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The Geothermal Power Plants of Amiata Volcano, Italy: Impacts on Freshwater Aquifers, Seismicity and Air

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Abstract

Production of geothermal energy for electricity at Amiata Volcano uses flash-type power plants with cooling towers that evaporate much of the geothermal fluid to the atmosphere to condense the geothermal vapour extracted. Because the flash occurs also within the geothermal reservoir, it causes a significant depressurization within it that, in turns, results in a drop of the water table inside the volcano between 200 and 300 m. The flow rates of natural springs around the volcano have also substantially decreased or ceased since the start of geothermal energy exploitation. Continuous recording of aquifer conditions shows substantial increases in salinity ($>20\%$) and temperature ($>2^{\circ}\text{C}$) as the water table falls below about 755–750 m asl. In addition to hydrologic impacts, there are also a large numbers of induced earthquakes, among which the M_L 3.9, April 1, 2000 earthquake that generated significant damage in the old villages and rural houses. Relevant impacts on air quality occur when emissions are considered on a per-MW basis. For example, $\text{CO}_2 + \text{CH}_4$ emissions at Amiata are comparable to those of gas-fired power plants, while the acid-rain potential is about twice that of coal-fired power plants. Also, a significant emission of primary and secondary fine particles is associated with the cooling towers. These particles contain heavy metals and are enriched in sodium, vanadium, zinc, phosphorous, sulphur, tantalum, caesium, thallium, thorium, uranium, and arsenic relative to comparable aerosols collected in Florence and Arezzo. Measurements have shown that mercury emitted at Amiata comprises 42% of the mercury emitted from all Italian industries, while an additional comparable amount is emitted from the other geothermal power plants of Tuscany. We believe that the use of air coolers in place of the evaporative cooling towers, as suggested in 2010 by the local government of Tuscany, could have and can now drastically reduced the environmental impact on freshwater and air. On the opposite side of the coin, air-coolers would increase the amount of reinjection, increasing the risk of induced seismicity. We conclude that the use of deep borehole heat exchangers could perhaps be the only viable solution to the current geothermal energy environmental impacts.

Keywords: geothermal energy, environmental impact, aquifer pollution, induced seismicity, air-quality deterioration

1. Introduction

Geothermal energy is the energy stored as heat within the upper crust of the Earth. Due to magmatism and hydrothermal circulation, rocks at high temperatures, in the 150–350°C range, can be found in specific areas at reasonably shallow depths. Because rocks are poor heat conductors, geothermal heat energy is most commonly extracted by circulating fluids in the pores and fractures of the hot rock using water injection and production (withdrawal) wells.

Geothermal energy is commonly perceived as environmentally friendly in Italy [1–3]. However, at Amiata Volcano in Southern Tuscany (**Figure 1**), geothermal energy exploitation has quantifiable and substantial local and more widespread environmental impacts, which suggest that this form of energy production needs substantial technical improvements before it may be considered eco-friendly.

At Amiata, there are six flash-type 20-MWe power-plants units, three for each of the two geothermal fields of Bagnore and Piancastagnaio (**Figure 1**). Briefly, the produced geothermal vapour (**Figure 2**) is used to spin a turbine to produce electricity. Immediately after, the vapour is condensed within a shower of cold geothermal fluid, and separated into two streams, a liquid brine condensate and a non-condensable gas, that are treated as follow:

1. The liquid brine is sent to the cooling tower where it is sprayed from the top, while 9-m-diameter fans pump air upward from the bottom of the towers (counter-current) thereby evaporating one-half to three-quarters of the geothermal fluid which is exhausted to the atmosphere (cf. [7], p. 2). The remaining cooled geothermal fluid, collected at the bottom of the tower is sent back to the condenser to condense again the vapour and complete the cycle; the excess geothermal fluid is sent to reinjection in the reservoir. The fluid balance in the reservoir is maintained through fresh-water recharge from the superficial freshwater aquifers (cf. [8]).
2. The non-condensable gases are passed through the Abatement of Mercury and Hydrogen Sulphide (AMIS) system to reduce the amount of these two pollutants; the H_2S is mixed with air and via catalytic oxidation is transformed into SO_2 , which, in turn, is dissolved into the geothermal fluid and sent to the condenser; the remaining gas stream is sent to the cooling towers to be exhausted to the atmosphere.

Because the geothermal fluid contains also a significant amount of ammonia, to mitigate the emissions, sulphuric acid is added to the geothermal fluids, if the SO_2 produced by the AMIS is insufficient, to convert ammonia into ammonium-sulphate salts. In the case that residual SO_2 is present, soda (Na_2CO_3) is added to the liquid stream. In short, the gaseous pollutants are converted to salts that are solubilised in the liquid stream and for the most part, reinjected into the reservoir. However, because of the substantial evaporation occurring in the cooling towers, an unknown fraction of the geothermal fluid droplets evaporate completely leaving fine particles that, with the fine particles contained in the non-condensable gas-stream [9], are emitted as aerosols to the atmosphere with the air-vapour flow. In addition, the majority of the non-condensable gases and smallest size-fraction of droplets of geothermal fluid are emitted to the atmosphere carried by the upward airflow.

