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Tracing Ancient Carbon Dioxide Emission in the Larderello Area by Means of Historical Boric Acid Production Data

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Abstract: The impact of natural CO₂ emissions in the development of geothermal areas is presently gaining more attention than ever before. In Italian geothermal fields, a reduction in the natural CO₂ emissions has been observed. This paper reviews and provides an analysis of the historical production data of boric acid from 1818 to 1867 used to calculate the natural emissions of CO₂ associated with boric acid production that pre-dates the use of geothermal resources for power production, which started in 1913. Boric acid was already being extracted from the natural geothermal fluids in geysers and natural ponds emitting steam and gases. After 1827 the ‘lagone coperto’ (covered lake) equipment optimized production, and the drilling of shallow wells (20–30 m) starting in 1836, which further increased the quantity of its extraction. The first geothermal reservoir was developed at the turn of the century and the Larderello geothermal field began to grow. The use of deep wells, keeping pace with the power production, led to the gradual disappearance of the natural ponds and the ‘lagoni’ (lakes) in the historical area, so the residual natural emission of CO₂ is presently restricted to diffuse soil emission. Comparisons of the ancient CO₂ emissions with those of the Geothermal Power Plant (GPP) in the Larderello area show that both amounts are in the same order of magnitude, suggesting a balance between the depletion of natural emissions and geothermal activity.

Keywords: sustainability; geothermal resources; CO₂ emission; soil emission; boric acid; lagone; lagone coperto; depletion; substitutive emission



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1. Introduction

The question about CO₂ emissions from geothermal power plants has become increasingly important as discussions on climate change have become more common. Historically, the emissions from geothermal energy utilization have been considered non-anthropogenic because they are natural source fluxes released into the atmosphere by natural surface venting.

Carbon dioxide is released to the atmosphere naturally from geothermal fields through: soil flux, steam vents, fractures, steam heated mud-pools, and thermal springs. CO₂ can also be transported by groundwater flow, absorbing and releasing the carbon dioxide (in the geothermal reservoir) by mineral precipitation or degassing. Although soil emission of CO₂ can occur in many ways, the emission rate strongly depends on the characteristics of the field and, thus, may vary greatly from one field to another.

The rate of natural emission can be altered by fluid extraction in the wells used for power production and district heating or, as has occurred in the past in the Larderello area, for boric acid production. In the Larderello area, natural emission from steam and gas vents progressively disappeared while the steam collection by wells grew, suggesting that the rate of natural soil emission depends on the interplay between the natural mechanism of gas emission from the soil and the utilization and extraction of steam in the geothermal field.

The sources commonly recognized as possible origins of CO₂ in a hydrothermal system are hydrolysis of carbonate rocks, crustal magmatism, subcrustal magmatism following partial melting of mantle rocks and metamorphic processes [1].

A study by Bertani and Thain (2002) [2] revealed that emission factors vary in a very wide range between 4 and 740 gCO₂/kWh, with a weighted average of 122 gCO₂/kWh. Recently, figures as high as 1300 gCO₂/kWh have been reported by Fridriksson (2017) for Turkish geothermal fields [3], while the emission from fossil fuel (natural gas, coal, oil), ranges from 350 to 1100 gCO₂/kWh. In other fields, such as those in the USA, the rate is reported to fluctuate with different resource management, namely the reinjection of separated fluid is found to dilute the resource and lower the emission rate from the GPP. An example from GPP Krafla in Iceland shows how the emission fluctuates according to volcanic action in the specific field, with additional utilization, and also shows how it declines and stabilizes with further operation of the GPP. It is, therefore, safe to assume that, even though the emissions of geothermal power plants originate from natural sources, the utilization of the geothermal field can affect the emission rate. According to present studies, the emission rate from GPPs can be both higher and lower than the natural rate, and, over time, utilization can further lower the emission rate.

The emission factors, usually expressed as CO₂ emission per kWh produced by a geothermal plant, or eventually as cumulative emission including methane, defined as the Carbon Dioxide Equivalent, only partially represent the contribution of a power plant to carbon dioxide emissions in the atmosphere; this is because the contribution of surrounding soil emission must be included in the total amount of emission, taking into consideration any depletion observed pre and post geothermal development. In any case, a detailed picture of soil emission in the field is required, and even though the CO₂ emissions are found to be of a natural source, it is understood that it is important to measure the natural surface emissions, as well as those coming from the power plant, which is an integral part of the field being monitored.

However, it must be understood that the present knowledge of the impact of geothermal utilization on the carbon cycle is not sufficient to justify a global methodology.

The comparison of natural soil emission in geothermal areas with respect to pre-development soil emission can be an interesting starting point to evaluate eventual depletion effects on soil emission induced by geothermal utilization. On the other hand, most of the geothermally developed areas in operation today have never evaluated the natural soil emission before the initial extraction and utilization of the fluids. In these cases, a pre and post comparison is not possible; however, a correlation between current soil emission of developed geothermal areas and the emission rates in contiguous areas is achievable. In Table 1, a brief overview of soil emission in geothermally developed areas and other volcanic and non-volcanic areas is reported.

The large range in emission rate reported underlines the variability between different volcanic and non-volcanic areas in the world and how they impact on the amounts of gases emitted through the soil. Furthermore, the estimates are conducted by using different methodologies and many include only diffuse degassing, or soil and groundwater emission measurements, which may lead to difficulties in the testing of different areas. However, a few studies on the subject dealing with soil emission in geothermal productive areas do exist and, in some cases, either a qualitative or quantitative comparative testing with plant emission has been performed, e.g., for Iceland [4], Italy [2,14,17], and New Zealand [16]; each of these is a pioneering country for geothermal energy use. In the case of Italy, these studies conclude that central Italy is a significant carbon dioxide emission area, where the metamorphic CO₂ emissions are believed to be significant [1].

Table 1. CO₂ emission in main volcanic and non-volcanic areas *.

