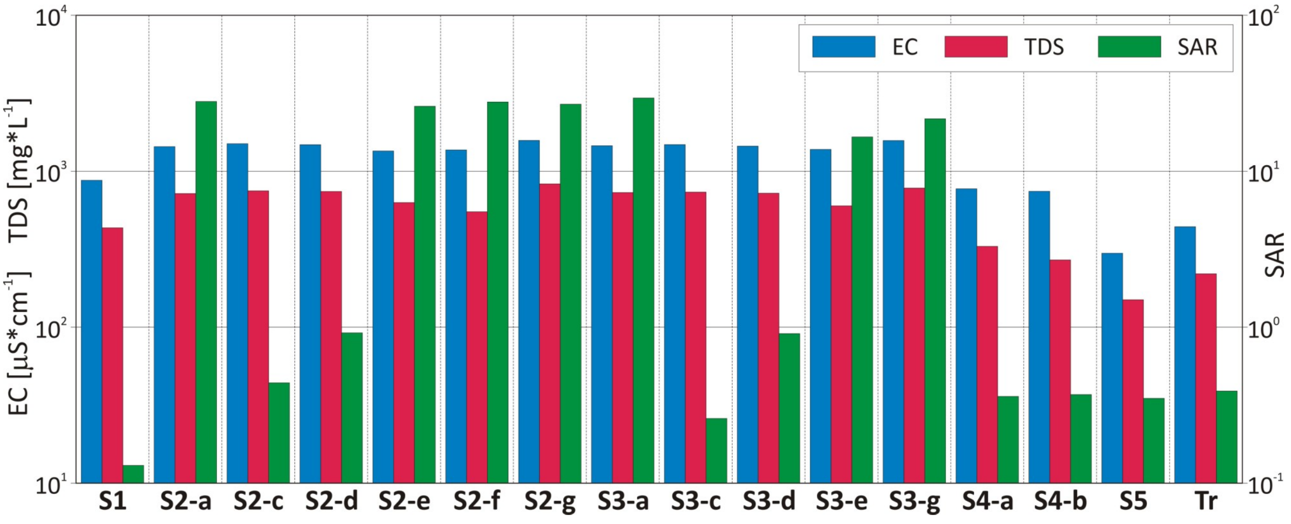


Fig. 10- The histogram shows values of electrical conductivity (EC), total dissolved solids (TDS) and sodium adsorption ratio (SAR) for the anomalous La Rossa pools of water (S2, S3), the adjacent springs (S1, S4, S5) and the Tramutola spring (Tr). Letters "a" to "g" are referred to the seven samplings of la Rossa groundwaters.

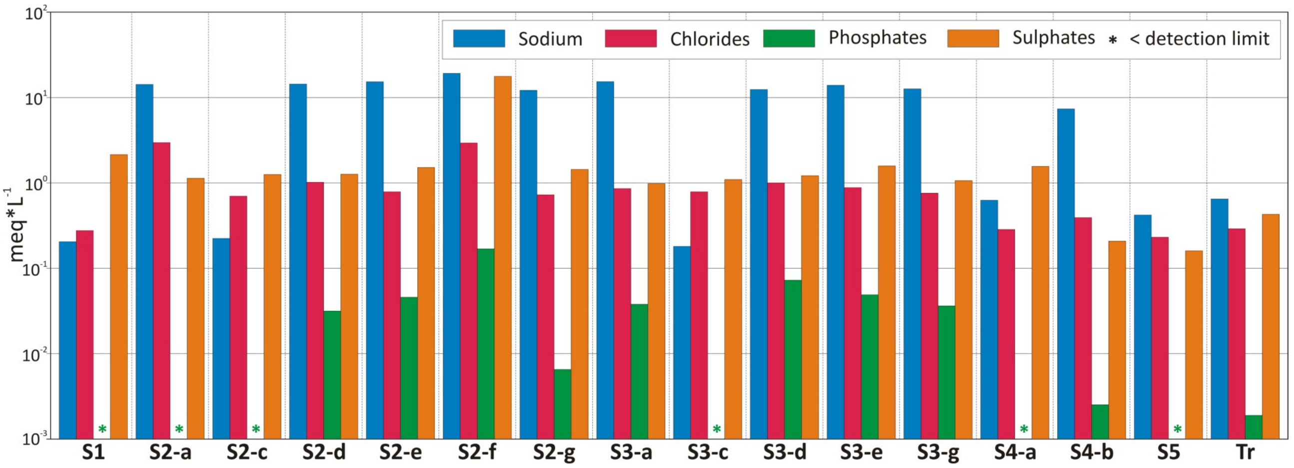


Fig. 11 - The histogram shows values of sodium, chlorides, phosphates and sulphates for the S2, S3 La Rossa pools of water, the adjacent springs (S1, S4, S5) and the Tramutola spring (Tr). Letters "a" to "g" are referred to the seven samplings of la Rossa groundwaters.

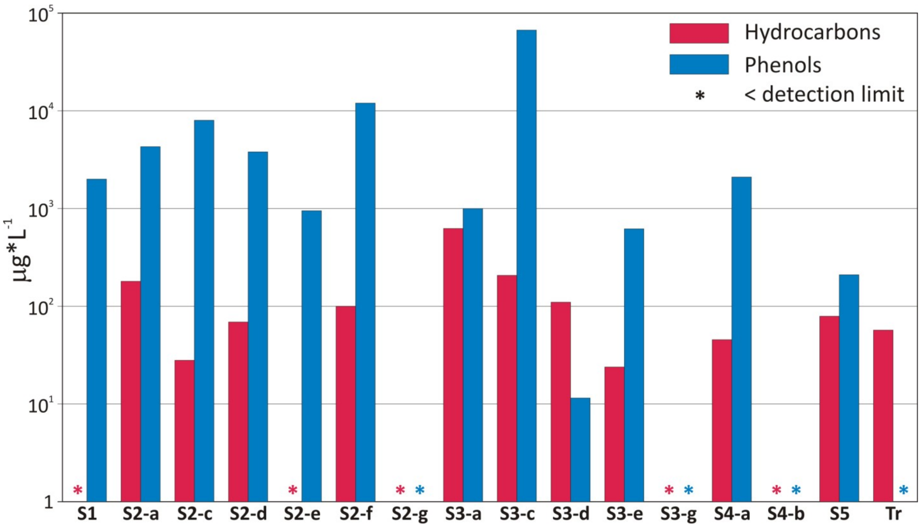


Fig. 12 - The histogram shows values of total hydrocarbons for the S2, S3 La Rossa pools of water, the adjacent springs (S1, S4, S5) and the Tramutola spring (Tr). Letters "a" to "g" are referred to the seven samplings of la Rossa groundwaters.