In this paper, we present data and explanation to show how, because of this specific type of geothermal energy exploitation, some significant impacts occur at Amiata as follows: (I) decline in the water table of the volcanic freshwater aquifer

Figure 1.
(a) Structure of the Amiata volcano area, after Borgia et al. [4]; the three geothermal areas are circled in blue; brown areas = permeable rocks, blue areas = impermeable rocks; black lines = normal faults, yellow lines = basal compressive structures, red lines = anticlines, green lines = synclines. The blue line is the cross-section of (b). Purple line is cross section of Figure 8; numbers are piezometers: 1 = Enel inferno, 2 = Lazzaretti, 3 = Enel4, 4 = Enel Castagno, 5 = Enel Valle, 6 = Galleria Nova drainage tunnel. Inset is the location of Amiata volcano in Tuscany (black line), Italy. (b) Cross-section through Amiata volcano and the Piancastagnaio geothermal field (after [4]); section trace is in (a). Note the doming structures of the anhydrites (AB-TU-1) that constitute the superficial geothermal field; TMC is the Tuscan metamorphic complex, VO are volcanic rocks, LT-TU2 are Tuscan units, LI is Ligurian units, M-P-Q are Miocene-Pliocene-Quaternary marine sediments. Numbers 1, 2, and 3 are the locations of local stress fields (indicated on top of the figure) consistent with volcanic spreading, which allow for activation of normal, strike-slip and thrust [5] faults, respectively.

because of geothermal fluid production and depressurization, (II) increase in induced seismicity mainly because of fluid reinjection, and (III) decrease of air quality because of the atmospheric emissions of gases and aerosols. Other environmental impacts may arise because of overall geothermal-field depressurization, such as subsidence and soil gas emissions, but are not discussed here.

Figure 2. (a) The PC5 (left-hand side of the photo) and PC4 (right-hand side of the photo) power plants at the Piancastagnaio geothermal field. Note the plumes emitted from the cooling towers and the steam pipes in the foreground. (b) Schematic of a flash geothermal power plant such as those at Amiata volcano (modified from [6]); the cooling towers are composed of three cells exhausting air with vapour, gases, droplets of water and fine particles to the atmosphere. See text for further explanation.

2. Geology

The geology of the Amiata Volcano and the surrounding areas was originally studied by Calamai et al. [8], Ferrari et al. [10], Brogi [11] and references therein. Borgia et al. [4, 12] presented a volcanic spreading model for the volcano-tectonic evolution of Amiata (**Figure 1**), expanding on the idea originally suggested by Ferrari et al. [10] and Garzonio [13], and that relates the deep-seated gravity deformation of the volcanic edifice with the formation of the geothermal fields. More recently, Principe and Vezzoli [14], prefer a three-phases volcano-tectonic-collapse model for the origin of the numerous faults that cut the volcanic edifice of

Amiata, a model originally proposed by Mazzuoli and Pratesi [15] and later by Calamai et al. [8]; these authors, however, fail to recognise the numerous compressive structures and anhydrite and shaley diapirs that are found around the base of the volcano [8, 16–19] and that tectonically balance the collapse and spreading of the volcanic edifice [4]. They also fail to recognise the faulting and grabens in the basement below the volcano [8] that do not correspond to their collapse structures within the volcano but are in good agreement with the volcanic spreading model. Active compressive tectonics away of the eastern base of Amiata Volcano are also shown by recent thrust and strike-slip focal mechanism solutions [20].

Aside from the details of the different interpretations of the volcanotectonic evolution of Amiata, there is a general agreement that a relatively large number of recent and active, normal faults cut the volcanic edifice and its basement at least down to the anhydrites at the base of the Tuscan Formation (in the case of the volcanic spreading model [4]), or to deeper levels above the plutons (in the case of the volcano-tectonic collapse model [14]), or even deeper into the crust (in the case of the regional tectonic model [11]). These faults and the volcanic conduits, in addition to the sandstones of the Ligurian Formations and limestones of the Tuscan Formations, constitute the permeable pathways that connect the shallow freshwater aquifer contained in the volcanic rocks with the regional-scale hydrothermal aquifer [4, 8, 12, 21–23]. This freshwater aquifer is often referred to as the superficial aquifer.

3. Impact on Amiata volcano freshwater aquifer

The Amiata Volcano freshwater aquifer—the name derives probably from Latin “ad meata”, which means “at the springs”—is one of the most important sources of potable water in southern Tuscany and Latium serving about 700 thousand people, particularly during the summers, in the provinces of Grosseto, Siena, Arezzo and Viterbo. The richness of this resource is due not only to the freshness and abundance of the water (with productions on the order of 1 m³/s) but also to the fact that it is located at a relatively high altitude (most springs are between 600 and 900 m asl) in such a way that the aqueducts from Amiata can deliver water to the surrounding country by gravity without the need of pumping.

The first comprehensive study of this aquifer about the development of geothermal power plants is the one by Calamai et al. [8] (**Figure 3a**). In this study, they used all available data from before geothermal exploitation, including an electrical resistivity survey, calibrated with deep boreholes, that had up to 10-km-long survey lines to define the water table in addition to the top of the shaley and sandstone basement (the so-called “impermeable” layer below the volcanic rocks), and the top of the carbonatic rocks (Tuscan Formation) where the geothermal fields are located. It is seen that the water table rises from the lower elevations toward the top of the volcano reaching 1200 m above sea level where at least one spring was known to exist. The maximum gradients of the water table are relatively high at around 10%.

Numerical models of the Amiata Volcano freshwater aquifer have been developed by Delcroix et al. [25] and Caparrini et al. [26]. They find that for adequate permeability of the volcanic rocks and recharge, the water table indicated by Calamai et al. [8] is appropriate.

After the first years of exploitation of the geothermal fields (the first wells were drilled in 1959), the pressure of the geothermal fields was reduced by about 15 bar [21] (**Figure 4**). Around the same time, many fresh-water cold springs had substantially decreased their flow rate or had dried out, without any comparable decrease in rainfall (**Table 1**) [27]. During the same period, several water-drainage

Figure 3. Piezometric surface of the Amiata volcano freshwater aquifer (a) before geothermal exploitation started in 1959 (redrawn from [8]), and (b) after the beginning of geothermal exploitation (redrawn from [24]). The grey-coloured extent of the drawing is the outcrop of volcanic rocks as in (a). The decrease in elevation of the volcanic water table after the beginning of geothermal exploitation is evident and in the range of 100–300 m. Note also in (b) the minimum in the water table that indicates how the water from the superficial aquifer is drained down to the rocks below the volcano, where the hydrothermal system is located.

tunnels had to be constructed to increase the amount of water put into the aqueducts to deliver to the water users. The flow rate of at least one of these drainage tunnels (“Galleria Nova”) at the beginning of geothermal production showed an inverse relation with the production of geothermal fluids (**Figure 5**). Namely, as the flow rate of geothermal fluid produced increases, the flow rate of the spring decreases and vice versa.

