# ISOTOPIC TECHNIQUES TO MONITOR GAS RELEASES AT DIADEMA UGS - ARGENTINA


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## 1. - ABSTRACT


Located 40 kms North from the city of Comodoro Rivadavia, Chubut, in the Argentine Patagonia, the Underground Natural Gas Storage is in its tenth period of operation.

From its beginning, in 2001, YPF leased from CAPSA a sector of its field, especially a horizon in the Salamanca Formation, a marine deposit of Tertiary sandstones, with a structural scheme of monoclines and multiple direct faults, which was a gas field that was developed until it was exhausted.

The Diadema Underground Natural Gas Storage (Diadema UGS) takes the gas carried in summer by the San Martín gas pipeline, which joins the island of Tierra del Fuego, at the South of the continent, with the City of Buenos Aires. After reducing its pressure from 60 to 25 bar, it is injected into the *Banco Verde Member* (BV), belonging to the Salamanca Formation, located about 600 m under the surface, by 12 wells. In winter it is extracted, compressed and dehydrated for delivery to consumption in the City of Comodoro Rivadavia.

Above the BV there are substantial reserves of fresh water supplying the local population. Below there are oil fields with associated gas, operated by CAPSA, with hundreds of wells of varying age, some over 80 years old.

For operating and environmental reasons, different types of monitoring are being carried out, such as: dynamic and static pressure, temperature, presence of explosive mixtures, quality of surface and ground water.

Even if these variables were insufficient to control migration, release or extraction of gas in oil wells, we should take into account that daily monitoring is done to about 25 wells, located among hundreds of wells in a mature field. Other analyses were then planned to determine the issues.

The following monitoring objectives were set:

- To determine the isotopic and geochemical constituents of the injected gas, of the gas originally remaining at the reservoir and the gas present in the aquifers, if any.
- If gas were found in the aquifer, to determine its origin
- To evaluate the mixing of native gas and stored gas in different sectors of the storage.
- To detect any gas from the UGS in development wells of the company itself, and neighboring companies.

We should note that, for reasons such as broken casings due to corrosion, or else poor finishing, located in the same stratum, both oil companies could extract a part of the gas from the UGS involuntarily. In order to control such risk, other techniques were used with analysis of stable isotopes from natural gas, and geochemical relations that permitted early detection of unreported gas extractions. As is well known, chemical and isotopic constituents of natural gases vary with their history of formation and migration, thermogenic and biogenic origin and mixtures, and acquire a fingerprint that, once found, can be used for such purposes. For these reasons, chemical and isotope composition analysis was carried out, including carbon and Hydrogen isotopes for hydrocarbons gases, carbon isotopes for CO2 and Nitrogen isotopes for N2.

Although with some variability, the injected/ produced gas has its own isotope and chemical fingerprint, different from the "local gas", including original gas from the reservoir, gas from overlying aquifers and gas associated with the oil production in the area. The use of geochemical techniques has shown to be able for distinguish the mixing of gases in minor proportions This can increase the knowledge about gas migration within the reservoir, the tracking of mixtures with native gas, reservoir compartmentalization, permeability of boundaries like faults, gas leaks and so forth. A practical use of this method was to be able to claim a financial indemnity in cases where storage gas was found to have been unduly extracted, by wells not belonging to the Storage. The obvious benefits from the method indicate that it should be used regularly as a monitoring tool for this type of operations.

## 1. - Location and Geology

### 1.1. - Location

Diadema UGS is located in the North Flank of the Gulf Basin, 40 km NW from the City of Comodoro Rivadavia. The storage location is shown in detail in Figure 1.

