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The first Brazilian Field Lab fully dedicated to CO₂ MMV experiments: from the start-up to the initial results

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Abstract

Currently one of the main challenges in CO₂ storage research is the development, testing and validation of accurate and efficient Measuring, Monitoring and Verification (MMV) techniques to be deployed at geological sequestration sites that are cost effective yet help minimize risk. This perspective motivated PETROBRAS, the National Oil Major in Brazil, through its R&D investments portfolio to prioritize research projects that would contribute to decreasing the technological gap in the area. The Company's periodic surveys indicated the lack of infrastructure, as well as expertise in CO₂ MMV, as two of the most critical issues at the national level. In order to bridge that gap, initial steps were taken in 2010 for the start-up and development of the first CO₂ MMV Field Lab in Brazil, fully sponsored by PETROBRAS, with a long term goal of enabling the ranking of the best, most cost-effective MMV technology alternatives to be deployed at commercial large scale CCGS sites scheduled to be installed in the country. In addition to providing basic infrastructure to carry out the CO₂ injection and controlled release experiments, the facility was designed for the simultaneous testing of multiple measuring methodologies. Additional benefits of the initiative are the creation of expertise and the acceleration of the know-how in MMV in Brazil, as well as the development of a deeper and more

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practical knowledge of CO_2 dynamics and impacts in a real world, open air scenario. Under the full support of the PETROBRAS R&D Center (CENPES), through its Climate Change Mitigation Technological Program (PROCLIMA), the Brazilian Pilot CO_2 MMV Lab was made possible through a joint 4-year research Project, conceived and carried out by PETROBRAS and local academia in Brazil, in close cooperation with international experts. An overview of the Project and the multiple research areas encompassed will be presented, together with the preliminary results of the first CO_2 injection campaign, which took place in 2013.

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1. Background

Substantial technological advances have taken place for the last decades in strategic areas of sustainable development (among others, energy conservation, decarbonization, biofuels, alternative energy etc), together with an overall rising in public awareness relative to the importance of engaging in a planetary commitment to curbing greenhouse gas emissions in order to minimize the impacts and risks associated with global warming. In spite of these developments, the challenge of greenhouse gas emissions reduction is yet to be overcome with mid- to long-term reduction targets likely being missed unless more radical corrective actions are undertaken according to the most recent IPCC Report[1].

The urgency to deploy effective climate change mitigation measures, encompassing collaboration literally among all sectors of modern society, is thus reinforced. In this perspective the contribution of Geological Carbon Sequestration for carbon dioxide emissions abatement is of undeniable importance for both heavy industry and the energy production sector, with special emphasis in the oil industry [2,3]. However, in order to establish GCS on a global scale as a major emissions control strategy, one of the most critical challenges is to ensure effective permanence and containment of the gas in the geological formation (sink), with the minimum quantifiable leakage risks that the gas might escape the storage reservoir and impact shallow groundwater aquifers or migrate back into the atmosphere. With this respect, the importance of CO_2 MMV is fundamental, providing technically sound and effective information for the verification, accounting and risk assessment of potential carbon dioxide releases at the storage site. The development of expertise and the improvement of robust technical tools ensuring the effectiveness of geological storage will also add to overall public acceptance[4].

In order to face the challenge of CO_2 emissions management, as well as to contribute to the Brazilian climate change mitigation strategies[5], PETROBRAS through its Corporate Strategic Plan [6], has been very actively involved in carrying out multiple initiatives including: (1) generating direct atmospheric emissions reductions by engaging in energy efficiency integrative projects and programs, benefiting from a long-term established and proprietary know-how in energy conservation; adopting both "in- plant" and "end-of-pipe" control approaches throughout the Company's facilities, as well as up-grading product specifications aiming the formulation of more environmental friendly fuels; (2) keeping an aggressive investments portfolio for the development of renewable energy sources and state-of-the-art installations, as well as in the production of greener fuels, building on the Company's world class efforts in the commercial scale production of biofuels, with emphasis in biodiesel; (3) engaging since early phases in strategic discussions, long term partnership projects, Joint Industry Projects and alliances targeting CCS as one major and critical route to climate change mitigation, both at the international and national levels. An example illustrating the last point is the 2007 launch of the PETROBRAS Research Center (CENPES) Technological Program (PROCLIMA), which both performs and sponsors R&D efforts in mitigation strategies, focusing on the value chain of the oil industry. One of the most emblematic action lines is the creation and full sponsorship of the Climate Change and Carbon Sequestration Network, encompassing technical partnership and collaboration with 14 research institutes in the Brazil, carrying out state-of-the-art R&D projects in the areas associated with this theme.