To study the water table among other things, ENEL carried out an electric resistivity survey [24] to detect changes in the phreatic surfaces of the superficial

Figure 4. Decrease in the shut-in pressure of the geothermal wells in the reservoirs after the first years of geothermal exploitation (redrawn from [21]). Note that the initial pressure of the wells changes from about 22 bar in 1959 to about 7 bar in 1964. B.# (closed blue dots) are the names of the various wells first drilled at Bagnore. Open dots are non-producing wells.

Spring ↓ Date →	1940	1950–1951	1960–1964	1970–1972	2001–2002
Acqua d’Alto or Ente	118.00	89.10	97.06	68.00	49.10
Acqua Bona	7.50	7.30	6.00	0.00	0.00
Fontine	13.00	13.00	13.00	1.50	0.00
Vena	31.80	29.30	13.50	6.00	4.00
Total	170.30	138.70	129.56	75.50	53.10

Table 1. Flow rates in l/s of major springs SW of Amiata volcano that decreased their flowrate or dried out after the beginning of geothermal exploitation (after [27]).

aquifer. This survey (**Figure 3b**) shows a very different water table from the original one (**Figure 3a**) and effectively indicates that the superficial freshwater aquifer was drained through the main faults and the eruptive chimneys that connect the volcano to the geothermal system. It also shows a major minimum in the water table, which the same authors indicate as a potential drainage at depth [24]. This minimum in the water table was later measured also with an electric resistivity survey by the Province of Grosseto [29] and its time-evolution was monitored from August 2003 to April 2006 twice a year using magnetotelluric measurements by the Tuscan Region [30] showing oscillations in the phreatic surface that varied between 700 and 600 m asl.

Delcroix et al. [25] find that fluid production from the geothermal field above 0.5 m³/s can create critical conditions in the superficial freshwater aquifer because many areas of the aquifer could dry out. Also, Caparrini et al. [26] notice a direct correlation between the level of the monitored water table and the pressure below the superficial volcanic aquifer, that is the pressure of the geothermal field.

Additional evidence of the impact of geothermal exploitation on springs comes from the observations of the flow rates at the “Poggetto” hot spring (**Figure 6a**),

Figure 5. Correlation between vapour extraction at Bagnore geothermal field (pink line, left-hand side scale increasing upward) and water flow rate at the “galleria Nova” (dark-blue line, right-hand side scale increasing downward). The minimum water flow rate at the “galleria Nova” during the years 1962–1964 corresponds to a maximum in vapour extraction from the geothermal field in the same period. Conversely, as the vapour extraction decreased in the following years, the water flow rate at “galleria Nova” increased again (vapour production from [28]; galleria Nova flowrate data are from a personal communication from Regione Toscana to a. Borgia).

located about 5 km from the geothermal fields northeast of Amiata Volcano (Poggio Zoccolino geothermal area, **Figure 1a**). The flow rate of this spring increased when the Piancastagnaio geothermal field was closed, and decreased again when the geothermal field was reopened. Similarly, the spring flow rate increased when the Bagnore geothermal field was closed and it dropped to zero when the geothermal field reopened with power production tripled. A parallel change in flow rate can be also observed in the flow rate of the “Galleria Nova” drainage tunnel (**Figure 6b**). Similar changes are also observed in the various piezometers.

To monitor the time evolution of the minimum in the water table, the local government and ENEL installed within the volcanic edifice a set of piezometers that continuously measure the water table, in addition to groundwater salinity, conductivity and temperature. Five of these piezometers are indicated in **Figure 1a**, which form the highest to the lowest elevations are: “Enel Inferno”, “Lazzaretti”, “Enel4”, “Enel La Valle”, “Enel Castagno”. In addition, the draining tunnel of “Galleria Nova” constitutes the lower point of emergence of the water table. **Figure 7** shows the elevations of the water table for these piezometers in December 2018 projected along the purple line in **Figure 1a**. Two observations may be made:

1. From the original (before geothermal exploitation) elevation, the water table has dropped about 200–250 m in the two piezometers found at the higher elevations. Mineral precipitates (mainly goethite) in the fractures of the lavas of the cores of the “Lazzaretti” piezometer are found at about 200 m above today’s water table (direct observations by the authors; cf. also [31, 32]). Because these precipitates can form only below the water table, this finding confirms that, since their precipitation, the water table has dropped by a similar elevation. Also, today’s water table elevation at the “Lazzaretti” piezometer is about 50–100 m higher than the elevation measured by Compagnia Mediterranea Prospezioni [24], Marocchesi [29], and Manzella [30].

Figure 6.
(a) Flowrate versus time of the spring “Poggetto” between 2003 and 2016. The spring flow rate varies inversely with geothermal fluids production of the Mt. Amiata fields. Data courtesy of Ing. Pagano. (b) Flow rate versus time of the galleria Nova drainage tunnel from 1990 to 2020. From 1990 to 2009, the flow rate has clear cycles with a 3–4 year periodicity. The anomalous 30% increase in flow rate that begins in the summer of 2010 (blue arrow) was just before the installation of the first piezometer (Figure 1a) and corresponded to the closure of the Piancastagnaio geothermal field. Also, the closure of the Bagnore geothermal field corresponds to a significant increase in flow rate, while the reopening of the fields matches decreases in flow rate. Data from Regione Toscana—Centro Funzionale Monitoraggio Idrologico-Idraulico.

2. The water table has a strong inflexion in the gradient with the water table sloping toward the interior of the volcano—as determined from the piezometers Enel Castagno/Enel Valle toward Enel 4—.