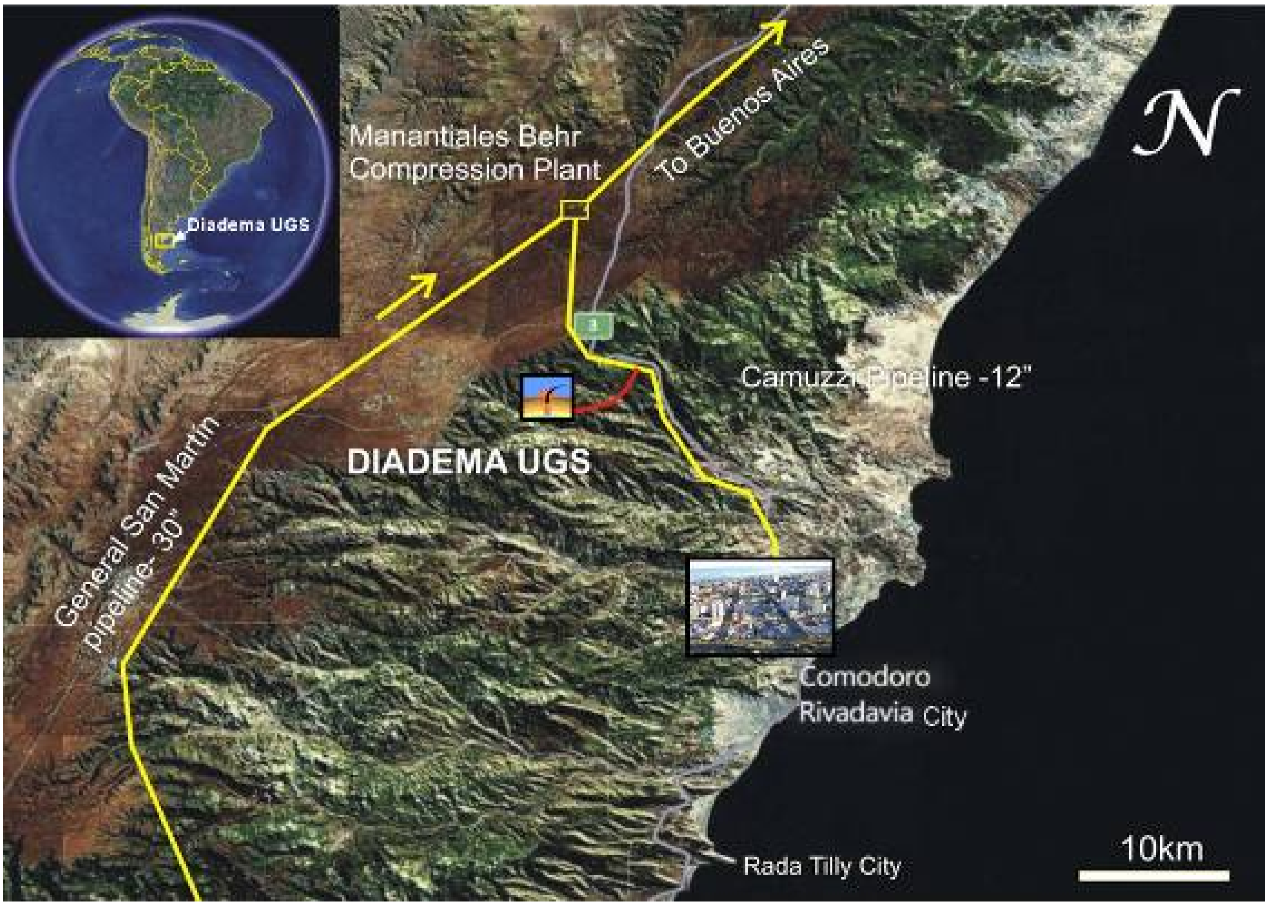



**Figure 1. -** Location of Diadema UGS.

The field was developed since the 30's until it was abandoned in the 90's. The site is an exhausted natural gas field, selected by reason of the properties of the original fluid, a useful volume in excess of 100 million $Sm^3$, located near one of the main gas pipelines between San Martín and Comodoro Rivadavia. Once the location was decided upon, the company conducted gas injection pilot tests, the existing wells were conditioned as injection wells (2) and monitoring wells (3), and assessments were made to determine its geophysical and hydrogeological conditions and economic feasibility. Diadema has been operating since 2001 and is the first UGS in Argentina. (Rodriguez et al, 2001, 2003, 2005, 2009)

## 1.2. - Geology

The stratigraphic column of the area is shown in Table 1. The geological level used by the UGS is a lithostratigraphic unit so-called “Banco Verde”, a part of the Hansen Member in the Salamanca Formation. It is located at an average depth of 650 meters below the well head. The Banco Verde consists of sandstones of medium to coarse grains, originally sea material, covered with clays arising from a lagoon environment. The horizon has a porosity of 25-30% and its permeability reaches values in excess of 1 Darcy. The Banco Verde has an underlying level so-called “Fragmentosa”, consisting of grey sandy shales and covered by dark shales from another unit so-called “Banco Negro”.

The Banco Verde is structurally divided into blocks, arising from direct faults having regional length and E-W NE-SW direction, with over 40 meters of vertical throw. These faults are permeable, so they permit hydraulic communication between adjacent blocks, so that the system behaves as one reservoir (Figure 2).