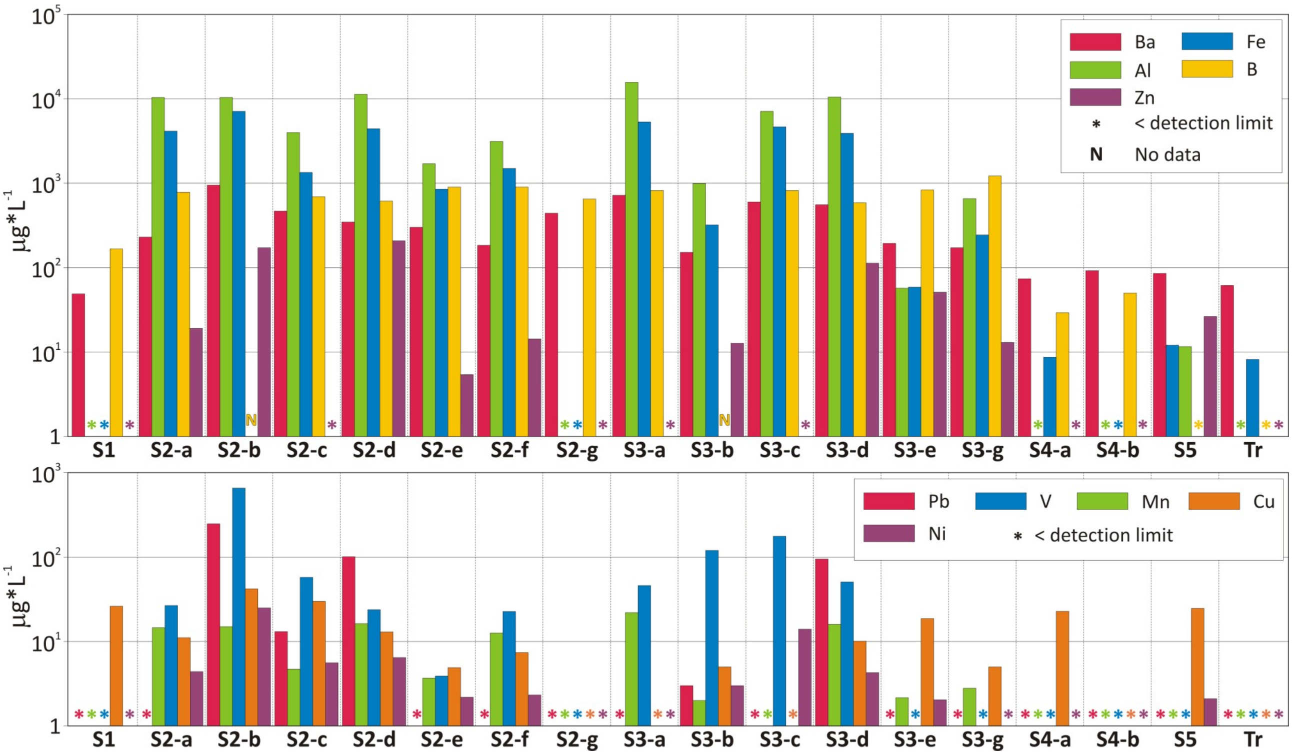


Fig. 13- The histograms show values of several significant metals for the S2, S3 La Rossa pools of water, the adjacent springs (S1, S4, S5) and the Tramutola spring (Tr). Letters "a" to "g" are referred to the seven repeated samplings of la Rossa groundwaters.

products, bacteria (Collins, 1975; Veil *et al*., 2004; Strømgren *et al*., 1995; Igunnu and Chen, 2014). Phenols are also present with concentrations generally < 20 mg/L (Neff *et al*., 2011; Neff and Foster, 1997; Utvik,1999; Utvik *et al*., 1999). Most produced water is more saline than seawater (Cline, 1998). Sodium is the dominant cation: for conventional wells sodium makes up 81% of the cations, but calcium also represents 14% of the cation makeup, while magnesium and potassium account for 5%. Salinity in conventional oil resources is due mainly to dissolved sodium and chlorides (Fakhru'l-Razi *et al*., 2009; Neff *et al*., 2011). Metals are typically represented by lead, barium, manganese, iron, zinc, chromium and nickel. Other metals can be boron, cadmium, copper, strontium, mercury, lithium, selenium, antimony, aluminum, arsenic (Collins, 1975).

Substances are often in a colloidal state (Farajnezhad and Gharbani, 2012) and waters are treated in order to realize coagulation or flocculation: aluminum sulphate, ferrous sulphate, ferric chloride and ferric chloro-sulphate are commonly used as coagulants (Amokrane *et al*.,1997). Formation water associated with petroleum is usually anoxic and has a negative redox potential (Donaldson *et al.,* 1985); most produced water has an Eh usually low (Collins, 1975). Collins (1969) reported that produced water from the Anadarko Basin, Texas-Oklahoma, had an Eh ranging from -270 to -300mV.