These observations should be analysed in light of the following simplified conservation laws:

Figure 7. Sketch of water table levels measured in December 2018. Red line is the approximate original water table from Figure 3a. The elevation of the water table inferred by projected piezometer data from “ENEL Valle” and “ENEL Castagno” is the linear interpolation between their two elevations. Note: (1) the reduction in the water table and (2) the flow of water that is from the Valle-Castagno piezometers (located at lower topographic elevations) toward the ENEL4 piezometer (located at a higher topographic elevation) shows an inversion in the original direction of water flow in the aquifer. Data from Regione Toscana—Centro Funzionale Monitoraggio Idrologico-Idraulico.

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} = 0 \quad \text{2D-mass conservation,} \quad (1)$$

$$v_x = -\frac{k}{\mu} \frac{\partial p}{\partial x} \quad \text{x-momentum conservation,} \quad (2a)$$

or

$$v_x = -K \frac{\partial H}{\partial x}, \quad (2b)$$

where

$$K = \frac{k\rho g}{\mu} \quad (2c)$$

and v_x and v_z are the groundwater Darcy’s velocities in the x and z directions respectively, k is the rock permeability, m and r are respectively the water viscosity and density, K is the hydraulic conductivity, $\frac{\partial p}{\partial x}$ and $\frac{\partial H}{\partial x}$ are respectively the pressure and head gradients in the x direction, and g is the acceleration of gravity.

Mass conservation (Eq. (1)) states that if the flow velocity changes in one direction, there must be an opposite change in the other direction. Momentum

conservation (Eq. (2); Darcy's law) states that the flow is in the negative direction of the pressure or head gradient, that is from high to low pressure or head.

From these observations and Eq. (2), we may see that, for constant hydraulic conductivity K , if the hydraulic gradient decreases in the x -direction (horizontal) so does the velocity. Therefore, from Eq. (2c), if the velocity decreases in the x -direction it must increase in the z -direction. That is, due to gravity, the groundwater can only flow to the minimum and then downward toward the geothermal system (indeed, there are no pumping wells in the area). This conclusion is made even more evident by the positive gradient between the piezometers Enel n.4 and Enel Castagno/Enel Valle that forces the groundwater to flow toward the interior of the volcano.

In addition, it can be observed that the temperature and salinity of the water at the ENEL "Castagno" piezometer substantially increases if the water table drops below about 748–757 m asl. In the first of these events, the salinity drops from 285 to 185 ppm as the water table rises from 754 to 767 m asl (**Figure 8a**). In the second event, the salinity rises from 170 to 210 ppm as the water table drops below 748 m asl; on the contrary, as the water table rises again in elevation to 755 m asl the salinity drops again to lower values. The changes in temperature during these events are even more pronounced (**Figure 8b**). In the first event, the temperature increases by 2°C as the water table drops from 762 to 749 m asl decreasing to the original temperature as the water table rises again. In the second event as the water table drops below 754 m asl the temperature increases by about 1.0°C, but when it drops below 746 m asl, there is a temperature increase of about 4.5°C. As the water table recovers to rise above 746 m asl, the temperature drops again by 2°C.

Both the salinity and temperature variations analysed in conjunction with the water table elevation changes indicate that as the water table falls below a given elevation, the pressure at the bottom of the aquifer decreases and, as suggested by Caparrini et al. [26], the hot saline fluids rise into the freshwater aquifer decreasing its quality. We point out that the piezometer ENEL "Castagno" is located at the intersection of two relevant faults (the "Le Mura" and "Poggio Pinzi" faults) created by the volcanic spreading processes (**Figure 1a**). These faults create particularly high-permeability pathways connecting the anhydrite and carbonate rocks of the geothermal field with the volcanic rocks of the freshwater aquifer.

Future work will attempt to quantify the actual volume of water that is drained from the superficial freshwater aquifers to the geothermal system. This calculation is at the moment hindered because flow rates from the various wells and the producing pressures and vapour/liquid water ratio in both geothermal systems are unknown.

4. Induced seismicity

An earthquake occurs when the shear stress (τ) accumulated on a fault plane exceeds its shear strength (τ_f), which opposes the relative motion along the fault and is mainly dependent on lithology, roughness of faults' surface and normal stress acting on it (e.g., [33]). The effective value of the normal stress (σ_n) acting on a fault surface is controlled by the local stress field (i.e., values and relative directions of principal stresses σ_1 , σ_2 and σ_3) and by the pore pressure (p_p) in the neighbourhood of the fault.

$$\tau > \tau_f = C + \mu(\sigma_n - p_p), \quad (3)$$

Figure 8. Piezometer Castagno. (a) Water table elevation and salinity versus time. (b) Water table elevation and temperature versus time. Note the rapid changes in salinity and temperature as the water table drops to the lower values. Data from Regione Toscana—Centro Funzionale Monitoraggio Idrologico-Idraulico.

where C is cohesion and μ is friction coefficient [34]. When values of p_p increase—for example, due to anthropogenic operations, such as fluid injection, in the vicinity of the fault—pore pressure acts against σ_n , lowering the value of τ_f and thus allowing for the generation of a seismic event at relatively low values of shear stress (for $\tau > \tau_f$).

Seismicity is said to be “induced” when a pore-pressure-increase brought about by underground human activities (e.g., fluid injection) reaches a fault plane (possibly at some distance from the injection well) increasing the value of p_p and allowing the fault to slip, thereby releasing seismic energy accumulated on the fracture plane in the form of elastic strain [33]. The literature presents many past examples of seismicity induced by anthropogenic operations (e.g., [35, 36]) and, focus of this chapter, geothermal energy exploitation [37, 38]. In general, induced events are

usually of low intensity, because fault planes are not reactivated for their full extent [39], with hypocenters commonly located at relatively short distances from the injection well [37, 40, 41].