Reference	Area of Study	Data as Reported in the Original Paper	Data Expressed in t/h
Bertani and Thain 2002 [2]	Global ranges for CO ₂ emission (GPP)	4–740 gCO ₂ /KWh	
Fridriksson 2017 [3]	Turkish geothermal fields	400–1300 gCO ₂ /KWh	
	Emissions of CO ₂ from fossil fuels	350–1100 gCO ₂ /KWh	
Armansson 2003 [4]	Natural emissions from Krafla, Iceland	200 gCO ₂ /d m ²	
Armansson 2005 [5]	Estimated CO ₂ annual emissions from several geothermal and volcanic systems around the world	0.01–1000 Mt/y	1.14–144,077
	Pantelleria Island	0.39 Mt/y	44.5
	Mid-Ocean Volcanic system	30–1000 Mt/y	3422–144,077
	New Zealand	0.44–0.95 Mt/y	50.2–108.4
Fron dini et al. 1999 [6]	Total estimated emission ranges	200–1000 Mt/y	22,815–144,077
	CO ₂ fluxes from central Italy		
	Stifone		30
	Clitunno		0.15
	Rasiglia		0.11
Rogie, Kerrick, Chiodini and Fron dini 2000 [7]	Canino		0.7
	Selvena		0.7
	Central Italy aquifers	1–3 × 10 ¹¹ mol/y	502–1506
Kerrick 2001 [8]	Discharge from focused emission, Central Italy	1 × 10 ¹⁰ mol/y	50
Carapezza 2011 [9]	Volcano Island	1350 t/d	56.3
Sbrana 2020 [10]	Amiata Area (225 km ²) emission shallow biogenic + deep origin carbon	13,350 t/d	556.3
Lenzi Caprai 2016 [11]	Emission CO ₂ from sharp soil venters in Amiata area		6.8
Chiodini 2020 [12]	Bagni San Filippo area (1.7 km ²), combined soil emission end springs emission	910 t/d	37.9
Chiodini 2004 [13]	Emission deep CO ₂ in Tuscan Roman Degassing Structure (TRDS)		703
	Emission deep CO ₂ in Campanian Degassing Structure (CDS)		351
Gambardella 2004 [14]	Flux of CO ₂ is released into the atmosphere in the entire anomalous area of Central Italy	9.7–17 Mt/y	1107–1940
Fron dini et al. 2008 [15]	Indirect estimation of CO ₂ flux from regional aquifers (tuscany and northern Latium)	0.9 × 10 ¹¹ mol/y	452
Armansson 2005 [5]	Maximum possible CO ₂ flux from geothermal and volcanic systems in Iceland	1.3 × 10 ⁹ kg/y	148
Werner et al. 2006 [16]	CO ₂ fluxes from the Rotorua system in New Zealand (8.9 km ²)	69.66 t/d km ²	26

* In addition to the above mentioned data, for the Italian case, some databases have been developed, such as the MagaDB database (<http://www.magadb.net/> (accessed on 12 May 2021)), which contains available data on the chemical composition, and sometimes the flow rates, of gas emitted from several types of gas sources.

1.1. CO₂ Emissions in Geothermally Developed Areas

The operation of the geothermal reservoir can impact natural emissions. Although no additional CO₂ is created where no combustion is involved, a change in the natural equilibrium of the carbon cycle can result in a modification in the rate of CO₂ emissions from the soil (Holm, Jennejohn and Blodgett, 2012) [18], (Ármannsson, 2016) [19].

The growing interest in the reduction in anthropic contributions of CO₂ through the use of geothermal fields has led to studies in some well-known geothermal areas. In many cases, soil emission decreases has been observed, as in the Italian case. In other cases, some authors have reported increased activity, such as those in Reykjanes, Iceland [4] and Wairakei and Ohaki, New Zealand (Fridriksson, Mateos, Audinet and Orucu, 2016) [20].

1.2. Iceland Case

Ármannsson et al., (2003) [4] reported natural emission and power plant emissions in several areas in an initial attempt to compare the two types of emission. According to their calculations, the Krafla area's natural emission (Figure 1) corresponds to 200 g m⁻² d⁻¹. For the entire area covered by Iceland, the author estimates that the maximum possible CO₂ flux from geothermal and volcanic systems to the atmosphere would be about 1.3 × 10⁹ kg/year (148 t/h) (Ármannsson et al., (2005)) [5]. The same author estimated that emissions from the three major geothermal power stations in Iceland correspond to more than 8–16% of the maximum annual total emission estimated, and therefore suggests that geothermal emissions cannot be neglected in Iceland. Observations in Reykjanes and Svartsengi geothermal areas indicate an increase in diffuse emission from the geothermal field after the beginning of power production. In the case of the Svartsengi plant, an increase in the emission factors has been observed due to the formation of a steam cap in the mid-1980s with high concentrations of CO₂. After this initial phenomenon, decreasing emissions have been observed as a result of a gradual decrease in the CO₂ concentration in the steam cap [4]. In the Krafla geothermal power plant (Figure 1), the CO₂ concentrations increased between 1975 and 1984 due to magmatic activity referred to as the Krafla fires. The increased emissions caused by a gas pulse due to magmatic intrusions increased the CO₂ content drastically. In 1999, the emission spiked again but that was due to increased power output when a second 30 MW unit was added. Since 2005, the emission has been gradually decreased, which clearly shows that both natural and developing processes can impact changes in emission due to geothermal operations [5,21]. In the Reykjanes field, an analogous increase has been observed and could be due to the field evolution, since the commissioning of the 100 MW plant, in 2006, where the CO₂ production from wells has indeed already started a slow decline (Fridriksson, Oladottir, Jonsson and Eyjolfsson, 2010) [22]. Other studies in Hengill and Krafla in Iceland indicate similar results where the emission increase is very small and only a negligible amount would be counted as added emissions [19].