Because of the considerable variability in water chemistry and the potentially large volumes involved, the management of produced water is an important and complex issue (Engle *et al*., 2014). Environmental effects of the produced water disposal can include contamination of soil, ground and surface water by salts, hydrocarbons, trace elements and NORM, with elimination of the agricultural uses of land (Keeland and McCoy, 2003; Gleason and Tangen, 2014). Sodium causes substantial degradation of soils and death of vegetation (Dutton *et al.,* 1989; Richter *et al.,* 1990). Irrigation waters with SAR levels greater than 12 are considered sodic and can adversely impact plant growth.

La Rossa groundwaters have a colloidal behavior, bad smell and gas bubbling, composition and flow rates quickly variable in time, basic pH (up 9.25), negative redox potential (up to -250 mV), high temperature (up to 23°C). They sometimes have high contents of total hydrocarbons, phenols, surfactants,

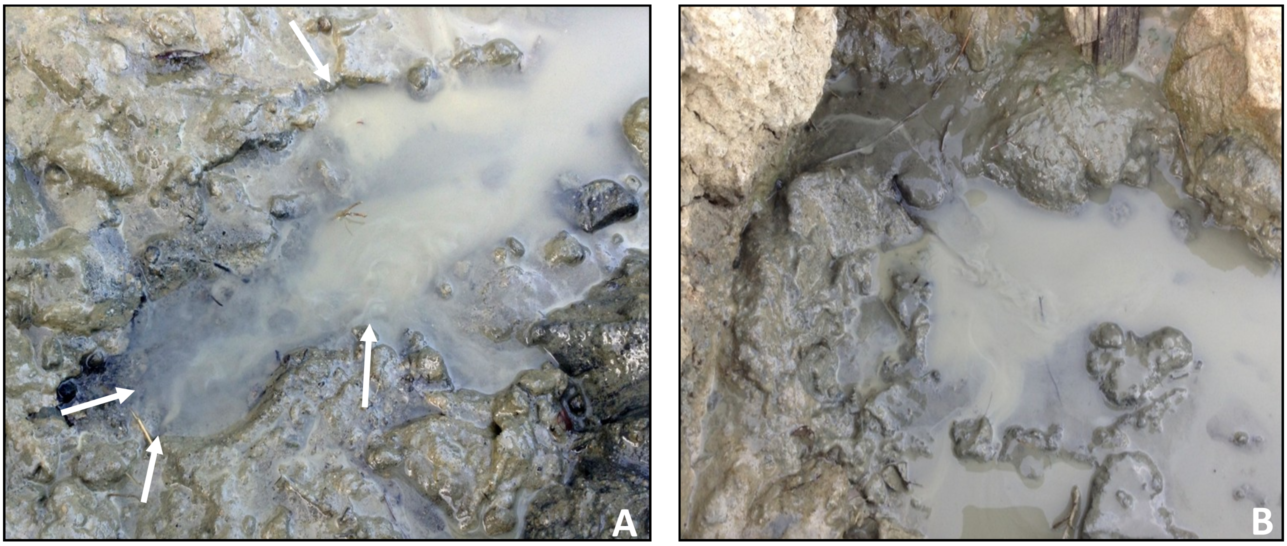


Fig. 14 - La Rossa S2, S3 pools of water: note the emergence of two distinct types of water, a turbid and a transparent meteoric groundwater (as indicated by arrows), that mix immediately downflow.

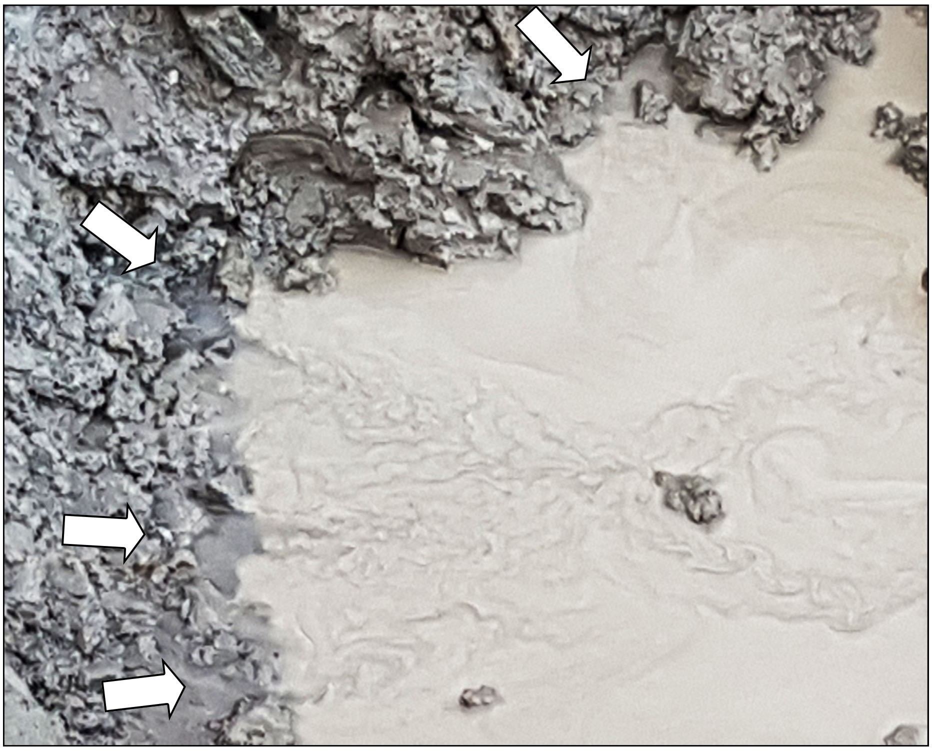


Fig. 15- The emergence of La Rossa groundwaters along a spring line.

sodium, salts and metals, such as aluminum, iron, manganese, boron, barium, lead, copper, zinc, strontium, vanadium, nickel. Aluminum is the most abundant metal in La Rossa waters, despite being almost insoluble from rocks in natural conditions. Sodium is the dominant cation, followed by calcium, potassium and magnesium; the dominant anions are (in descending order) bicarbonates, sulphates, chlorides and phosphates. La Rossa waters are sodic and cause degradation of soil along their flow path, making it infertile and producing salt crusts on soil and clasts (Figg. 9a,b). Sometimes the mixing of La Rossa murky groundwaters with those meteoric has been distinctly observed at their emergence from the underground (Fig. 14).

