Metrological assessment of on-site geochemical monitoring methods within an aquifer applied to the detection of H_2 leakages from deep underground storages

Elodie Lacroix[1], Stéphane Lafortune[2], Philippe Donato[1], Philippe Gombert[3], Zbigniew Pokryszka[3], Marie-Camille Caumon[1], Xuan Liu[4], and Odile Barres[1]

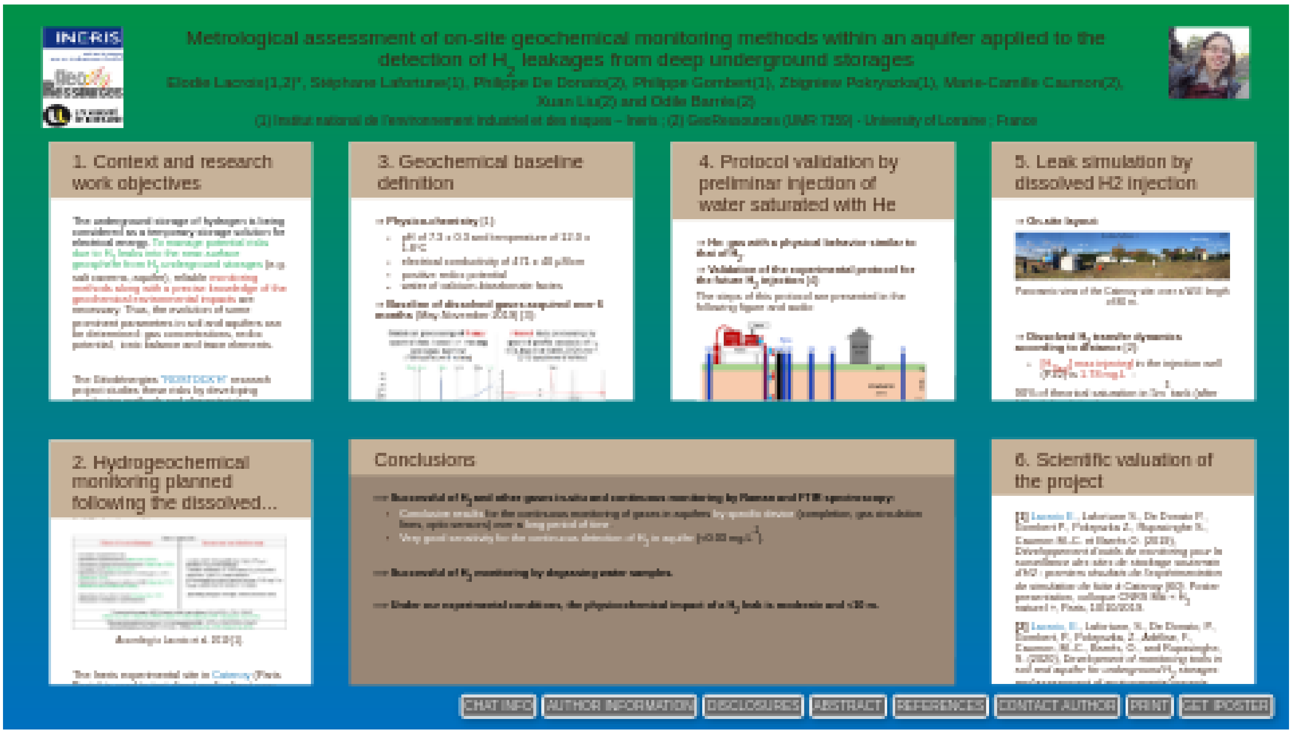
[1]University of Lorraine Nancy
[2]INERIS Institut National de l'Environnement Industriel et des Risques
[3]Ineris
[4]Univeristy of Lorraine

November 22, 2022

Abstract

To manage potential risks due to H_2 leaks into the near-surface geosphere from H_2 underground storages (e.g. salt caverns, aquifer), reliable monitoring methods along with a precise knowledge of the geochemical environmental impacts are necessary. Thus, the evolution of some prominent parameters in soil and aquifers can be determined: gas concentrations, redox potential, ionic balance and trace elements. As part of the ROSTOCK'H project, Ineris simulated H_2 leakage by injection of dissolved H_2 into a shallow aquifer (~20 m deep) in an experimental site within the Paris basin. This experiment aimed to testing advanced monitoring techniques and studying hydrogeochemical impacts at shallow depths. The aquifer water has calcium-bicarbonate facies and a neutral pH. Eight piezometers were aligned over 80 m according to the aquifer main flow (west-east). Hydrogeochemical monitoring devices were set up. One of the piezometers was equipped with a completion connected to a Raman probe and a specific Mid-IR cell for continuous measurement of aqueous gases. At the experiment outset, 5 m^3 of water were extracted from the aquifer to be saturated with H_2 under atmospheric conditions, before being reinjected through the injection well. About 100 L^{STP} of dissolved H_2 (concentration of 1,8 mg/L) was injected in the aquifer. The H_2 injection was preceded by the injection of underground water containing tracers ($He_{(aq)}$, uranine and LiCl) in order to warn the H_2 plume arrival in the piezometers located downstream of the injection well. The concentrations of aqueous gases (He, H_2, N_2, O_2, CO_2, H_2S and CH_4) were measured in a control piezometer (20 m upstream) and in six piezometers up to 60 m downstream. Thus, the maximum H_2 contents were detected up to 20 m downstream of the injection well: 0.6 mg/L at 5 m, 0.17 mg/L at 7 m then 1.8 µg/L of H_2 at 10 and 20 m during the first week. Following the $H_{2(aq)}$ addition, the aquifer physico-chemistry has been modified: low increase in pH, high decrease in redox potential and $O_{2(aq)}$. These results confirm the feasibility of detecting and monitoring H_2 in shallow aquifers in very low concentration conditions and highlight the potential impacts. This is of first importance for establishing the surveillance and security aspects related to with H_2 storage.