It has been assumed that the impact of geothermal power plants may actually be near zero, as the CO₂ discharge has been enhanced in the initial phases, which are immediately followed by a long period of relatively low gas output and, thereafter, left to function, permitting a natural equilibrium to be re-established (Holm, Jennejohn and Blodgett, (2012)) [18].

However, not many studies have been conducted with direct measurements of natural emissions, and this information rarely exists for currently operating power plants, as pointed out by, e.g., Ármannsson et al., (2005) [5] and Fridriksson et al., (2016) [23].

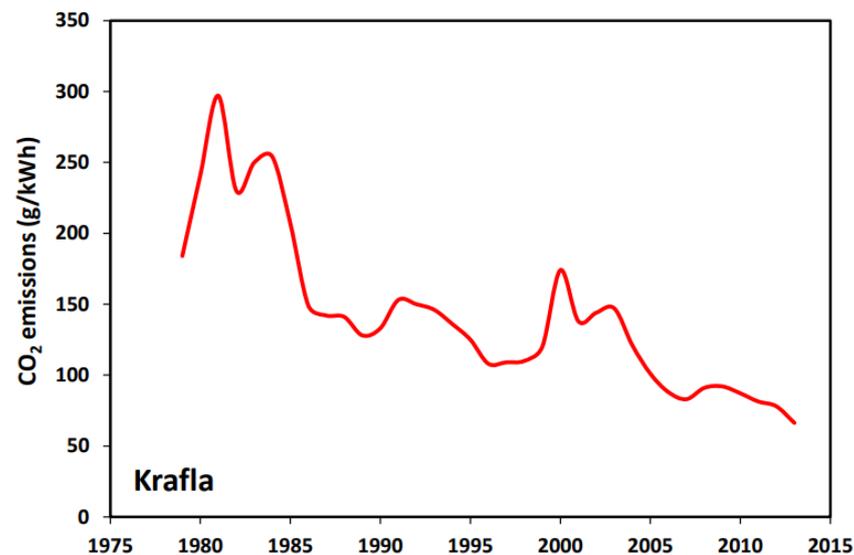


Figure 1. Evolution of CO₂ emissions from Krafla geothermal power plant (after Fridriksson et al. [20]).

1.3. New Zealand Case

Werner et al., (2006) [16] conducted a survey on CO₂ fluxes from the Rotorua system in New Zealand, calculating a carbon dioxide emission of 620 t/d (26 t/h) in an 8.9 km² area with a flow rate 69.66 t/d km², and concluded that while diffuse emissions from the magmatic system could be considered fairly high (1000 t/d), they would, if normalized by land area, be comparable to all other volcanic and geothermal areas worldwide. However, Sheppard and Mroczek (2004) [24] suggest that a significant increase in diffuse CO₂ emissions has come about in the Wairakei field in New Zealand due to exploitation, with this being of almost the same order as emissions from power production.

1.4. Italian Case

Bertani and Thain (2002) [2] showed that the natural emission of ‘lagoni’ (a local term used at Larderello for natural water, steam and mud pools derived from the condensation of steam escaping from the very shallow carbonatic, evaporitic geothermal reservoir) and the ‘fumaroles’ have undergone a substantial depletion since the industrial development of the Larderello area began causing the total disappearance of the ‘lagoni’ in 1922 [25]. They estimated that gas discharge from power production in Larderello is balanced by a reduction in natural emissions, and that the overall difference is insignificant.

For the Amiata area, Frondini et al., (2009) [17] showed that a calculated estimate of minimum CO₂ emission due to natural soil emission (~14.5 t/h) was slightly higher than the direct measurements (~10.5 t/h), with a difference of approx. 4 t/h for the entire Amiata area. The authors suggest that this is probably caused by geothermal power production, which may have reduced natural emissions.

From the above-mentioned studies we can understand that the emissions can fluctuate substantially due to both natural changes and utilization, but some have speculated that the emissions may decrease over long periods of time as the production of fluid serves to degas the natural reservoir [18]. Very few studies have been conducted to estimate changes in natural emissions due to geothermal development and whether or not emissions from geothermal power plants should be considered natural or anthropogenic depends on the fields involved.

1.5. Depletion and Substitutive Emission

It has become evident that carbon dioxide emissions from volcanic and non-volcanic areas, regardless of whether they host geothermal fields, are part of the global carbon cycle and occur naturally. Obviously, definite conclusions regarding this topic need much

more research. Until we can be absolutely certain about the precise nature of geothermal emissions, a field-based approach is advised.

In the Larderello area, a comparison of the current data for the geothermal power plant emissions with respect to ancient surface carbon dioxide emission data is not possible, due to the lack of registered information regarding the direct soil measurements that should have been taken during the initial phases of the utilization of the geothermal steam 200 years ago. Thus, an indirect method has been applied, based on the data of boric acid production, available since the start of industrial development in the Larderello area and its surrounding areas. Furthermore, thanks to some early data available on the steam composition, such as the Non-Condensable Gases (NCG) content and boric acid concentration in the steam, we can calculate steam flow rates and carbon dioxide emission as reported above.

From Bertani's studies, we are able to evaluate the amount of depletion of natural CO₂ emission in the Larderello area according to an indirect evaluation of the steam and NCG emission associated with the industrial production of boric acid. The basic idea of this model is that geothermal development can induce a depletion of natural gas emission in the area hosting geothermal wells and plants. The degree of depletion, namely the differences of soil emission rates, expressed as flow rates per unit area (e.g., ton*day/km²), can be figured out by registering the natural emissions in a green field ($\varnothing_{archaic}$) and taking note of the same quantities after industrial development ($\varnothing_{developed}$):

$$Depletion = \varnothing_{archaic} - \varnothing_{developed} \quad (1)$$

When the data of a green field are not available, a comparison between developed areas and nearby non-developed areas (areas hosting non-developed fields or areas with already known high rates of CO₂ soil emissions, not far from the reference areas and with analogous deep geological structures, in the order of no more than 10–20 km) can be calculated as:

$$Depletion = \varnothing_{nearby\ areas} - \varnothing_{developed} \quad (2)$$

In both cases, the degree of depletion represents the amount of natural emission that has been partially or totally replaced by plant emissions, according to a criteria of 'substitutive emission' (SE).

