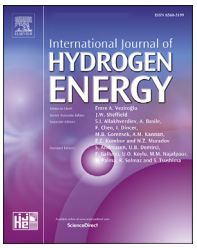
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Long-term monitoring of natural hydrogen superficial emissions in a brazilian cratonic environment. Sporadic large pulses versus daily periodic emissions

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HIGHLIGHTS

- Large quantities of H_2 are leaking from the Sao Francisco basin.
- Few hundred kg of H_2 per day/km^2 escape from the emitting structures.
- High Pulses are emitted sporadically and part of the H_2 remains trapped in the soil.
- Remaining H_2 is then slowly released following daily changes in temperature and pressure.

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ABSTRACT

In many basins, hydrogen-emitting structures are now observed, but the estimation of the H_2 flow leading to their formation remains poorly constrained since all data show that the H_2 emissions are variable in space and time. We present here the data of a long-term monitoring campaign with a high density of permanent hydrogen detectors installed in 2 structures in the Minas Gerais State (Brazil). Results show that two kinds of signals are recorded, large sporadic pulses that affect the H_2 content of the soil for one or two days and smaller ones, with a daily periodicity, that last 6 h and during which the near surface soil concentration usually does not exceed 200 ppm. This last signal is very regular in frequency, less in amount, and the daily maximum happens around noon or in the early afternoon. We interpret the large pulses as evidences of a deep hydrogen flux, leaking either from a reservoir located in the subsurface, from an aquifer which is degassing or, although it seems unlikely, directly from the H_2 generation area.

The time correlation between the pulse and the increase of the daily signal suggests that this last one corresponds to the slow release of the gas that has been captured by the soil during its transport towards the surface. This daily signal is most likely influenced by external factors such as atmospheric pressure and sub-surface bacterial activity. In map view, the lack of correlation between the highest hydrogen concentrations over time

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suggests that the soil is very heterogeneous and that preferential pathways exist. The results confirm that long-term monitoring, over a few months, is mandatory to catch a certain number of high pulses and so to have a better estimation of the real flow. Data also suggests that sensors with a large concentration range should be used (from 10 to several 10^4 ppm). Even if quantification of leakage doesn't help to quantify the subsurface reserves, these new data allow a more precise evaluation of the quantity of H_2 released in surface by these structures, few hundred of kilo per day, and confirm the high H_2 prospectivity of this basin.

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Introduction

Natural H_2/towards a carbon-free fuel

The dihydrogen gas H_2, that we will call hydrogen, is getting more and more important in the new carbon-neutral energy mix. Made from water electrolysis, it is a way to store electricity but H_2 is also a clean fuel. Cars, trucks, buses, trains and even ships using H_2 fuel cells are becoming commonplace in European cities as well as in California, Japan or Korea. The advantages are numerous but there are still impediments as the lack of policy framework covering the environmental impacts [1]. However, the production of H_2 is today almost always based on hydrocarbons and, in order to reduce the CO_2 balance of this fuel, clean alternatives for H_2 production are looked for. Exploration & Production of natural hydrogen looks as one of the most promising ways to get large quantities of green hydrogen cheaper than the "grey" one produced from methane [13,19,25]. In that context, exploration started in various geological settings and exploration strategy as well as tools are under development [26]. Up to now, the few known H_2 reserves have been found by chance whereas looking for water or hydrocarbons but, as for all natural resources, we should be able to do better by understanding the generation, transport and accumulation processes.

Hydrogen can be naturally produced by various processes in subsurface. In most of them, H_2 is coming from the water and is separated from the oxygen by diagenetic process [7,36] or by radiolysis [32]. Since Hydrogen is the most abundant element of the solar system, the degassing of large reserves of deep seated H_2, issued from the mantle or the Earth's core, has been also proposed [15,39] and references inside. The better well-known reaction is the oxidation of, for instance, ferrous material that results in the release, through water reduction, of H_2 contained in this water. The origin of the H_2 flow is not the aim of this paper and the reader may refer to Ref. [14,16] and references inside for a complete overview of the origin of H_2 in subsurface. We aim here to better define the H_2 surface emanations that are observed in some basins. These emanations are numerous, in Russia [16,31], in USA [38], in Brazil [27], in Ukraine [39] in Australia [20] but the measurements, usually the H_2 concentrations in the soil, happen to be very variable in time and space, making them difficult to interpret. In Brazil, a permanent monitoring of H_2 emitting structures have been carried out for two years and this paper summarizes the results and conclusions of this long-term data acquisition.

The knowledge and understanding of these variabilities in time and space is mandatory to propose an exploration methodology and an accurate surface monitoring strategy. That is also one of the goals of the present work. However, we will first synthetize what has been already published and discussed about these structures that are usually called *fairy circles* from which H_2 is leaking. The wording *fairy circle* is derived from the biology where researchers also study this kind of structures that correspond to a gap of vegetation [12].

Fairy circles – state of knowledge

Since H_2 concentration in the soil of the emitting structures is, for a long time, known to change in time and as a function of the position within the structure [16,38], a permanent monitoring has been started in 2018 in Brazil by Engie (see location of the studied area Fig. 1). The company developed for this purpose their own sensors which are autonomous and connected and send daily the measurement to the researchers [18]. The initial campaign, presented in Refs. [27] took place for few weeks with 9 sensors in July/August 2018. Since, in parallel to the monitoring, the tools have been continuously upgraded and the last major data acquisition campaign of this research project came to an end in May 2020. The first acquisitions in 2018 clearly confirmed the heterogeneity of the H_2 concentration within the structure and emphasized for the first time the various time frequencies of this signal. For most of the sensors, when the H_2 concentration was not zero, a daily periodic signal was recorded with values usually around 200 ppm at midday and null by night. In addition, we have recorded much larger high pulses of few thousands of ppm. They are not periodic and do not occur at any specific hour, Refs [27] presented the data of a 6 weeks monitoring campaign (July/August 2018). They show large pulses, occurring in that case at night in one detector, and the daily signal which is present in all the other detectors. Since hydrogen is a known energy source for many bacteria, a characterization of the soil of this structure has been carried out and the H_2 consumption by the bacteria in this specific soil has been measured (0.05–0.1 mol H_2/kg of soil/day, i.e. about 30 l/week for 1 m^3 of soil). This kinetic has been integrated in a model of H_2 transport in the soil with hydrogenase and the modeling proves that about half of the H_2 may be consumed by the microorganisms before reaching the surface [21].

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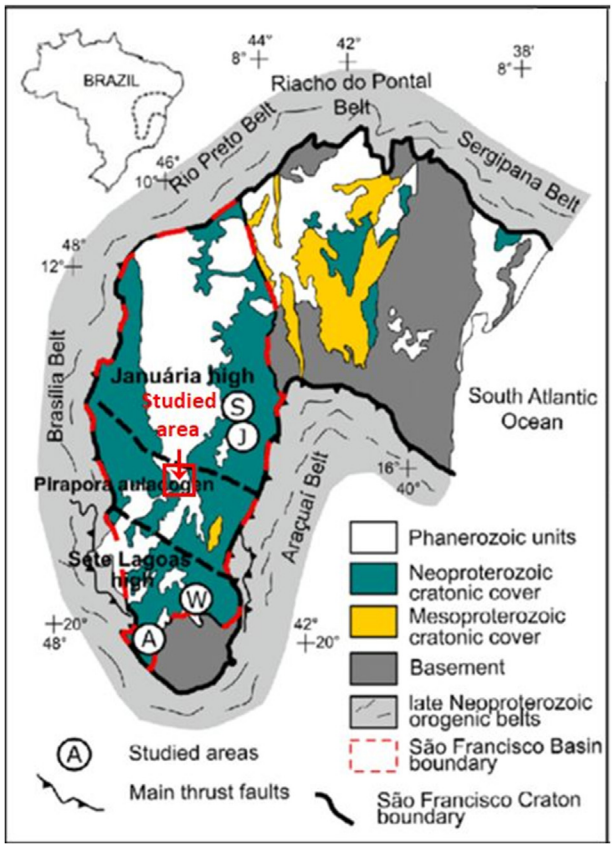


Fig. 1 – Structural map of the São Francisco Basin showing the two orogenic belts that border it and the location of the studied area. Modified from Ref. [28].