The high concentration of aluminum is intriguing: the average concentration in principal VA springs is 9.30 μg/L, whereas in La Rossa S2,3 groundwaters reaches 15,700 μg/L. Aluminum in oil industry is used in drilling muds (NRC, 1983), in oil desolforation processes, for coagulation and flocculation of colloids of produced waters (Amokrane *et al*., 1997; Pinotti and Zaritzky, 2001; Sahu and Chaudhari, 2013), ecc. Aluminum is very abundant in rocks but it is almost insoluble in waters at natural conditions. Aluminum low mobility, however, is strongly pH-dependent: its solubility increases at pH < 5.5, but aluminum may be also mobilized from rocks under strongly alkaline conditions at pH values > 8 (Shiller and Frilot, 1996), just like those of La Rossa waters.

La Rossa S2,3 groundwaters share many of the general properties of oil produced water, despite obvious differences that can be due to several factors, such as: 1) the underground processes (water mixing, water-rock interaction, ecc.) that can modify the original physico-chemical properties of waters flowing trough rocks. The isotopic composition of mixed waters, for example, becomes intermediate between the composition of the end members (Kendall and Caldwell, 1998); 2) the compositional variability in time of produced water; 3) the low velocities of the underground flows: they often occurs as a slow seepage through the pore spaces between particles of unconsolidated materials, or through networks of fractures and solution openings in consolidated rocks. A velocity of 1 foot per day or greater is a high rate of movement for groundwater and velocities can be as low as 1 foot per year or 1 foot per decade (Alley *et al*., 1999); 4) the treatment processes of produced water at facilities like COVA. This treatment implies, among others, the use of chemicals, like soda, that can increase water pH. La Rossa groundwaters have a pH ranging from 8.21 to 9.25.

It is therefore confirmed that the potential source of the anomalous La Rossa groundwaters could be the Val d'Agri oil produced water treated at COVA, injected in the Costa Molina 2 well and migrated in the underground. We made a comparison of the properties of La Rossa S2,3 groundwaters with two analyses of the oil wastewater treated at COVA. We found several similarities, even though such a type of comparison is highly questionable, because of: 1) the underground physico-chemical processes that can modify some of the original properties of the injected water; 2) the high variability in time of the oil produced water; 3) the long time interlapsed between the wastewater injection and its emergence at a distance of 2.3 km, considering the general low velocities of underground flows. The analyses of COVA produced water show negative redox potential, high values of temperature, TDS, EC, total hydrocarbons, phenols, sodium, salts, surfactants, metals like boron and strontium; phosphates are also present.

The most frequent causes in the world of underground migration of injected wastewater are: 1) improperly plugged abandoned oil and gas wells within the radius of influence created by the injection wells, that act as conduits for these fluids. In our study area the CM3 abandoned well occurs ~ 2.06 km from La Rossa S2,3 pools of water (Fig. 5); 2) well leakage, that can be due to insufficient length of the metallic casing, or to problems of well integrity due to damages to the metallic casing for corrosion or cracks, or to the force of injection that accidentally shatters the rock meant to contain it (Nicot *et al.,* 2006), then allowing fluids to seep through induced fractures into the earth. Underground fluid migration and consequent contamination of water supplies can be favoured by the geologic structure of the area, with faults and fractures. In Osage County (Oklahoma, USA) many injection, waterflooding and pressure maintenance wells encountered problems with equipment failures, leakage across geologic structures and from improperly plugged and abandoned older production wells (Otton *et al.,* 1997). Groundwater contamination by leakage of injection wells is diffused in the world. Among others, the GAO study (1989) found 23 confirmed studies of groundwater contamination from produced water injection wells. Radioactive contaminated groundwater was discovered in August 1984 in two groundwater monitoring wells drilled 300 m far from a deep injection well (Haase *et al.,* 1987). Leaking wells can also go undetected. Payne *et al.*(1999), looking for the cause of high salinity in soil, found that at least 22 brine injection wells in the Hatchel area in West Texas (USA) were likely sending a plume of salt water up into the ground unnoticed.

5.2 Geologic Structure, Induced Seismicity and Fluid Migration

The CM2 injection well is located in the area of the destructive M7 seismic event of 1857, that caused 3,000-4,000 victims in the Montemurro village. In the basement Quaternary faults are still active: they controlled the development of the Val d'Agri graben, but their scientific knowledge is still poor.

Recently Stabile *et al*. (2014) and Improta *et al*. (2015) documented the occurrence of microseismicity induced by the injection of Val d'Agri oil produced water in the CM2 well, up to a depth of ~ 9 km inside the carbonate Apulian Platform (Fig. 16).

Improta *et al*. (2015) documented also the presence of two faults just below the CM2 well (Fig. 16B). The NE-dipping fault should be located between 3.5 and 4.5 km depth, fully contained within the carbonate reservoir of the Apulian Platform, topped by flysch and shale successions. This fault is a matter of debate with Stabile *et al*. (2014), that have attributed the induced seismicity to the reactivation of this NE-dipping fault that reaches the surface. This reconstruction has been so challenged by Improta *et al.* (2015): "*Our 3-D locations suggest that the preexisting NE-dipping fault is fully contained within the carbonate reservoir and topped by flysch and shale sequences because only a few sparse, small events (M_L <1) occurred above the AP. No NE-dipping fault is reported in the geologic maps of the area, and the structural relationship of the fault illuminated by induced microearthquakes with the known Quaternary normal faults is not clear (Figures 4a and 4b). The fault is located in the footwall block of the SW dipping normal fault that bounds the basin [Lazzari and Lentini, 1991] and crops out 1.4 km SW of the well (Figures 4a and 4b). Therefore, its geometry is incompatible with a antithetic secondary strand of the basin-bounding fault system, as hypothesized by Stabile et al. (2014)".*

We reconstructed the Quaternary tectonic structure of the CM2 area (Fig. 17), and identified a morphostructure controlled by normal faults oriented NNE-SSW dipping ESE, and NNW-SSE dipping to WSW, with a vertical displacement of each fault of some hundreds of meters. The induced seismicity mostly occurs in the area bounded by the mapped normal faults.