In this case, the SE is calculated as:

$$SE = actual\ plant\ emission - Depletion \times geothermal\ field\ area \quad (3)$$

In this context, we have calculated the depletion of natural emission in the Larderello area that had been observed by Bertani et al., (2002) [2], all of which has been historically documented (Figure 2). In particular, all the early activities involved in boric acid extraction, in the area surrounding Larderello, as well as within itself, were conducted by extracting H₃BO₃ from condensed fluid present in the 'lagoni', accumulated in the form of mud or hot water ponds from which large amounts of steam were continuously and naturally emitted (Figure 3).



Figure 2. Picture of the Larderello area at different times.

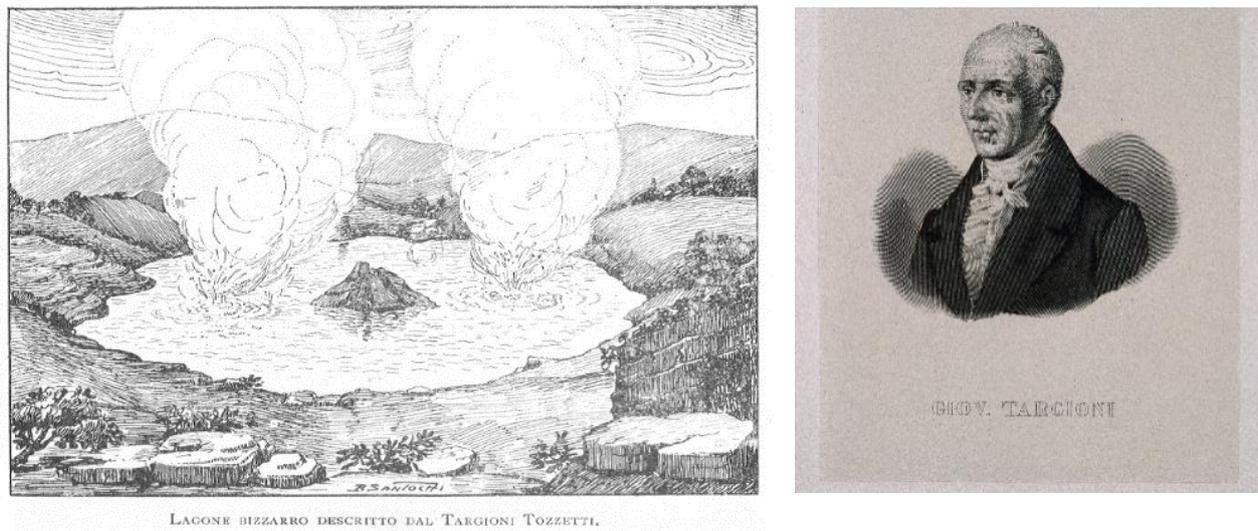


Figure 3. The first described ‘lagone’ called ‘lagone bizzarro’ (bizarre lake—left) from Targioni Tozzetti and a picture of the author (right).

Some early compositional data from shallow wells were made available at the end of the 19th century (Table 2). Based on the aforementioned data regarding the ratio between the condensable phase and the NCG and boric acid concentration in condensates, the steam and the NCG flow emissions have been calculated by the amount of boric acid extracted in the production area.

1.6. Historical Background on the Larderello Area

Boron is one of the important constituents of geothermal fluids and can be observed as boric acid (H_3BO_3). Its concentration spans from few to hundreds of mg/L depending on water–rock interaction and potential deep magmatic inputs. Boric acid is naturally contained in Larderello geothermal steam, and due to its high affinity with the liquid phase, it reaches high levels of concentration in steam condensation (up to 600 mg/L).

In Italy, the extraction of boric acid, discovered in 1702 by G. Homberg [26], began at the end of the 18th century, following its discovery in the ‘Lagone Cerchiaio’ in Monterotondo Marittimo, a few kilometers south of Larderello, by Hubert Franz Hofer [27]. Boric acid was, at the time, known as the sedative Homberg salt [28]. Boric acid was collected in natural ponds containing muds and mixtures (called ‘lagoni’) and from geysers, whilst natural fumaroles were initially used as an energy source to evaporate waters enriched with boric acid (Figures 4 and 5). The ‘lagoni’ were first described by Italian naturalist Giovanni Targioni Tozzetti [29]; their size and dimension ranged from a few meters up to more than 30 m. It is probable that each ‘lagone’ was the result of steam rising from the deep geothermal reservoir and condensing in the very few meters below the surface to form a shallow pool (perched aquifer) hosted in the geothermal system cover, made up of flysch facies containing sandstone and carbonatic rocks.



Figure 4. The ancient 'lagoni' in Larderello (outlined in circle) from a topographic map dated before 1827.