The 24 h frequency, which was unexpected by the team, lead to various additional works. First the H_2 sensors temperature dependence has been retested in laboratory, the results show the accuracy of the measurements between 5° and 45 °C [29]. Outside of this window the accuracy is decreasing and the error may reach 30%. This accuracy remains acceptable to test the presence or absence of H_2 in the soils: as a comparison the bacteria are able to consume half of the H_2 signal in few hours so a change of the soil permeability that will increase the transport time of the H_2 towards the surface will result in a higher uncertainty on the deep signal. It is demonstrated that the midday large values are not due to any flaw in the sensibility of the sensors, linked to external parameters as air temperature. Moreover, taking into account the soil thermal conductivity, the soil temperature at 80 cm depth, where the gas is pumped, is not affected by these daily changes. This daily frequency remains then to be explained. A bibliographic review shows that such a 24 h frequency has been noted in other contexts of gas monitoring for instance in mines or along active faults for safety issues [23,30] and on evapotranspiration of the soils. These similitudes suggest that the daily signal is not related to the H_2 generation but to the transport mode of the gas towards the surface.

[30] who monitored H_2 along the San Andreas faults recorded also these diurnal variations, the maximum is at the beginning of the afternoon and the amplitude is between 50 and 300 ppm (See Fig. 4 in their publication) [30]. Also checked the reality of this signal and concluded that it is not due to the instruments. The signal that these authors was looking for and which is related to the earthquakes appears in addition of this diurnal signal and is much stronger. We will see further how we propose, based on our new data set, to link these deep-source-related emissions and the daily signals.

[6] tested the influence of the atmospheric pressure daily variation and concluded that it may explain this periodicity, as the decrease of atmospheric pressure during each afternoon pumps away the gas from the soil, with some delay due to the soil porosity, whereas the increase of the atmospheric pressure at night blankets partially the gas present in the soil porosity. Other external causes, i.e. not related to the initial H_2 emissions, could be proposed, as the earth tide, the variation in water content in the soil but also a change in the near surface bacterial activity. In the studied structure in Brazil, sampling has been done within the first 40 cm [21] and the near surface living bacteria's that have been identified may use different sources of energy and therefore could consume less H_2 in the middle of the day. This suspected variability of the H_2 consumption has not yet been quantified; likewise, a full modeling with all the external causes has not yet been done. Meanwhile [22], tested how a pulse of H_2 at a given depth with a given frequency propagates through the soil. Their model is taking into account the bacterial consumption in the soil, potential heterogeneities of the soil in terms of porosity and permeability and the initial pressure of the H_2 pulse. Their results show that.

(1) Published data, especially in Brazil, are not compatible with a constant flow source or with a high frequency one (less than 12 h)
(2) Gas transport in the soil partially saturated with water is a slow process, with « regular » hypothesis for the permeability of the soil the vertical velocity is in the range of 2–4 m/h. Some hours between the maximum at the pulse origin and the higher concentration near the surface are therefor expected.
(3) In case of low permeability zone, clayey area versus sandy one, the H_2 is selecting another migration pathway and so the invasion of the soil by the gas is partial. This is reinforced by the bacterial activity, if the transport is slow, all the H_2 is consumed and it never reach the surface.
(4) The size of the structure is mainly function of the transport time between the localized pulse and the surface. There is so no simple "inversion" of the size of the circle versus the depth of the pulse.

The pathway from the H_2 source to the leaking point is not modeled in that approach, the authors consider that it could be through aquifers since the H_2 is rather soluble in water when the pressure increases with depths [4]. Migration of a gas phase from the source cannot be excluded. Aquifers anyway are degassing when approaching the surface since the H_2 solubility is decreasing when the pressure and temperature decrease [17]. Alternatively, the emitting structures may be above an accumulation from which the gas escapes through microfractures that have a valve behavior when the pressure increases. Such a behavior has been described in many gas

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accumulations, in volcanic, geothermal or hydrocarbon-rich provinces [33].

In parallel of these modeling efforts, the Engie Lab Crigen developed a second version of the sensors and a hundred of them have been installed on the field, roughly half on the same structure called Campinas and half on another nearby structure, also emitting hydrogen, called Baru. A few others have been installed outside of the structures in order to analyze the regional background signal (Fig. 2).

Geological setting and methods

São Francisco Basin

The São Francisco Basin is a N–S oriented structure that corresponds to a double foreland basin, located on the São Francisco Craton, bounded by two orogenic belts, the Brasilia Belt westward and the Araçuai Belt eastward (Fig. 1). Both belts were created during the Brasilian Orogeny, at the end of the Proterozoic [2,28].

Substantial portion of the cratonic area is covered by the basin and shows two regional highs, Januaria High in the north and Sete Lagos High in the south, separated by a wide depression of general direction NW-SE, called Pirapora Aulacogen. The studied area is located on the northern edge of Pirapora Aulacogen, bordering the Januaria High (Fig. 1).

The stratigraphic column includes rocks from Archean metamorphic basement (>1.8 Ga), they can reach up to 7.000 m in thickness, and end with the Neoproterozoic Tres Maria Formation (576 Ma. Old) of the Bambui Group [3].

These sediments can be divided into different sequences:

1. A thick package deposited on the Archean basement, during the Paleoproterozoic rifts;
2. Thick sedimentary sequence deposited inside new rifts that reactivates the area during the Mesoproterozoic. At the end of the Mesoproterozoic there was an intense igneous activity, causing intrusions (dikes and sills) in the sedimentary layers previously deposited;
3. A lower Neoproterozoic sequence, deposited in a rift/sag environment and generically called Macaubas Sequence and;
4. A marine sequence, generically called Bambui Sequence, deposited in a foreland basin environment at the end of the Neoproterozoic. Phanerozoic sediments with small thickness and continuity occur covering the sequences specified above.

The structures of the monitored area are on Cenozoic terrains composed of a thin sand layer (few tens of meters thickness) that covers the Bambuí and older sequences. The area is far from the main thrust faults and, from a structural point of view, it is on a regional basement high, little deformed between the two paleo forelands.

The rocks that could be the source of H_2 are either the iron rich formations that are exploited in the mines southeastward (Banded Iron Formation among others) but also ultrabasic intrusions [9] or other mineral rich levels. Other sources of H_2 could be proposed but the new data that we present in this paper are only related to the amount of H_2 in the soil, not to its chemical and isotopic characteristic and so will not help to discriminate between the potential sources. We will not comment here either on the source or the migration pathway toward the studied area. Our favorite model is, at this stage of our knowledge, a generation of the H_2 eastward, a long-distance transport within deep aquifers and a degassing below the studied area. We do not know if there is a free H_2 gas accumulation below the monitored area or if the H_2 is degassing directly from an aquifer.