Improta *et al*. (2015) state that microseismicity is induced by rapid communication of pore pressure perturbations along an intensely fractured and highly permeable fault zone. The latter likely corresponds to a hydraulically conductive pathway that promotes pore pressure diffusion. The response of the system is very rapid and the seismicity begins with a delay of only 3 hours after the injection initiation. Stabile *et al.* (2014) and Improta *et al*. (2015) show various elements that can be adequately evaluated from the geoenvironmental point of view.

Wastewater injection induced earthquakes up to a depth of ~ 9 km (Fig. 16 B1, event *DE*) in the carbonate rocks and in the overlying flysch and shale rocks, and up to 5 km horizontally from the bottomhole (Fig. 16, B1 event *b*), a distance that comprises the area of Cd. La Rossa, located only 2.3 km from the injection well to the NE. The injected fluids thus migrated through a large volume of carbonate and overlying siliciclastic rocks, as suggested by the distribution of induced microseismicity. The upward fluid migration through flysch and shale rocks, evidenced by induced seismicity as shown in fig. 16 B of Improta *et al*. (2015), reached about 800 m from the surface. It is consequently not excluded that these fluids may have arrived at the surface in many sites (as in Cd. La Rossa). Moreover injected fluids have migrated into flysch and shale rocks without causing induced seismicity for a distance > 1 km (Fig. 16 B1event c). This means that the lack of induced seismicity does not necessarily implies the lack of fluid migration. On the other hand massive water injection has the potential to elevate pore pressures within porous and fractured formations and to reactivate faults, either seismically or aseismically (Gan and Ellsworth, 2014; Cappa and Rutqvist, 2011; Segall and Rice, 1995). It is then highlighted that the flysch and shale cover does not guarantee the isolation of injected fluids from the surface.

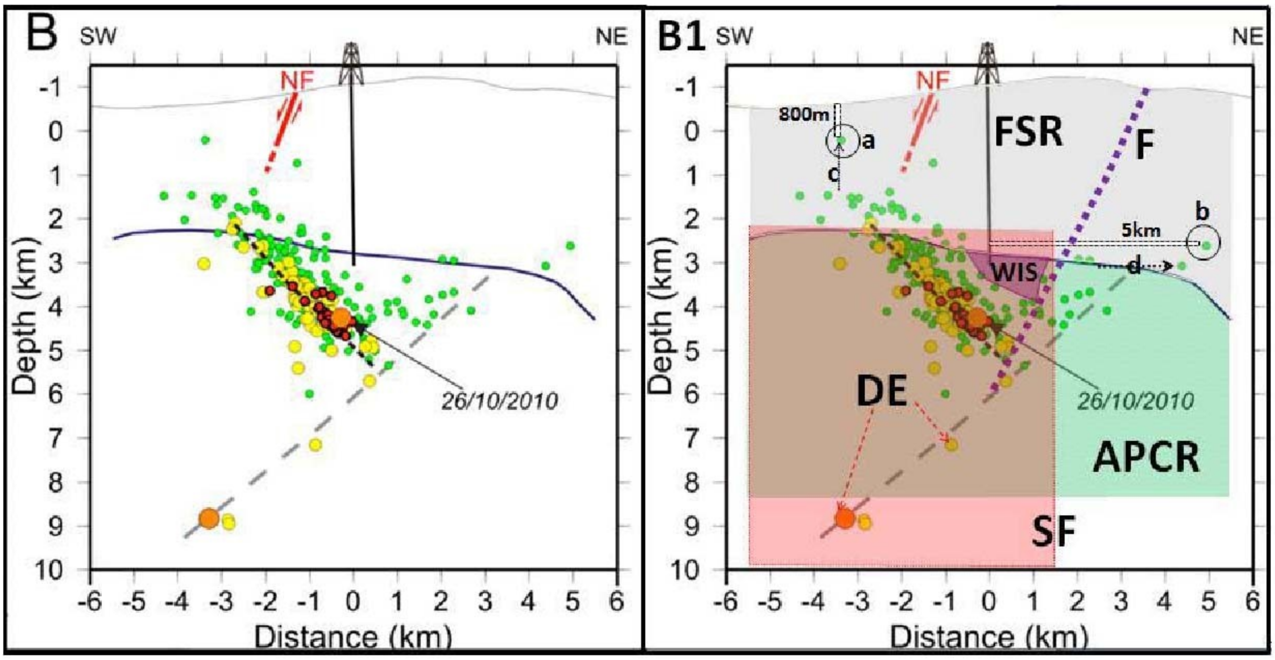


Fig. 16. Left image B is fig. 4B of Improta *et al.* (2015), right image B1 is the interpretation of geoenvironmental data according to us. FSR: flysch and shale rocks; APCR: Apulian Platform calcareous rocks; SF: rocks that can be affected by the seismogenic fault of the 1857 earthquake; WIS: rocks that have been affected by injected fluids without induced seismicity; DE: earthquakes induced by wastewater injection about 9 km deep and about 5 km from the bottomhole; a, b: earthquakes induced by injection respectively at about 800 m (a) from the surface and 5 km (b) from the bottomhole; c: migration of fluids injected for about 1 km, rising toward the surface without causing earthquakes; d: migration of injected fluids for about 2 km without causing induced seismicity. F: eastern normal fault system that borders the Val d'Agri graben.