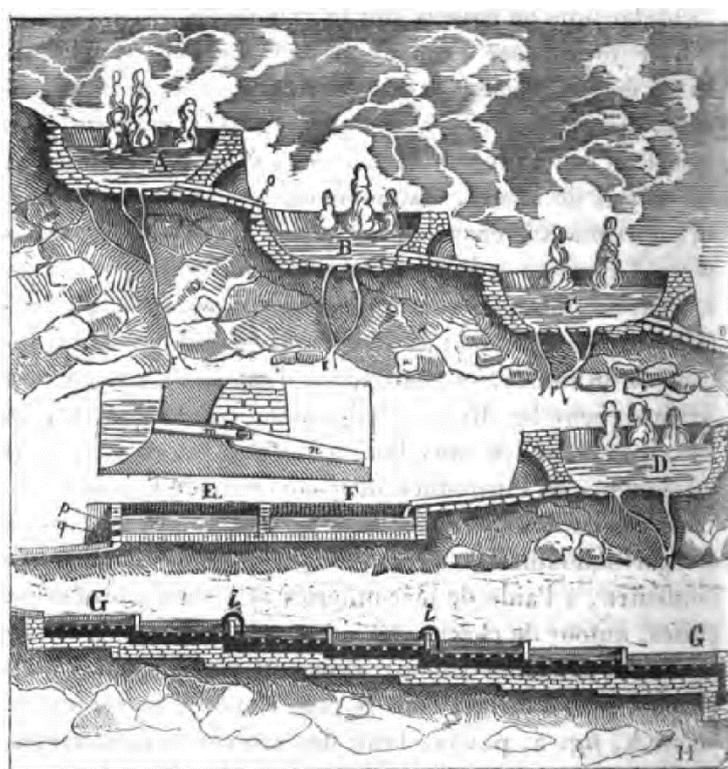


Figure 5. The first 'lagoni' (natural lakes and ponds) were limited and connected to allow brines to be collected for further evaporation.

With the introduction of industrial utilization of geothermal fluids, starting from 1818, the natural 'lagoni' were surrounded by a restricting wall and limited in order to enrich the descending saline waters. After the invention of a 'lagone coperto' (covered

geothermal lake, Figures 6 and 7) in 1827 by Francesco Larderel, the natural saline waters were evaporated by the steam entrapped by the concrete and brick dome-shaped lids, which give the pools the name ‘lagone coperto’. The geothermal fluid was collected and conducted into pipelines to use the steam as a source of energy and boric acid. In this sense, 1827 can be considered a milestone in the history of renewable energy sources, insomuch as it saw the first use of steam as an energy source.

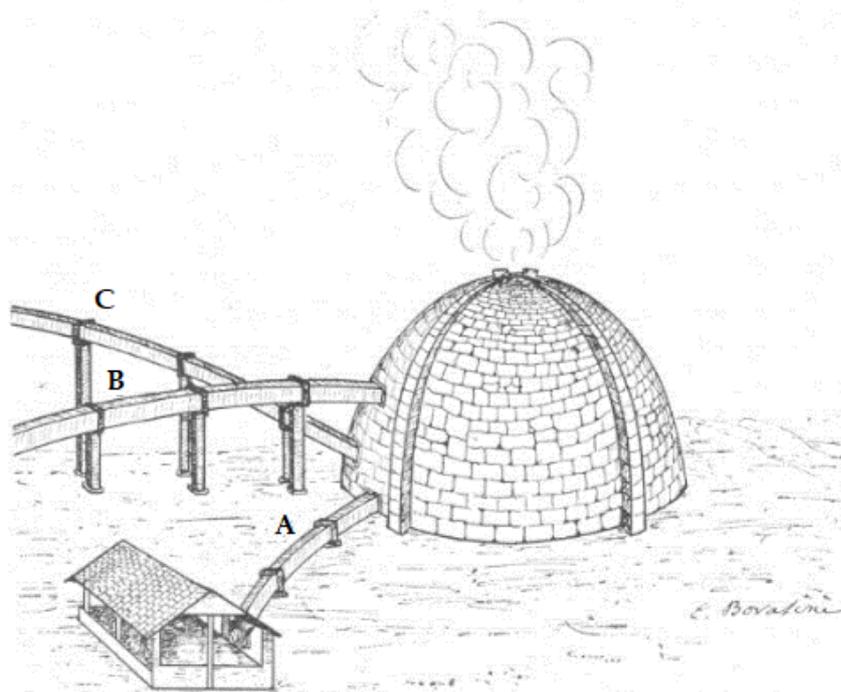


Figure 6. The ‘lagone coperto’ (covered lake) used to collect steam and hot waters containing boric acid. (A) boric water exit; (B) steam exit; (C) hot water inlet.

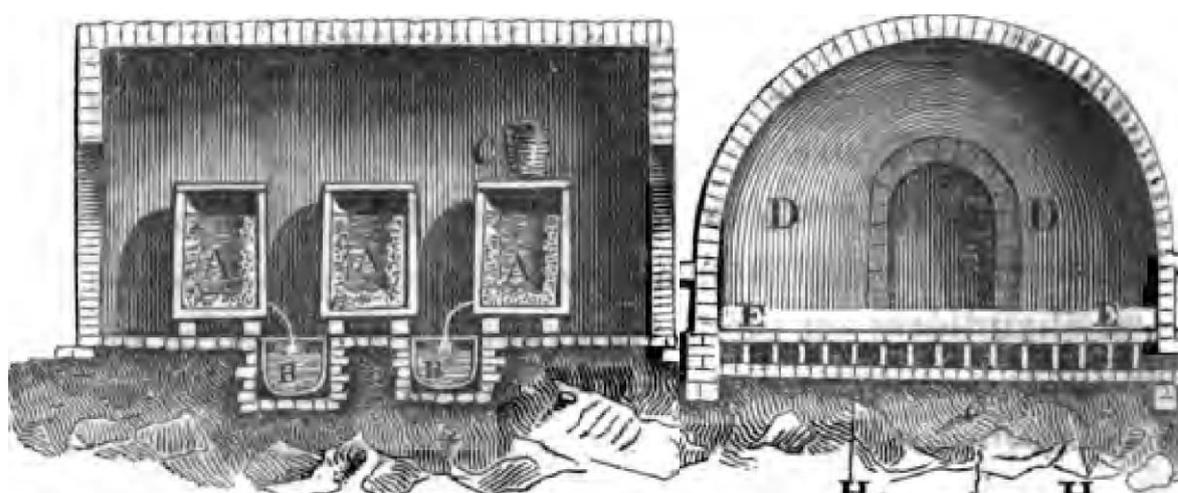


Figure 7. A section of the ‘lagone coperto’ (covered geothermal lake).