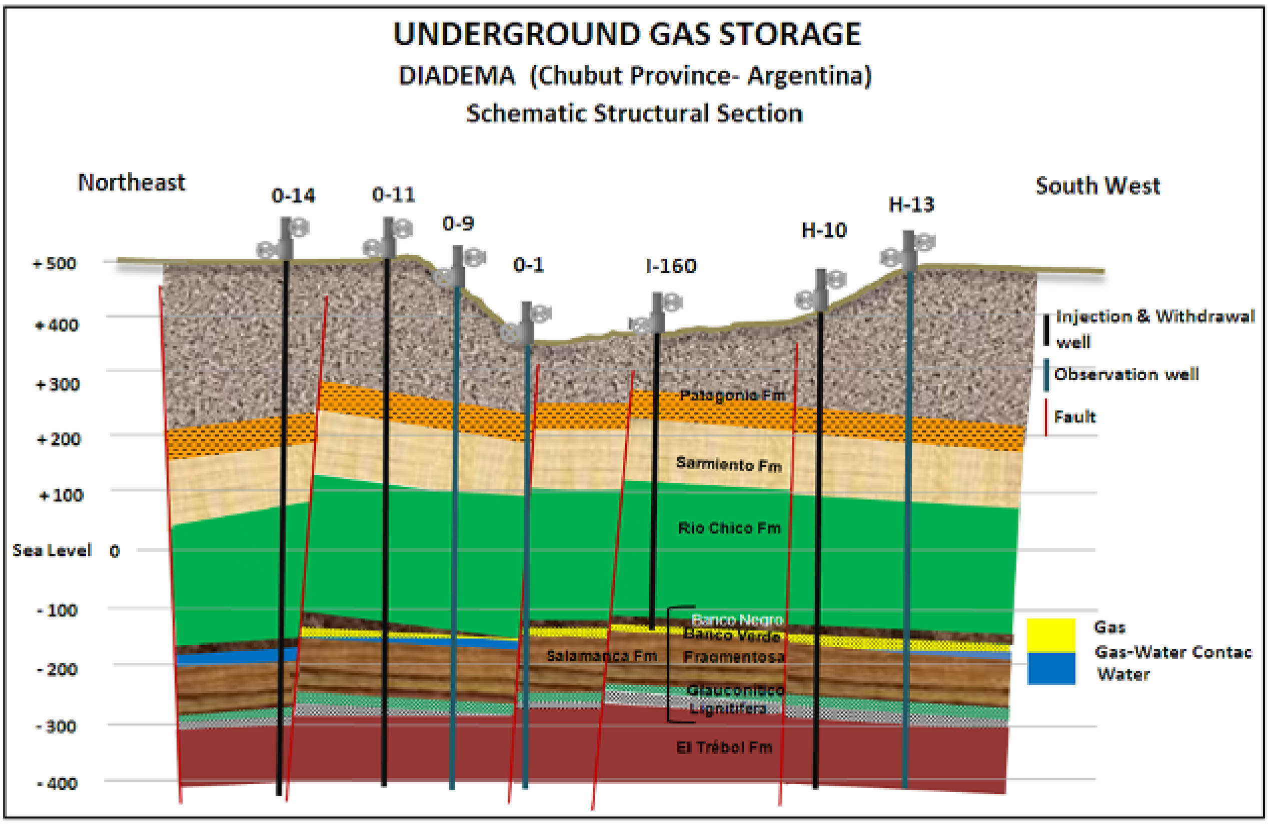



**Figure 2. -** Structural cross-section of the storage

Table 1 shows the stratigraphic sequence of the Diadema area. It should be noted that the seal rock comprises basal shale levels of the Banco Negro.