Monitoring implementation

The H_2 detectors Parhys@ were installed in the area presented in Fig. 2:

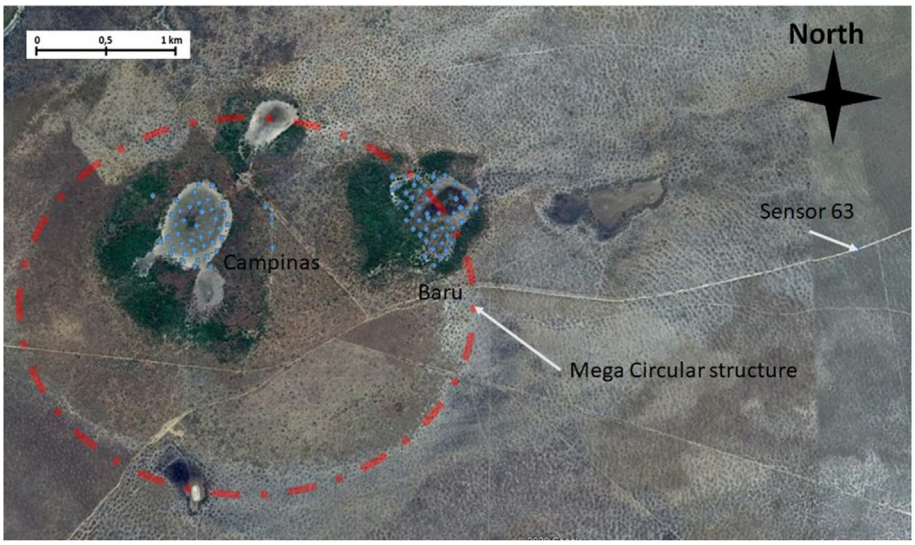


Fig. 2 – Satellite photo of the studied area, with the two structures of Campinas and Baru. Blue dots: position of the sensors during the monitoring campaign presented here, inside and outside of the circular structures. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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- 39 are positioned in the Campinas structure, with an average distance between them around 70 m,
- 5 detectors are set in the vicinity of the Campinas structure, but outside of it.
- 50 detectors are localized in the Baru structure, with an average distance between them around 60 m. At last,
- One detector (Sensor 63) is installed outside of the mega-circular structure englobing Campinas and Baru (Fig. 2).

We present in this paper the monitoring of the Campinas structure during 8 months and the monitoring of the Baru structure (and the sensor 63) during 6 months.

As presented in Ref. [27]; each detector is programmed to analyze the H_2 concentrations at a depth of 80 cm every hour. A pump is activated for 2 min with the same pumping rate than the commercial GA5000© detector in order to facilitate the comparison (i.e. 400ml/mn). The maximum H_2 value for each of these measurements is recorded and forms the basis for the following discussion.

During the 2 mn of measurement, the pump extracts gas at a depth of about 80 cm and pumps it to the surface where the detector is positioned (Fig. 3). The analyzed H_2 concentrations present a bell-shaped curve versus time (Fig. 3). Because of the range of possible H_2 measurements with the detectors, the large H_2 concentrations may happen to be truncated, when they exceed the maximum threshold (Fig. 3). The recorded concentration represents in this case a minimum value compared to the real one which cannot be measured. One of the sensors has a higher threshold, 15000 ppm, and allowed us to record higher pulses.

Results

Time variation of the H_2 soil concentration

The long-term monitoring confirms the coexistence of two signals that have been documented at the start of the experiment with few weeks of monitoring (see Fig. 5 in Ref. [27] but the new data also allows us now to see the relationship between these two signals. Since the periodic daily signal (the positive peak at the middle of the day) has been largely described previously we are going to pay more attention here to the global signal. On Fig. 4 we extracted the data of 3 individual sensors during 1 month. For a better visibility of the figure, we zoomed in a one-month time interval, but these large pulses are occurring randomly during the whole-time interval of the measurement acquisition campaign. Fig. 5 shows a cumulative view of all the sensors on one of the structures, Campinas, during 200 days. Both images show the two signals, high pulses, sporadic, that last between 1 and 3 days and the daily variation with 6 h of diurnal emissions every 24 h. Since the two signals have quite different intensity, in order to increase the readability of the curves on Fig. 4, two scales have been used. Fig. 4b corresponds to a sensor installed in Baru and is the unique sensor that may reach 15 000 ppm. The main peaks on Fig. 4a and c may then represent only a minimum value of H_2, as a saturation is probable. Although adding concentrations does not really make any physical sense, as only absolute quantities should be added, the relation between concentrations and absolute quantities are in our specific case always proportional, as the pumping rate and time of pumping is similar for any detector at any time. Also, we did it to get a global picture of the temporality of the emissions in the structures. If the flow of H_2 were constant and only its migration path in the soil variable, one would expect this sum to be almost constant since the sensors are the same, pumping at the same rate and homogeneously distributed in the structure. It is not the case and the frequency of this sum gives us information. The absolute value is not significant and doesn't have to be considered as representative of the global emission of this structure. On Fig. 5a, all the emissions recorded by the sensors on the Campinas structure have been added up, the daily signal is clearly visible but appears as secondary versus the large signal. On the individual curves it could be observed that the daily signal does not disappear during the pulse although it is not very visible because it is quite lower in intensity. At the opposite, on that 3 examples of Fig. 4, one may also note that the large pulses are immediately followed by a weakening of

