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Article

Natural H₂ Transfer in Soil: Insights from Soil Gas Measurements at Varying Depths

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Abstract: The exploration of natural H₂ is beginning in several countries. One of the most widely used methods for detecting promising areas is to measure the H₂ percentage of the air contained in soils. All data show temporal and spatial variabilities. The gradient versus depth is not usually measured since the standard procedure is to drill and quickly install a tube in the soil to pump out the air. Drill bits used do not exceed one meter in length. These limitations have been overcome thanks to the development of a new tool that enables percussion drilling and gas measurements to be carried out with the same tool until 21 feet deep. This article shows the results obtained with this method in the foreland of the Colombian Andes. The variation of the gradient as a function of depth provides a better understanding of H₂ leakage in soils. Contrary to widespread belief, this gradient is also highly variable, and, therefore, often negative. The signal is compatible with random and discontinuous H₂ bubbles rising, but not with a permanent diffusive flow. Near-surface bacterial consumption should result in a H₂ increase with depth; it may be true for the first tens of centimeters, but it is not observed between 1 and 5 m. The results show that, at least in this basin, it is not necessary to measure the H₂ content at depths greater than the conventional one-meter depth to obtain a higher signal. However, the distance between the measured H₂ peaks versus depth may provide information about the H₂ leakage characteristics and, therefore, help quantify the near-surface H₂ flow.



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Keywords: natural hydrogen; soil gas measurement; H₂ emanation; Colombia; Llanos; Putumayo

1. Introduction

As part of the quest for a carbon-free energy mix, or at least one that is less CO₂-intensive, H₂, once a chemical product, is now being considered as a means of storing intermittent electricity and decarbonizing certain industrial processes. H₂ is still manufactured, but its presence underground, long known but poorly understood, has been reassessed [1]. Indeed, H₂ is not only an energy carrier but also a source of energy, and continuous production from a field, discovered by chance in Mali, has confirmed this for over 10 years [2,3]. Many countries have adapted their mining legislation to allow prospecting for this new resource, and companies have embarked on exploration [4,5].

The understanding of hydrogen systems is still in its infancy although the main generating rocks have begun to be inventoried and mapped [5,6]. The main reactions are also fairly well known (see [6,7] and reference therein), even though their kinetics remain to be better defined. The main reaction is the oxidoreduction (reduction of water and oxidation of an Fe rich mineral), which may be active in different geological contexts. Radiolysis also leads to the generation of H₂ from water [8]. Additional H₂ generating rocks are the organic rich facies, such as coal, as the late maturation of the organic matter generates H₂, which may remain as a free gas at high temperatures (above 200 °C) [9,10]. When subsurface data exist, the presence and current depth of these generating rocks can be investigated.

For hydrocarbon exploration, the presence of reservoirs, traps and seals is verified before drilling. For the H₂ system, the characteristics of the seal and even the existence of perfect seals are still debated. At Bourakebougou, in Mali, the only field currently in production, the seals of the various reservoirs are dolerites and shale [11,12]. However, some authors doubt the sealing capacity of regular poor permeability rocks against H₂ dismigration [13], while others note that salt could be an excellent cap rock [14]. Thus, the presence of H₂ leaks is being investigated for the time being. These leakages are interpreted as proof of an existing and active H₂ system. The fault zones, as with all fluids, are a preferential pathway for H₂ migration [15,16], where the fault valve effect could result in pulses [17]. In these areas, leakages are usually greatest, and more continuous.

Various tools enable the H₂ explorationist to map H₂ presence in the soil. As H₂ is virtually absent from air (0.5 ppm), the presence of H₂ in the soil is interpreted as evidence of a leakage from a deeper system, generating rock, degassing aquifer, accumulation or migration pathway. As H₂ presence affects vegetation and sometimes soil geometry, remote sensing can be used. This includes satellite images (such as Google Earth), Digital elevation models (DEM), and vegetation indexes often based on infrared acquisition. Sub Circular Depression (SCD) with abnormally high H₂ content in the soil, also called fairy circle, where vegetation disappears or is different, has been described first in Russia [18] and, then, in the USA [19], Brazil [20], Australia [21,22] and Namibia [23]. The total absence of vegetation observed in Brazil [20] is not universal and just different; less tall, vegetation can also be observed as in Colombia [24], where sugarcanes continue to grow but plants are smaller in the H₂ leakage zones. Usually, field acquisitions are prepared on the basis of the existence of potential H₂-generating rocks in the areas where vegetation anomalies have been noted [6]. This methodology is basic but appears to be effective and, very often, the soil in these areas of missing or anomalous vegetation contains an unusual H₂ percentage.

Since [18,25], the vast majority of soil gas measurements have been carried out in the same way, with just a few variations [6,26]. This method is known to have some limitations [27,28], but it is the only one that is easy to implement. In this paper, after describing the usual way of measuring H₂ content in the soil, we present a new tool that has been developed to overcome these limitations. We will discuss what we have learned thanks to it and, especially, the depth-dependent measurement of H₂ content that the tool allows. The developed tool can also be used to sample gases present in the soil. Different containers could be used and the comparison between them will be presented in another publication.

The measurements published in this article all come from the Colombian Andean foreland; see the location in Figure 1, called the Llanos Basin for the northern part and the Putumayo Basin for the South [29]. The Llanos Basin is a flat area of about 200,000 km² that extends eastward to the Guiana craton. It corresponds to the foreland of the today Eastern Cordillera, a Mesozoic depocenter inverted during the Tertiary [29,30]. This basin is rich in hydrocarbons and, therefore, the subsurface geometry is rather well known [31]. Between the basement and the tertiary deposits, the Paleozoic and the Mesozoic are still present in the western part but pinch out eastward. The Putumayo Basin southward extends to the Ecuadorian border; it is less deep, the oil and gas exploration is, however, active [32]. The exact H₂ potential of these two basins, and repairing their more prospective areas, is not the subject of this article. For reasons of confidentiality, we will not provide further details about the location of the studied areas or on the generating rocks we are considering.

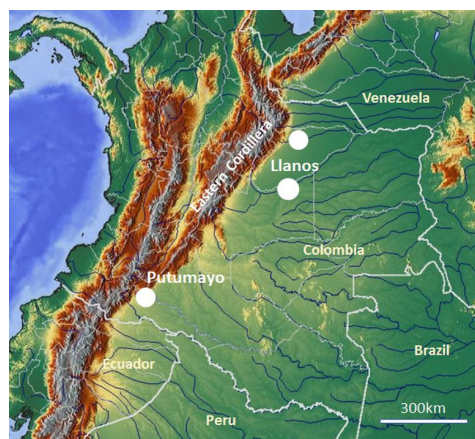


Figure 1. Map of Colombia with the location of the Llanos and Putumayo basins. The studied areas are indicated by the white circles.

2. Existing Soil Gas Measurement Methods

Soil H_2 content is measured using sensors that analyze the gas contained in the soil porosity. This gas is largely air—around 20% of O_2 and 80% of N_2 —but it can vary if deep sources bring other gases to the near surface, or if microorganisms generate gases in the soil. The typical additional gases are CH_4 and CO_2 . The sensors used analyze all these gases. Specifically, they analyze O_2 , CH_4 and CO_2 , in % and calculate a “balance” that is interpreted as N_2 . The sensors chosen for H_2 exploration also measure H_2 , in ppm, as this gas is in smaller quantities in the soil. The GA5000 or BIOGAS5000 (manufactured by QED Geotech) used by many authors [19,33,34] may also be equipped to measure H_2S and CO , which is mainly a safety feature when working in volcanic zones, as these two gases are toxic. Other commercial gas analyzers are also performing the same kind of measurements; in our case, we used an Optimax (manufactured by MRU Instruments Inc.), and laboratories such as the CSIRO in Australia are developing their own tools [27,33]. Permanent H_2 sensors, called Parhys, have been also developed by Engie [20].

Microorganisms are always present in the soil and many of them are known to consume H_2 [35–38]. These authors have shown that correcting this consumption to calculate a flow rate at depth from surface measurements is not easy, as it depends on many factors, including, for instance, permeability and water content. The consumption has been measured in the laboratory in volume per time. As a result, the speed of the transport of the H_2 is a key parameter; if it is too slow, the microorganisms have the time to consume all the H_2 [36]. Inverting the signal to deduce from surface flow the existence or depth of a leaking reservoir or degassing aquifer is highly speculative [6,35]. To compute a flow from punctual data, even numerous, 50 sensors on a single SCD recorded H_2 for 8 months in Brazil, also required hypotheses [20]. Even if these H_2 near-surface data sets (80–100 cm depth) cannot be directly inverted, they are key to eliminating unrealistic hypotheses on the deep H_2 flow. For instance, in Albania, the H_2 flow measured in a mine is too high to be directly related to a H_2 generation zone and is interpreted in terms of leakage from a deeper reservoir [39].

In the field, all the teams who performed soil gas measurements have noticed that H_2 contents are low when measurements are taken very close to the surface (10 to 20 cm), and all measurements are generally taken at around 80/100 cm from the surface (see additional material in [6]). This value has no scientific basis, but is the result of various constraints, such as the length of the drill bit that you can buy and take with you in your luggage. Furthermore, to penetrate the ground with a drill bit, we have to put weight on the tool, which is impossible with a tube that is too long. In some cases, where the ground is too hard, soil may be missing in some basins; we are unable to drill as deeply and measurements are taken at a shallower depth.

2.1. Tube Installation

How the hole should be made is debated, as H_2 can be generated by perforation, as it is well known on a larger scale in the oil industry [40]. Some authors suggest avoiding the rotary mode with the drill [28], while others note that results are generally insensitive to this factor [6]. From the experience of one of the authors, the key factors are the water content in the soil (after or during a rain for instance) and the temperature of the drill bit, usually related to the drilling time or rotation speed; the H_2 , in this case, comes from the oxidation of the drill bit.