| Local Stratigraphic Chart | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Geo-chronological Units | | | | Stratigraphic Unit | | | | Geology |
| **Erathem Era** | **System period** | **Series Epoch** | | **Formation** | **Member** | **Salamanca Fm. Levels** | **Thickness (Meters)** | **Facies** |
| Cenozoic | **Quaternary** | **Holocene** | | Alluvial Deposit | — | — | — | Fluvial |
| | | **Pleistocene** | | Patagonian Shingle | No formal member | — | 10-40 | Fluvial-Glacial |
| | **Neogene** | **Pliocene** | **Upper** | | | | | |
| | | | **Lower** | Discordance | — | — | — | — |
| | | **Miocene** | **Upper** | | | | | |
| | | | **Medium** | Santa Cruz Fm. | No formal member | — | 100 | Continental |
| | | | **Lower** | Patagonia Fm. | No formal member | — | 200 | Marine |
| | **Paleogene** | **Oligocene** | | Sarmiento Fm. (Spalletti y Mazzoni) (1979) | Colhué-Huapi Member | — | 100 | Continental |
| | | **Eocene** | | | Puesto Almendra Member | — | | |
| | | | | | Gran Barraca Member | — | | |
| | | **Paleocene** | **Upper** | **Rio Chico Fm.** | No formal member | — | (200-300) | Continental |
| | | | **Lower** | **Salamanca Fm.** | **Hansen Member** | Banco Negro | **20** | **Marine** |
| | | | | | | **Banco Verde** | **20** | |
| | | | | | | Fragmentosa | **(130-140)** | |
| | | | | | **Member Bustamante** | Glauconitico | **(10-30)** | |
| | | | | | | Lignitifero | **20** | |
| Mesozoic | **Cretaceous** | **Upper** | **Chubutian** | Yacimiento el Trebol Fm. | — | — | — | Fluvio-Deltaic |
| | | | | Comodoro Rivadavia Fm | — | — | — | Fluvial |
| | | **Lower** | | Mina el Carmen Fm. | — | — | — | Fluvial-Lagoon |

**Table 1**. - Simplified Stratigraphy of Diadema area.

The photograph in Figure 3 shows a Banco Verde outcrop located on the marine coast near the hill known as Pico Salamanca and the related contacts with the underlying and overlying horizons.

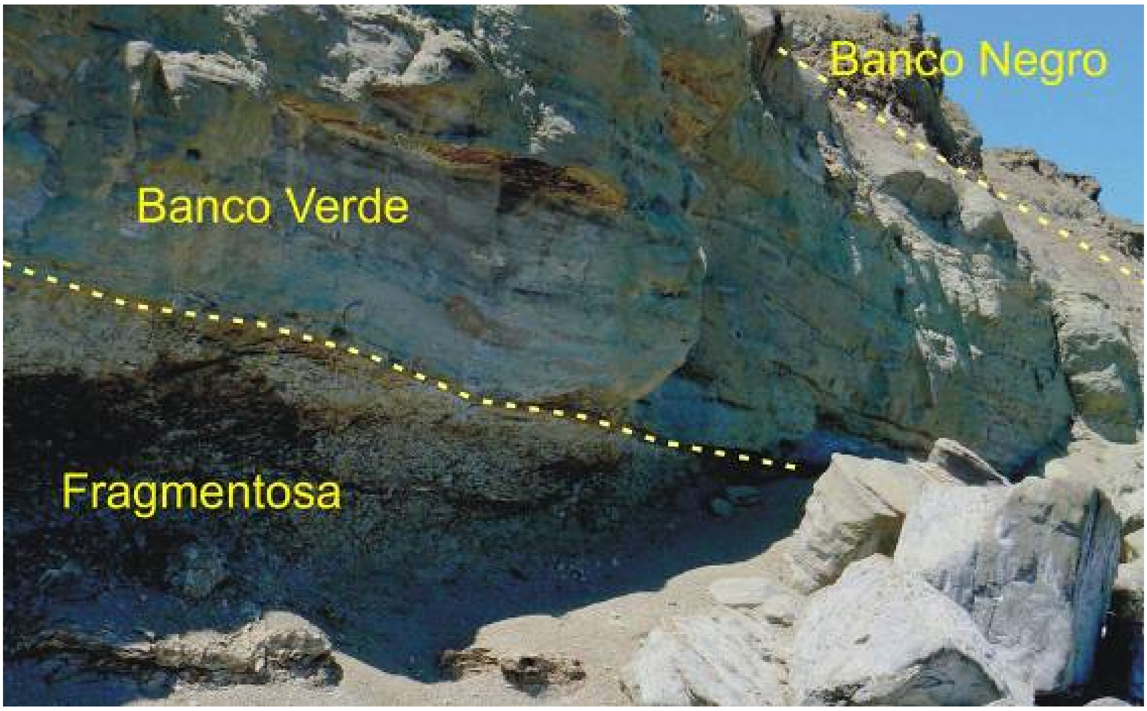



**Figure 3**. - Banco Verde Outcrop. The yellow lines indicate roof and base between Banco Negro and Fragmentosa, respectively

The geological structures associated to the gas storage, which include the main faults in E-W direction crossing the reservoir, are shown on the map corresponding to Figure 4. The map shows the areas defined as Sampling O-I-H and H West, where the gas bubble has developed. NE of the map is a volcanic intrusion crossing the storage, which is a boundary of the reservoir.