Seismicity is termed ‘triggered’ when the fault intersected by the pressure increase, due to gravity or tectonic loading, is already in a critical state in terms of shear stress (close to failure, i.e., critically stressed). In this case, τ is almost equal to τ_f on the fault plane and even a small increase of p_p activates a slip that interests the whole surface, releasing the entire stress accumulated on the structure in the form of seismic waves [39, 42]. A prerequisite for this to happen is the optimal orientation of the fault with respect to the principal stresses, with the normal to its surface lying in the plane $\sigma_1 \sigma_3$, where the differential stress is higher [38].

Previous studies (e.g., [33, 39, 43–45]) suggest that faults when in critically stressed conditions, can be more conductive to fluids (and to poroelastic stress changes). Barton et al. [45] present strong evidence that, in crystalline rocks, faults that are optimally oriented for shear failure and critically stressed have increased permeability and conduct fluid along their planes. Non-critically stressed faults appear to provide no fluid migration pathways. The concept of periodic fluid flow along growth faults (within sedimentary basins) was introduced by Sibson [43] and Hooper [45] who show how fluid motion along fault planes is restricted during periods of fault activity. At Paradox Valley, Colorado, USA, injection for disposal of high-salinity water induced seismicity (with several events of $M_L > 4$) which separated in two distinct zones: a principal one (>95% of events) asymmetrically surrounding the injection well and to a maximum radial distance of ~ 3 km, and a second zone covering an area of about 10 km^2 and centred ~ 8 km northwest of the injection [46]. Active faults and fractures at the edges of the valley allow for the stress change caused by the injection to reach the secondary seismic zone.

During the period 1982–2009, ENEL has recorded a large number of earthquakes with magnitudes in the range between 0 and 4 (**Figure 9**) [47]. These earthquakes, which appear to be induced by geothermal fluid production/

Figure 9. Earthquakes epicentres recorded by ENEL from 1982 to 2009 (modified after [47]). The volcanic rocks are pink coloured; triangles are seismic stations. Note the large number of earthquakes that concentrate in and around the geothermal fields, most of which seem to be induced by geothermal exploitation; red star is the epicentre of the 1st April 2000 $M = 3.9$ earthquakes.

reinjection, are concentrated mainly within the geothermal fields and most of them are close to the production and injection wells. Some earthquakes even of significant magnitudes are located in proximity to extensional structures within the volcanic edifice.

Mazzoldi et al. [48] described the microseismic activity recorded in 2000–2001 around the Piancastagnaio geothermal field. They show how long-time geothermal fluid production with strong depressurization of the geothermal fields (see **Figure 4**) could have augmented the effective shear strength of faults and the potential magnitude of triggered or induced earthquakes. Perhaps this could have been the mechanism for the April 1st 2000 triggered earthquake in the Piancastagnaio Geothermal Field that had $M_L > 3.9$, damaging buildings in the Piancastagnaio and Abbadia San Salvatore municipalities and alarming the population [40, 41, 49].

During the last century, the strongest earthquake around Amiata Volcano occurred in 1919, with an epicentre at Piancastagnaio and with an estimated magnitude between 5.1 and 5.4. Two other events of magnitudes 5 and 4.6, with epicentres at Mt. Amiata (1948) and near Radicofani (some 10 km E of the volcano, 1958), respectively, have been reported. The latter is also the last event of $M > 4.5$ recorded in the area after the beginning of the geothermal exploitation (1959) [48].

During 14 months, Mazzoldi et al. [48] recorded about 600 seismic events of M_L between -1 and 3 . The recorded events could be split into two groups: (a) tectonic events and (b) hydraulic-fracturing events. The largest part of the record (about $3/4$ of them) were microseismic events ($M_L < 1$) belonging to group (a) with epicentres located within an area of 5 km in radius, centred within the geothermal field (around the PC16 injection well). Among microearthquakes, events with higher energies tended to be located within the area on the side of the volcano at very shallow hypocenter depths and close to the extensive structure of the edifice (cf. **Figure 1**). Hypocenter depths increase from the volcano toward the geothermal field where earthquake hypocenters are at and a few kilometres below exploitation depths (2–3 km). A small but significant part of the record (about 5%) consisted of group (b) events, which could not be accounted for by a pure brittle-fracture mechanism but rather seem indicative of hybrid events, generally related to fluid-filled fracture dynamics, typical of volcanic areas and geothermal fields [50]. Hypocenters of these events were tracked down with a grid-searching method based on the maximum energy distribution at the four stations [51] and were mainly concentrated within the geothermal field, on the south-eastern side of Amiata volcano still at exploitation depths.

Previous seismic analyses of recorded events [52, 53] and seismic observation by Mazzoldi et al. [48] show that the SE base of Mt. Amiata has the highest density of tectonic events in correspondence of the geothermal field location, the extensional structures that dissect the volcanic edifice (SE of the edifice) and the compressive structures at the base of the volcano—the last two formed by the volcanic spreading process [4].

Sorgenia [20] recorded microseismicity at the Eastern base of Amiata Volcano for 6-months. They located two distinct thrust-fault events (with a four-month delay between them) of approximate $M = 2$ and hypocenter depth of 8 km. These seismic events show active compression within the Siena-Radicofani Graben, which is consistent with the work of Bonini and Sani [18] and Borgia et al. [4].

Because of active volcanic spreading, after major earthquakes, faults tend to recover in time their critically stressed conditions according to the local Maxwell time (t) [54]. Using for the evaporites a Young's modulus $\lambda = 10^9$ Pa [55] and a viscosity $\mu = 10^{18}$ Pa s [4], this recurrence time is found to be:

$$t = \frac{\mu}{\lambda} = 10^9 \text{ s} = 31.7 \text{ a.} \quad (4)$$

Given the approximations in Eq. (4) and using the Gutenberg-Richter curve given by Mazzoldi et al. [48], this recurrence time corresponds to earthquakes magnitudes between 4 and 5. These values of volcanic-spreading earthquake magnitudes, although on the smaller side, are comparable to the magnitudes given by Mazzoldi et al. [48]. Assuming our approximation for recurrence time is correct, and considering that the latest earthquake with a magnitude of about 4 occurred in 2000, we may suggest that a similar earthquake is expected to occur in the next few decades. Experience suggests that geothermal exploitation could perhaps trigger such an earthquake.