Once the hole is made (Figure 2), it normally remains open if the soil is not too loose, and a cannula is inserted into the ground. This tube, made in copper or stainless steel, is pierced laterally at the end which is in the soil. The drill has usually a diameter of 14 or 16 mm; the tube, which is slightly thinner, is inserted into the vacuum as soon as possible after drilling and the measurement is taken: the sensor pump pumps air which is into the soil and analyzes it.

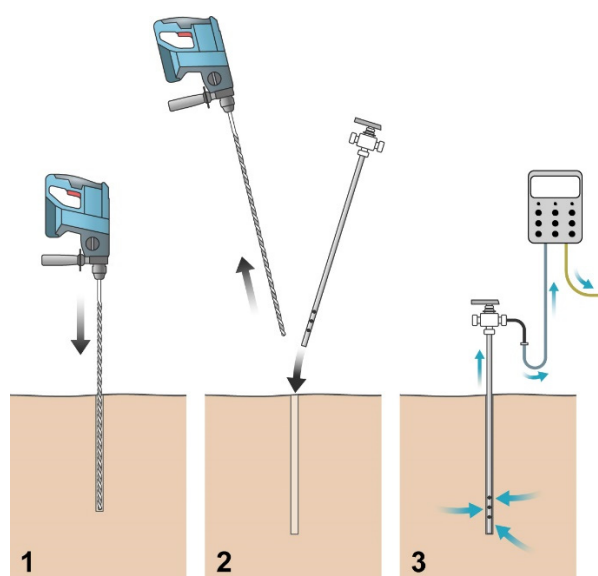


Figure 2. Traditional way to measure the soil gas. 1: Drilling, 2: tube installation and 3: measurement, eventually sampling through the valve. The blue arrows indicate the gas flow when pumping.

There are two stages in the procedure: first, drilling, and then, inserting the tube as quickly as possible. This process is clearly handcrafted, but it was the best that could be performed with the available equipment. When permanent monitoring is not possible, an alternative to obtain complementary data is to leave the tube in the ground, close its upper end, and measure the H_2 content several times over a day or two, to ensure that the initial drilling no longer affected the measurement. Field constrains do not always allow this but, usually, a recharge of at least 1 or 2 h long could be tested. By experience, recharge could be visible after just 1 h and permits optimism regarding the fact that the H_2 leakage is active. Long-term monitoring has the advantage of ensuring that the flow is continuously active, as opposed to measuring residual H_2 adsorbed, as in shale minerals in the soil, but such data sets are still rare [20]. Conversely, you can be unlucky and measure zero at a location where a few hours or days later, the H_2 content of the soil could have been high, as all monitoring data have shown [20].

The fact that the measurement changes near the surface has been noticed by many authors, but as they also noted that, in SCDs, soil H_2 content varies throughout the day and spatially across the structure; they did not attempt to quantify these variations.

2.2. Gas Measurement and Sampling

In terms of commercial gas analyzers, many field campaigns have been conducted with the GA2000, GA5000 or BIOGAS5000 equipped with various sensors. The difference between the three tools is mainly their age and the presence, or absence, of an integrated GPS. They are robust devices; the laboratory tests that many teams have carried out with known blends of gases are good, and in the field, they do not seem to be affected by weather conditions. They need, however, to be protected from the dust and the water and filters have to be installed. H₂S has also to be avoided, but this kind of gas is rather scarce outside of volcanic contexts. When we want to sample soil gas, taking advantage of the sensor pump is useful, even if vacuum tubes have a slight gas-sucking effect. The gas can be sampled either at the inlet or outlet of the sensor, but it has been found that there is a bias at the outlet, it is better to carry this out before the gas circulate in the sensor. So, the various researchers have either fitted a T-junction on the pipe between the rod and the sensor, or inserted a spike directly into the silicone pipe, which means changing it from time to time [6]. The correlations between the field measurements and the measurements that could be performed in laboratory are usually good [6,19] but may slightly differ. The reasons for this shift are, essentially, the gap between the timing of the measurements and the filling of the exetainer. The maximum of H₂ content is usually reached after 40 s, which is mainly due to the sensor response time, although the speed of the gas transport in the soil and up to the analyzer may also play a role. As a result, the best time to sample the gas is unclear. If we wait until the maximum is recorded on the sensor, the H₂ content of the circulating gas is lower. Here too, everyone's technique for obtaining a representative sample is based on trial and error. Exetainers are rather small and this method of sampling also precludes some analyses.

In our case, in Colombia, we worked with an Optimax, a multi-gas sensor sold by MRU Instruments Inc. The analyzed gases are the same as with the GA, four, by default, with others optional, and the computation of a balance is interpreted as N₂; in addition, the temperature is displayed. The application provides a time-indexed record, allowing users to visualize changes in gas concentrations through graphical representations that could be interesting for the sampling. Figure 3 shows the available display for two measurements. Measuring may start before actioning the pump (Figure 3b). As already stated, N₂ is not measured but deduced from the other gases, implying that its variations follow mainly O₂ peaks. With this sensor, the O₂ measurement is fine after 10 to 15 s and the H₂ measurement needs about 40 s. The shift between the O₂ and H₂ peaks is likely due to the sensors. With this real-time measurement, one may select the point and depth to take samples for laboratory analysis. These laboratory analyses have a cost and carrying out many field measurements without additional cost is key to selecting the right samples. One may note that without pumping, the signal reflects only air composition, which is coherent with the fact that one needs to extract the gas from the porosity of the soil. Since the soil permeability is not large, the pressure gap between the surface and 1 or a few meters is not large enough to create an immediate flow. This observation raises doubts about the ability of certain laboratories to carry out good analyses without a pump. Based on the pump power and the soil characteristics, the authors computed the volume of the soil that is drained around the tube, which is a cylinder about 8 cm in diameter [20]. The height of the drained cylinder corresponds to the perforated part of the stem. This very small volume is reduced to nearly zero without pumping. Before the pump is started (Figure 3b), the analyzer only measures the air in the stem.

In conclusion, it appears that the four main limitations of the current protocol are that (1) it separates drilling from setting up the measurement tube, (2) it limits the measurement depth, (3) it does not include monitoring and (4) the quantity and container of the gas samples are limited. The proposed solution addresses points 1, 2 and 4.

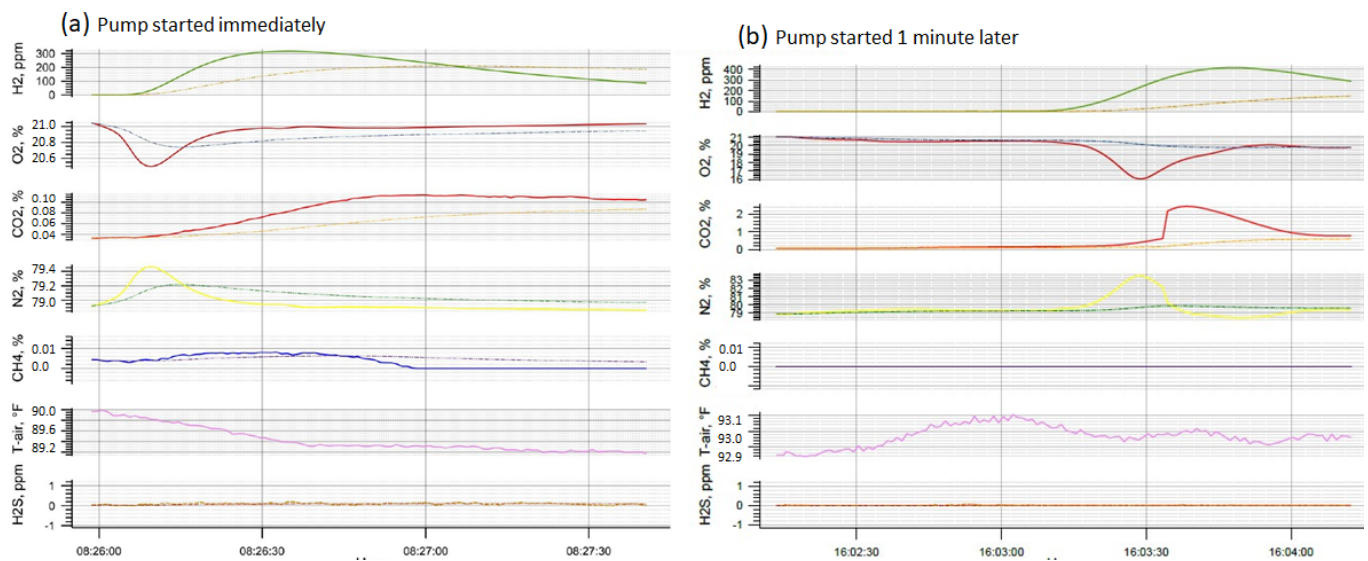


Figure 3. Measurement versus time during 2 min. **(a):** The pump and the gas analysis have been started jointly. The soil gas arrives after 10 s in the sensors (with variation in O₂, note that the N₂ is deduced from the other gas concentration and is, therefore, in line). **(b):** The gas analyzer has been started at 16.02 before the beginning of the deep air circulation (pump at 16.03.15).