Under the umbrella of PROCLIMA, the Brazilian CO_2 MMV Field Lab was initiated as the first of its kind in the country, as well as at the South American Continent level, and was designed to fill the knowledge gaps of CO_2 management technologies and aiming to level-off Brazil in the international scenario. The overall expectations are high for long-term partnership of PETROBRAS and the Brazilian academic community to provide technical solutions for the country's climate change mitigation strategies.

2. Project and site overview

2.1. Site choice, location and main features

The 157 ha Ressacada Experimental Farm (Figure 1) under the responsibility of UFSC, Santa Catarina State Federal University was chosen to as the site for the CO_2 MMV field lab. Located in Florianopolis, the capital of Santa Catarina, a state in the Southern part of Brazil the Ressacada Farm facility has already hosted several controlled release experiments of solid and liquid contaminants, as well as soil and aquifer remediation research projects, sponsored by PETROBRAS, with the endorsement of the local environmental agent (FATMA).

The CO₂ MMV field lab experimental cell ($27^{0}41'02.19$ "S latitude; $48^{0}32'41$ " W longitude; 1.84 m elevation; see Figure 2), occupies a 6,280 m² area, located next to the main administration and lab facilities building, and was made available to this Project by the local university Agronomic Sciences Department (UFSC/CCA).

The area is situated at 2 km South the Hercilio Luz International Airport, in a rural area with a strong nonanthropogenic CO₂ source profile predominantly from local native vegetation including various types of grasses as well as C4 (which include *Cynodon dactylon*, *Paspalum notatum*, *Centella asiatica*.)

Local climate is Subtropical Humid [7]. According to the information made available through the Brazilian National Meteorology Institute (INMET) Database[8] typical surface temperatures range from 13 to 25° C, average rainfall is 1,627 mm per year, well distributed throughout the seasons. There is a clear prevalence of winds coming from the Northern quadrants. During summer time, most frequent winds come from North (15.5%) and NNE(10.3%) with 90% of the records below 6 m/s; during the winter, prevailing winds come from the N (27.3%) and NNE (10.4%) and 90% of the records fall below 7.0 m/s.

The study area is represented mainly by quaternary deposits composed primarily of sandy, unconsolidated sediments[9]. However, local soil sampling carried out at an earlier phase of this study [10], show that there is a substantial degree of heterogeneity at the very local levels, with up to 18% clay composition which appears as lenses between the sandy layers. Three types of lithology were identified: clay, silt and sand. Based upon particle size analysis, the local soil sediments were mostly classified as fine to medium sand, with less contribution of fine sand. For further details refer to [11], published in this issue.

The aquifer, as detailed in[10], is unconfined and very shallow, ranging from 0.4 m to 1.3 m depth, with a low gradient (0.4%) and flows E-W, at 6.3 m.year⁻¹ on average.



Fig. 1. Location maps of Ressacada Experimental Farm in perspective in Brazil and at mesoscale; (b) Ressacada Farm and surroundings



Figure 2. CO₂ MMV field lab experimental cell detailing (a) the injection well; (b) CO₂ cell location highlighted in yellow; (c) main administration building at which equipment requiring controlled temperature conditions were sheltered.

2.2. Carbon dioxide injection infrastructure and 2013 release campaign

While various well designs were considered, including a horizontal well similar to the ZERT site [12, 13], it was decided that a simpler configuration would reduce infrastructure costs and installation time while yielding significant information [14].

Figure 2 shows the location of the 3-meter depth vertical well for the CO_2 injection carried out in the 2013 Campaign, at the coordinates (6935.466 N), (742.183 E), together with the limits of the experimental cell made available for CO2 research purposes. Refer to the next topic for the detailed spatial deployment of the different monitoring devices and tools, with the respective sampling grids.