Metrological assessment of on-site geochemical monitoring methods within an aquifer applied to the detection of H_2 leakages from deep underground storages



Elodie Lacroix[1,2]*, Stéphane Lafortune[1], Philippe De Donato[2], Philippe Gombert[1], Zbigniew Pokryszka[1], Marie-Camille Caumon[2], Xuan Liu[2] and Odile Barrès[2]

[1] *Institut national de l'environnement industriel et des risques – Ineris*
[2] *GeoRessources (UMR 7359) - University of Lorraine ; France*

Presented at:

1. Context and research work objectives

The underground storage of hydrogen is being considered as a temporary storage solution for electrical energy. To manage potential risks due to H_2 leaks into the near-surface geosphere from H_2 underground storages (e.g. salt caverns, aquifer), reliable monitoring methods along with a precise knowledge of the geochemical environmental impacts are necessary. Thus, the evolution of some prominent parameters in soil and aquifers can be determined: gas concentrations, redox potential, ionic balance and trace elements.

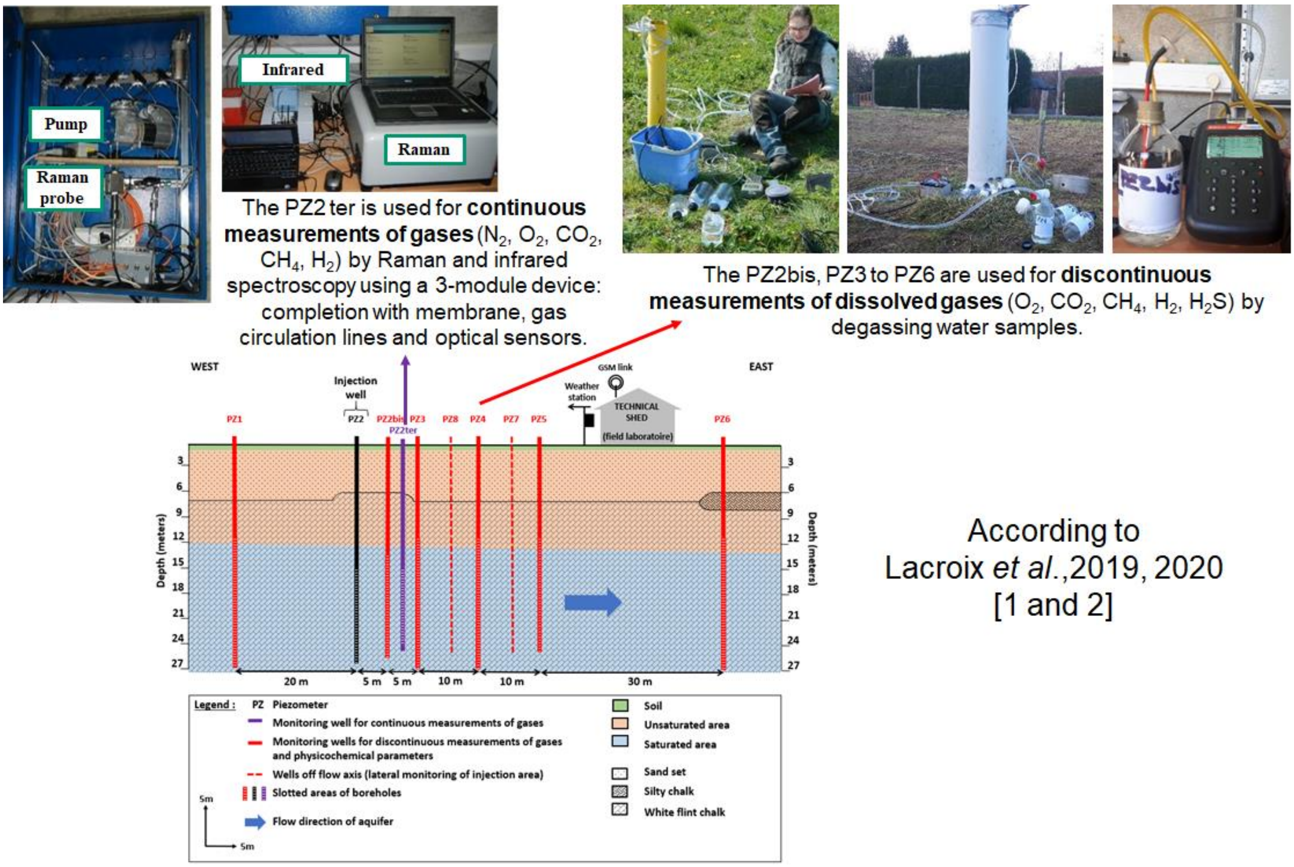
The Géodénergies "ROSTOCK'H" research project studies these risks by developing monitoring methods and characterizing potential impacts of H_2 leaks. A simulation of leak by dissolved H_2 injection into a water table in the Paris Basin was carried out.

2. Hydrogeochemical monitoring planned following the dissolved H_2 injection

Satured area (S.A.)	
Effects of H_2 arrival (leakage)	Sensors used and detection range
- Increase of [dissolved H_2] - Decrease of [dissolved O_2] (Berta *et al.* 2018). - Decrease of potential oxidoreduction (Berta *et al.* 2018). - Increase of pH (Berta *et al.* 2018). - Reduction of nitrates to nitrite or to nitrogen or NH_4^+ (Berta *et al.* 2018). - Reduction of sulfates to sulfites or H_2S (Bai *et al.* 2014, Berta *et al.* 2018, Truche *et al.* 2009). - Reduction of Fe (III) in Fe (II) (Truche *et al.* 2010). - Dissolution of metallic trace elements.	- 2 probes AMT of AquaMS (0-2 mg/L of $H_{2(aq)}$) : [dissolved H_2] measurements. - 2 portable analyzers (0-1000 ppmv $H_{2(g)}$) by partial degassing : [gas H_2] measurements. - Multiparameter physicochemical probes: 0-50 mg/L for [$O_{2(aq)}$], ± 2000 mV for redox, 0-14 of pH. - Laboratory analyzes of major, minor and trace ions.
Production/increase of [CH_4] due to biotic interactions: $4H_2 + CO_2 = CH_4 + 2H_2O$ (Berta *et al.* 2014, Berta *et al.* 2018, Ebigbo *et al.* 2013, Tarkowski 2019, Toleukhanov *et al.* 2015).	
Other possible interactions such as acetogenesis ($4H_2 + 2CO_2 = CH_3COOH + 2H_2O$) and acetotrophy ($CH_3C00^- + H^+ = CH_4 + 2H_2O$) (Berta *et al.* 2018, Ebigbo *et al.* 2013).	