3. H₂ Soil Gas Measurement at Various Depth

For the field campaigns done in Colombia, Expro introduces the H₂ Extractor Pro[®], an innovative solution for soil gas analysis and sampling, featuring three key advancements:

- Soil penetration without rotation and direct opening for gas measurement without removing the stem: This feature allows for gas measurements to be taken directly through the sampling system without the need to remove the stem. This streamlines the process and minimizes potential disruptions.
- Depth adjustment and measurement without repositioning the equipment: This advancement enables measurement and sampling at greater depths without repositioning or removing the equipment. This approach reduces unnecessary disturbances and enhances operational efficiency.
- Sampling conditions: the system is designed to ensure that gas sampling occurs under optimal conditions, thereby improving the accuracy and reliability of the measurements.

These innovations collectively enhance the effectiveness and ease of soil gas sampling operations. The methods have been patented (Application #63/506,148).

3.1. Description of the Methodology

The soil fluid sampling system includes various tools and accessories designed for drilling and installing a sampling string at various depths through a 1/4" nylon tube (Figure 4).

The main advantage of this new device is that drilling the hole and measuring the gas are carried out simultaneously. There is no need to remove the drill bit to place the collection tube. The nylon tube placed in the center of the drill tube remains the same for the entire measurement; it is planned to be long enough from the start and emerges laterally under the cap, which enables percussion to be applied (Figure 4d). When the requested depth is reached, the system is opened by a slight upward movement, applied by hand or with a crowbar depending on the soil. Only the nylon tube is attached to the tip and the gas is then pumped through the grid and side holes by the sensor pump. The field campaigns are carried out with a couple of tool tips that allow us to change it at each position and to clean it before a second use. To avoid the risk of contamination, the nylon tube is used only once.

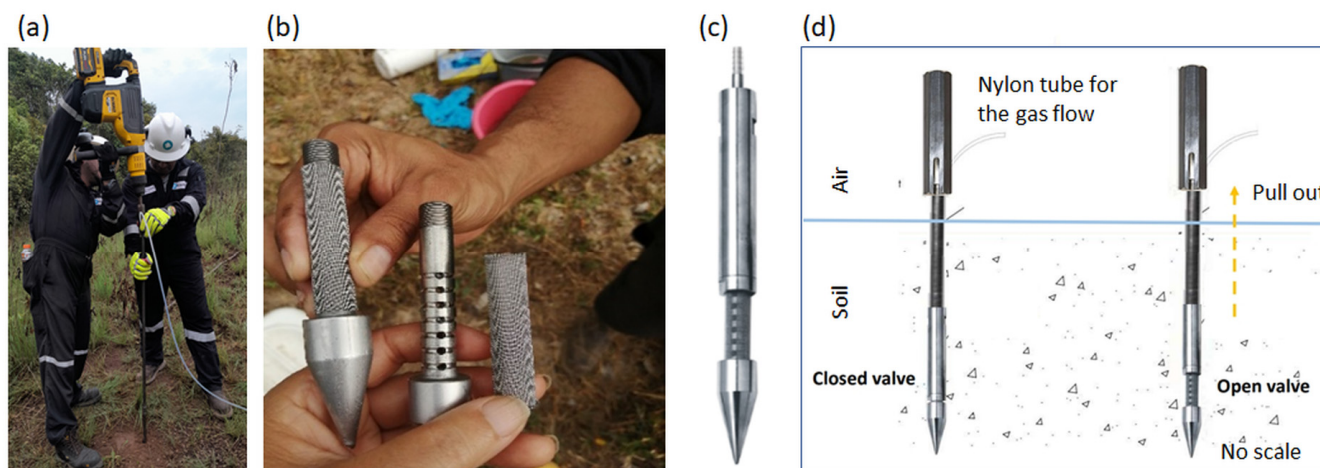


Figure 4. Equipment for measuring in situ and the sampling areas. (a) Penetration in percussion mode only. (b) Tip of the tool disassembled and in position, (c) photo of mounted tip with moving part in open position and (d) field use diagram showing the close and open positions.

3.2. Equipment Used

3.2.1. Surface Drilling Equipment

The drilling method employed from the surface is not rotational but uses axial percussion (Figure 4a); as a result, it works as a hammer. This technique minimizes high-temperature friction with formation minerals and reduces the direct oxidation of the steel by water in the soil but also allows for deepening the void even when measuring the gas. In the Colombian foreland, soil is always present. If the rock is very close to the surface, percussion is unlikely to work for a couple of meter deep hole. The equipment offers a rather portable and practical solution. It is all battery powered, and although the equipment is heavier and more cumbersome than the traditional method, it can be carried some distance away from cars by the team.

The equipment allows us to drill down to about 5 m (15.7 ft) depth, and up to 20 ft, in fact, and various measurements and sampling could be performed during the deepening.

The final depth is determined based on the H_2 concentration identified but also the limitations or complications encountered during drilling. In case of very clayey soil, we noticed that the grid (Figure 4b,c) that protects the lateral voids can become blocked; the grid is stuck within a “mud cake” and the air no longer passes through. The number of open/close cycles may be limited by this issue.

From experience, the maximum depth is 15 feet; at greater depths, at least with the soil in these basins, the gas does not pass through, and the deepening may cause damage to the tools; it could be different in another type of soil.

3.2.2. Sampling Manifold

The surface manifold consists of a set of valves designed for flow control during sampling. It enables the diversion of gas from the bottom of the microwell to either the sample container or the meter. This setup supports the visualization of H_2 concentrations over time by allowing the meter to be directly connected to the Nylon flow hose, which is attached to the top of the drill string. Additionally, the manifold facilitates the connection of one or more types of containers to the system, enabling the creation of the necessary vacuum for pre-sample integrity testing.

3.2.3. Method 1: Vacuum Sampling/Bypass

Equipment includes the biogas meter, pressure gauge, cylinder and a valve arrangement, as depicted in Figure 5. In this procedure, the sample cylinders are subjected to a vacuum of approximately -20 to -26 inHg. Once the meter detects the presence of

hydrogen-rich gas, the valve arrangement is opened so that the cylinder is filled until the pressure in the vacuum gauge reaches 0 psi, as per the schematic.

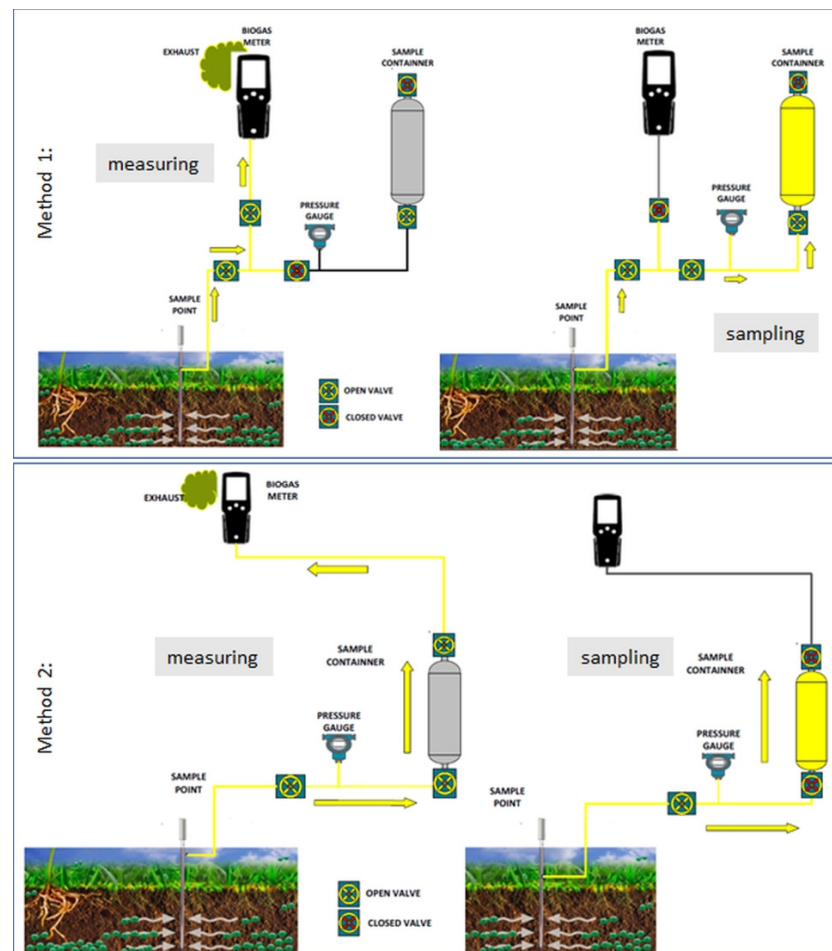


Figure 5. (Top): Method 1 for soil vapor sampling: A derivative is created. (Bottom) Method 2: The container is permanently there, and its exit is locked when we wish to sample. Arrows indicate the gas flow path.

Despite Method 1 being based on established best practices and research related to sampling in the oil industry, and despite integrating new technologies, the analysis of the first campaign's results highlighted potential loss between the meter measurement and the capture during flow diversion. This realization underscored the need for a second method to improve accuracy.

3.2.4. Method 2: Tandem Sampling of Container and Meter

We used the same equipment as in Method 1, but the arrangement is modified, as shown in Figure 5. The method operates on the principle of placing a cylinder under vacuum at -27 inHg within the sampling setup, aligning it with the subsurface drilling system before positioning the sampling probe to the drilled sample point. If the H_2 concentration during flow measurement proves to be representative, the flow is already aligned with the cylinder, which can then be closed to capture the sample.

Once the alignment is set in the surface manifold, drilling begins. Real-time readings from the meter allow for the detection of H_2 concentrations exceeding a chosen threshold. At this point, the valves of the container are closed, and the gas sample is captured.