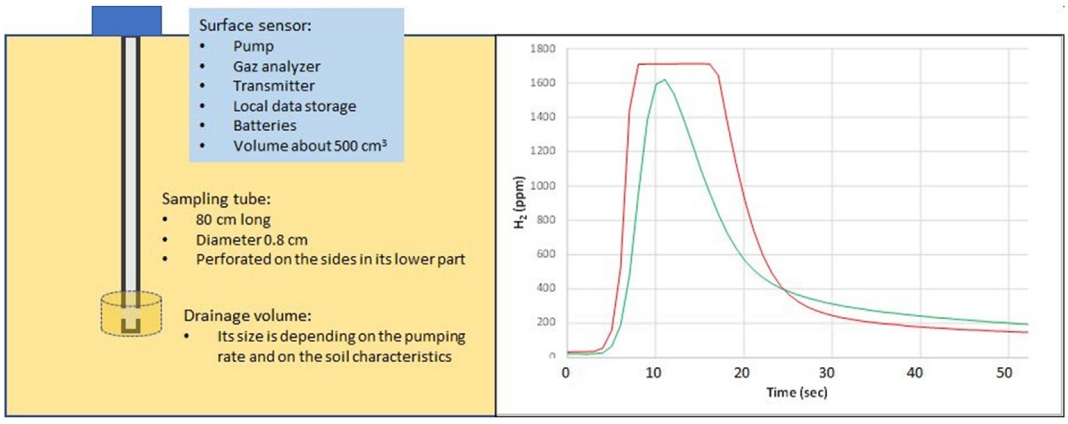


Fig. 3 – Left: monitoring setting; right: Schematic hydrogen measurement during the 2 min run occurring each hour. Only the first 50 s of the run are presented in the figure, as the signal is decreasing monotonously after this time. Sometimes the signal is non-saturated (green curve) whereas some others times it presents a clear saturation (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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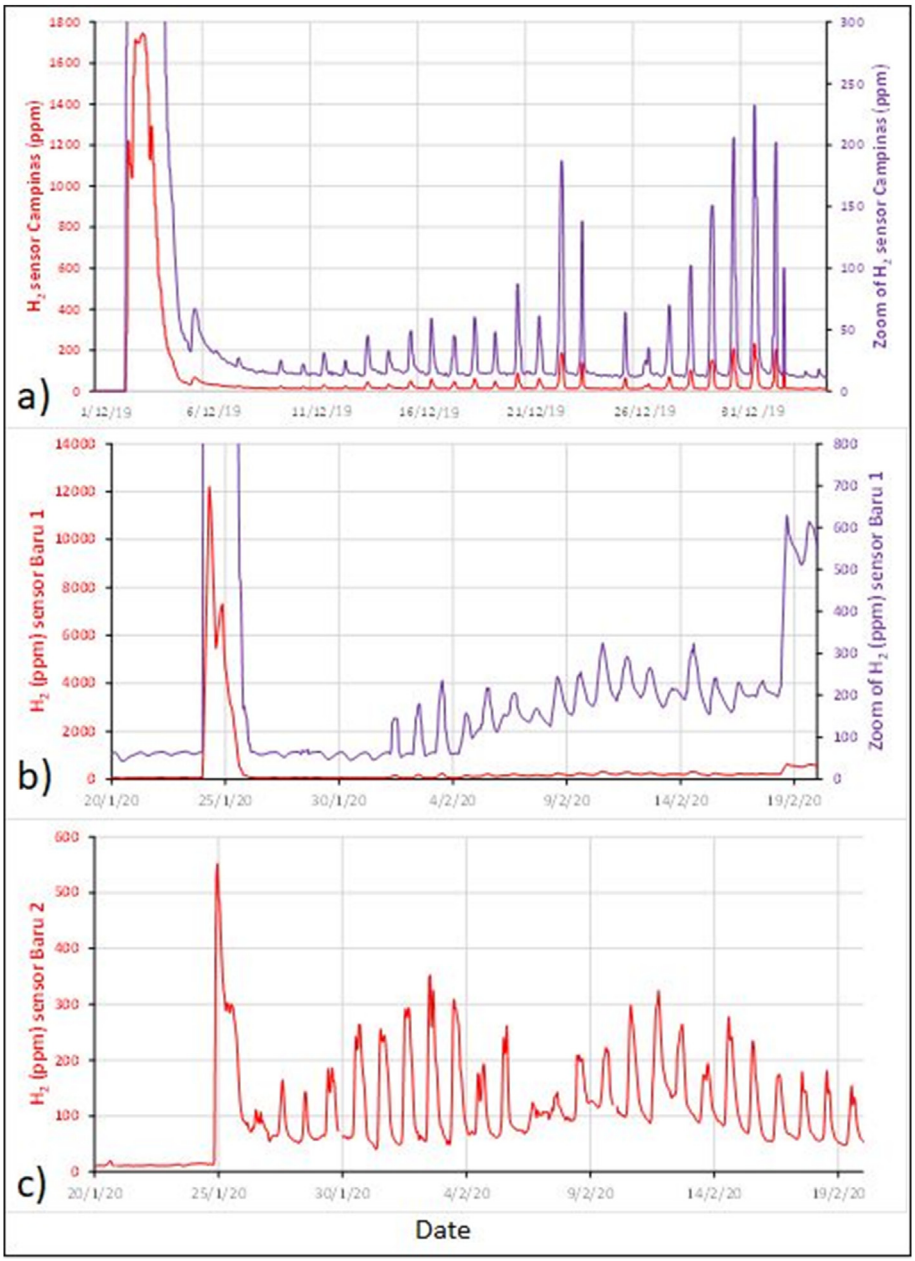


Fig. 4 – Three examples of isolated large H_2 emissions, followed by periods of low emissions, then by a daily oscillation of the H_2 concentrations with maximal values around 200–300 ppm. a) example from one of the sensors of the Campinas structure. b and c) Examples from the Baru's structure. Each of the three recordings are presented during a one-month period.

the daily signal for few days, the concentrations go down to less than 100 ppm and remain low for 3 or 4 days. It is only later that the daily oscillations increase again in intensity.

On Fig. 5 we also displayed the amount of rain during the acquisition campaign. The water is assumed to influence the H_2 content in the soil in two ways. First on the generation side in the hypothesis of a H_2 produced by superficial water/rock interaction and then on the transport side. The generation may take place far away of the emitting structure but one may wonder if the soil humidity after rain influences the H_2 transport to the surface and if the oscillation of the water table influences the degassing. The precipitation data are collected from a meteorological station located at 32 km from the monitored structure. It seems clear that the correlation, if it exists at all, takes place at another level. At the scale of the week, the influence of the weather in terms of precipitation on the H_2 soil concentration is not noticeable.

The sum of the emissions on Fig. 5a shows also a decrease after 4 months. For the sake of transparency, and as H_2 monitoring data on a fairy circle are rare, we publish here all

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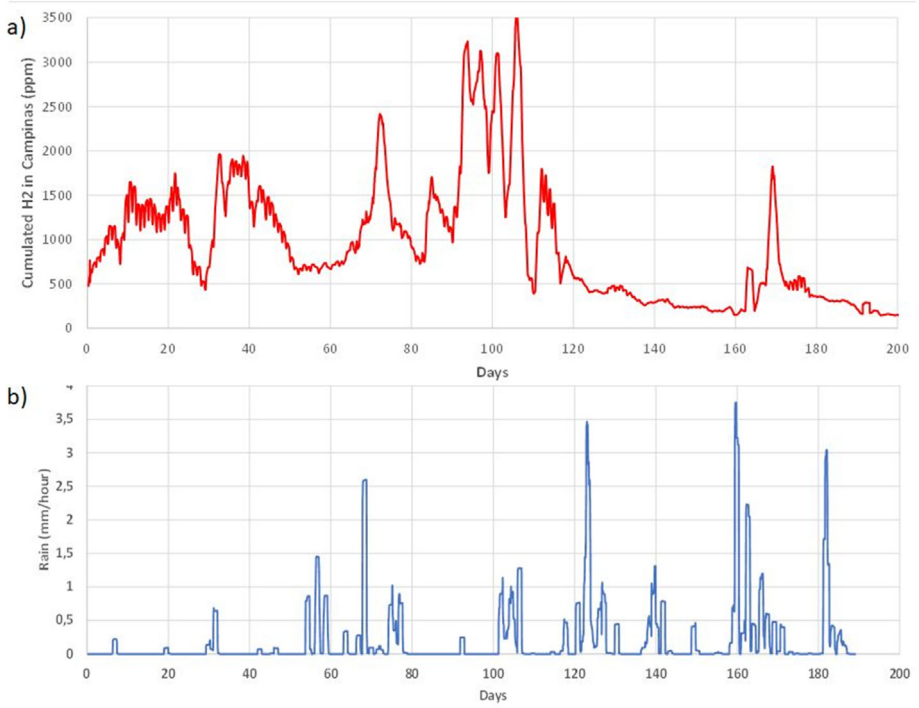


Fig. 5 – a) Sum of the hydrogen emission versus time in the Campinas structure. b) precipitations in the area during the same time interval.

the measurements over 8 months, but our interpretation is that the last months of measurement are degraded. We will come back to this later.

Spatial variation of the H_2 soil concentration

- Maps of subsurface H_2 emissions

With all the installed detectors, it was possible to assess the positions of H_2 emission through time. It confirms that the major area of emission is located at the periphery of the structures identified by the vegetation changes, see Fig. 2. However, the rim itself does not present either uniform values and what seems most clear about this spatial compilation of emissions is that some parts of the structure do not emit (Fig. 6). There are preferential migration pathways.

In term of elevation, the topography of the two structures are slightly different; the center part of Campinas is depressed of few meters versus the border and as a result often full of water during the raining season. When this part is dry, clay deposits in this center could be observed whereas the surrounding areas are sandy. On the opposite, the Baru structure is almost flat with a less pronounced depression, the dark area in its center that could be noted in the satellite images corresponds to an area which have been partially burnt.