According to Lacroix et al. 2019 [1].

The Ineris experimental site in Catenoy (Paris Basin) is used to test direct and indirect near-surface monitoring methods relating to dissolved H_2 [2]:



According to Lacroix *et al.*,2019, 2020 [1 and 2]

3. Geochemical baseline definition

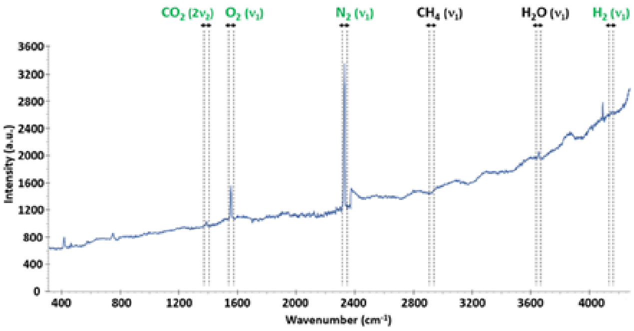
⇒ **Physico-chemistry** [1]:

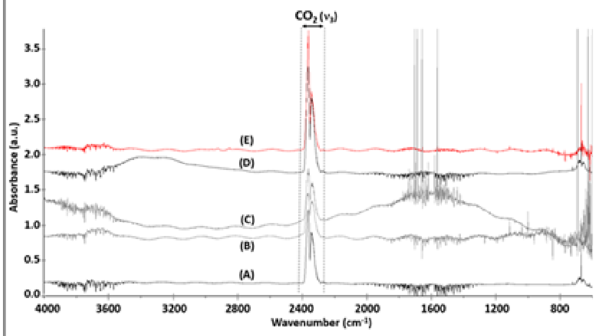
- pH of 7.3 ± 0.3 and temperature of 12.0 ± 1.8°C
- electrical conductivity of 471 ± 40 µS/cm
- positive redox potential
- water of calcium-bicarbonate facies

⇒ **Baseline of dissolved gases acquired over 6 months** (May-November 2019) [3]:

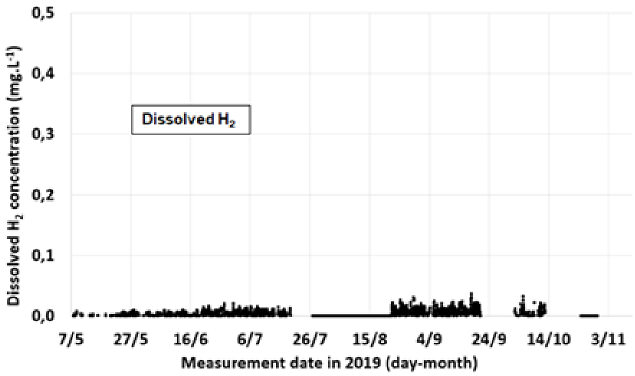
Statistical processing of Raman spectral data based on moving averages method
(7966 spectra over 6 months)

Infrared data processing by spectral profile analysis of ν_3 CO_2 band at 2400-2220 cm^{-1}.
(3150 spectra over 6 months)

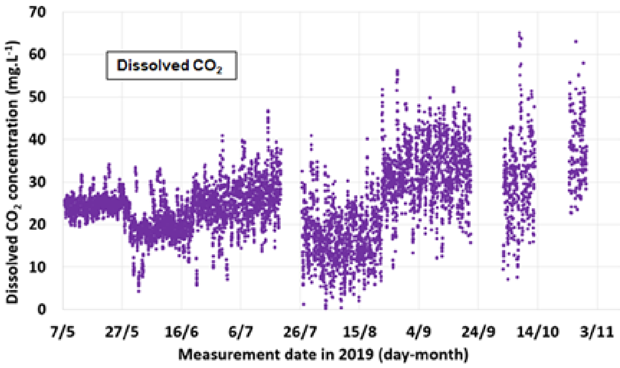




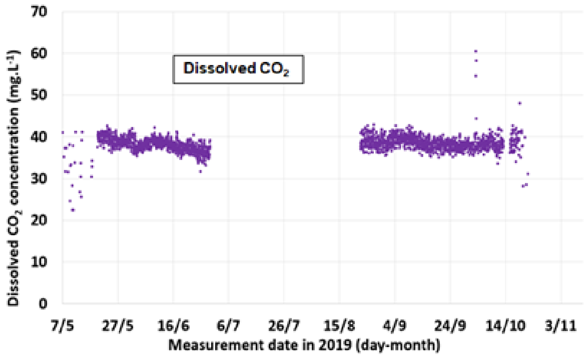
Average $[N_{2(aq)}] \approx 17.0$ $mg.L^{-1}$
Average $[O_{2(aq)}] \approx 7.6$ $mg.L^{-1}$
Average $[H_{2(aq)}] \approx 0$ $mg.L^{-1}$