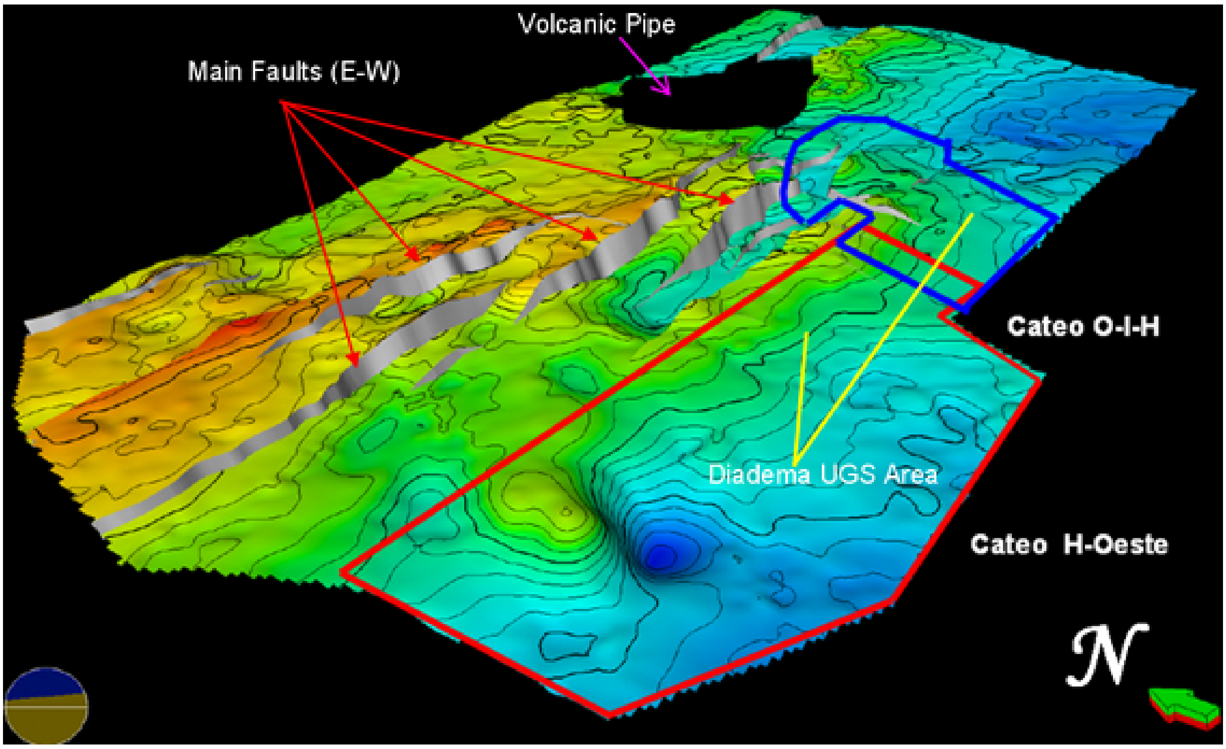


**Figure 4. -** Structural Map top Banco Verde.

## 2. - Operation

The UGS is linked to the main gas pipeline San Martín (TGS) and Camuzzi Gas del Sur S.A.'s natural gas distribution system, as shown in Figure 5.
The stored gas originates in Onshore and Offshore fields in the Austral Basin, located in the provinces of Santa Cruz and Tierra del Fuego, at the southern end of the Patagonia.