Fig. 7 shows some of the daily emissions in the two structures, days where large pulse occur have been selected for the figures. One may note that sporadically, some large emissions may occur near the center (Fig. 7) in Campinas. It appears also that the main emitting area is moving through time along a rim close to the border of the structure, with various intensities. In the Baru structure, which consists of three coalescing structures, the structure located Northeast is emitting in the same way than Campinas, whereas the two other substructures, located South and West, appear to be less active in terms of H_2 emission during the 6 months of monitoring. Values are averaged per day so the yellow correspond roughly to the sensors where only the diurnal signal, the midday pick, was present that specific day.

One may note two characteristics on that images, some H_2 pulses are visible on more than one sensor, or more exactly it happens that different sensors record a pulse on the same day, but it is extremely rare that adjacent sensors record the same pulse. The distance between the sensors is about 80 m, so at small scale it means that the gas pathways are small fingers for the large pulses. At the opposite, the daily signal affects a large part of the rim every day.

Discussion

Relationship between large pulses and remaining periodic pulsing emission

The new data confirmed the tendency observed in the Campinas structure since the beginning of the monitoring in 2018 and described in Ref. [27]: the most common behavior of H_2 emission is the diurnal daily periodic oscillation of the H_2 concentrations, and the exceptions consist on much larger H_2 peaks. The news data set also confirms that the H_2 concentration in the soil could be very low several hours a day, usually at night, even the structure is emitting H_2. However,

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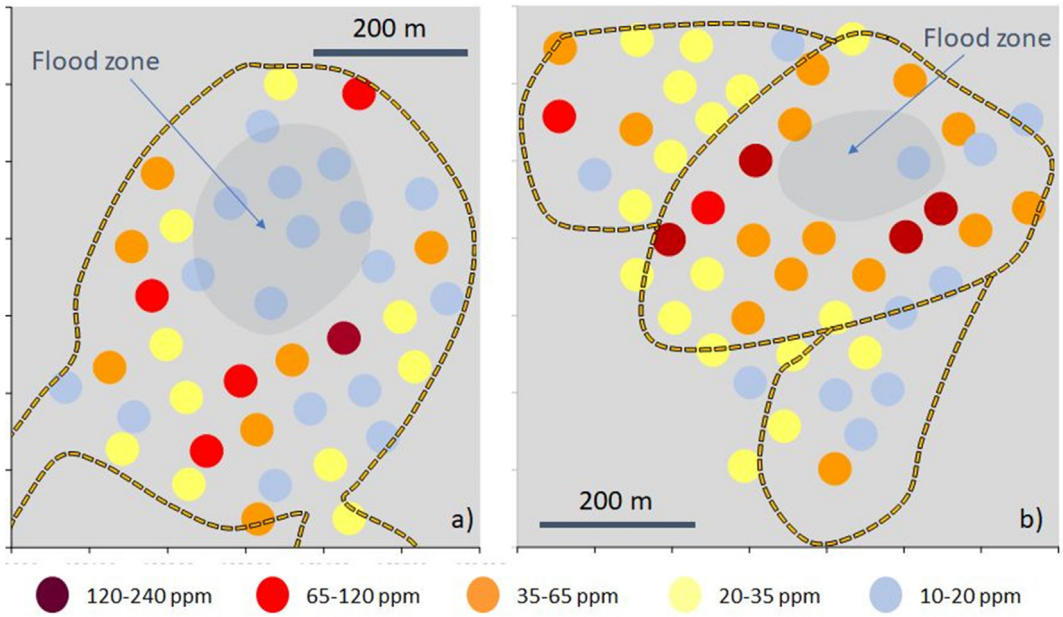


Fig. 6 – Maps of the average emissions for each sensor of the 2 structures during the 8 and 6 months of monitoring for Campinas (a) and Baru (b) respectively.

the very dense sensors array allowed us now to prove that these large pulses take place almost every day in the structure at different places. They are not as common as the daily smaller signal, but quite relative as exceptions since they are observed almost daily as soon as the density of the sensors is high.

Trying to find a spatial logic in these gas emissions seems difficult and, from our point of view, is not significant to evaluate the hydrogen potential of the area. When a pond bubbles due to gas escapes, trying to predict the position of the next bubble is of little interest. The key point is the flow of H_2 through the full structure. Nevertheless, this new continuous recording data, where the days before the peak and the days after the peak can be observed, provide information on the whole system and the interactions between the soil and this gas flow.

The model of gas transport within a heterogeneous soil published by Ref. [22] explains this lack of high value in the depressed center of the structure by the presence of low permeability clay and remains relevant, however the 3D heterogeneity of this soil is clearly more complex that the simple published 2D model.

The large pulses of H_2 seem to recharge the system and appear as the precursors of the beating emissions, of lesser

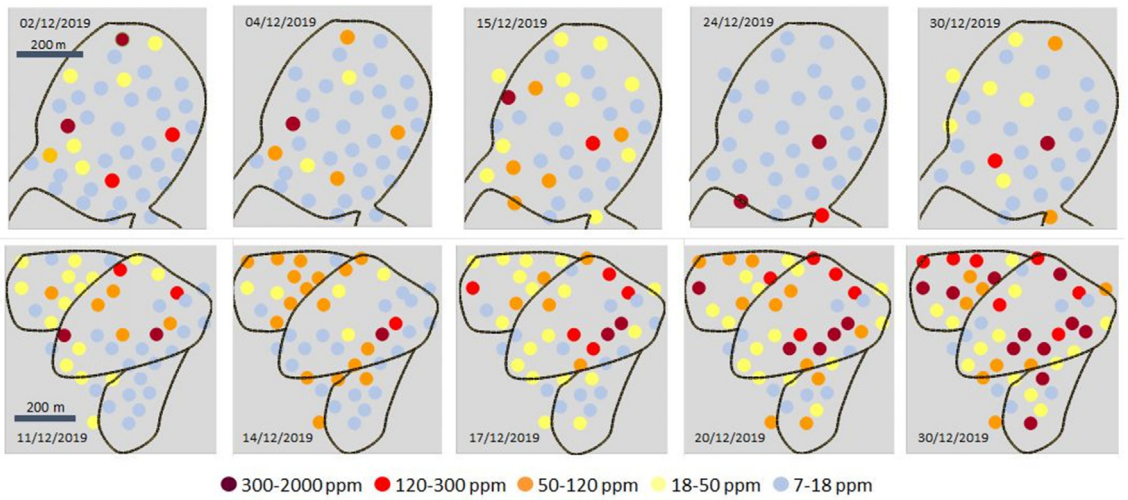


Fig. 7 – Average emissions in Campinas (above) and Baru (below) during one day for 5 different days during December 2019 month.