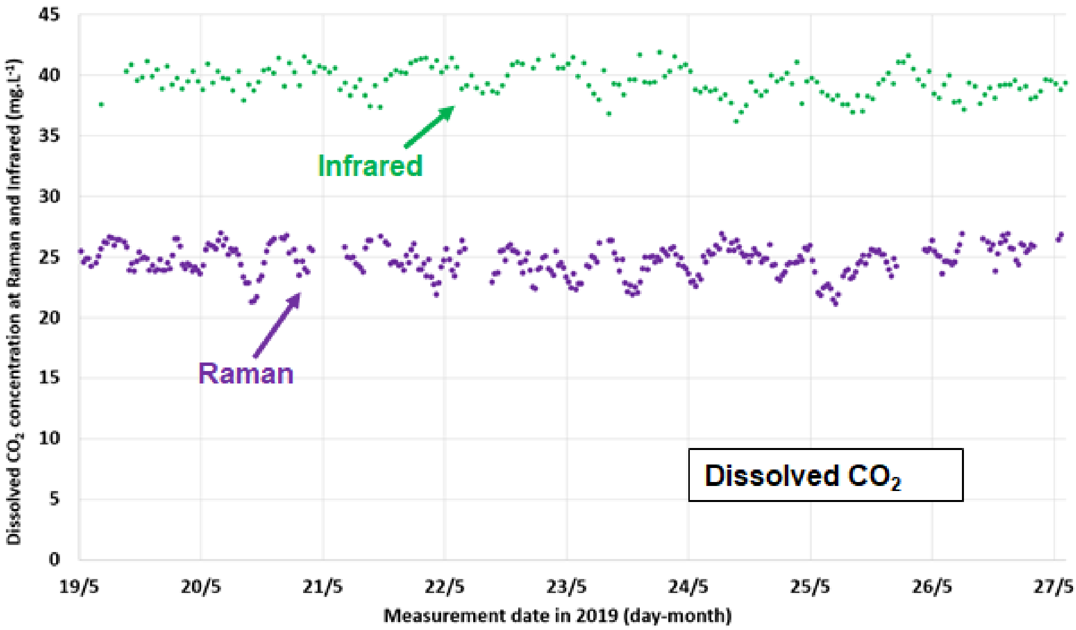
Average $[CO_{2(aq)}] \approx 20\text{-}35$ $mg.L^{-1}$



Average $[CO_{2(aq)}] \approx 40$ $mg.L^{-1}$



⇒ **Combined Raman/Infrared metrology validated on site** [3]:

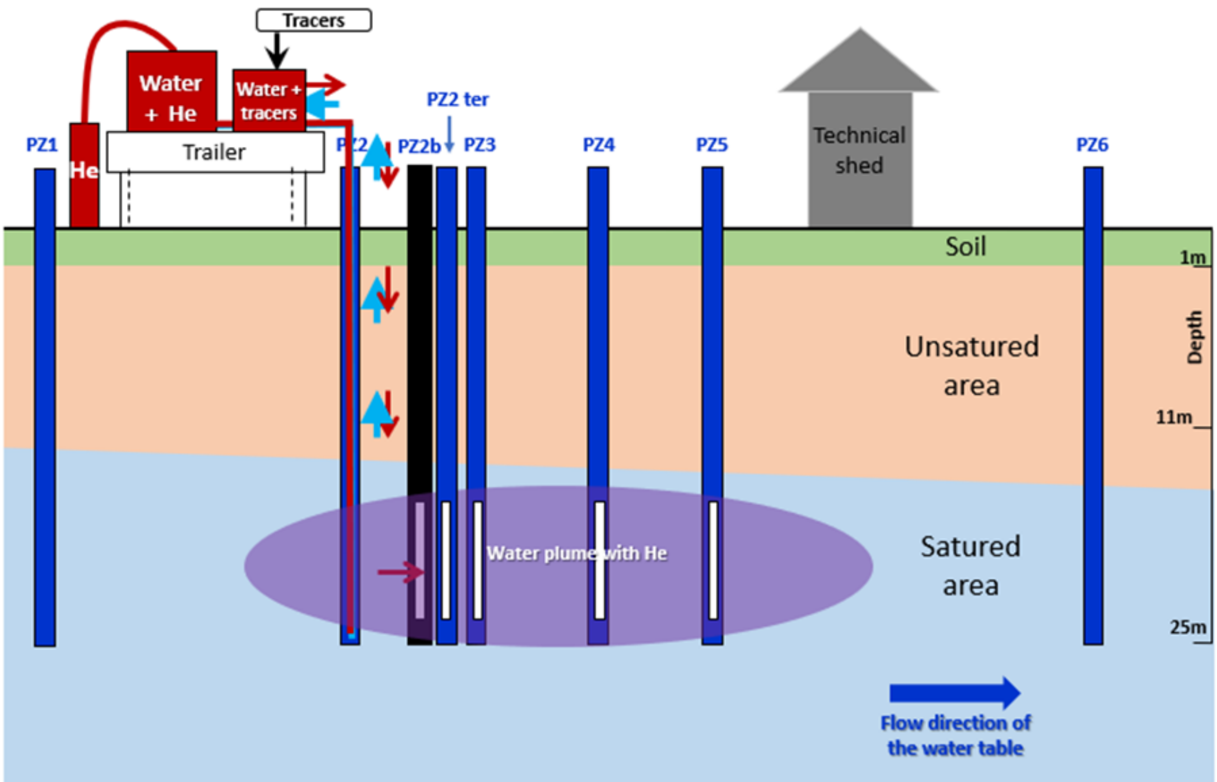


4. Protocol validation by preliminar injection of water saturated with He

⇒ **He: gas with a physical behavior similar to that of H_2.**

⇒ **Validation of the experimental protocol for the future H_2 injection** [4]:

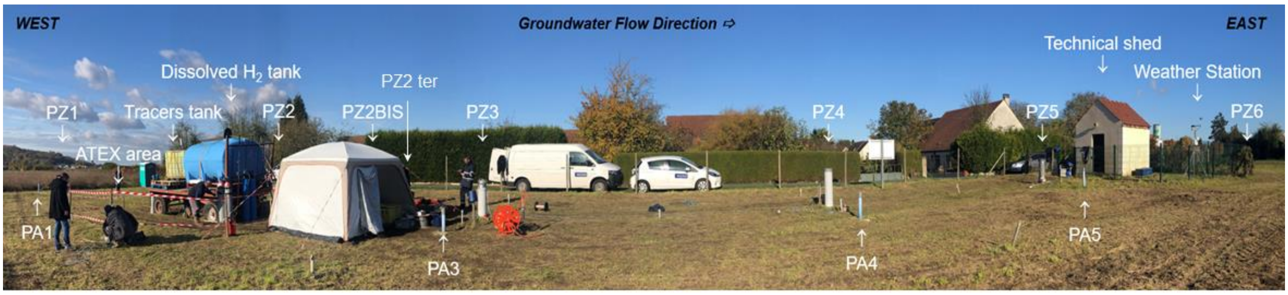
The steps of this protocol are presented in the following figure and audio



- success of this injection experimental protocol with monitoring of the He plume migration in the water table and up to 20 m downstream.
- choice of 2 hydrogeological tracers among the 5 used during this preliminar injection (uranine and lithium).
- characterization of the 2 distinct hydrodynamic regimes linked to a matrix and a fissure porosities.
- protocol adaptability: change in the injection preparation and modification of the monitoring organization.