5. Atmospheric emissions

Currently, there are six flash-type 20-MWe power-plant units at Amiata Volcano, three for each of the two geothermal fields of “Bagnore” and “Piancastagnaio” (cf. **Figures 1** and **2**). In addition, for both fields, there is a secondary use of the residual heat for home and greenhouse heating.

To force evaporation of the geothermal fluid, the three fans of each cooling tower pump about 4–6 ($\times 10^6 \text{ Nm}^3/\text{h}$) of fresh air into the base of the tower (cf. **Figure 2b**) [9, 56], and emit the same amount of air plus a fraction of geothermal fluid (much of which is evaporated into the airflow) from the top of the towers (**Figure 2b**). Because from about one-half to three-quarters (cf. [7, 9]) of the geothermal fluid that enters a power plant is emitted to the atmosphere from the cooling towers, a total in the range of 360–585 t/h of geothermal fluids is lost to the atmosphere. In addition to carbon dioxide (CO_2), and even if there are abatement technologies for mercury (Hg) and hydrogen sulphide (H_2S) (the AMIS—Abatement of Mercury and Hydrogen Sulphide) and for ammonia (NH_3) (with the addition of sulphuric acid) the emissions still have high contents of these pollutants and of additional pollutants such as sulphur dioxide (SO_2), methane (CH_4), arsenic (As), antimony (Sb), boric acid (H_3BO_3), selenium (Se), cadmium (Cd), chromium (Cr), manganese (Mg), nickel (Ni), lead (Pb), copper (Cu), and vanadium (V) (**Table 2**).

In particular, CO_2 and CH_4 emissions are over 6.7×10^5 and $1.4 \times 10^4 \text{ t/a}$, respectively. These two compounds produce an equivalent greenhouse-gas effect that is calculated to be comparable to the emissions of gas-fired power plants per Mega Watt of electrical energy produced [57]. Orlando et al. [58] suggest that this CO_2 is generated by the interaction of the geothermal fluids with magnesian siderite in the phyllites of the geothermal reservoir. In addition, the emissions of H_2S that amount to $1.2 \times 10^3 \text{ t/a}$, of SO_2 that consist of 2.7 t/a, and of boric acid have an acid-rain potential that is about twice that of coal-fired power plants per MW of electrical energy produced [57].

In addition, the emissions of NH_3 amount to $2.1 \times 10^3 \text{ t/a}$ (**Table 2**) and constitute a notable contribution to the formation of secondary fine particles (aerosols). In 2017 these emissions were close to half of the total Tuscany ammonia emissions [5, 59]. Relative to mercury, the emissions are indeed relevant even with the abatement technology in place; including mercury and mercury compound, they total 1.17 t/a. While the emissions of arsenic and arsenic compounds sum to about 79 kg/a. To better emphasise the relevance of these values, the only mercury and arsenic emissions are, respectively, 42.5% and 7.5% of the total emissions of these pollutants from all Italian industries [5]. Note that an amount approximately equal to that of

	Bagnore	Piancastagnaio	Total
H ₂ S Hydrogen sulphide (t/a) ⁺	4.86E+02	7.25E+02	1.21E+03
CO ₂ Carbon dioxide (t/a) ⁺	3.77E+05	2.97E+05	6.74E+05
SO ₂ Sulphur dioxide (t/a) ⁺	0.61	2.07	2.68E+00
NH ₃ Ammonia (t/a) ⁺	1.21E+03	9.51E+02	2.16E+03
CH ₄ Methane (t/a) ⁺	1.03E+04	4.10E+03	1.44E+04
CO Carbon monoxide (t/a) ⁺	57.29	29.17	86.46
H ₃ BO ₄ Boric acid (t/a) ⁺	4.50	12.18	16.68
As Arsenic (kg/a) ⁺	24.49	9.99	34.48
Arsenic compounds (kg/a) ⁺	13.98	27.49	41.47
Hg Mercury (kg/a) ⁺	106.7	258.07	364.77
Mercury compounds (kg/a) ⁺	85.15	722.52	807.67
Sb Antimony (kg/a) ⁺	24.28	24.07	48.35
Se Selenium (kg/a) ⁺	9.20	20.46	29.66
Cd Cadmium (kg/a) ⁺	0.02	0.01	0.03
Cr Chromium (kg/a) ⁺	0.13	0.86	0.98
Mg Manganese (kg/a) ⁺	0.18	0.11	0.29
Ni Nickel (kg/a) ⁺	0.36	0.50	0.86
Pb Lead (kg/a) ⁺	0.14	0.04	0.18
Cu Copper (kg/a) ⁺	0.20	0.12	0.32
V Vanadium (kg/a) ⁺	0.10	0.04	0.14
⁺ Data derived from: Ref. [57].			
⁺ Data derived from: Ref. [2].			

Table 2.
Today’s approximate emissions per year of some compounds and metals from the power plants of the two Amiata volcano geothermal fields of “Bagnore” and “Piancastagnaio”.

the Amiata Volcano area is emitted by the geothermal power plants of the Larderello area in central Tuscany. Before the emplacement of the mercury abatement technology, the emissions for mercury were probably an order of magnitude higher. The actual amount of mercury emitted from geothermal power plants as a total in the Amiata Volcano geothermal area is not known. However, a gross estimate can be made based on the available data published yearly by the Agenzia Regionale per la Protezione Ambientale della Toscana (ARPAT) since 2002, and the set of measurements made by ENEL [60]. Based on these measurements the total Mercury emitted by the Amiata Volcano power plants could be in the order of 50–60 t in the past 60 years.