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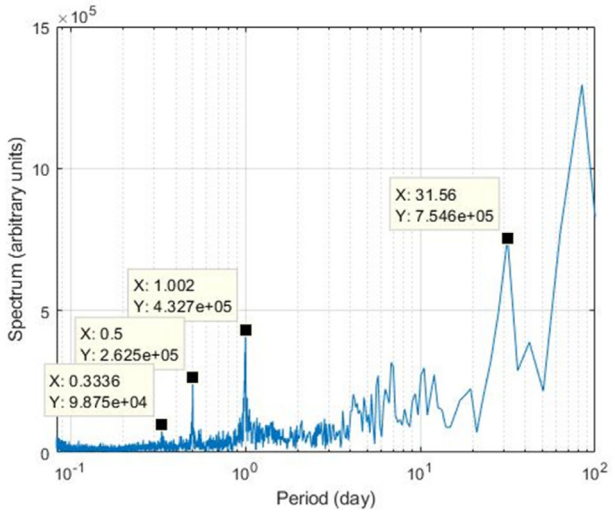


Fig. 8 – Spectrum of the Fourier transform of the global signal Fig. 5.

importance but of longer effect. Within the different modeling that have been published so far on the data of 2018 [6,21, 22]; the trapping of the H_2 within the soil were not taken into account. On both approaches the soil is a porous medium through which the flow passes and the characteristic of his media, as well of the external conditions, slow down or speed up the flow and, in addition, in the two Myagkiy et al. papers the bacterial activity that consumes the H_2 is taken into account. As the opposite, other H_2 consumption processes, chemical consumption through reactions for instance and the potential role of the retention of hydrogen in the soil and its release according to the conditions (pressure, thermicity, chemical concentration gradient…) has not yet been quantified in our knowledge. Trapping of hydrogen on clay mineral is however a known phenomenon that has been described among others in Canada in a similar context (H_2 emitting structures above an old craton); values up to 0.25 mol kg-1 of rock (i.e. about 500 ppm in that case) have been proposed for the thermal desorption [35]. These values are mineral dependent and cannot be extrapolated to the Brazilian case study but suggest that the capacity of sorption process should be investigated for the soils, and maybe the sediments, below

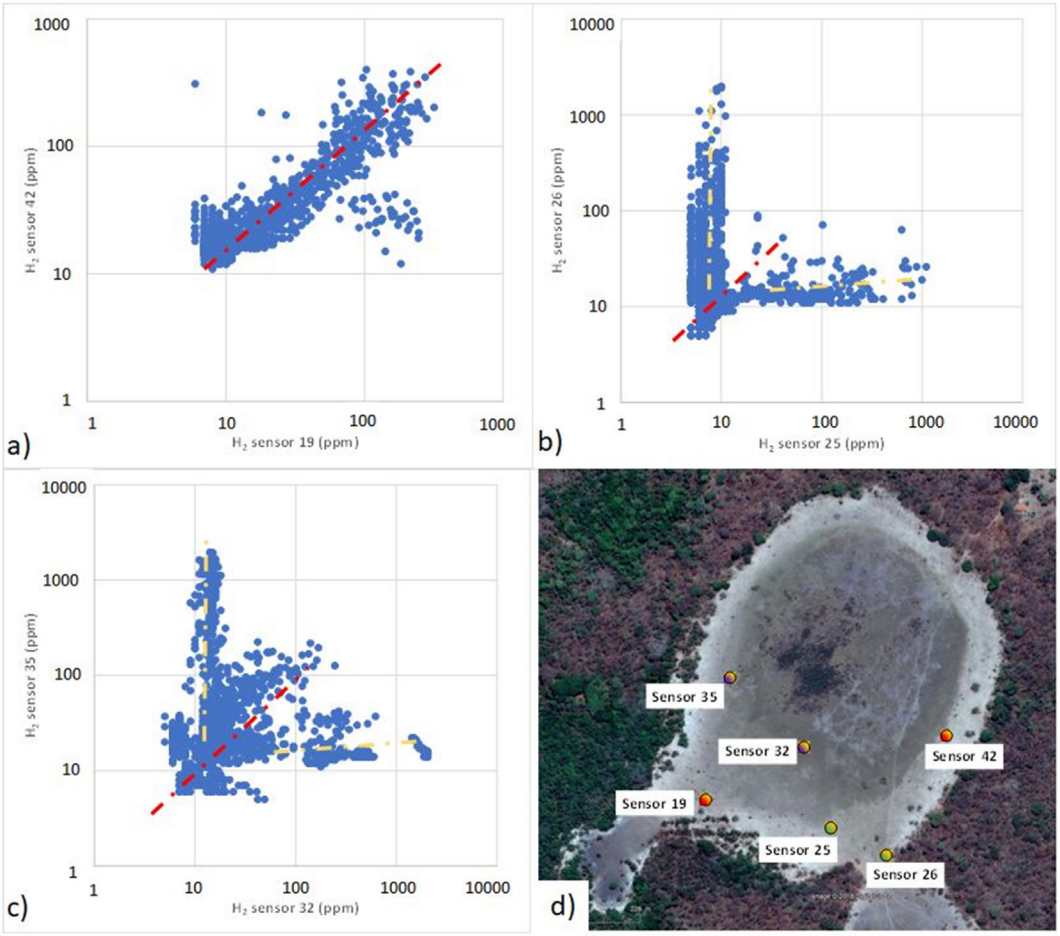


Fig. 9 – Correlation between some sensors. For low values, corresponding to the periodic daily maximum, less than 200 ppm, the correlation exists, red dashed lines. As soon as high values are recorded, they correspond to the pulses, there is no correlation, yellow lines. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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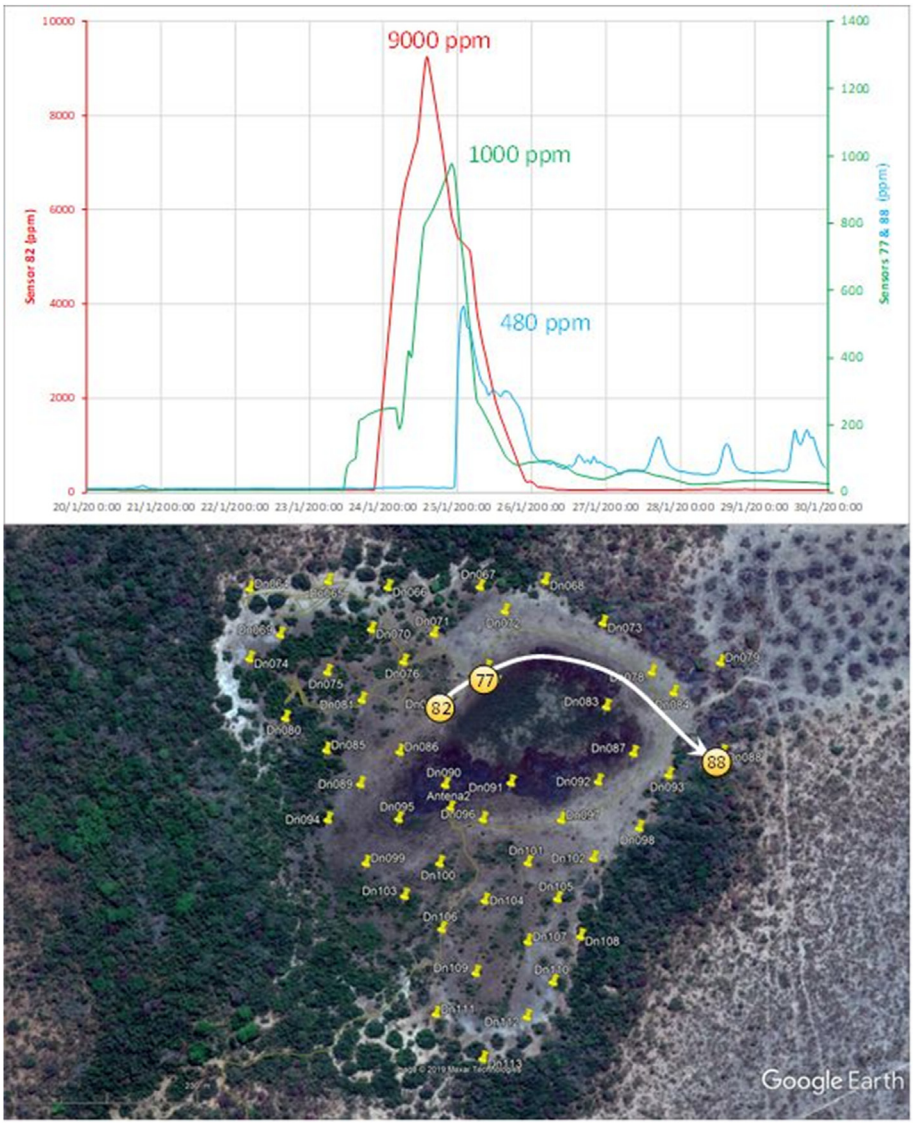


Fig. 10 – An example of measurement on three different sensors that may have caught the same high pulse at different time. The time shift means that the H_2 spends more time in the soil (longer distances and/or lower speed) as a result, due to H_2 consumption in the soil, the intensity decreases.

the São Francisco basin. Desorption is highly temperature dependent and the experiment from these authors show that H_2 desorption may start at low temperature.