4. Results: H₂ Content in the Soil of the Colombian Forelands

Four field campaigns have been organized between April 2022 and October 2023. More than 530 in situ soil gas measurements have been performed and the values are presented in Figure 6. The data show the excellent potential of these two basins, with more than 290 values above 100 ppm and 170 above 200 ppm. There is, as usual, a large number of near-zero values. Even a few hundred ppm may look like a small quantity; H₂ emanations in the soil are not random nor ubiquitous. The average value of 158 ppm and the maximum value of 1629 ppm indicate that hydrogen generation is active in these basins. However, the goal of this article is the understanding of H₂ displacement in the soils, so we will only focus on the presentation of the results and discussion of those points.

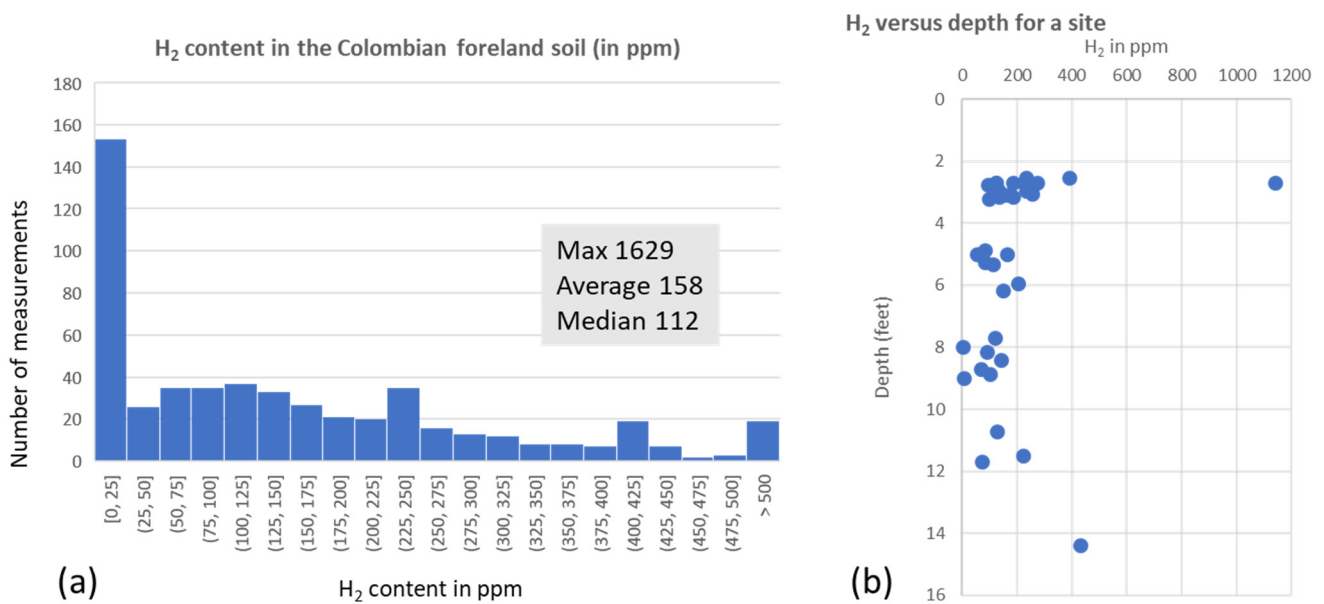


Figure 6. (a) Statistical representation of the H₂ concentration in the soil during the various campaigns. (b) H₂ versus depth for a given site (maximum distance between the various vertical profiles less than 300 m).

In terms of the variability of the results, the fact that we have values at various depths does not change the general feature noted by previous authors: H₂ content in the soil is highly variable, even in the areas, or especially in the areas, where leakage is ongoing. In other areas, the data are uniformly zero or near zero. This means that many measurements must always be made when evaluating an area.

Figure 6b shows this variability versus depth on a given zone. In the studied areas, there are no fairy circles but some vegetation anomalies, and the measures have been planned in cluster around selected locations. The distances between the measured points in a given site are, therefore, rather small, ranging from a few tens of a meter to less than 300 m. We can reasonably consider that the subsoil is fairly homogeneous at this scale, and the absence of any noticeable variation with depth suggests that the soil’s characteristics do not allow H₂ to accumulate on a specific layer. We can, therefore, interpret the vertical profiles as due to variations in H₂ flow.

4.1. Maximum H₂ Content Versus Depth

The data set presented here includes values measured from near surface to 21 feet. As explained previously, when we open and close the system too many times to pump the gas, due to the characteristics of the soil in the studied areas, the grid that protects the tube often becomes plugged by a sort of mudcake and the gas cannot get through. Except for a few trials, the data have been recorded with a maximum of five extensions (i.e., 15 feet—4.6 m). The data for O₂ and H₂ contents in the soil are presented in Figure 7. The first important

information is that there is no general trend versus depth. In neither of the two basins shown here does the H_2 content of the gas clearly increase with depth. Conversely, the H_2 content is variable whatever the depth. It should also be noted that there are no major differences between the areas studied. For comparison, the O_2 content has been displayed; it is also variable and not depth-dependent. In these basins, the CH_4 is almost always close to zero and it is the CO_2 that balances the O_2 .

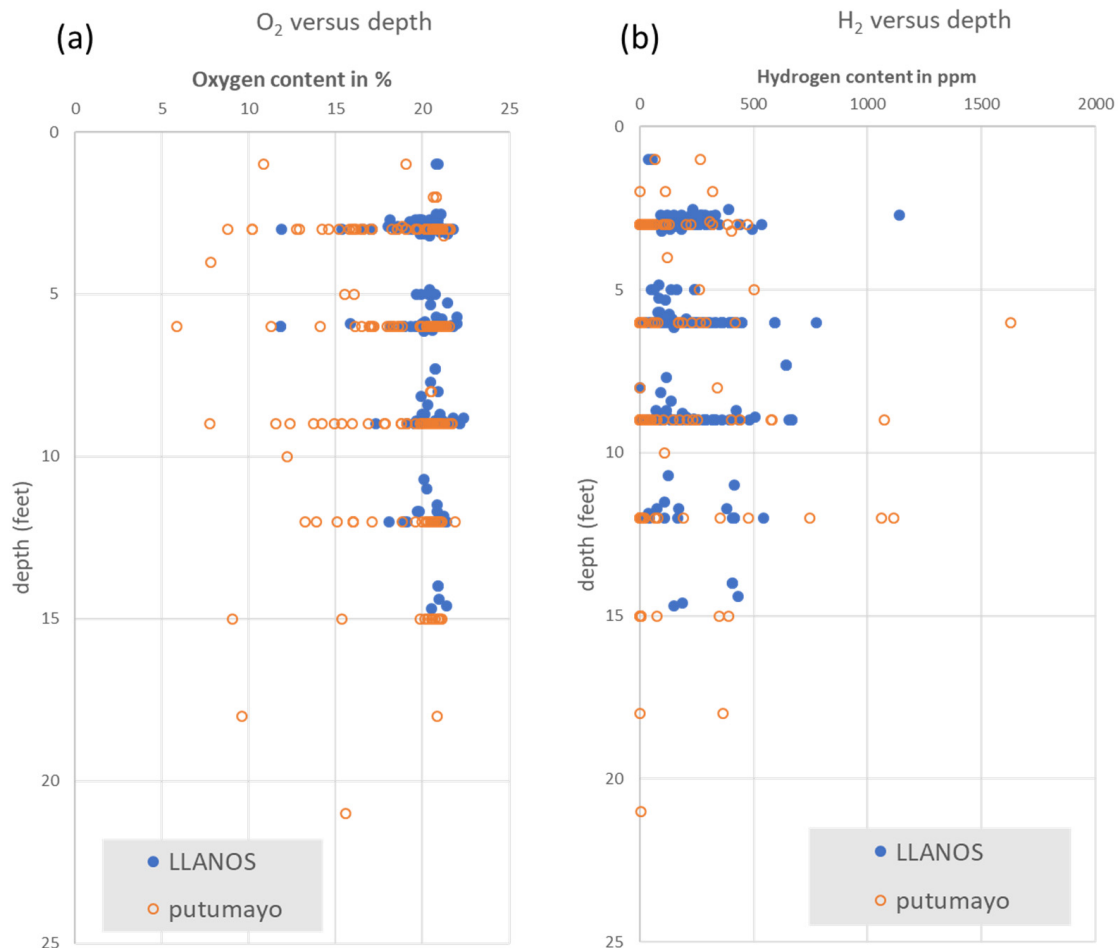


Figure 7. Evolution of the gas within the soil at various depths. (a) O_2 in %. (b) H_2 content in ppm. Data of the various campaigns are displayed together but the origin of the data between the two basins is highlighted by the color.

4.2. Relation to Other Gases

As stated before, various gases are measured, and one may study the relationship between the H_2 and other gases. Figure 7 shows the O_2 values versus depth and Figure 8 shows the CH_4 and CO_2 versus H_2 . Surprisingly, since Llanos and Putumayo Basins are petroleum provinces, the CH_4 content is always close to zero. The CO_2 content also remains fairly low in the Llanos Basin, at less than 6%, with an average of less than 0.5%. In the Putumayo Basin, the maximum is 13% and the average is 1.7%. Regarding the methane content, except for one point at 10% (located at a depth of 4 feet), all the values are close to zero, and the average is 0.09%. Interestingly, Figure 8 shows that there is no relation between the CH_4 and H_2 content.