6. Conclusions

Oil produced water has the potential to affect the quality of drinking water resources if it enters into a surface or groundwater body intended for human use. We examined the physico-chemical and hydrogeological characteristics of two anomalous turbid and saline pools of groundwater that suddenly appeared in 2011 on soils of Cd. La Rossa in the Val d'Agri oil field, at 2.3 km from the CM2 injection well, and we reconstructed the geological structure of the area.

Our data confirm that La Rossa S2,3 groundwaters share many of the general properties of oil produced water, despite the obvious differences due to the processes that occurred during their underground flow. Our fieldwork shows that La Rossa groundwaters flow out in pressure along a spring line visible at a depth of ~ 2 m, where a change of rock type occurs between permeable sandstone and overlying low-permeability mudstone that allows some feeble flow to reach the surface forming the S2,3 La Rossa pools of water. Field observations show also: 1) the occurrence in the two pools of a mixing between turbid saline and meteoric groundwaters at their emergence to the surface ; 2) the lack of interconnection between the S2,3 pools of water, that have apparently different underground flow paths; 3) the spread of contamination in the springs adjacent to La Rossa pools.

About the potential mechanisms that favoured the underground flow and emergence of La Rossa S2,3 waters, Improta *et al.* (2015) documented a large-scale underground migration of the oil wastewater injected in the CM2 well, that caused induced microseismicity for kilometers in the carbonate and overlying flysch and shale rocks. The Authors recognized the occurrence of faults just below the injection well, with intensely fractured and highly permeable fault zones, that represent hydraulically conductive pathways for the diffusion of the injected produced water. The latter migrated and induced microseismicity up to a depth of about 9 km, at a distance of about 5 km from the CM2 well and at about 800 m from the surface. Induced microseismicity seems to be confined in the morphostructure we recognized in the CM2 area, controlled by normal faults oriented NNE-SSW dipping ESE and NNW-SSE dipping WSW.

Potential contributory causes of the underground wastewater migration and emergence to the surface, could be abandoned oil wells within the radius of influence created by the injection well, like the CM3 well, and/or leakages of the CM2 well for problems of well integrity. A parliamentary question in 2011 mentioned that the CM2 injection well had problems of well integrity in 1999.

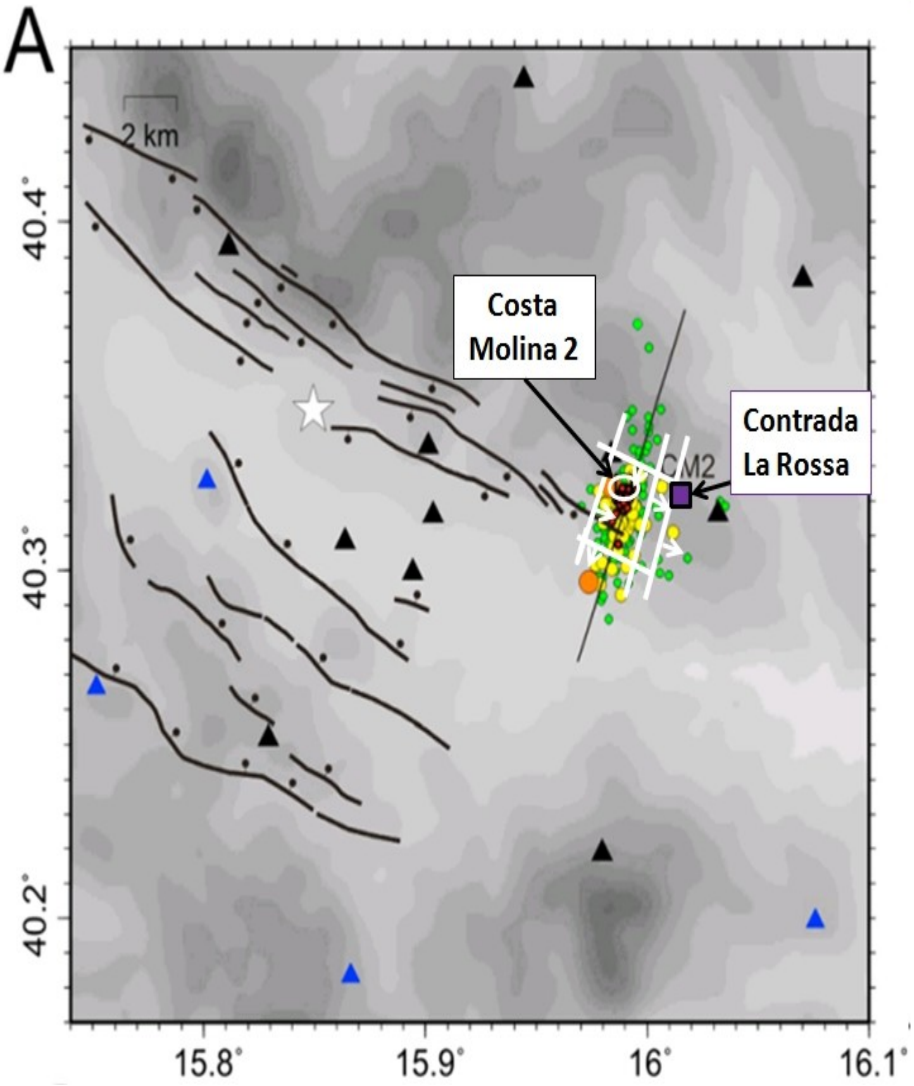


Fig. 17 - The figure illustrates our modification of fig. 4A of Improta *et al. (*2015): white lines indicate the normal faults we recognized in the field. Black and blue triangles are relocated earthquakes recorded by ENI and INGV permanent stations from June 2006 to December 2013, respectively. The figure reports events within a horizontal distance of 5 km from the CM2 well and shallower than 10 km. Orange, yellow, and green dots indicate events with ML ≥ 2, 1 ≤ ML < 2, and ML < 1, respectively. Red small dots denote DD locations of the 69 events recorded by the INGV temporary network between 2 and 12 June 2006. The white star is the epicenter of the 1857 M7 earthquake.