Large pulses: frequency and intensity

As noted previously, almost all our concentration measurements are truncated at 1800 ppm, resulting that often, we don't measure the maximum concentration of the pulse. The measured quantity of H_2 emitted on each point is then a minimum. However, in the Baru structure, one of the sensors is able to measured values up to 15 000 ppm and in fact it reached this value several times.

The high pulses appear during 1–3 day long. We didn't notice any relationship between their duration and their intensity but, as we have just discussed, very often the large peaks overpass the maximum authorized concentrations of the sensors and so the intensity is not properly measured.

In a structure like Campinas these large pulses (above 1000 ppm) appear once or twice for a given detector, but considering the whole structure, it is a quite common behavior through time, as shown on Fig. 5a. Only some time intervals of some weeks are without large pulses, which may be due to a not-enough dense gridding of the structure with the detectors.

In order to better define the frequency of the global signal we extracted the Fournier transform of it. The results are presented Fig. 8 and clearly highlight again the daily signal, the 24 h (1 day) is strong as well as the 12 h and 8 h ones. In addition, for the long-term signal, a close to one month (31,56

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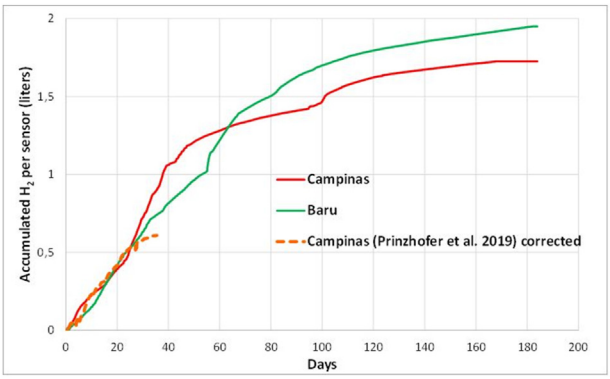


Fig. 11 – Average H_2 emission (in liters) recorded by sensors on each structure. The sum of the emission recorded for each structure has been divided by the number of installed sensors, for each of the three datasets. The absolute amount of H_2 was obtained, from the H_2 concentrations (in ppm) considering the amount of total gas passing through the pump (mainly air) and the detection system of each detector, knowing the flow rate of the detector's pumps.

days) pick is visible suggesting again an influence of the Earth tides that we didn't explore yet. This has been done by other researchers on equivalent signals [39].

Correlations and absence of correlations between detectors

We presented the daily small variations as periodic and the high pulses as sporadic. If it is the case, we may expect no correlation between the H_2 soil concentration between the different sensors and at the opposite some correlations for the low values. It is what can be observed on Fig. 9 that compares the H_2 concentrations measured each hour during 8 months between different detectors.

In Fig. 9a, the two sensors located on the ring (as seen Fig. 9d) mainly recorded low values, less than 200 ppm and are relatively well correlated. On Fig. 9b and c, the sensors measured couples of high values, over 500 ppm and these high values are completely uncorrelated.

It must be noted that the correlations are not related to the proximity of two detectors, as detectors 19 and 42 are very distant on the map of Campinas (Fig. 9d), whereas detectors 25 and 26 are next to each other. It confirms what we can observed on the maps Figs. 6 and 7, the distance between two sensors, even short, 60–70 m, is large enough to get completely different signal between the two sensors. It is an indirect evidence of the high variability of the soil characteristics and that there is no global invasion by the gas when a pulse reaches the surface. It also confirms what we expected, taken into account the pump power and the soil characteristics that the drainage area around the sensors is very small.

However, temporal correlation of some pulses, may also suggest that various migration pathways exist from a given leakage point to the surface, depending of the heterogeneities of the soil. When the travel time is longer, the maximum at 80 cm depth is reached later and the intensity is lower, due to the H_2 dispersion and consumption, by bacterial activity among other. Fig. 10 shows an example of this correlation, the pulse reaches the sensor 82 at 8 a.m. the 24th of January, the sensor 77 at 11pm the same day and the sensors 88 at 1 a.m. the following day. The decrease of intensity, from 9000 ppm to 480 ppm, and the time gap of 17 h are qualitatively compatible with the model of pulse migration proposed by Ref. [22]. In that model a pulse at 30 m deep reaches the surface above the leaking point 12 h later and a near surface point shifted 30 m laterally 18 h later, the decrease of intensity in that model is of about 45%. To reach a quantitative fit, a complete description of the soil heterogeneity will be necessary and is clearly out of the scope of this paper. One may just notice that the decrease of intensity is much larger, which means that the H_2 consumption or retention in the soil is higher than in that model. Having more high pulses that can be correlated will help to characterize these values: soil heterogeneity and consumption/retention in the soil but they are rare. In that case the high pulse has been recorded with the only sensor that goes over 1800 ppm and it is maybe why we may observe its lateral propagation meanwhile the strong intensity decrease.

Conclusions

The data of this first long-duration survey of H_2 emissions in "fairy circles" improves our knowledge of the H_2 emitting structures and it allows us to better interpret the partial data that have been collected so far and which could appear inconsistent.

Deep control of H_2 flux versus soil control and atmospheric control

As a matter of fact, since the first punctual measurements of H_2 concentrations in soils [16,38] the signal was shown to be variable. Data of the short-term monitoring [27] highlighted the systematic oscillation of the H_2 signal through time characterized by 6 h long H_2 emissions at the middle of the day and poorly characterized high pulses following an unknown logic. We have seen from the long duration monitoring presented here that this daily oscillatory signal, is indeed the most common but that the large and longer hydrogen pulses are not so rare, a day or a week is short for a geological time and that these large pulses are likely to represent the charge of the near surface system. The fact that we registered only one pulse in July 2018 was due to the weak density of our sensors array at that time. Part of the H_2 of the high pulses escapes immediately and a part invades the ground from which it is slowly released through a kind of daily breathing during which the frequencies of 8, 12 and 24 h are significant.

At this stage, the fact that the initial charge of the soil in H_2 is only happening though the events of large pulses is a hypothesis, strongly suggested by the time relationship between both signals for the individual sensors. An alternative interpretation would be the coexistence of high intensity pulses and a more diffuse flow towards which the soil would be able to act as a buffer at certain times of day. Having sensors at different depths, few meters deep versus near surface, could help to eliminate one of these hypotheses.