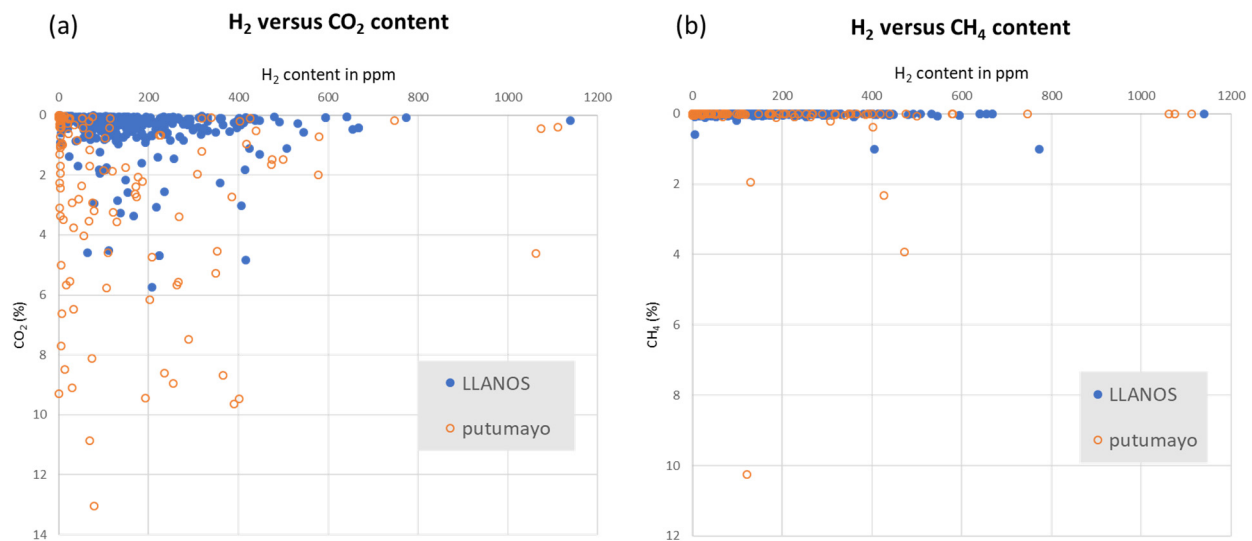


Figure 8. Relation between CH_4 , CO_2 and H_2 . (a) H_2 versus CO_2 . (b) H_2 versus CH_4 .

4.3. Gradient of the H_2 Content Versus Depth

With the new tool developed for this study, the H_2 content in the soil has been measured in 180 points with an average of three measurements at different depths by points. Figure 9 shows the vertical profiles of a couple of these points. The dots correspond to the data and the curve is an extrapolation to allow visualizing the H_2 gradient versus depth. Clearly, there is no constant and no typical profile. The gradients are sometimes negative and sometimes positive, and they change according to the depth. In the vast majority of cases, the H_2 content profiles display maximum and minimum values even along this rather short distance. Only in three cases is the gradient constantly positive; it means that the H_2 content is increasing between three and 12 feet. Due to the spacing of the measurements, one every 3 feet, the width of the peaks is, obviously, of little significance, but the presence of maximum and minimum values, close to zero, over similar vertical distances (P4, P5, L7) draws attention. Variation at wavelengths shorter than 3 feet cannot be quantified with this approach, but at one location, we performed a higher-frequency measurement to ensure that the values were representative (Figure 10).

Leakage, and, therefore, H_2 emanations, are a dynamic system. For the large part, the H_2 is moving in the soil. To avoid the overinterpretation of these data, we have to keep in mind that the curves in Figure 9 do not exactly represent vertical profiles at a given time. The time required to drill and measure four points is around $\frac{1}{2}$ h. The duration of measurement was, for instance, 35 min for P1, 20 min for P2 and 36 min for P6, which was the deepest point, with five measurements. Interpreting this vertical profile as a picture at a given time is, therefore, an approximation, but it is the best we can do without having all the soil characteristics to recompute the signal. As an indication of the time required for the H_2 pulse to be transported upwards by 30 m, in the modeling carried out previously, it was around 6 h [35]. It means that, for the 5 m displayed here, the gas will need 1 h in sandy soil; in shaly soil, the gas transport velocity is lower. The curves are, therefore, squeezed in comparison to the vertical profile at a given instant.

In the Putumayo Basin, the wavelength is between 5 and 9 feet, about $2.5 \text{ m} \pm 20\%$, whereas, in the Llanos, it is larger, about 12 feet. The difference could be due to different pulsing rates or different velocities in the upward transport. These values cannot be considered as quantitative, but they show the signal shape. The peak width is related to data spacing, but Figure 10 gives a better definition of the signal; it corresponds to an acquisition almost every foot (the spacing has not been regular due to acquisition constraints). The H_2 peaks are much narrower, since, in Figure 9, they were only defined by one value. The oxygen and CO_2 curves are more linear, with just three or four anomalous

values, in comparison to the average value. A more global trend seems to start below 15 feet, with a decrease in O₂ content from 20 to 15%, but we do not have enough data to be definitive on that conclusion. The non-decrease in oxygen content for the first meters is, however, confirmed. It could be also noticed that the H₂ ambient noise, the minimum between the peaks, is around 100 ppm, which is a rather high value in comparison to that of many basins [6,26].

The H₂ content in the soil is known to be variable in time and space [41]. All the published data confirm this observation, and various explanations have been proposed, which are all related to the way the H₂ is transported in the soils. This transport is influenced by the atmospheric pressure [42], by the soil permeability and the microorganism consumption [35,36] and by the water content [27]. Some scientists also tested the Earth and Moon tide effects [43]; their conclusions were negative but other investigators think it is important. The 24 h wavelength highlighted by the Brazilian data set [20] is correctly explained by the atmospheric pressure and the spatial variation by changes in soil characteristics (mineralogy, permeability, water content and microorganism consumption). For instance, lower permeability or an increase in water content will slow down the upward H₂ transport to the surface, resulting in a larger consumption by the microorganism, as quantified by Myagkiy and coauthors [35,36]. However, the charge of H₂, which rises from the rocks below the soil, can also be sporadic, if, for instance, if it is linked to a deeper fault valve effect [17].

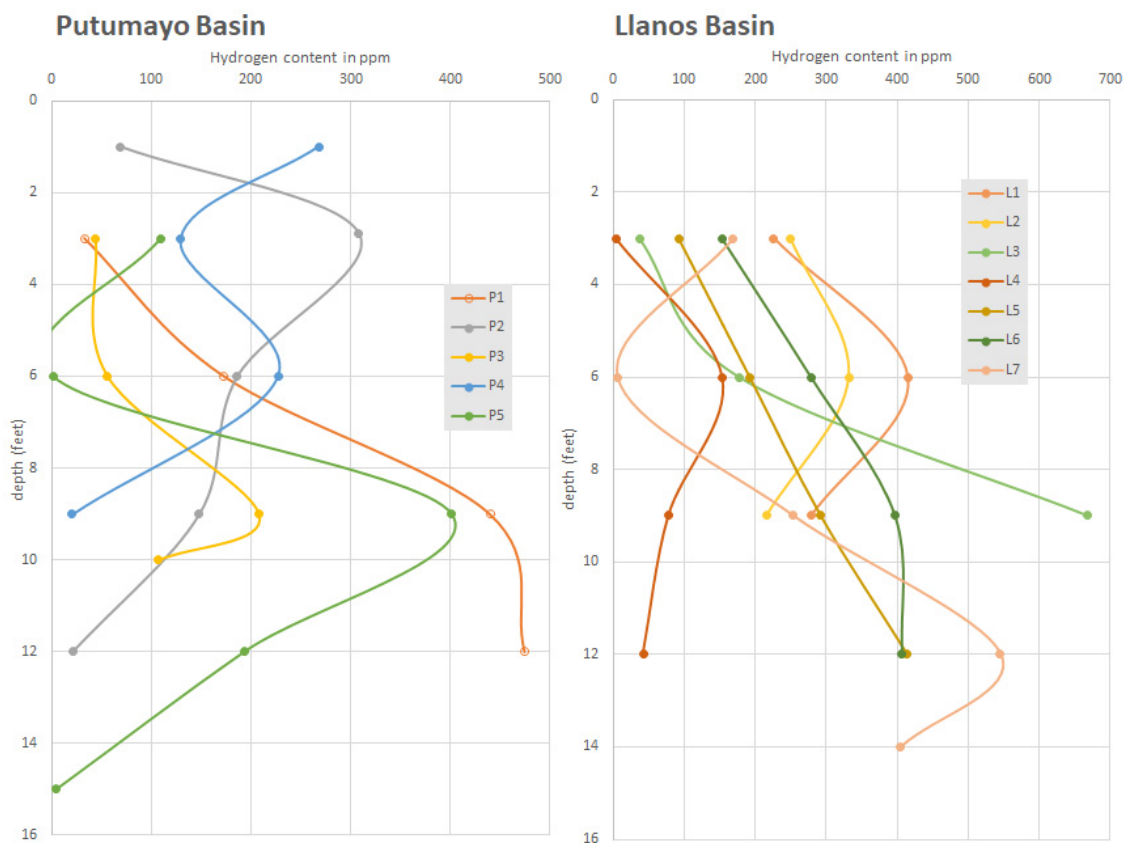


Figure 9. Individual profiles of H₂ versus depth. The requested time for drilling and measuring is between the first measurement and the fourth one is about 30 mn. (Left): Putumayo, (Right): Llanos.