References

Alley, W.M., Reilly, T.E. and Franke, O.L. (1999) - Sustainability of Ground-Water Resources. *U.S. Geological Survey Circular 1186*.

Amokrane, A., Comel, C. and Veron, J. (1997) - Landfill Leachates Pre-Treatment by Coagulation Flocculation. *Water Res*., 31, 2775 - 2782.

Cappa, F. and Rutqvist, J. (2011) - Modeling of coupled deformation and permeability evolution during fault reactivation induced by deep underground injection of CO2. *Int. J. Greenhouse Gas Control*, 5, 336-346.

Cello, G., E. Tondi, L. Micarelli and L. Mattioni (2003) - Active tectonics and earthquake sources in the epicentral area of the 1857 Basilicata earthquake (southern Italy). *J. Geodyn*., 36, 37–50.

Civita, M., De Maio, M. and Vigna, B. (2003) - Studio delle risorse sorgive degli acquiferi carbonatici dell'Alta Val d'Agri. In: A. Colella (Ed.), *Le risorse idriche sotterranee dell'Alta Val d'Agri, Collana Editoriale di Studi e Ricerche dell'Autorità Interregionale di Bacino della Basilicata,* 3, 221-452.

Cline, J.T. (1998) - Treatment and Discharge of Produced Water for Deep Offshore Disposal. Presented at the *API Produced Water Management Technical Forum and Exhibition*, Lafayette, LA, 17-18.

Colella, A. (2014) - Anomalous deep waters gurgling to the surface and impacting soils in the Val d'Agri oil field, southern Italy. *International Journal of Ecosystems and Ecology Science*, 4/4, 533-542.

Colella, A., Lapenna, V. and Rizzo, E. (2004) - High-resolution imaging of the High Agri Valley basin (Southern Italy) with electrical resistivity tomography. *Tectonophysics*, 386 (1–2), 29–40.

Colella, A and Agrifluid Group (2003) - Le risorse idriche sotterranee dell'Alta Val d'Agri. In: A. Colella (Ed.), *Le risorse idriche sotterranee dell'Alta Val d'Agri, Collana Editoriale di Studi e Ricerche dell'Autorità Interregionale di Bacino della Basilicata,* 3, 1-495.

Collins, A.G. (1975) - *Geochemistry of oilfield waters*. Elsevier Scientific Publishing, Amsterdam, 496 pp.

Collins, A.G. (1969) - Chemistry of some Anadarko Basin brines containing high concentrations of iodide. *Chemical Geol*., 4,169-187.

Donaldson, E.C., Chilingarian, G.V. and Yen, T.F. (1985) - *Enhanced Oil Recovery, I: Fundamentals and Analyses*. Elsevier, 603 pp.

Dutton, A.R., Richter, B.C. and Kreitler, C.W. (1989) - Brine discharge and salinization, Choncho River Watershed, West Texas. *Ground Water*, 27, 3, 375-383.

Engle, M.A., Cozzarelli, I.M. and Smith, B.D. (2014) - USGS Investigations of Water Produced During Hydrocarbon Reservoir Development. *USGS Fact Sheet*, 2014–3104.

ENI (2014) - ENI in Basilicata. *Local Report*, 107 pp.

ENI (2015) - *https://www.eni.com/eni-basilicata/home.page.*

Fakhru'l-Razi, A., Pendashteh, A., Abdullah, LC., Biak, DR, Madaeni, SS. and Abidin., ZZ. (2009) - Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.,*170, 530-551.

Farajnezhad, H. and Gharbani, P. (2012) - Coagulations treatment of wastewater in petroleum industry using poly aluminum chloride and ferric chloride. *IJRRAS* 13(1).

Gan, Q. and D. Elsworth (2014) - Analysis of fluid injection-induced fault reactivation and seismic slip in geothermal reservoirs. *J. Geophys. Res. Solid Earth*, 119, 3340–3353.

GAO (1989) - Safeguards Are Not Preventing Contamination from Oil and Gas Wastes. *RCED*, 89-97.

Gleason, R.A. and Tangen, B.A. (2014) - Brine contamination to aquatic resources from oil and gas development in the Williston Basin, United States. *U.S.Geological Survey Scientific Investigations Report 2014–5017*, 127 pp.

Haase, C.S., Von Damm, K. L. and Stow, S.H. (1987) - Closure of the Oak Ridge National Laboratory Hydrofracture Facility: an Opportunity to Study the Fate of Radioactive Wastes Disposed by Subsurface Injection. *Report Oak Ridge National Laboratory*, Oak Ridge, Tennessee.

Igunnu, E.T. and Chen, G.Z (2014) - Produced water treatment technologies. *International Journal of Low-Carbon Technologies*, 9, 157–177.

Improta, L., Valoroso, L., Piccinini, D. and Chiarabba, V. (2015) - A detailed analysis of wastewater-induced seismicity in the Val d'Agri oil field (Italy). *Geophys. Res. Lett.,* 42.

Improta, L., Ferranti, L., de Martini, P.M., Piscitelli, S., Bruno, P.P, Burrato, P., Civico, R., Giocoli, A., Iorio, M., D'Addezio, G. and Maschio, L. (2010) - Detecting young, slow-slipping active faults by geologic and multidisciplinary high-resolution geophysical investigations: A case study from the Apennine seismic belt, Italy. *J. Geophys. Res.*, 115.

Keeland, B.D. and McCoy, J.W. (2003) - Effects of produced water and hydrocarbon releases on vegetation at site A of the Osage-Skiatook petroleum environmental research project, Osage County, Oklahoma. In: *2003 10th Annual International Petroleum Environmental Conference,* Houston, Texas, November 11-14, 2003: IPEC.

Kendall., C. and Caldwell, E.A. (1998) - *Isotope Tracers in Catchment Hydrology*. Elsevier Science B.V., Amsterdam, 839 pp.