5. Leak simulation by dissolved H_2 injection

⇒ **On-site layout:**

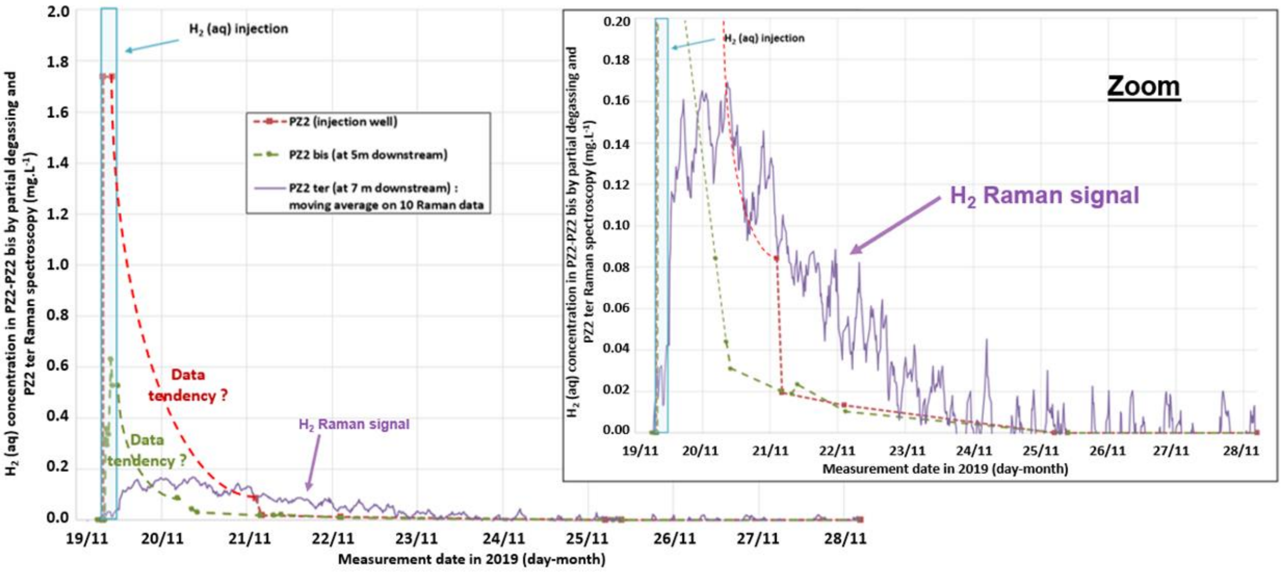


Panoramic view of the Catenoy site: over a W-E length of 80 m.

⇒ **Dissolved H_2 transfer dynamics according to distance** [2]:

- [$H_{2(aq)}$] max injected in the injection well (PZ2) is 1.78 mg.L^{-1}:

90% of theorical saturation in 5m^3 tank (after 16h of dissolution)



- 1114 Raman spectra acquired during the period following the H_2 injection from 19 to 30 November 2019.

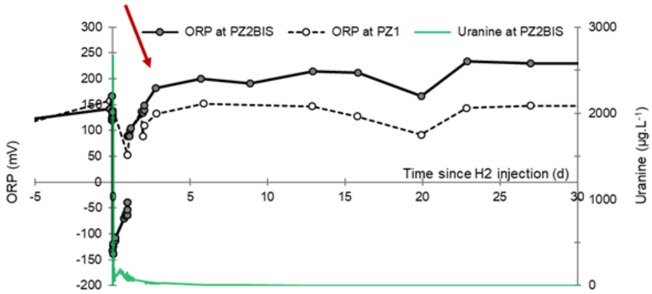
- Detection of $H_{2(aq)}$ up to 20 m downstream and at very low concentrations 1.8 µg.L $^{-1}$

Piezometer	Distance from the injection well (m)	Breakthrough time after the start of the H_2 injection (hour)	$[H_{2(aq)}]_{max}$ detected
PZ1	-20	-	0 mg.L^{-1} (DL of $H_{2\ (aq)}$ = 0,05 µg.L^{-1})
PZ2	0	0	1,78 mg.L^{-1}
PZ2 bis	+5	2	0,6 mg.L^{-1}
PZ2 ter	+7	≈ 10 and during 19 hours	0,17 mg.L^{-1}
PZ3	+10	71	1,8 µg.L^{-1}
PZ4	+20	90	1,8 µg.L^{-1}
PZ5	+30	-	0 µg.L^{-1} (DL of $H_{2\ (aq)}$ = 0,05 µg.L^{-1})
PZ6	+60	-	0 µg.L^{-1} (DL of $H_{2\ (aq)}$ = 0,05 µg.L^{-1})

⇒ **Behavior of Redox and dissolved O_2 in PZ2bis (5 m downstream) monitored over 1 month** [5]:

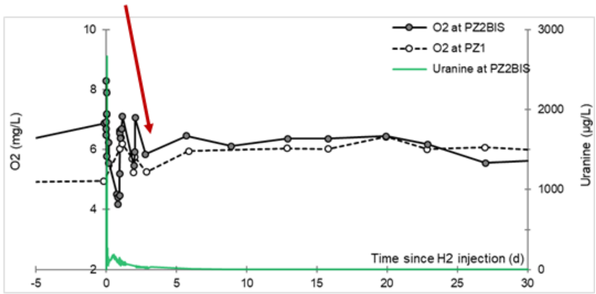
Redox evolution

Back to normal after 3 days following injection (similar to baseline)



Dissolved O_2 evolution

Back to normal after 3 days following injection (similar to baseline)



<u>Conclusions</u>

⟹ **Successful of H_2 and other gases in-situ and continuous monitoring by Raman and FTIR spectroscopy:**

- Conclusive results for the continuous monitoring of gases in aquifers by specific device (completion, gas circulation lines, optic sensors) over a long period of time.
- Very good sensitivity for the continuous detection of H_2 in aquifer (<0.03 mg.L^{-1}).