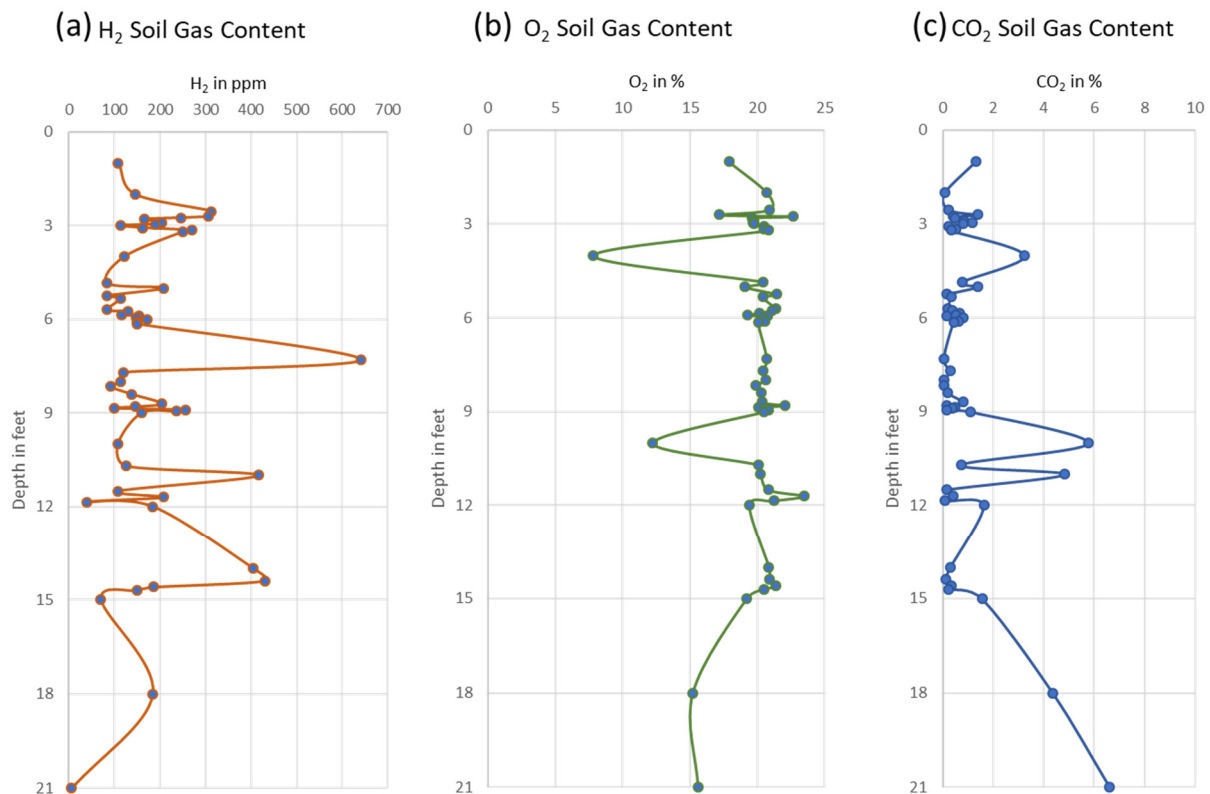


Figure 10. High-density profile of the various gas content versus depth, (a) H₂, (b) O₂ and (c) CO₂, at a given location in the Putumayo Basin.

4.4. Model of H₂ Rising Through a Soil

The two signals, soil breathing and deep flow, are distinct. In the context of native H₂ exploration, only the deep flow is of interest to us, whether sporadic or not. Spending too much time discussing what is happening at the near surface is irrelevant, but it must be understood in order to abstract from it. The data set of the long-term monitoring recorded in Brazil is compatible with the breathing of the soil, influenced by the air pressure with a signal on the order of 100 ppm and subject to the 24 h cycle and sporadic pulses, with much higher values and often less regular ones (see [6,20] for the details of the discussion and the data).

The origin of the deep H₂ flow may be diverse, directly from the rock that generates the H₂, but more likely, from a migration pathway or from a reservoir. The solubility of H₂ in water is high at large depths but decreases when the pressure, and so the depth, decreases [44,45]. In the case of H₂ dissolved in an aquifer, degassing will take place when the H₂ dissolved amount overpasses the solubility. The free gas thus released rises, like bubbles in an aqueous medium. The measured signal strongly suggests that this is what we are seeing in Colombia.

To our knowledge, data on H₂ content versus depth have only been published once, in the Carolina Bay in the US [19]. The numerous data of H₂ versus depth recorded in Colombia are, therefore, a new and complementary element to the spatial variability already described many times over, and to the variability along the day and according to the dryness of the season, which are also well known [27].

A linear increase in H₂ content with depth would have been compatible with a constant, or at least permanent, deep upward H₂ flow attenuated by near-surface consumption by microorganisms. This is not what has been observed. Gradient variations with depth strongly suggest a sporadic source. Such a deep signal results in variable gradient, both positive and negative, as modelling has already shown [35].

In terms of pulse frequency, observing two maxima over 5 m, or at least one minimum and one maximum over 2 m, gives an indication of this frequency. It has to be higher than the 24 h or 6 h as in the simple model published by these authors [35]. Reversing this signal would require in-depth knowledge of soil permeability, hydrometry (both in 3D) and H₂ transport mode (advection vs. diffusion). It could help to be more quantitative to pass from the data set of H₂ content in the soil to an H₂ flow rate, but acquiring so many data to characterize the soil will not help to decrease the uncertainties about the H₂ resources. Similarly, good quantification of oil or gas seeps does not help to prove reserves. We interpret these depth variations as proof that the signal is dynamic and, therefore, as proof that leakage is active today.

The hypotheses in Figure 11 are that microorganism consumption decreases with depth, and that a clay layer close to the surface slows down the H₂ flow and causes it to be consumed. The zero near-surface signal in the center comes from these hypotheses. The signal decay from 100% at 30 m to 35% 8 h later at 7 m is due to consumption, but also to the spreading of the H₂ flow. This decrease in the maximum does not fit at all with the Colombian data set. Of course, there is no guarantee that the pulses are of the same intensity every time, but the fact that, on average, the maxima do not increase with depth (Figure 8) also indicates that the consumption is not as assumed in this previous study [35,36].

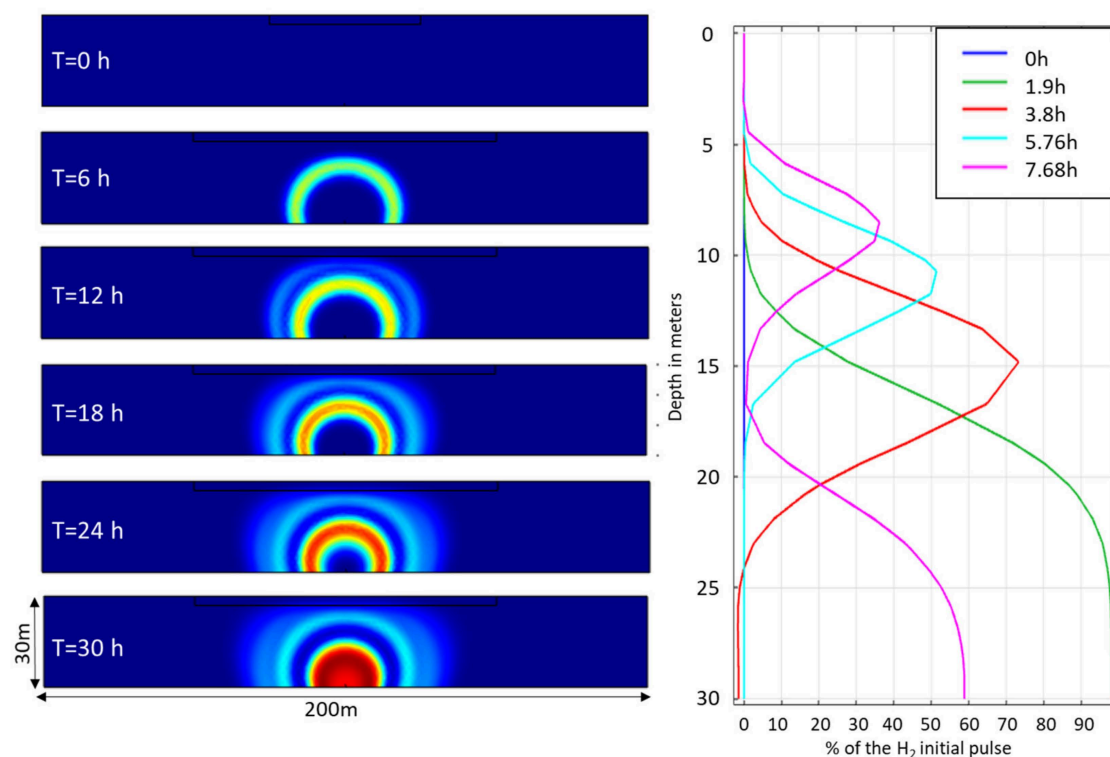


Figure 11. Signal with 4 pulse a day (6 h of gap); in that case, the distance between the two peaks is about 15 m. These figures come from the work performed in 2019 by A. Myagkiy but were not included as figures in the original paper [35]. In this model, a shaly bed in the central part of the model slows down the upward flow and precludes H₂ escape due to high microorganism consumption. It is not the case in the Colombian foreland. Left, the color code from red (100%) to blue (0%) indicates the ratio of the H₂ pulse that reach this point.

When bubbling is observed in lakes or at sea, we see gas bubbles, and it is easy for anyone to realize that the gas content is not constant and cannot be. This has been pictured in New Caledonia [46] and, more recently, in Indonesia [47]. In soil, diffusion and variations in the permeability and/or absorption capacity of certain elements will make gas transport

more complicated, but the source is probably just as sporadic. Figure 12 is a simplified diagram, unlike Figure 11, which is the result of a calculation, but it illustrates what is observed with these vertical profiles with rising pulse of H_2 .