After 1836–1838, some very shallow (20–30 m) [30] hand-driven drilling wells started to enhance the steam output from the natural ‘lagoni’ and their surrounding area. The first deep-drilling system used to reach steam in the first reservoir (200–700 m) started at the

beginning of the 20th century, when the electrical use of steam was applied to machinery. With this modern drilling practice, the natural ‘lagoni’ underwent a progressive decline, and the last ‘lagone’ disappeared in 1922. In the Secolo Valley, the core of the Larderello field, also known as Devil’s Valley, no surface manifestation exists anymore. The last of the remaining natural manifestations can still be seen in the Sasso Pisano and Monterotondo areas.

A more detailed overview of the historical development can be found in Burgassi et al. [31].

2. Material and Methods

In the most recent studies, the ancient carbon dioxide emissions have needed to be virtually reconstructed using the indirect method to evaluate emissions ‘within the area’, based on the amount of boric acid collected in each mining site around the Larderello area.

The Tyrrhenian margin of Italy is known to be affected by a large CO₂ diffuse soil emission [13], linked to its geodynamical setting that gives rise to mantle upwelling, crustal thinning and subsequent extension and normal faulting. All of these characteristics are well highlighted and correlated in a recent paper by Vannoli et al., (2021) [32]. Larderello, one of the world’s rarest superheated, steam-dominated systems, is located in central-western Tuscany, a Tyrrhenian region dominated by high heat flow, widespread hydrothermal features, and a large flux of deep CO₂ [13]. The site was already known in Etruscan times due to its natural surface manifestations: thermal springs, steaming ground, hot pools, geysers, and fumaroles all related to the geothermal system at depth.

The upper reservoir of the Larderello geothermal field is composed of sedimentary rocks, carbonates, dolomites and anhydrides at shallow depth (from 300 m below ground level), while the second reservoir is hosted in metamorphic rocks such as phyllites, mica schists, schists and gneisses to a depth of 3500 m below ground level and other varying depths within the field. On the basis of δ¹³C and ³He, isotopic study on wells in Larderello Gherardi et al., (2005) [33] concludes that CO₂ (>90%) is mainly of crustal origin, related to the large thermal anomaly affecting the area.

Boric acid is naturally contained in Larderello geothermal fluids, and it is quantitatively transferred into brine during steam condensation. This is the reason why it is still used to evaluate drift (droplets of condensable phase transported out of the cooling tower) through a simple mass balance.

The available data on ancient fluid composition have been used to calculate: (a) the amount of geothermal fluid flowing in the areas, calculated by dividing the yearly production of boric acid by boric acid concentrations in the fluid, (b) the amount of Non-Condensable Gases (NCG), calculated according to the ancient geo-fluid gas content data and, finally, (c) the carbon dioxide emissions, calculated using gas compositional data.

The available data include the annual boric acid ($Q_{H_3BO_3}$) production of the ancient Larderello area industries that have been running since 1818 [34–36], as well as an analysis of production data up to 1867 [37], but data on boric acid production after 1900 are not available due to the beginning of electric power production and deep drilling [38]. By the value of measured [39] boric acid concentration in steam, $[H_3BO_3]$, and the oldest available data of gas content in steam (G/V), the amount of gas and steam natural emission has been calculated. The production and boric acid concentration can be combined to calculate the amount of condensable fluid carrying boric acid with the following criteria:

$$Q_{cond.} = \frac{Q_{H_3BO_3}}{[H_3BO_3]} \quad (4)$$

where $Q_{cond.}$, $Q_{H_3BO_3}$ and $[H_3BO_3]$ are, respectively, the condensable flow rate, the boric acid production and the boric acid concentration in the condensable phase. The total

amount of fluid (condensable phase + NCG), Q_{fluid} , including the non-condensable gases' (NCG) flow rate, Q_{NCG} , is then calculated.

$$Q_{fluid} = Q_{cond} \frac{1}{1 - G/V} = \frac{Q_{H_3BO_3}}{[H_3BO_3]} \frac{1}{1 - G/V} \quad (5)$$

$$Q_{NCG} = Q_{cond} \frac{G/V}{1 - G/V} = \frac{Q_{H_3BO_3}}{[H_3BO_3]} \frac{G/V}{1 - G/V} \quad (6)$$

Table 2. Early steam characterization data according to ref. [39].

STEAM FROM WELLS	G/V (%wt/wt) ^(a)	[H ₃ BO ₃] (‰) ^(b)	[H ₃ BO ₃] (mg/L) ^(c)
Foro forte (del Capanno)	5.00	0.58	580
Foro dei Visconti (Piazza Anna)	5.00	0.50	500
Foro forte di Piazza Anna	11.80	0.53	530
Foro di S.Arturo in Piazza Anna	10.30	0.47	470
Foro Venella	6.70	0.52	520
Foro del Cannello	6.00	0.16	160
Foro dei lagoni	6.00	0.42	420
II° foro lagoni	10.50	0.65	650
Foro dell'ammoniaca	5.80	0.35	350
Foro dei tini	6.00	0.48	480
Foro del Terrazzo	6.30	0.42	420
Foro della turbine	5.80	0.60	600
Foro umido, debole, tra i lagoni	0.82	2.80	2800
Foro umido di Piazza Anna	14.60	4.60	4600
Average	7.19	0.934	934

^(a) Gas content expressed as a percentage of the total fluid (condensable phase + NCG), ^(b) boric acid concentration as part in each thousand in the condensable phase, ^(c) boric acid concentration as milligrams per liter in the condensable phase.