The choice of 3m as the depth level to carry out the injection is justified by the results of a prior reduced scope experimental study, carried out in 2012 [15] that used a 8-m deep vertical well. In this 2012 preliminary survey, resistivity and soil flux measurements indicated significant spreading of the CO_2 in the subsurface caused by the existence of clay lenses that significantly reduced vertical permeability compared to horizontal permeability. Soil characterization indicated that clay lenses at shallower depths are thinner so a shallower release would likely result in less lateral spreading, shorter retention times, and earlier release to the atmosphere.

Key well parameters are 3 m total depth, PVC casing, and a 30 cm screened section. Well construction is shown in Figure 3.

The unconsolidated nature of the local soil and the use of a single injection well meant care had to be taken to avoid the risk of collapsing the sediments and creating an undesirable chimney effect. This was accomplished by estimating the maximum allowable injection pressure using the Payne equation [16] then applying a safety factor of roughly 60% factoring in some additional head loss. These calculations resulted in an injection rate range from 90 to 150 g/h.

The 2013 injection campaign was carried out during 12 consecutive days, 24 hours a day, starting on the 10th of September 2013. The CO_2 supplied was food grade, 99.99% purity and fed to the injection well through a gas cylinder housed away from general personnel site circulation. Technical personnel carried portable gas monitors when heading into less ventilated areas. Injection rates were far too low to cause any health or safety hazards, with an overall emission throughout the whole campaign less than the amount of gas released by c.a. 3 idling light-duty vehicles (LDV) on a daily basis[14].

Both pressure and mass flow were continuously controlled and monitored. A double stage pressure regulator, together with an electronic mass flow controller, were coupled to the cylinder.

Figure 4 portrays the hourly variations of the recorded injection pressure, as well as the mass flux throughout the campaign.



Figure 3. Injection well constructive details



Figure 4. Carbon dioxide mass flux rates and injection pressure hourly values during the 2013 release campaign

3. Experimental techniques deployed on site and main results

Site properties monitored and institutions involved include:

- atmospheric fluxes and concentration, using an Eddy Covariance System and a Carbon Isotope Gas Analyzer in collaboration with IPEN, Research Institute on Nuclear Energy);
- soil gas fluxes and concentration using accumulation chambers; soil and headspace gas analysis by gas chromatography and isotopic analysis; same for the gases dissolved in the water; tracer studies in collaboration with PUCRS/CEPAC, Pontifical Catholic University of Rio Grande do Sul;
- electro- resistivity anomalies in the soil and subsurface, in collaboration with UNESP-RC/LEBAC, University of the State of Sao Paulo-Rio Claro;
- shallow aquifer water quality, in collaboration with UFSC-REMA, University of the State of Santa Catarina
- complementary studies on botanic stress, potentially derived from the exposure to excess CO₂ in the environment, in a joint collaboration with PUCRS and UFSC-CCA (Agronomic Sciences Department at UFSC).

Additionally PROCLIMA funded, by means of the current PETROBRAS CENPES R&D Project, technical collaboration with ZERT (Zero Emissions Research Technology)/MSU (Montana State University), as well as a cooperation with LBNL (Lawrence Berkeley National Laboratory)/US DOE (Department of Energy), currently being formalized under a joint R&D Project sponsored by the Brazilian CO2 Net.

This paper presents an overview of the methodologies deployed at the Ressacada site in 2013, providing the main results of the 2013 release campaign. Given space limitations, the focus will be on the integration of the main results and aspects of CO_2 fluxes and concentrations in the atmosphere and soil, the geophysics assessment and some parameters of the shallow aquifer water quality study.

3.1. Atmospheric fluxes and concentration

Atmospheric assessment of CO₂ dynamics, described and discussed in detail in [17], included: (1) measuring CO₂ fluxes at the micrometeorological scale using an Eddy-Covariance System (ECS, IRGASON-EB-IC), installed 8 m upwind of the injection well, set on a meteorological tower (Campbell UT30) recording all the standard surface meteorology parameters; (2) performing carbon isotopic composition analysis (¹³ C, ¹² C isotopic concentrations and ratio) using the Isotope Gas Analyser (IGA) , manufactured by Los Gatos Inc, Model 9120003, based upon an Off-Axis Cavity Ring Down System (CRDS), sheltered in the main administration building at the site downwind of the injection point, as shown in Figure 5.