⟹ **Successful of H_2 monitoring by degassing water samples.**

⟹ **Under our experimental conditions, the physicochemical impact of a H_2 leak is moderate and <10 m.**

6. Scientific valuation of the project

[1] Lacroix E., Lafortune S., De Donato P., Gombert P., Pokryszka Z., Rupasinghe S., Caumon M.-C. et Barrès O. (2019), *Développement d'outils de monitoring pour la surveillance des sites de stockage souterrain d'H2 : premiers résultats de l'expérimentation de simulation de fuite à Catenoy (60)*. Poster presentation, colloque CNRS Miti « H_2 naturel », Paris, 10/10/2019.

[2] Lacroix, E., Lafortune, S., De Donato, P., Gombert, P., Pokryszka, Z., Adélise, F., Caumon, M.-C., Barrès, O., and Rupasinghe, S. (2020), D*evelopment of monitoring tools in soil and aquifer for underground H_2 storages and assessment of environmental impacts through an in-situ leakage simulation*, EGU General Assembly 2020, Online, 4–8 May 2020, EGU2020-17949, https://doi.org/10.5194/egusphere-egu2020-17949.

[3] Lacroix E., de Donato P., Lafortune S., Caumon M.-C., Barres O., Derrien M., Piedevache M. and Liu X., *Metrological development based on in situ and continuous monitoring of dissolved gases in an aquifer: application to the geochemical baseline definition for hydrogen leakage survey*. Analytical Methods. To be submitted.

[4] Lafortune S., Gombert P., Pokryszka Z., **Lacroix E.**, de Donato P., Nevila Jozja N., (2020), *Monitoring Scheme for the Detection of Hydrogen Leakage from a Deep Underground Storage. Part 1: On-Site Validation of an Experimental Protocol via the Combined Injection of Helium and Tracers into an Aquifer*. Appl. Sci., 10, 6058, https://doi.org/10.3390/app10176058

[5] Gombert P., Lafortune S., Pokryszka Z., **Lacroix E.**, de Donato P., Jozja N. *Monitoring scheme for the detection of hydrogen leakage from a deep underground storage. Part 2: Chemico-physical impacts of hydrogen injection into a shallow chalky aquifer.* Appl. Sci. To be submitted.

Disclosures

Images are author's own unless otherwise stated.

Author Information

Presentation :

Elodie Lacroix is PhD student in geosciences in the field of geochemical monitoring methods for the risk prevention of a future underground gas storage. During this doctorate, she carried out my research work on two main geographical sites: (i) at Ineris (institute and experimental site belonging to it: Catenoy in Oise department, next to Paris) and (ii) at the University of Lorraine (Nancy).

Email : elodie.lacroix@ineris.fr / elodie.lacroix@univ-lorraine.fr

Acknowledgments:

The results presented in this poster were acquired within the framework of the ROSTOCK-H research project funded by the Scientific Interest Group GEODENERGIES.

Thanks also go to the co-authors and people involved in this research subject such as Ineris without whom the on-site experiments wouldn't have taken place, the University of Lorraine and its subcontractor, the Solexperts company for technical development and scientific analysis tools but also the CETRAHE laboratories of the University of Orléans and Chrono-environnement of the University of Burgundy Franche-Comté for carrying out hydrochemical analyzes of the water samples taken.

Abstract

To manage potential risks due to H_2 leaks into the near-surface geosphere from H_2 underground storages (e.g. salt caverns, aquifer), reliable monitoring methods along with a precise knowledge of the geochemical environmental impacts are necessary. Thus, the evolution of some prominent parameters in soil and aquifers can be determined: gas concentrations, redox potential, ionic balance and trace elements.

As part of the ROSTOCK'H project, Ineris simulated H_2 leakage by injection of dissolved H_2 into a shallow aquifer (~20 m deep) in an experimental site within the Paris basin. This experiment aimed to testing advanced monitoring techniques and studying hydrogeochemical impacts at shallow depths. The aquifer water has calcium-bicarbonate facies and a neutral pH. Eight piezometers were aligned over 80 m according to the aquifer main flow (west-east). Hydrogeochemical monitoring devices were set up. One of the piezometers was equipped with a completion connected to a Raman probe and a specific Mid-IR cell for continuous measurement of aqueous gases.

At the experiment outset, 5 m^3 of water were extracted from the aquifer to be saturated with H_2 under atmospheric conditions, before being reinjected through the injection well. About 100 L^{STP} of dissolved H_2 (concentration of 1,8 mg/L) was injected in the aquifer. The H_2 injection was preceded by the injection of underground water containing tracers ($He_{(aq)}$, uranine and LiCl) in order to warn the H_2 plume arrival in the piezometers located downstream of the injection well. The concentrations of aqueous gases (He, H_2, N_2, O_2, CO_2, H_2S and CH_4) were measured in a control piezometer (20 m upstream) and in six piezometers up to 60 m downstream. Thus, the maximum H_2 contents were detected up to 20 m downstream of the injection well: 0.6 mg/L at 5 m, 0.17 mg/L at 7 m then 1.8 µg/L of H_2 at 10 and 20 m during the first week. Following the $H_{2(aq)}$ addition, the aquifer physico-chemistry has been modified: low increase in pH, high decrease in redox potential and $O_{2(aq)}$. These results confirm the feasibility of detecting and monitoring H_2 in shallow aquifers in very low concentration conditions and highlight the potential impacts. This is of first importance for establishing the surveillance and security aspects related to with H_2 storage.