The ratio (R) of the geothermal steam fluid rate and boric acid production rate is finally calculated as follows:

$$R_f = \frac{Q_{fluid}}{Q_{H_3BO_3}} = \frac{1}{[H_3BO_3]} \frac{1}{1 - G/V} \quad (7)$$

Furthermore, the analogous ratio R_{NCG} of NCG emissions to boric acid production is calculated using the following equation:

$$R_{NCG} = \frac{Q_{NCG}}{Q_{H_3BO_3}} = \frac{1}{[H_3BO_3]} \frac{G/V}{1 - G/V} \quad (8)$$

According to the definitions in equations 7 and 8, the R_f and R_{NCG} are dimensionless expressions representing the amount of steam associated with the production of a given amount of the tracer adopted boric acid (annual production rate in the data Tables 3–5). In Table 2, the first steam characterization data of boric acid and gas content (G/V) for different wells from ref. [39] are reported and, from the average of the data, the R_f and R_{NCG} values are calculated:

$$R_f = 1153.2$$

$$R_{NCG} = 82.9$$

Table 3. Calculated steam flow rates and NCG flow rates from boric acid production data according to ref. [34].

Year	Boric Acid Production (Kg/y)	Boric Acid Production (t/y)	Steam Calculated from R_f (t/y)	NCG Emission Calculated from R_{NCG} (t/y)	Average Steam Flow rate (t/h)	Average NCG Flow Rate (t/h)
1818–1828	50,000	50	57,661	4144	6,6	0.47
1829–1838	466,666	467	538,169	38,679	62	4.4
1839	717,333	717	827,243	59,455	95	6.8
1840	841,584	842	970,531	69,753	111	8.0
1841	849,268	849	979,393	70,390	112	8.0
1842	885,046	885	1,020,653	73,356	117	8.4
1843	885,067	885	1,020,677	73,358	117	8.4
1844	885,000	885	1,020,600	73,352	117	8.4
1845	885,066	885	1,020,676	73,357	117	8.4
1846	1,000,000	1000	1,153,220	82,884	132	9.5
1847	1,000,000	1000	1,153,220	82,884	132	9.5
1848	1,000,000	1000	1,153,220	82,884	132	9.5
1849	1,000,000	1000	1,153,220	82,884	132	9.5
1850	1,000,000	1000	1,153,220	82,884	132	9.5
1851	1,166,666	1167	1,345,423	96,697	154	11.0
1855	1,333,333	1333	1,537,626	110,511	176	12.6
1857	1,633,333	1633	1,883,592	135,376	215	15.4

Table 4. Calculated steam flow rates and NCG flow rates from boric acid production data according to ref. [36].

Year	Tuscan Libbra/y	Boric Acid Production (Kg/y)	Boric Acid Production (t/y)	Steam Calculated from R_f (t/y)	NCG Emission Calculated from R_{NCG} (t/y)	Average Steam Flow Rate (t/h)	Average NCG Flow Rate (t/h)
1826	149,000	50,591	51	58,343	4193	6.7	0.48
1827	66,000	22,410	22	25,843	1857	3.0	0.21
1828	197,000	66,889	67	77,138	5544	8.8	0.63
1829	376,000	127,667	128	147,228	10,581	16.8	1.21
1830	602,000	204,403	204	235,722	16,942	26.9	1.93
1831	789,000	267,897	268	308,944	22,204	35.3	2.53
1832	1,103,000	374,513	375	431,895	31,041	49.3	3.54
1833	1,347,000	457,360	457	527,437	37,908	60.2	4.33
1834	1,725,000	585,707	586	675,448	48,545	77.1	5.54
1835	1,841,000	625,093	625	720,870	51,810	82.3	5.91

Table 5. Calculated NCG emission from data from boric acid production data according to ref. [37] and their distribution in factories in 1867.

Plant Name	Boric acid Daily Production (kg/d)	Boric Acid Production (Kg/y)	Boric Acid Production (t/y)	Steam Calculated from R _f (t/y)	NCG Emission Calculated from R _{NCG} (t/y)	Average Steam Flow Rate (t/h)	Average NCG Flow Rate (t/h)
Larderello	1740	634,841	635	732,111	52,618	83.6	6.0
Castelnuovo	304	111,235	111	128,278	9220	14.6	1.1
Sasso	710	259,267	259	298,992	21,489	34.1	2.5
Monterotondo	317	115,524	116	133,225	9575	15.2	1.1
Lago-Collacchia, S. Edoardo, S. Federigo	1180	430,931	431	496,958	35,717	56.7	4.1
Lustignano	310	113,067	113	130,391	9371	14.9	1.1
Serrazzano	348	127,389	127	146,908	10,558	16.8	1.2
Total	4909	1,792,254	1792	2,066,863	148,548	236	17.0

The boric acid production data from several datasets, reported in Tables 3–5, have been used to calculate the flow rates of fluid and NCG in the 1818–1867 period (during which data were available). In particular, Table 3 contains the first list of boric acid production data reported by Francesco De Larderel in reference [34] and the data reported on the suitability of calculations in this study make it a document of very high historical importance.

Similar data have been calculated from Repetti [36] and are reported in Table 4.

While in Table 5 data from Meneghini [37] give a picture of distribution of the production according to the existing fabrications in 1867.

In our calculation, we have assumed that the G/V data values—available since the end of the 1800s when Prof. Raffaello Nasini was charged [35] with implementing the early studies started by Payen [40] and the subsequent studies conducted by Meneghini [37], and performed the first complete and extensive chemical and physical characterization of Italian geothermal fluids—are comparable or have declined only slightly since the period covered in the earliest boric acid production data. In any case, the calculated NCG values are underestimated.