Lazzari, S. and Lentini, F. (Eds.) (1991) - *Carta Geologica del Bacino del Fiume Agri.* Scala 1:50.000, S.EL.CA, Firenze.

Lustgarten, A. (2012) - Are fracking wastewater wells poisoning the ground beneath our feet? *Scientific American.*

Maschio, L., Ferranti, L. and Burrato, P. (2005) - Active extension in Val d'Agri area, Southern Apennines, Italy: Implications for the geometry of the seismogenic belt. *Geophys. J. Int*., 162(2), 591–609.

Mongelli, G., Paternoster, M. and Frittella, F. (2003) - Caratterizzazione geochimica delle acque di sorgente dell'Alta Val d'Agri. In: A. Colella (Ed.), *Le risorse idriche sotterranee dell'Alta Val d'Agri. Collana Editoriale di Studi e Ricerche dell'Autorità Interregionale di Bacino della Basilicata*, 3, 177-197.

Morandi, S. and Ceragioli, E. (2002) - Integrated interpretation of seismic and resistivity images across the Val d'Agri graben (Italy). *Annals of Geophysics*, 45(2), 259-271.

Neff, J.M., Lee, K. and DeBlois, E. (2011) - Produced Water: Overview of Composition, Fates, and Effects. In: Lee, K., Neff, J.M. (Eds.), *Produced Water.* Springer New York, 3-54.

Neff., J. M. and Foster, K. (1997) - Composition, fates and effects of produced water discharges to offshore waters of the Java Sea, Indonesia. *Report to Pertimena/Maxus*, Jakarta, Indonesia, 103 pp.

Nicot, J.P, Saripalli, P., Hovorka, S.D. and Lakshminarasimhan, S. (2006) - Leakage Pathways from Potential Storage Sites in the Texas Gulf Coast and Implications for Permitting. Abstract in: *Fifth Annual Conference on Carbon Capture & Sequestration,* Alexandria, Virginia. GCCC Digital Publication Series#06-09.

NRC (1983) - Drilling discharges in marine environment. *National Research Council National Academy Press*, Washington D.C., 180 pp.

Osservatorio Val d'Agri - *http://www.osservatoriovaldagri.it/*

Otton, K.J. (2006) - Environmental aspects of produced-water salt releases in onshore and coastal petroleum-producing areas of the conterminous U.S. *U.S.Geological Survey Open-File Report 2006-1154*, 221 pp.

Otton, K.J., Asher-Bolinder, S., Owen, D.E. and Hall, L. (1997) - Effects of produced waters at oilfield production sites on the Osage Indian Reservation, northeastern Oklahoma. *U.S. Geological Survey Open-File Report 97-28*.

Paine, J.G., Dutton, A.R. and Blum, M.U. (1999) - Using Airborne Geophysic to identify salinization in West Texas. *Report of Investigation n. 257, Bureau of Economic Geology*, *The University of Texas*.

Pinotti, A. and Zaritzky, N. (201) - Effect of aluminum sulfate cationic polyelectrolytes on the destabilization of emulsified wastes. *WASTE MAN*, 21(6), 535-542.

Richter, B.C., Dutton, A.R. and Kreitler, C.W. (1990) - Identification of sources mechanisms of salt water pollution affecting ground-water quality: a case study, West Texas. *The University of Texas, at Austin, Bureau of Economic Geology Report of Investigations,* No. 191, 43 pp.

Sahu, P. and Chaudhari, P.K. (2013) - Review on Chemical treatment of Industrial Waste Water. *J. Appl. Sci. Environ. Manage,* 17 (2) 241-257.

Segall, P. and Rice, J. R. (1995) - Dilatancy, compaction and slip instability of a fluid-infiltrated fault. *J. Geophys. Res.*, 100(B11), 22,155–22,171.

Shiller, A.M. and Frilot, D.M.(1996) - The geochemistry of gallium relative to aluminum in californian streams. *Geochimica et Cosmochimica Acta*, 60(8), 1323-1328.

Stabile, T. A., Giocoli, A., Perrone, A., Piscitelli, S. and Lapenna, V. (2014) - Fluid injection induced seismicity reveals a NE dipping fault in the southeastern sector of the High Agri Valley (southern Italy). *Geophys. Res. Lett.,* 41, 5847–5854.

Strømgren, T., Sørstrøm, S.E., Schou, L., Kaarstad, I., Aunaas, T., Brakstad., O.G. and Johansen, Ø. (1995) - Acute toxic effects of produced water in relation to chemical composition dispersion. *Mar. Environ.Res.*, 40,147–69.

Trice, R. (1999). Application of borehole image logs in constructing 3D static models of productive fracture network in the Apulian Platform, Southern Apennines. *Borehole Imaging: Applications and Case Histories*, edited by M. A. Lovell, G. Williamson and P. K. Harvey, *Geol. Soc.London Spec. Publ.*, 159, 156–176.

UNMIG (2016) - *http://unmig.sviluppoeconomico.gov.it/*

USGS (1999) - General Facts and Concepts about Ground Water. *http://pubs.usgs.gov/circ/circ1186/index.html*

Utvik, T.I.R. (1999) - Chemical characterization of produced water from four offshore oil production Platforms in the North Sea. *Chemosphere*, 39, 15, 2593-2606.

Utvik, T.I.R., Durell, G.S. and Johnsen, S. (1999) - Determining produced waters originating PAH in North Sea water: Comparison of sampling techniques. *Marine Pollution Bulletin*, 38 (11), 977-989.

Veil, J.A., Puder, M.G., Elcock, D. and Redweik, R.J. (2004) - A white paper describing produced water from production of crude oil, natural gas, coal bed methane. *Technical Report, Argonne National Lab.,U.S. Department of Energy.*

Aknowledgments

We are grateful to Prof. Massimo Civita and Dr. Adriano Fiorucci of Politecnico di Torino for suggestions and discussions on the hydrogeological aspects of the study area.