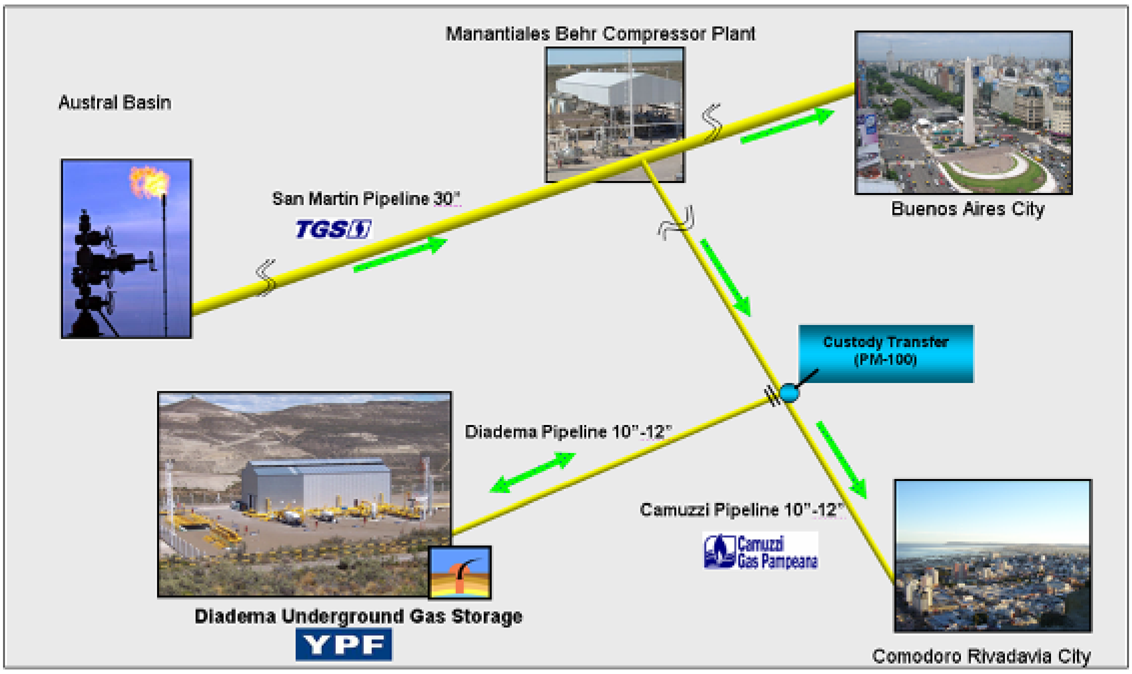



**Figure 5. -** Diadema UGS pipeline interconnections.

The operation consists in delivering natural gas to the reservoir, from excess production, in the summer months (November / March) and extracting it in the winter period (April / September). Delivery / extraction capacity is in the order of 1.0 million $m^3$/day. This is done by 12 dual operation wells.

Delivery / extraction of natural gas to/from the reservoir is done in a controlled manner, keeping the pressures uniform for optimum development, and observing the original maximum pressures in the reservoir (26 kg/$cm^2$).

The gas extracted from the reservoir is conditioned at a plant with capacity to process 1.2 Million Sm3/day, provided with two (2) gas-liquid separators, three (3) motor compressors, two (2) coalescent filters to withhold liquid and solid particles and two (2) dehydrating towers. Upon being conditioned, the gas is delivered to the local distribution company (Camuzzi) for consumption in the City of Comodoro Rivadavia.

Developments in the different summer and winter cycles, as well as the inventory gas, can be seen in Figure 6. It can be noticed that in the last four (4) years there has been a substantial increase in gas inventory as a consequence of adding a new storage block (Sampling H-West).