 CO_2 atmospheric fluxes and surface meteorological parameters (local wind speed and direction; atmospheric temperature and pressure; rainfall) were collected and registered on a field datalogger (Campbell CR1000) on a continuous basis for the ECS. Once the ECS was mounted upwind of the CO_2 injection well, thus providing a local picture of the ecosystem fluxes at the micromet scale, the experimental data obtained was tagged according to the wind direction in order to be used for leakage assessment, coupling the filtered ECS results with the output from the IGA- CRDS.

The IGA-CRDS was sheltered in a controlled-temperature room located inside the main administration building, shown in Figures 2 and 5. Sampling for the IGA was carried out: (1) routinely from that fixed location (shelter) and (2) exploratorily in order to enhance the leakage detection, daily screening studies were also conducted during the release experiment, in which 2-4 h continuous data acquisition was performed at areas identified by other techniques as likely to have a high flux (CO_2 hot spots)

Figure 5 details the spatial distribution of the atmospheric measurement kits, as well as the subsurface monitoring grid (electrical imaging, geophysisc, detailed in topic 3.3) and the soil flux chamber grid (detailed in topic 3.2). The highest records of CO_2 -induced anomalies provided by these two grids were incorporated as much as possible as indicators of potential CO2 hot spots or most probable atmospheric leakage locations. The blue dots depicted in Figure 5 are the likely hotspots at which surveying was performed using the IGA-CRDS.



Fig. 5. Atmospheric detection trains and respective locations at the site; geophysics (electrical imaging) and soil flux chamber grids; IGA CRDS screening sampling locations, as indicated by the highest anomalies obtained through the former two methods.

Figure 6 shows a plot of carbon dioxide atmospheric concentration readings, covering the three periods: background (from September 1st to 9th), injection (September 10th to 21st) and post-injection (from September 22nd onwards) compiling the results from both ECS and IGA-CRDS.



Figure 6. Atmospheric CO₂ concentration measurements from the Eddy Covariance System (ECS) and the Isotopic Gas Analyzer (IGA-CRDS)

Figure 7 portrays the records for the CO_2 atmospheric fluxes obtained from the ECS, covering the same period as described by Figure 6. The areas hatched in light green correspond to the rainy days.

As shown in Figures 6 and 7, background values readings for CO_2 concentration were 388 ± 5 ppmV; isotopic delta ¹³ C ranged from -6 to -15 ppmil. The average atmospheric flux was predominantly negative in the vicinities of -20 µmols.s⁻¹.m⁻², thus indicating a strong "sink" behavior of the site, consistent with the abundance of local green areas. During the release experiment the measured values started to increase in a very discrete, but steady fashion, achieving a peak reading of 1200 ppmV and delta C^{13}/C^{12} of -25 ppmil (maximum leakage, also perceived by the methodologies carried out by the other research groups). The atmospheric flux recorded values showed the same overall trend, and ranged from ca.-30 to + 20 µmols.s⁻¹.m⁻².Nevertheless these numbers may be compromised to some extent by the high local atmospheric humidity; abundant rainfall was recorded especially on 21st September 2013 during the release experiment.

FLUX



Figure 7: Atmospheric CO₂ flux measurements from the ECS covering the same period as in Figure 6.

After the injection ceased the measured atmospheric concentration values gradually returned to the background levels, consistent with other measurements carried out in this study.

Discrete atmospheric CO_2 build-up was registered during the campaign in spite of the low injection rates used and the substantial local atmospheric scavenging (abundant rainfall, atmospheric dispersion and high inversion heights), as reported in the preliminary meteorological survey [18].

3.2. Soil flux measurements

 CO_2 soil fluxes were measured, as detailed in [11], using LI-COR LI8100-A Automated Soil CO_2 Flux System. Measures were taken 3 times a day (9am; 11:30am; 3pm), on a 80-point grid, which location was already presented in Figure 5. The accumulation chambers were used during the background survey, the injection experiment and the post-injection period.

Maximum background levels for CO_2 soil flux were 34 mmol/m²/s. During the injection period an increase in these values was detected, being almost eightfold higher than background values (9 days after the injection started). The maximum reading during the injection period was 267,12mmol/m²/s. After the release stopped, CO_2 flux gradually started to decrease back to background values again.