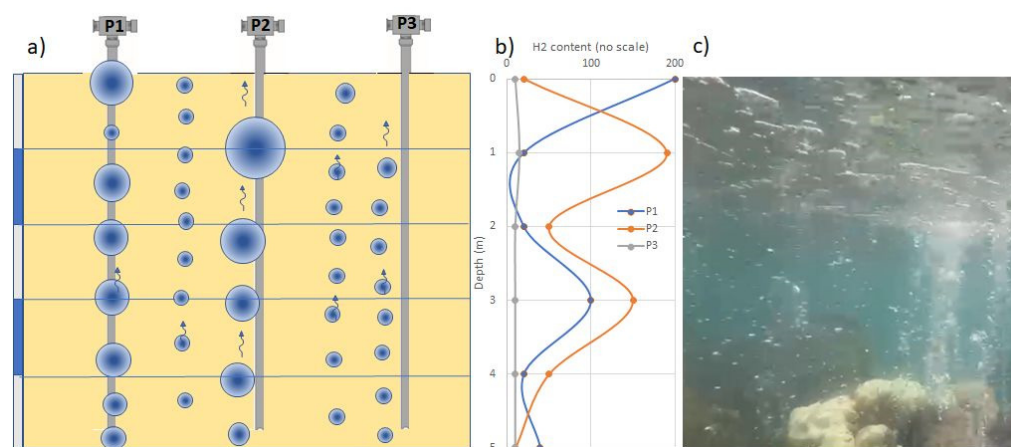


Figure 12. Visualization of the H_2 content heterogeneity in subsurface and in water. (a) H_2 pulses rising in a soil and random position of a measurement stem. (b) Expected vertical profiles of H_2 in these 3 positions. (c) Image of bubbling gas (40% H_2) in Indonesia.

5. Conclusions

- New tool

One of the main advantages of this new tool is the continuous measurement capability. There is no opening of the system and, therefore, no gas escape during perforation. The stem is pressed in without rotation and the measurements could be performed at various depths without reopening the hole. This method, therefore, enables accurate measurement of H_2 concentrations at depths of up to 15 feet. It also allows us to sample the gas at various depths and the methods developed and presented in this paper offer enhanced reliability.

In return, the equipment is heavier, its use requires more time for a single measurement performed with the classical method (as presented in Figure 2) and, since it is purely “hammer like”, in the case of outcropping rocks, the penetration will be limited. One good policy could be to use both methods in parallel, dividing up the team in the field. Quick and numerous measurements to make a map and deeper measurements could be performed on certain points to see the profile in depth.

- H_2 Gradients vs. depth

Our dataset (180 different locations, 535 measurements) does not show, on average, higher values at 4 m than at 1 m. The H_2 content values at 1 m look representative and it seems reasonable to continue to perform H_2 concentration mapping with the classical method. However, the data clearly show the pulses of the H_2 leakages. This confirms, once again, that you need to take different measurements at different times to know whether there is a flow of H_2 . The wavelength of the signal versus depth may be interpreted in terms of flow but only with a numerical tool.

- H_2 Consumption by microorganisms

The expected increase in H_2 with depth is not observed between 1 and 5 m. This may mean that microorganism consumption is only very active in the near surface and/or that, in that case, the upward H_2 flow is fast enough to not be affected. As a range of values, in the modeling performed previously, the upward H_2 near-surface velocity was in the range of 1 m per hours (strongly dependent on the water content and diffusion/advection ratio). The data do not show any correlation between the CO_2 , CH_4 and H_2 content (Figures 8 and 10), which is also not very compatible with a signal strongly influenced by microorganisms.

- Variability of the H₂ signal

It was already known that the H₂ signal within the soil is variable in 3D, (time and two spatial directions). We show, with these new data, that it is variable in 4D. This stands as another good reason to be careful not to interpret this type of data too quickly and, above all, not to consider scattered and too-sparse data as quantitative.

In addition, it could be noted that the H₂ potential of these two basins, where H₂ emanations are numerous and high, is very good.

6. Patents

H2 Extractor Pro: Uspto—UNITED STATES PATENT AND TRADEMARK OFFICE—Application #63/506,148—NATURAL HYDROGEN GAS SAMPLING SYSTEM AND METHOD/Superintendencia de Industria y Comercio NC2023/0008355—National Patent—SISTEMA Y METODO DE MUESTREO DE GAS HIDROGENO NATURAL.

Author Contributions: Conceptualization, I.M. and C.P.; methodology and tools development, D.P. and E.C.; data curation, E.C. and I.M.; writing—original draft preparation, review and editing, I.M.; project administration and funding acquisition, C.P. and K.A. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: Authors Cesar Patino and Katherine Aristizabal were employed by the company Ecopetrol (Colombia), Dora Piedrahita and Elkin Colorado were employed by the company Expro. The remaining author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Smith, N.J.P.; Shepherd, T.J.; Styles, M.T.; Williams, G.M. Hydrogen Exploration: A Review of Global Hydrogen Accumulations and Implications for Prospective Areas in NW Europe. *Pet. Geol. Conf. Ser.* **2005**, *6*, 349–358. [CrossRef]
2. Prinzhofer, A.; Tahara Cissé, C.S.; Diallo, A.B. Discovery of a Large Accumulation of Natural Hydrogen in Bourakebougou (Mali). *Int. J. Hydrogen Energy* **2018**, *43*, 19315–19326. [CrossRef]
3. Diallo, A.; Cissé, C.S.; Lemay, J. La Découverte de l'hydrogène Naturel Par Hydroma, Un «Game Changer» Pour La Transition Énergétique. *Ann. Mines* **2022**, 154–160. Available online: <https://www.annales.org/ri/2022/ri-novembre-2022/2022-11-26.pdf> (accessed on 7 September 2024). [CrossRef]
4. Rigollet, C.; Prinzhofer, A. Natural Hydrogen: A New Source of Carbon-Free and Renewable Energy That Can Compete with Hydrocarbons. *First Break* **2022**, *40*, 78–84. [CrossRef]
5. Truche, L.; McCollom, T.M.; Martinez, I. Hydrogen and Abiotic Hydrocarbons: Molecules That Change the World. *Elements* **2020**, *16*, 13–18. [CrossRef]
6. Lévy, D.; Roche, V.; Pasquet, G.; Combaudon, V.; Geymond, U.; Loiseau, K.; Moretti, I. Natural H₂ Exploration: Tools and Workflows to Characterize a Play. *Sci. Technol. Energy Transit.* **2023**, *78*, 27. [CrossRef]
7. Klein, F.; Tarnas, J.D.; Bach, W. Abiotic Sources of Molecular Hydrogen on Earth. *Elements* **2020**, *16*, 19–24. [CrossRef]
8. Lollar, B.S.; Onstott, T.C.; Lacrampe-Couloume, G.; Ballentine, C.J. The Contribution of the Precambrian Continental Lithosphere to Global H₂ Production. *Nature* **2014**, *516*, 379–382. [CrossRef]
9. Horsfield, B.; Mahlstedt, N.; Weniger, P.; Misch, D.; Vranjes-Wessely, S.; Han, S.; Wang, C. Molecular Hydrogen from Organic Sources in the Deep Songliao Basin, P.R. China. *Int. J. Hydrogen Energy* **2022**, *47*, 16750–16774. [CrossRef]
10. Boreham, C.J.; Edwards, D.S.; Feitz, A.J.; Murray, A.P.; Mahlstedt, N.; Horsfield, B. Modelling of Hydrogen Gas Generation from Overmature Organic Matter in the Cooper Basin, Australia. *APPEA J.* **2023**, *63*, S351–S356. [CrossRef]
11. Maiga, O.; Deville, E.; Laval, J.; Prinzhofer, A.; Diallo, A.B. Trapping Processes of Large Volumes of Natural Hydrogen in the Subsurface: The Emblematic Case of the Bourakebougou H₂ Field in Mali. *Int. J. Hydrogen Energy* **2024**, *50*, 640–647. [CrossRef]
12. Maiga, O.; Deville, E.; Laval, J.; Prinzhofer, A.; Diallo, A.B. Characterization of the Spontaneously Recharging Natural Hydrogen Reservoirs of Bourakebougou in Mali. *Sci. Rep.* **2023**, *13*, 11876. [CrossRef] [PubMed]