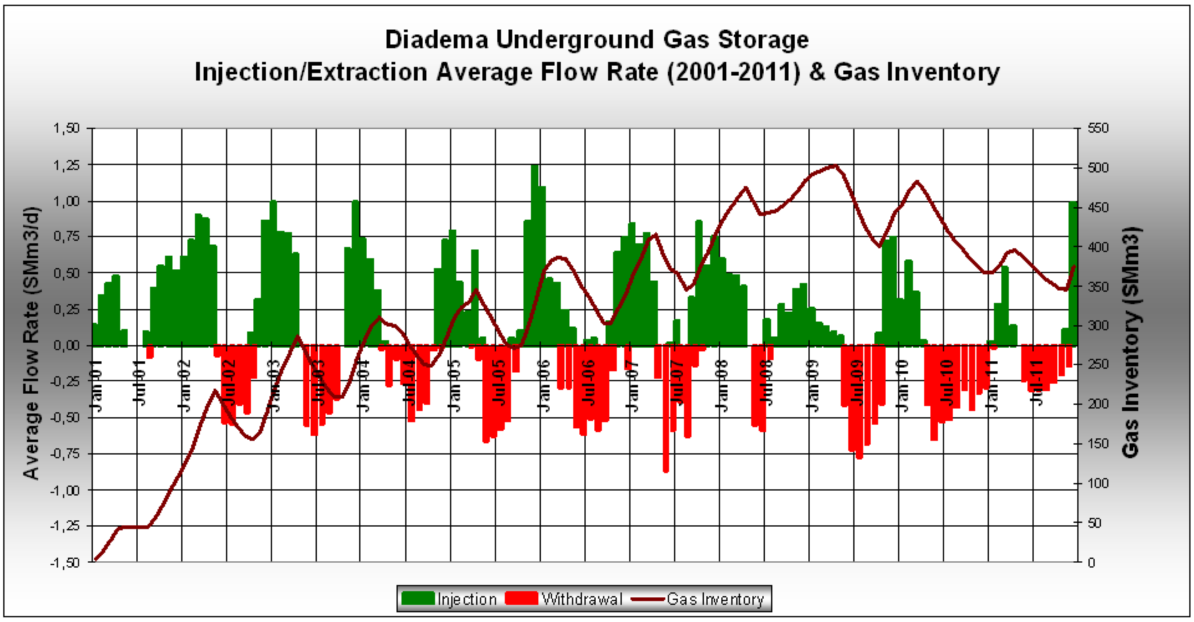



**Figure 6. -** Gas Injection – Withdrawal Cycle and Gas Inventory

**3. - Monitoring process**

This process consists in controlling pressure at the well top on a daily basis, and also regularly, determining other physical and chemical parameters so as to be able to follow up developments in the gas bubble in the reservoir, such as static pressure gradients, molar composition, isotopic analysis, etc.

As the Diadema UGS area is used to develop oil and associated gas from deeper reservoirs, for monitoring purposes, any possible presence of gas is verified regularly between the guide piping and the casing of such development and non-development (to be abandoned) wells.

Table 2 shows the types of wells existing at the UGS.

| **Diadema Storage Wells** | | |
|---|---|---|
| Type | AIM | Number |
| Gas Injection / Withdrawal | Banco Verde | 9 / 11 |
| Gas Bubble Monitoring | Banco Verde | 11 |
| Gas Levels Monitoring | Rio Chico Fm | 1 |
| Aquifer Levels Monitoring | Patagonia Fm | 2 |
| **TOTAL** | | 22 |

**Table 2**. - Type of wells used for storage operations and monitoring.

Figure 7 shows a general schematic of monitoring activities on the wells in the area, including overlying aquifers. Figure 8 shows the location of different types of wells and the prevailing direction of natural gas migration within the reservoir. Each well is logged on a daily basis, by entering any developments in the different parameters (pressure, gas inventory, etc.), as shown in Figure 9.