Regarding the composition of the fine particles collected in the Piancastagnaio area Tommasini et al. [9] show that they are enriched relative to the fine particles collected in Firenze and Arezzo (these are among the Italian cities that have the largest concentrations of fine particles in the air) in sodium, vanadium, zinc, phosphorous, sulphur, tantalum, caesium, thallium, thorium, uranium, and arsenic (**Figure 10**). Barazuoli et al. [61] report a set of analyses of the condensates produced by several geothermal wells in the Bagnore and Piancastagnaio geothermal fields. From these data, we calculate that the condensate from the geothermal fluids can have a total solid concentration (C_s) in solution that is in the order of 1 g/l.

Figure 10. Enrichment factor (EF) of heavy metals in the fine particles collected at Piancastagnaio geothermal field (after [9]). The arrow point to the elements that are enriched in the Piancastagnaio area in comparison to the concentrations found at Firenze (traffic station) and Arezzo (urban background station). Note that the EF scale is logarithmic: Small upward increases in the positions of points on the graph correspond to significant enrichments.

Recalling that the volume of condensate emitted to the atmosphere (V_c) is estimated to be in the order of two-third of the about 130 t/h of geothermal fluid used in a 20 MWe geothermal power plant and that the airflow through the cooling towers

(A_f) is about $5 \text{ Mm}^3/\text{h}$, doing the appropriate units conversion and assuming an equivalence between litres and kg for liquid water solutions, we may calculate:

$$C_{PM} = \frac{C_s \times V_c}{A_f} = \frac{10^6 (\mu\text{g/l}) \times 87 \times 10^3 (\text{l/h})}{5 \times 10^6 (\text{m}^3/\text{h})} \approx 17 \times 10^3 (\mu\text{g/m}^3). \quad (5)$$

That is, the order of magnitude estimates of fine particles concentration (C_{pm}) emitted from the cooling towers of a 20-MWe geothermal power plant should be in the order of $17 \times 10^3 (\mu\text{g/m}^3)$, which is a significant amount. This value should be incremented by the fine particles that are present in the non-condensable gas stream [9]. The primary and secondary fine particles resulting from the geothermal power plant emissions seem to be visible in the haze that is left after the evaporation of the H_2O cloud (**Figure 11**). During periods that the power plants are out-of-service emissions to the atmosphere are even more significant and are unaccounted for (**Figure 12**). In fact, during these periods, because the vapour production from the geothermal wells cannot be stopped, the geothermal fluids are emitted directly to the atmosphere without any pollutant abatement technology.

At the moment, there is no available direct measurement of the concentration of fine particles at the exit of the cooling towers of each power plant. Thus, we can only compare the value calculated above with the fine-particle concentrations of $10\text{--}30 \mu\text{g/m}^3$ (average $15 \mu\text{g/m}^3$) measured by Tomassini et al. [9] in the Piancastagnaio geothermal field area approximately 1–2 km uphill of the power plants. Given the approximations made and the fact that we are calculating a potential maximum fine-particle concentration in the emissions, to find a dilution factor of about a thousand, from the emission towers to the place where measurements were taken (1–2 km uphill of the power plants), appears to be consistent with atmospheric modelling of the power plant emissions (cf. [6]). In this respect, we observe that the power plants are located all around the village of Piancastagnaio from NE to E to SW and to S at a distance smaller than 2 km. In addition, in the western direction there are the three power plants of the Bagnore geothermal field at just over 10 km distance. Therefore, no matter from what direction blows the wind (apart from NW and N) the fumes from the power plants always reach the village of Piancastagnaio. It is only when there are strong winds from the north and northwest that the concentration of fine particles decreases [9]. We think that during winter thermal inversion events, when the fumes of the power plants can accumulate and linger in the lower atmosphere even for a few days, the concentration of fine particles could increase significantly above the values that have been occasionally measured up to now.

Finally, we have to recall that some of the elements emitted to the atmosphere, in addition to radon, are radioactive. Geothermal energy production has been included already many years ago [62] among the human activities that generate Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM). In this respect, very little is known about the geothermal power plants of Amiata Volcano.

6. Discussion and conclusions

Geothermal exploitation for the production of electricity at Amiata Volcano uses flash-type power plants with cooling towers that evaporate much of the geothermal fluid to the atmosphere with minor reinjection, that is from about one-quarter to one-half, of the fluid produced [7, 9]. In addition, the flash of the geothermal fluid is mainly occurring at depth forcing a significant depressurization of the geothermal system from the original undisturbed conditions (cf. [21]).

Figure 11.
Emissions from (a) the PC3 (b) the PC4-PC5 geothermal power plant units with the village of Piancastagnaio in the background. Note how after the evaporation of the water vapour in the atmosphere, a cloud of fine particles persists, much like the fumes emitted from major coal- or oil-fired power plants.

As a consequence, this depressurization propagates upward inducing a corresponding decrease in pressure at the base of the freshwater aquifer contained in the volcanic edifice [26]. Accordingly, the water table has substantially dropped, reaching in the centre of the volcano a decline of about 250 m (compare

Figure 12.
(a) The emissions during the out-of-service of the PC3 geothermal power plant occurred on the 10 of may 2005.
(b) Cloud of toxic geothermal fluids, emitted from the Bagnore 25 geothermal well, flowing toward home on 21 November 2007; the inhabitants had run away from their houses.