13. Prinzhofner, A.; Cacas-Stentz, M.-C. Natural Hydrogen and Blend Gas: A Dynamic Model of Accumulation. *Int. J. Hydrogen Energy* **2023**, *48*, 21610–21623. [[CrossRef](#)]
14. Leila, M.; Loiseau, K.; Moretti, I. Controls on Generation and Accumulation of Blended Gases (CH₄/H₂/He) in the Neoproterozoic Amadeus Basin, Australia. *Mar. Pet. Geol.* **2022**, *140*, 105643. [[CrossRef](#)]
15. Prinzhofner, A.; Rigollet, C.; Lefeuvre, N.; Françolin, J.; Valadão De Miranda, P.E. Maricá (Brazil), the New Natural Hydrogen Play Which Changes the Paradigm of Hydrogen Exploration. *Int. J. Hydrogen Energy* **2024**, *62*, 91–98. [[CrossRef](#)]
16. Baciú, C.; Etiope, G. A Direct Observation of a Hydrogen-Rich Pressurized Reservoir within an Ophiolite (Tişoviţa, Romania). *Int. J. Hydrogen Energy* **2024**, *73*, 402–406. [[CrossRef](#)]
17. Donzé, F.V.; Bourdet, L.; Truche, L.; Dusséaux, C.; Huyghe, P. Modeling Deep Control Pulsing FLux of Native H₂ throughout Tectonic Fault-Valve Systems. *Int. J. Hydrogen Energy* **2024**, *58*, 1443–1456. [[CrossRef](#)]
18. Larin, N.; Zgonnik, V.; Rodina, S.; Deville, E.; Prinzhofner, A.; Larin, V.N. Natural Molecular Hydrogen Seepage Associated with Surficial, Rounded Depressions on the European Craton in Russia. *Nat. Resour. Res.* **2015**, *24*, 369–383. [[CrossRef](#)]
19. Zgonnik, V.; Beaumont, V.; Deville, E.; Larin, N.; Pillot, D.; Farrell, K.M. Evidence for Natural Molecular Hydrogen Seepage Associated with Carolina Bays (Surficial, Ovoid Depressions on the Atlantic Coastal Plain, Province of the USA). *Prog. Earth Planet. Sci.* **2015**, *2*, 31. [[CrossRef](#)]
20. Moretti, I.; Prinzhofner, A.; Françolin, J.; Pacheco, C.; Rosanne, M.; Rupin, F.; Mertens, J. Long-Term Monitoring of Natural Hydrogen Superficial Emissions in a Brazilian Cratonic Environment. Sporadic Large Pulses versus Daily Periodic Emissions. *Int. J. Hydrogen Energy* **2021**, *46*, 3615–3628. [[CrossRef](#)]
21. Frery, E.; Langhi, L.; Maison, M.; Moretti, I. Natural Hydrogen Seeps Identified in the North Perth Basin, Western Australia. *Int. J. Hydrogen Energy* **2021**, *46*, 31158–31173. [[CrossRef](#)]
22. Boreham, C.J.; Edwards, D.S.; Czado, K.; Rollet, N.; Wang, L.; van der Wielen, S.; Champion, D.; Blewett, R.; Feitz, A.; Henson, P.A. Hydrogen in Australian Natural Gas: Occurrences, Sources and Resources. *APPEA J.* **2021**, *61*, 163. [[CrossRef](#)]
23. Moretti, I.; Geymond, U.; Pasquet, G.; Aïmar, L.; Rabaute, A. Natural Hydrogen Emanations in Namibia: Field Acquisition and Vegetation Indexes from Multispectral Satellite Image Analysis. *Int. J. Hydrogen Energy* **2022**, *47*, 35588–35607. [[CrossRef](#)]
24. Carrillo Ramirez, A.; Gonzalez Penagos, F.; Rodriguez, G.; Moretti, I. Natural H₂ Emissions in Colombian Ophiolites: First Findings. *Geosciences* **2023**, *13*, 358. [[CrossRef](#)]
25. Sukhanova, N.I.; Trofimov, S.Y.; Polyanskaya, L.M.; Larin, N.V.; Larin, V.N. Changes in the Humus Status and the Structure of the Microbial Biomass in Hydrogen Exhalation Places. *Eurasian Soil Sci.* **2013**, *46*, 135–144. [[CrossRef](#)]
26. Lefeuvre, N.; Truche, L.; Donzé, F.; Ducoux, M.; Barré, G.; Fakoury, R.; Calassou, S.; Gaucher, E.C. Native H₂ Exploration in the Western Pyrenean Foothills. *Geochem. Geophys. Geosyst.* **2021**, *22*, e2021GC009917. [[CrossRef](#)]
27. Davies, K.; Esteban, L.; Keshavarz, A.; Iglauer, S. Advancing Natural Hydrogen Exploration: Headspace Gas Analysis in Water-Logged Environments. *Energy Fuels* **2024**, *38*, 2010–2017. [[CrossRef](#)]
28. Halas, P.; Dupuy, A.; Franceschi, M.; Bordmann, V.; Fleury, J.-M.; Duclerc, D. Hydrogen Gas in Circular Depressions in South Gironde, France: Flux, Stock, or Artefact? *Appl. Geochem.* **2021**, *127*, 104928. [[CrossRef](#)]
29. Bayona, G.; Cortes, M.; Jaramillo, C.; Ojeda, G.; Aristizabal, J.J.; Reyes-Harker, A. An Integrated Analysis of an Orogen-Sedimentary Basin Pair: Latest Cretaceous-Cenozoic Evolution of the Linked Eastern Cordillera Orogen and the Llanos Foreland Basin of Colombia. *Geol. Soc. Am. Bull.* **2008**, *120*, 1171–1197. [[CrossRef](#)]
30. Cooper, M.A.; Addison, F.T.; Alvarez, R.; Coral, M.; Graham, R.H.; Hayward, A.B.; Howe, S.; Martinez, J.; Naar, J.; Penas, R.; et al. Basin Development and Tectonic History of the Llanos Basin, Eastern Cordillera, and Middle Magdalena Valley, Colombia. *Bulletin* **1995**, *79*, 1421–1442. [[CrossRef](#)]
31. Gonzalez-Penagos, F.; Moretti, I.; Guichet, X. Fluid Flow Modeling in the Llanos Basin, Colombia. *AAPG Mem.* **2017**, *114*, 191–217.
32. Gonçalves, F.T.T.; Mora, C.A.; Córdoba, F.; Kairuz, E.C.; Giraldo, B.N. Petroleum Generation and Migration in the Putumayo Basin, Colombia: Insights from an Organic Geochemistry and Basin Modeling Study in the Foothills. *Mar. Pet. Geol.* **2002**, *19*, 711–725. [[CrossRef](#)]
33. Mainson, M.; Heath, C.; Pejčić, B.; Frery, E. Sensing Hydrogen Seeps in the Subsurface for Natural Hydrogen Exploration. *Appl. Sci.* **2022**, *12*, 6383. [[CrossRef](#)]
34. Lefeuvre, N.; Truche, L.; Donzé, F.-V.; Gal, F.; Tremosa, J.; Fakoury, R.-A.; Calassou, S.; Gaucher, E.C. Natural Hydrogen Migration Along Thrust Faults in Foothill Basins: The North Pyrenean Frontal Thrust Case Study. *Appl. Geochem.* **2022**, *145*, 105396. [[CrossRef](#)]
35. Myagkiy, A.; Moretti, I.; Brunet, F. Space and Time Distribution of Subsurface H₂ Concentration in so-Called “Fairy Circles”: Insight from a Conceptual 2-D Transport Model. *BSGF Earth Sci. Bull.* **2020**, *191*, 13. [[CrossRef](#)]
36. Myagkiy, A.; Brunet, F.; Popov, C.; Krüger, R.; Guimarães, H.; Sousa, R.S.; Charlet, L.; Moretti, I. H₂ Dynamics in the Soil of a H₂-Emitting Zone (São Francisco Basin, Brazil): Microbial Uptake Quantification and Reactive Transport Modelling. *Appl. Geochem.* **2020**, *112*, 104474. [[CrossRef](#)]
37. Thaysen, E.M.; McMahon, S.; Strobel, G.J.; Butler, I.B.; Ngwenya, B.T.; Heinemann, N.; Wilkinson, M.; Hassanpouryouzband, A.; McDermott, C.I.; Edlmann, K. Estimating Microbial Growth and Hydrogen Consumption in Hydrogen Storage in Porous Media. *Renew. Sustain. Energy Rev.* **2021**, *151*, 111481. [[CrossRef](#)]
38. Ménez, B. Abiotic Hydrogen and Methane: Fuels for Life. *Elements* **2020**, *16*, 39–46. [[CrossRef](#)]

39. Truche, L.; Donzé, F.-V.; Goskolli, E.; Muceku, B.; Loisy, C.; Monnin, C.; Dutoit, H.; Cerepi, A. A Deep Reservoir for Hydrogen Drives Intense Degassing in the Bulqizë Ophiolite. *Science* **2024**, *383*, 618–621. [[CrossRef](#)]
40. Strapoć, D.; Ammar, M.; Abolins, N.; Gligorijevic, A. Key Role of Regearing Mud Gas Logging for Natural H₂ Exploration. In Proceedings of the SPWLA 63rd Annual Symposium Transactions; Society of Petrophysicists and Well Log Analysts, Stavanger, Norway, 11 June 2022.
41. Moretti, I.; Brouilly, E.; Loiseau, K.; Prinzhofer, A.; Deville, E. Hydrogen Emanations in Intracratonic Areas: New Guide Lines for Early Exploration Basin Screening. *Geosciences* **2021**, *11*, 145. [[CrossRef](#)]
42. Cathles, L.; Prinzhofer, A. What Pulsating H₂ Emissions Suggest about the H₂ Resource in the Sao Francisco Basin of Brazil. *Geosciences* **2020**, *10*, 149. [[CrossRef](#)]
43. Simon, J.; Fulton, P.; Prinzhofer, A.; Cathles, L. Earth Tides and H₂ Venting in the Sao Francisco Basin, Brazil. *Geosciences* **2020**, *10*, 414. [[CrossRef](#)]
44. Lopez-Lazaro, C.; Bachaud, P.; Moretti, I.; Ferrando, N. Predicting the Phase Behavior of Hydrogen in NaCl Brines by Molecular Simulation for Geological Applications. *BSGF Earth Sci. Bull.* **2019**, *190*, 7. [[CrossRef](#)]
45. Soreide, I.; Whitson, C.H. Peng-Robinson Predictions for Hydrocarbons, CO₂, N₂, and H₂S with Pure Water and NaCl Brine. *Fluid Phase Equilib.* **1992**, *77*, 217–240. [[CrossRef](#)]
46. Deville, E.; Prinzhofer, A. The Origin of N₂-H₂-CH₄-Rich Natural Gas Seepages in Ophiolitic Context: A Major and Noble Gases Study of Fluid Seepages in New Caledonia. *Chem. Geol.* **2016**, *440*, 139–147. [[CrossRef](#)]
47. Sanjaya, I.; Fatturakhman, M.L.; Arifin, A.S.; Maryanto, S.; Kim, H.S. Evaluating the Natural Hydrogen System in Ampana Basin, Central Sulawesi; An Implication for Natural Hydrogen Exploration in Indonesia. *J. Geol. Sumberd. Miner.* **2024**, *25*, 135–149. [[CrossRef](#)]

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