As shown in Figure 8, which couples the results from the soil flux chambers as well as the electrical imaging from the geophysics, the highest surface flux anomalies were observed mainly in the southwestern portion of the monitoring grid. These results are consistent with higher resistivity anomalies at the shallowest levels (50 cm) detected by geophysics which indicated subsurface CO₂ lateral spread predominantly beyond the flux grid, and also with some groundwater quality parameters, mainly acidity and conductivity.



Figure 8. Highest anomalies with respect to background levels, integrating geophysics and CO2 soil flux from the accumulation chamber measurements.

3.3. Geophysical monitoring

3D Electrical Imaging with a Wenner Array, as well as a time-lapse variation of the methodology, (4D Electrical Imaging) were performed at the site as detailed in [11]. Measurements were carried out using a resistivity meter model Super Sting R8/IP+28 (Advanced Geoscience,Inc) on a daily basis, at 10 a.m. local time, during all three periods, prior to the injection, during the whole injection , and for one week after stopping the injection. Prior to the 2013 release campaign, pre-characterization field studies were performed[10, 18] in which the same set of tools was deployed, aiming to assess the applicability of geophysics to the site, which was proved to be feasible.

Figure 9 illustrates the anomalies in electrical resistance/conductivity, attributed to the excess CO_2 concentration within the experimental cell around the vicinity of the injection well. The map view shown in the figure is the shallowest 50 cm chosen for purposes of comparison with flux accumulation chamber measurements. As consistent with the previous research carried out on site [10,15,18] deploying the same methods, this work shows an increase in the soil electrical resistivity associated with an increase of gaseous CO_2 concentration in the pore structure. Throughout the experimental cell, an overall increase in the geophysical anomaly was recorded, consistent with an increase in the gas concentration during the injection period. Average resistivity background level ranged from 300 ohm.m to 2,500 ohm.m. During the injection period, the maximum increases in resistivity recorded were 100% above background levels and the highest anomalies detected at the shallowest level (50 cm depth), located at the Southwest portion of the grid, were consistent with an enhancement in CO_2 concentration and flux in the soil.



Figure 9. Spatial distribution within the CO2 cell of resistivity anomalies at the shallowest levels, obtained with the 3D Electrical Imaging

3.4. Water quality

Water sampling was performed prior, during and after the CO_2 injection. Sampling was performed on a daily basis; the samples were collected manually on the spot, using a Merck Millipore Easy-Load® Peristaltic Pump, from 5 sampling wells, at three different depth levels (2, 4 and 6m). Parameters were measured using a MicroPurge® MP20 Flow Cell and included temperature, dissolved oxygen, electrical conductivity, pH, redox potential and salinity. Additionally, micro and macronutrients in the soil and water were monitored.

No significant vertical spread was detected for most of the parameters measured, meaning that ground-water collected at the three different depths showed similar properties, based upon the reported results. A slight increase in the acidity was observed, consistent with an increase in the CO₂ content and the dissolution process increasing the carbonic acid formation, thus decreasing the pH; the highest groundwater pH changes detected were in the range of 0.5 pH units lower than background levels and the most acidic samples (pH equal to 4.1) were drawn from the sampling wells closer to the injection well during the release campaign ...Refer to [11]and references therein for further details on methodologies deployed, as well as results and discussions.

4. Conclusions and perspectives

For most methods, the low release rates and short duration of the experiment would be expected to result in signals near the detection limit. Additional challenges are presented by the high precipitation levels, high natural variability of the site background CO_2 levels, and high atmospheric dilution levels due to the local meteorology. In spite of these challenges and the low injection rates, most methods implemented at the site were able to detect CO_2 above background and were in qualitative agreement regarding the location of the highest anomalies indicating that they are likely suitable for deployment on larger scales.

This experiment provided valuable experience in deploying near surface detection technologies in a high precipitation, highly variable background ecosystem. The small footprint, low rate controlled release helped

establish detection limits for the suite of detection methods chosen. We suspect the system did not reach steady state which made comparison of methods which have different integration times challenging.

Future injection campaigns will be carried out at higher release rates and have longer lasting campaigns to address these issues.

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