Figure 3a and b) and forming in the Southeastern sector of the volcanic edifice a minimum in the water table (**Figure 3b**), as it has been measured by Compagnia Mediterranea Esplorazioni [24], Marocchesi [29], and its time changes monitored by Manzella [30] with oscillations between 700 and 600 m asl. In December 2018, this minimum had an elevation of 746.39 m asl at the ENEL4 piezometer (**Figure 8**). The presence of this minimum demonstrates that the water is drained downward from the volcano into the rocks that contain the geothermal systems (the Anhydrites and the metamorphosed Tuscan Units; **Figure 1b**) via the many faults and the

volcanic conduits that cut the edifice and its basement (cf. [4, 8], and references therein). This impact of geothermal fluid production on freshwater aquifers need to be evaluated in detail when commissioning geothermal power plants. On the other hand, if a balanced production-reinjection volume of geothermal fluids were to become mandatory, for instance by using air-coolers in place of the evaporative towers, the impact on the superficial aquifers would be substantially reduced because the recharge from freshwater aquifers would need to compensate, as a first-order approximation, only for the reduced volume of the cold water reinjected relative to hot-water produced.

At Amiata Volcano, geothermal fluid production with its associated small amount of reinjection results in several induced earthquakes that are rarely felt by the population. However, a $M_L = 3.9$ induced earthquakes occurred on April 1st 2000 [40, 41, 49], which generated significant damages to houses and buildings in general but luckily no deaths. Given the volcanic spreading process, we suggest that an $M_L = 4-5$ earthquake could be triggered in the next few decades. Even if these magnitudes are not indeed large, the fact that the buildings of the many medieval villages in the area are old and not constructed to modern seismic standards, there is the likelihood of significant damages and potential deaths. Thus, increasing the amount of reinjected fluid relative to produced geothermal fluid could increase the earthquake risk, because it has been suggested that earthquake magnitude is related to the volume of fluids reinjected [63]. The suggestion of increasing reinjection to reduce the impact on the freshwater aquifer runs counter to reducing induced seismicity. Retrofitting all buildings, although very expensive, could be in the long term a reasonable answer because even larger-magnitude earthquakes unrelated to geothermal energy production, may occur in this area.

The non-condensable gases, in addition to the evaporation of a large fraction of the geothermal fluid in the cooling towers, produce significant emissions to the atmosphere [2, 5, 57]. In the first place, the CO_2 and CH_4 emissions produce greenhouse effects that are calculated to be comparable to the emissions of gas-fired power plants per electrical energy produced; therefore, we are forced to consider that the Amiata volcano geothermal power plants are not adequate to substantially reduce greenhouse gas emissions per electric energy produced. In addition, the emissions of H_2S , SO_2 and H_3BO_4 , have an atmospheric acidification potential (acid rain) that is also similar to coal-fired power plants per electrical energy produced. Also, the emissions of NH_3 , a notable contribution to secondary fine particles formation, in 2017 were close to half the whole emissions in Tuscany of such pollutant. Relative to Mercury, the emissions are relevant even with the abatement technology in place. Before, the emplacement of the Mercury abatement technology (AMIS) in the years two-thousands, the emissions were around an order of magnitude higher. The emissions of Arsenic and Arsenic compounds are also significant. While these emissions are generally monitored only for about a few hours per year, no controls are made for the rest of the time, even when the AMIS is not adequately functioning. In addition, the emissions that occur as fine particles (aerosol) are unaccounted for since there are no limits imposed by law for them. Primary and secondary fine particles related to the geothermal power plants could account for the relatively high level of fine particles (on average about $15 \mu\text{g}/\text{m}^3$) in the air of this, by all means, rural area that practically has no large emissions from other industries. In the Piancastagnaio area fine particles are enriched in Sodium, Phosphorous, Sulphur, Zinc, Tantalum, Caesium, Thallium, Thorium, and Uranium relative to the particles sampled in Florence and Arezzo [9] suggesting a direct contribution from the geothermal power plants.

Although the concentrations of fine particles measured in the air have been sporadically measured below the law limits, the pollutants contained in these

particles tend to be toxic metals, making these aerosols potentially dangerous for the health of the population living in the area. The WHO REVIHAAP [64], states that all the studies conducted to date show that there is no threshold level below which the effects of pollution on health are not evident. Therefore, in the application of the precaution principle, we suggest that the emissions from the geothermal power plants, in combination with an increase in pollutant content in the freshwater and soil, could be a concomitant cause for the excesses in hospitalizations and deaths in the Amiata Volcano geothermal area (cf. [65]).

In conclusion, the use of air-coolers in place of the evaporative cooling towers, like the ones used today, would drastically reduce the potential impact on the health of the population residing in the Amiata Volcano geothermal area. This technical solution has been already indicated in 2010 by the local government of Tuscany [66], but it has not been applied yet. This technology, which is now proposed for most binary-cycle geothermal power plants in Italy, would substantially reduce both the impact on the superficial freshwater aquifers because all the produced fluid would be reinjected reducing the need for recharge from the superficial volcanic aquifer, and on the atmosphere. After all, the emissions would practically be minimal. On the contrary, the much larger volume of reinjected fluid may increase the risk of inducing or triggering earthquakes. We think that future Life-cycle assessments of the geothermal power plants should attempt at including the environmental impacts reported in this paper and the consequent health risk for the residing population. We stress that the new emerging technologies, such as the deep-borehole heat exchangers should receive more attention and incentives; they produce less energy per unit time but on the other hand, the energy production could probably last for much longer than conventional geothermal power plants, with a minimal environmental impact.

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Conflict of interest

As a technical consultant, Borgia has served the Public Prosecutor of Grosseto, and worked for the Regione Toscana, the Comunità Montana Amiata Val d'Orcia, the municipalities of Piancastagnaio, Arcidosso and Radicofani, Macchia Faggeta, and several citizens to define the pollution and the environmental impact induced by the geothermal power plants.

Micheli has worked for 35 years in the geology and hydrogeology sections of the Regione Toscana and is now retired.

Carlo Balducci lived his whole life at the foot of Amiata Volcano and is now retired and in the process of creating a public comprehensive database of scientific and government documentation on the geothermal power plants of Amiata.

Notes

This paper is dedicated to the memory of Alice, Emidio, and all Amiata citizens that become ill and died.

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