REFERENCES

Abdin, Z., Zafaranloo, A., Rafiee, A., Mérida, W., Lipiński, W., Khalilpour, K.R., 2020. *Hydrogen as an energy vector*. Renewable and Sustainable Energy Reviews 120, 109620. https://doi.org/10.1016/j.rser.2019.109620

Bai, M., Song, K., Sun, Y., He, M., Li, Y., Sun, J., 2014. *An overview of hydrogen underground storage technology and prospects in China*. Journal of Petroleum Science and Engineering 124, 132–136. https://doi.org/10.1016/j.petrol.2014.09.037

Barthelemy, H., Weber, M., Barbier, F., 2017. *Hydrogen storage: Recent improvements and industrial perspectives*. International Journal of Hydrogen Energy 42, 7254–7262. https://doi.org/10.1016/j.ijhydene.2016.03.178

Berta, M., Dethlefsen, F., Ebert, M., Schäfer, D., Dahmke, A., 2018. *Geochemical Effects of Millimolar Hydrogen Concentrations in Groundwater: An Experimental Study in the Context of Subsurface Hydrogen Storage*. Environ. Sci. Technol. 52, 4937–4949. https://doi.org/10.1021/acs.est.7b05467

Caglayan, D.G., Weber, N., Heinrichs, H.U., Linßen, J., Robinius, M., Kukla, P.A., Stolten, D., 2020. *Technical potential of salt caverns for hydrogen storage in Europe*. International Journal of Hydrogen Energy 45, 6793–6805. https://doi.org/10.1016/j.ijhydene.2019.12.161

Cailteau, C., de Donato, P., Pironon, J., Vinsot, A., Garnier, C., Barres, O., 2011a. *In situ gas monitoring in clay rocks: mathematical developments for CO2 and CH4 partial pressure determination under non-controlled pressure conditions using FT-IR spectrometry.* Anal. Methods 3, 888. https://doi.org/10.1039/c0ay00622j

Cailteau, C., Pironon, J., de Donato, P., Vinsot, A., Fierz, T., Garnier, C., Barres, O., 2011b. *FT-IR metrology aspects for on-line monitoring of CO2 and CH4 in underground laboratory conditions*. Anal. Methods 3, 877–887. https://doi.org/10.1039/c0ay00623h

de Donato, P., Pironon, J., Barrès, O., Sausse, J., Quisel, N., Thomas, S., Pokryszka, Z., Laurent Alain, 2012. *Lessons Learned from Pratical Application of Geochemical Monitoring Methodology to CO2 Storage Site: Specific Case of Claye-Souilly project, Paris Basin, France*. Carbon Management Technology conference 1–10. https://doi.org/CMTC CMTC-150308-PP

de Donato, P., Pironon, J., Sterpenich, J., Laurent, A., Piedevache, M., Pokryszka, Z., Quisel, N., Barrès, O., Thomas, S., Rampnoux, N., 2011. *CO2 flow baseline: Key factors of the geochemical monitoring program of future CO2 storage at claye-souilly (Paris basin)*. Energy Procedia 4, 5438–5446. https://doi.org/10.1016/j.egypro.2011.02.529

Ebigbo, A., Golfier, F., Quintard, M., 2013. *A coupled, pore-scale model for methanogenic microbial activity in underground hydrogen storage*. Advances in Water Resources 61, 74–85. https://doi.org/10.1016/j.advwatres.2013.09.004

Gal, F., Julie, L., Zbigniew, P., Philippe, G., Solenne, G., François, P., Yacine, D., Patrice, S., 2014. *CO2 leakage in a shallow aquifer – Observed changes in case of small release*. Energy Procedia 63, 4112–4122. https://doi.org/10.1016/j.egypro.2014.11.442

Gal, F., Le Pierres, K., Brach, M., Braibant, G., Beny, C., Battani, A., Tocqué, E., Benoît, Y., Jeandel, E., Pokryszka, Z., Charmoille, A., Bentivegna, G., Pironon, J., de Donato, P., Garnier, C., Cailteau, C., Barrès, O., Radilla, G., Bauer, A., 2010. *Surface Gas*

Geochemistry above the Natural CO2 Reservoir of Montmiral (Drôme, France), Source Tracking and Gas Exchange between the Soil, Biosphere and Atmosphere. Oil Gas Sci. Technol. – Rev. IFP 65, 635–652. https://doi.org/10.2516/ogst/2009068

Garcia-Baonza, V., Rull, F., Dubessy, J., 2012. *Raman Spectroscopy of Gases, Water and other Geological Fluids*, in: Ferraris, G., Dubessy, J., Caumon, M.-C., Rull, F. (Eds.), Raman Spectroscopy Applied to Earth Sciences and Cultural Heritage. European Mineralogical Union, pp. 279–320. https://doi.org/10.1180/EMU-notes.12.8

Gombert, P., Pokryszka, Z., Lafortune, S., Lions, J., Gal, F., Joulian, C., Grellier, S., Prevot, F., Darmoul, Y., Squarcioni, P., 2014. *Selection, Instrumentation and Characterization of a Pilot Site for CO2 Leakage Experimentation in a Superficial Aquifer*. Energy Procedia 63, 3172–3181. https://doi.org/10.1016/j.egypro.2014.11.342

Ineris, 2016. *Le stockage souterrain dans le contexte de la transition énergétique*. Downloadable from the website: www.ineris.fr/sites/ineris.fr/files/contribution/Documents/ineris-dossier-ref-stockage-souterrain.pdf

Kervévan, C., Beddelem, M.-H., Galiègue, X., Le Gallo, Y., May, F., O'Neil, K., Sterpenich, J., 2017. *Main Results of the CO2-DISSOLVED Project: First Step toward a Future Industrial Pilot Combining Geological Storage of Dissolved CO2 and Geothermal Heat Recovery*. Energy Procedia 114, 4086–4098. https://doi.org/10.1016/j.egypro.2017.03.1549

Kim, J., Yu, S., Yun, S.-T., Kim, K.-H., Kim, J.-H., Shinn, Y.-J., Chae, G., 2019. *CO2 leakage detection in the near-surface above natural CO2-rich water aquifer using soil gas monitoring*. International Journal of Greenhouse Gas Control 88, 261–271. https://doi.org/10.1016/j.ijggc.2019.06.015