3. Results and Discussion

In Tables 3–5, the amounts of carbon dioxide in the NCG are reported, representing carbon dioxide emission as the average CO₂ content in Italian geothermal fluids, with values ranging between 95 and 98%, calculated from boric acid production. Considering that H₃BO₃ was extracted from highly emitting ponds ('lagoni') and fumaroles, the calculated amounts are under-estimated, neglecting the contribution of the non-industrially exploited ponds and other sources. Moreover, the availability of chemical composition of steam was started only in 1841 by Payen, who first measured (Figure 8) only the gas portion of the vented steam (CO₂ 57.30%, H₂S 1.32%, N₂ 34.81%, O₂ 6.57%). Nevertheless, although some contamination of air is present in these first studies, the original data can be corrected by air contamination, leading to a composition of 97.7% CO₂ and 2.3% H₂S. Data on boric acid concentration in steam and gas content are more recent. Even if the reported data are underestimated, they give an idea of the amount of carbon dioxide that progressively depleted at the surface with the development of the industrial use of steam for boric acid production and, since 1913, for electrical use. The emerging picture of steam and NCG emission calculated in the 1818–1867 period shows steam values continuously increasing during early geothermal development, starting at 6.6 t/h, and increasing to 215 t/h, and eventually reaching 236 t/h in 1867. The rates of NCG emission range between 0.47 t/h and 15.4 t/h up, reaching 17 t/h in 1867, with a ratio of about 7.2 tons of carbon dioxide (NCG) per 100 t/h of naturally emitted steam. These emissions from natural 'lagoni' have gradually depleted and are substituted by power plant emission. A comparison

with current emission can be performed by considering an average performance of Italian Geothermal Power Plants currently running with turbine efficiencies of 7 to 8 tons of steam per MWh produced. The largest natural NCG emissions flux calculated in this work reaches 17 t/h, carried by 236 t/h of venting steam. This amount of steam is equivalent to about 30–34 MW of a standard geothermal power plant, representing a significant estimation of the degree of substitution of natural emission. Considering that in the Larderello area, a substantial depletion of gas content has been observed after the systematic application of condensate reinjection practice, by reducing the gas content in steam, in some cases to 2% or less, the same 17 t/h of ancient NCG emission would be equivalent to 850 t/h steam or about 106 to 121 MW power production. This calculated amount of steam represents a gas discharge through the soil that has progressively disappeared in the Larderello area (Depletion) during the geothermal development and can be adopted as a proof of the concept of ‘Substitutive Emission’ of a power plant. By this hypothesis, the observed Depletion of the natural soil emission is a consequence of the fluid extraction from the depth and its discharge through the power plant with an equivalent and balanced rate between soil emission depletion and plant NCG discharge to the atmosphere. The data are undoubtedly incomplete due to neglecting the contribution of steam emitted from non-productive sites, the portion of boric acid contained in the vapor phase, lost by discharge into the atmosphere through the ‘lagoni’, and the diffuse emission through the soil that covered very wide areas in Larderello and the surrounding productive areas at the time of the initial geothermal era. Nevertheless, we suggest that the current data can be a valid starting point to evaluate the soil emission depletion, e.g., the effective contribution to the atmosphere of geothermal power plants calculated by subtracting the emission depletion of the natural NCG gas flows from the soil from the actual plant emission rate, which is at the base of the concept of ‘Substitutive Emission’ for Italian Geothermal Power Plants.

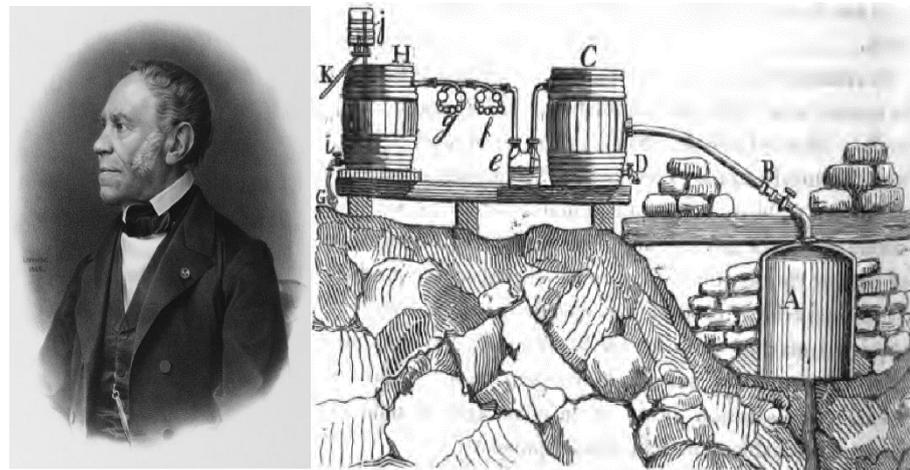


Figure 8. Francois Anselme Payen and his equipment that was used to perform the first analysis of geothermal gases.

4. Conclusions

The CO₂ emitted from geothermal plants is part of the natural CO₂ cycle and no new CO₂ is being produced, as in the case of fossil fuel use as an energetic source. Furthermore, the CO₂ is simply released by geothermal plants because it is associated with the geothermal fluids utilized in power generation. Thus, the CO₂ is subtracted from the cycle in areas where vigorous surface degassing from natural manifestations took place. In this case, it is possible that the effective contribution to the atmosphere is negligible.

With Larderello being the oldest geothermal field in the world, exploited since the 19th century for boric acid production and for power generation since 1913, quantitative measurements of depletion of naturally occurring surface manifestations carrying carbon dioxide could not be calculated as defined in the above section. Even so, the detailed

boric acid production data available since the industrial development of Larderello and surroundings areas, and early compositional data on the steam emitted from the field, has allowed a calculation of steam and NCG emissions in the area, which, although underestimated, are useful in evaluating the depletion rate in terms of steam (and associated NCG) that gradually and completely disappeared.

Our calculations indicate that about 236 t/h of venting steam, equivalent to about 30–34 MW of a standard geothermal power plant with 17 t/h of associated NCG, fed the ancient boric acid production factories, representing a significant estimation of the degree of substitution of natural emissions in the Larderello area.

Finally, the relationship between geothermal development and soil emission is a complex subject, even more so for very ancient fields where measurements before exploitation are missing. In such cases, a proxy, such as boric acid, can be used in order to obtain a rough but realistic estimation of surface emissions prior to development.

NOTE: all the data are expressed with dots (.) as a decimal separator.

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