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Strategy for surface monitoring

In summary, we have monitored this area of the Séão Francisco Basin for 2 years. This effort has been done conjointly to the development of this new sensor ParHys@ and the progressive resolution of field acquisition issues. It is obvious that in an industrial exploration process, because ultimately what we're looking for are natural hydrogen exploration tools, this acquisition time has to be reduced and the number of sensors optimized (i.e. as small as possible but without taking risk on the final quality of the data set). Here are the guidelines that could be proposed:

- First, as already highlighted, sporadic values measured during short field trips, cannot be quantitatively interpreted. An isolated null value does not mean anything and a very high value should not be taken for an average,
- Few weeks-long monitoring will be enough to see the periodic signal but the high pulses may be missed,
- The large pulses are sporadic and local, it means that, in order to catch the larger ones, one may either choose to have a high density of sensors for few months, or less sensors for a longer period.

Our experience is that the field conditions are harsh for the sensors, the quality of the signal may decrease with time, or the signal may disappear in the case of electronic problems, water flooding, batteries or pump breakage, etc. Choosing to have a large number of sensors for few months, 6 for instance, will be enough in a context similar to the São Francisco Basin.

A mix between sensors having a high sensitivity but a low saturation and some with a higher concentration range could be a good policy.

We have to note that this strategy is specific for the fairy circles, our experience on H_2 emission in other context such as emitting fractures in geothermal areas are completely different. First, the percentage of H_2 may be much larger (several percents, [10]; for Larderello area in Italy) and second, the H_2 concentrations appear less variable through time, at least for some days as it has been experimented in Djibouti [24].

New quantification of H_2 deep flux

Data acquisition always aims to reduce uncertainty on key parameters. Let see how, using the long-term monitoring in the Campinas structure as well as in the Baru structure, these new measurements allow reducing the large uncertainty on the quantification of possible H_2 flow deduced from the short-term monitoring done in July–August 2018 [27].

In order to compare and normalize these 3 recordings (first recording of [27]; and the two new records presented above from the two structures), we first computed the average amount of H_2 detected by each sensor, for one given structure. This calculation is done multiplying the obtained H_2 concentrations with the total gas volume passing though the pumps of the detectors. Converting the hydrogen concentrations into absolute amount was possible using the value of the pump flow for each detector. We present in Fig. 11 thes absolute average amount of analyzed hydrogen per detector, for each of these 3 datasets. These values represent the total amount that a detector has "seen" passing through its detection system. This measure is very much a minimum because (1) the concentrations are often clipped and (2) the very local rate of pumping is fast compared to the very local flux of H_2 (so the H_2 concentration drops dramatically in 2 min of pumping).

Three main observations may be done:

- The initial slope of H_2 amount increase is quite equivalent, whatever structure or time interval is taken. It appears that the flux of H_2 seeping out remains constant, at least during the first months of monitoring, in this studied area with two circular structures.
- The increase of H_2 amounts is smaller after 60–80 days. This fact was already noticed on the cumulative view of Fig. 5. Since the value of the initial slope obtained in July 2018 is the same than the two obtained in December 2019, we consider that only the first part of the curves has to be considered. The decrease may be due to a fatigue of the drilled well, whose porosity and permeability could be altered by the repetitive pumping of the detectors every hour during months. Argillaceous material or diagenetic processes due to an emphasized water/rock interaction may affect the flux of hydrogen reaching the detector. The small difference in this cushioning may be related to different soil in each structure.
- The Baru and Campinas slope shows some clear positive jumps at different times, such as after 55 and 85 days for Baru, or 100 days for Campinas. This suggests episodic replenishments, more visible for the Baru monitoring, as in this structure, one detector may reach concentrations above 10 000 ppm, on the contrary of Campinas, where all the detectors are clipped below 2000 ppm. What me measured now is then a minimum.

In order to extrapolate the amount of H_2 seen per detector to compute the total flux of H_2 in a whole circular structure, a key parameter already discussed in Ref. [27] is the volume of soil which may be drained by one tubing associated with one detector.

We suggest in this work a new approach to this problem, using the newly acquired whole curves of H_2 measurements during 2 min as presented in Fig. 3. For the detectors which didn't suffer H_2 saturation (as the green curve in Fig. 3 for example), the integral of the curve represents the whole amount of H_2 pumped during 2 min (changing the concentrations into amount thanks to the value of the pumping flux). Considering that the first 5–10 s of measurement correspond to the dead volume of the tubing, the maximum H_2 concentration corresponds to the initial concentration in the soil. Using both the total amount of H_2 (surface of Fig. 3) and the concentration of H_2 in the total gas (maximum concentration measured), one may compute the volume of total gas (mainly air) which has been pumped. The relation between the gas volume V, the H_2 quantity Q and the H_2 concentration C may be written:

$$Q = VC$$

As we know the quantity of H_2 (integral of the measured

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curve during the pulse with the bell-curve normalized with the gas flux through the pump), the initial concentration (maximum of the curve), it is possible to calculate for each detector the whole gas volume pumped during its emission. It should correspond to the volume of the cylinder at the base of the tube as presented in Fig. 3, even obviously it is only a scheme, the drainage volume is surely more complicated in shape and more or less extended in each direction depending of the permeability of the soil. However, we note a homogeneity of the calculated values, for all the sensors, this gas volume is systematically between 40 and 60 cm^3. Considering an average porosity of the soils of 50%, and a pumping height of 10 cm (size of the perforated part of the tubes, see Fig. 3), it means that the average drainage of each detector is about 8–12 cm^2. It corresponds to a radius between 1,6 and 2 cm but the drainage area is not a circle since the voids in the tubes, that are just few, create preferential pathways. This new value clearly reduced the uncertainty of the drainage of each sensor that was evaluated between 1 and 25 cm^2 in Ref. [27].

With this information, it is possible to calculate an average flux of hydrogen around 0.03 and 0.04 $m^3/day/m^2$. This is consistent, and in the lower range, with the estimation done previously by Ref. [27] of 0.04–0.9 $m^3/day/m^2$. For the Campinas structure which is 220 000 m^2 large it means than around 700 kg ± 20% are escaping daily and for the Baru structure about 530 kg ± 20%.

In the modeling paper of [6]; a deep hydrogen flux estimate was mandatory, as boundary condition, in order to fit the periodic daily H_2 emission curves. In that paper, the flux allowing this fit, taking into account the data of the daily atmospheric pressure variation, is 0.05 $m^3/day/m^2$. That is quite close and clearly in the same order of magnitude than our new estimate of 0.03–0.04 $m^3/day/m^2$.

It must be noted that the calculated flux from this work does not take into account the hydrogen consumption by bacterial activity in the soils. According to Ref. [21] who worked in the same structures in the São Francisco Basin, more than half of the migrating H_2 from deeper horizons may be consumed by bacterial activity. This indicates that the number may be just half of the real hydrogen flux at a larger depth in this cratonic environment.

As a comparison, this value for the emissions (35 000 $m^3/day/km^2$ ± 20%) is slightly higher but remains in the same range that the ones proposed by Ref. [16] for the fairy circles in Russia (10 000 $m^3/day/km^2$). This increase versus the previous publications is explained by the fact we caught the high pulses that was usually missed on the field due to a too short monitoring campaign.

Currently the debate about the natural H_2 emissions is getting intense. Some authors are convinced that is negligible, some others think that this flow is important (see review of [37]. Some authors focused on the source processes, they try to quantify what could be produced by such or such reaction [5,8], whereas some other ones try to interpret the leakage processes [39]; ourselves). Obviously, the data are missing to conclude, but obviously also, the surface data, for any kind of natural resources oil, gas, gold, iron, diamonds, has never allowed the explorationist to estimate reserves. So, in terms of exploration, the present monitoring shows that an active H_2 system is present in the Minas Gerais. The leakages we measure could be 10%, 1% or even 0.1% of what is generated in depth and only exploration wells will now allow us to define reserves.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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