Lafortune, S., Pokryszka, Z., Bentivegna, G., Farret, R., 2013. *From Geochemical Baseline Studies to Characterization and Remediation of Gas Leaks: Experiences and Case Studies of the French Institute for Risk Management (INERIS)*. Energy Procedia 37, 4391–4399. https://doi.org/10.1016/j.egypro.2013.06.344

Le Duigou, A., Bader, A.-G., Lanoix, J.-C., Nadau, L., 2017. *Relevance and costs of large scale underground hydrogen storage in France*. International Journal of Hydrogen Energy 42, 22987–23003. https://doi.org/10.1016/j.ijhydene.2017.06.239

Li, L., Zhang, X., Luan, Z., Du, Z., Xi, S., Wang, B., Cao, L., Lian, C., Yan, J., 2018. *Raman vibrational spectral characteristics and quantitative analysis of H 2 up to 400°C and 40 MPa.* J Raman Spectrosc 49, 1722–1731. https://doi.org/10.1002/jrs.5420

Lombardi, S., Annunziatellis, A., Beaubien, S.E., Ciotoli, G., 2006. NEAR-SURFACE GAS GEOCHEMISTRY TECHNIQUES TO ASSESS AND MONITOR CO2 GEOLOGICAL SEQUESTRATION SITES, in: Lombardi, S., Altunina, L.K., Beaubien, S.E. (Eds.), Advances in the Geological Storage of Carbon Dioxide. Kluwer Academic Publishers, Dordrecht, pp. 141–156. https://doi.org/10.1007/1-4020-4471-2_13

Moradi, R., Groth, K.M., 2019. *Hydrogen storage and delivery: Review of the state of the art technologies and risk and reliability analysis*. International Journal of Hydrogen Energy 44, 12254–12269. https://doi.org/10.1016/j.ijhydene.2019.03.041

O'Malley, K., Ordaz, G., Adams, J., Randolph, K., Ahn, C.C., Stetson, N.T., 2015. *Applied hydrogen storage research and development: A perspective from the U.S. Department of Energy*. Journal of Alloys and Compounds 645, S419–S422. https://doi.org/10.1016/j.jallcom.2014.12.090

Ozarslan, A., 2012. *Large-scale hydrogen energy storage in salt caverns*. International Journal of Hydrogen Energy 37, 14265–14277. https://doi.org/10.1016/j.ijhydene.2012.07.111

Pironon, J., de Donato, Ph., Barrés, O., Garnier, Ch., Cailteau, C., Vinsot, A., Radilla, G., 2009. *On-line greenhouse gas detection from soils and rock formations*. Energy Procedia 1, 2375–2382. https://doi.org/10.1016/j.egypro.2009.01.309

Riding, J.B., Rochelle, C.A., 2009. *Subsurface characterization and geological monitoring of the CO2 injection operation at Weyburn, Saskatchewan, Canada*. Geological Society, London, Special Publications 313, 227–256. https://doi.org/10.1144/SP313.14

Schädle, T., Pejcic, B., Mizaikoff, B., 2016a. *Monitoring dissolved carbon dioxide and methane in brine environments at high pressure using IR-ATR spectroscopy.* Anal. Methods 8, 756–762. https://doi.org/10.1039/C5AY02744F

Schädle, T., Pejcic, B., Myers, M., Mizaikoff, B., 2016b. *Portable Mid-Infrared Sensor System for Monitoring CO2 and CH4 at High Pressure in Geosequestration Scenarios*. ACS Sens. 1, 413–419. https://doi.org/10.1021/acssensors.5b00246

Taquet, N., Pironon, J., De Donato, P., Lucas, H., Barres, O., 2013. *Efficiency of combined FTIR and Raman spectrometry for online quantification of soil gases: Application to the monitoring of carbon dioxide storage sites*. International Journal of Greenhouse Gas Control 12, 359–371. https://doi.org/10.1016/j.ijggc.2012.10.003

Tarkowski, R., 2019. *Underground hydrogen storage: Characteristics and prospects. Renewable and Sustainable* Energy Reviews 105, 86–94. https://doi.org/10.1016/j.rser.2019.01.051

Tarkowski, R., Czapowski, G., 2018. *Salt domes in Poland – Potential sites for hydrogen storage in caverns*. International Journal of Hydrogen Energy 43, 21414–21427. https://doi.org/10.1016/j.ijhydene.2018.09.212

Toleukhanov, A., Panfilov, M., Kaltayev, A., 2015. *Storage of hydrogenous gas mixture in geological formations: Self-organisation in presence of chemotaxis.* International Journal of Hydrogen Energy 40, 15952–15962. https://doi.org/10.1016/j.ijhydene.2015.10.033

Total, 2015. Carbon capture and storage: The Lacq pilot (project and injection period 2006-2013).

Truche, L., Berger, G., Destrigneville, C., Guillaume, D., Giffaut, E., 2010. *Kinetics of pyrite to pyrrhotite reduction by hydrogen in calcite buffered solutions between 90 and 180°C: Implications for nuclear waste disposal*. Geochimica et Cosmochimica Acta 74, 2894–2914. https://doi.org/10.1016/j.gca.2010.02.027

Truche, L., Berger, G., Destrigneville, C., Pages, A., Guillaume, D., Giffaut, E., Jacquot, E., 2009. *Experimental reduction of aqueous sulphate by hydrogen under hydrothermal conditions: Implication for the nuclear waste storage*. Geochimica et Cosmochimica Acta 73, 4824–4835. https://doi.org/10.1016/j.gca.2009.05.043

Vinsot, A., Appelo, C.A.J., Lundy, M., Wechner, S., Cailteau-Fischbach, C., de Donato, P., Pironon, J., Lettry, Y., Lerouge, C., De Cannière, P., 2017. *Natural gas extraction and artificial gas injection experiments in Opalinus Clay, Mont Terri rock laboratory (Switzerland)*. Swiss J Geosci 110, 375–390. https://doi.org/10.1007/s00015-016-0244-1