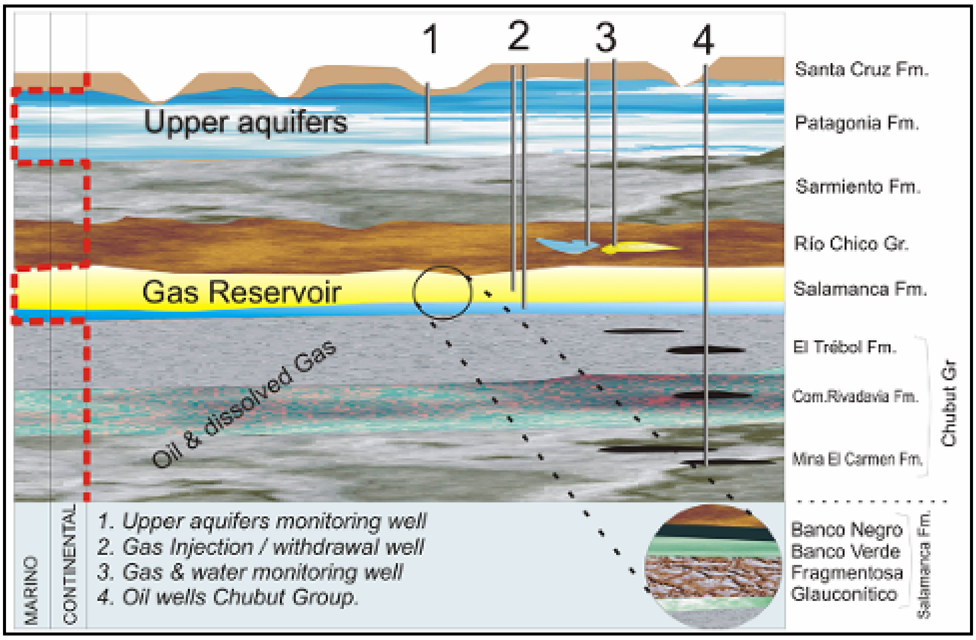



**Figure 7. -** Monitoring Wells at Diadema UGS area.

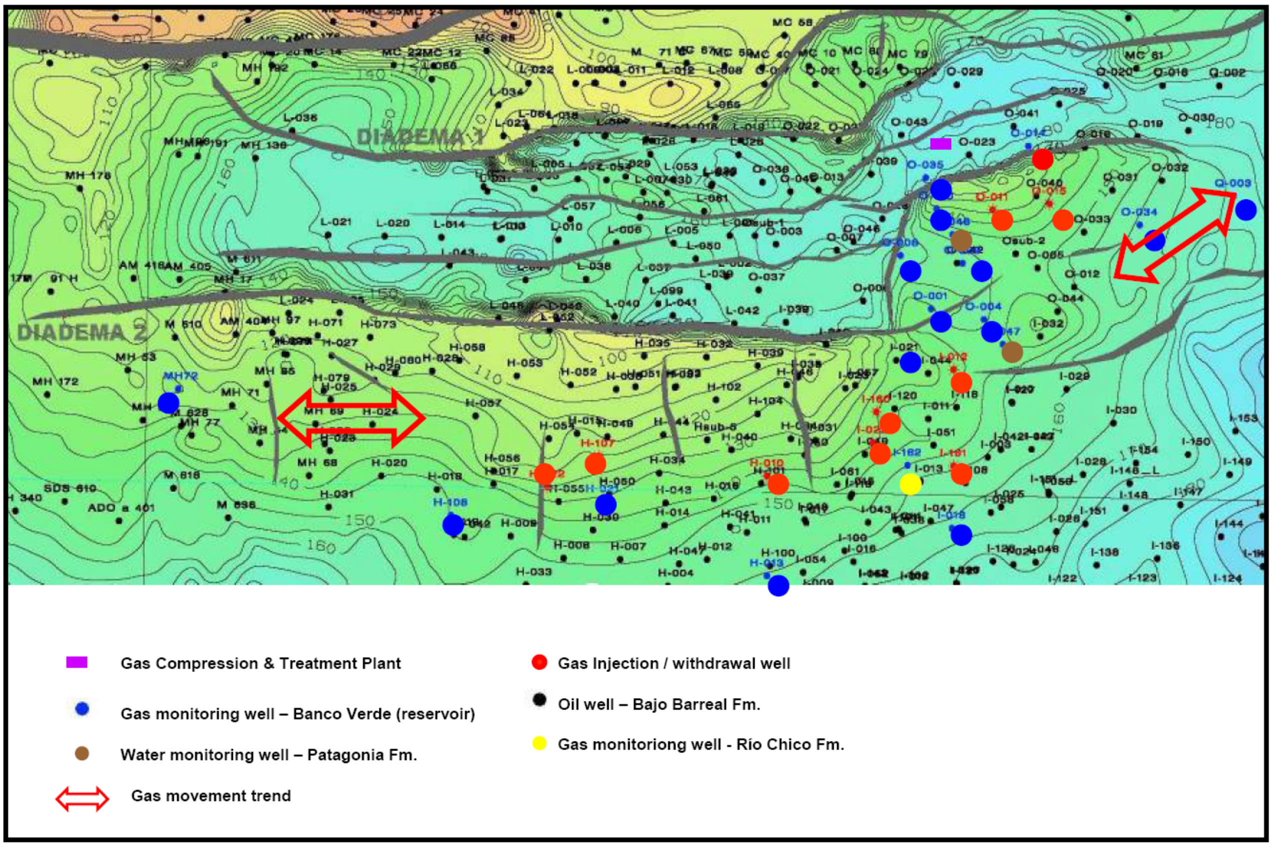



**Figure 8. -** Location of Injection / Withdrawal and monitoring wells.

The stored gas has reached a maximum volume of 500 MSm$^3$ in 2009, which gradually decreased towards the end of 2011 because there was little gas available for storage. This situation is being reversed since January 2012 (Figure 9).

Reservoir pressures have varied from a minimum value of 10 kg/cm$^2$ and a maximum of 25 kg/cm$^2$ for 10 years of continuous operation. Pressures found at monitoring wells I-12 and H-10, located in the central storage area, are clearly consistent with variations in natural gas inventory in each operating cycle, whereas at the well MH-72, at the West end of the storage, we find an initial delay in pressure increase until 2006 and a subsequent change in proportion to developments in natural gas inventories, which is explained by an actual hydraulic interconnection within the reservoir.

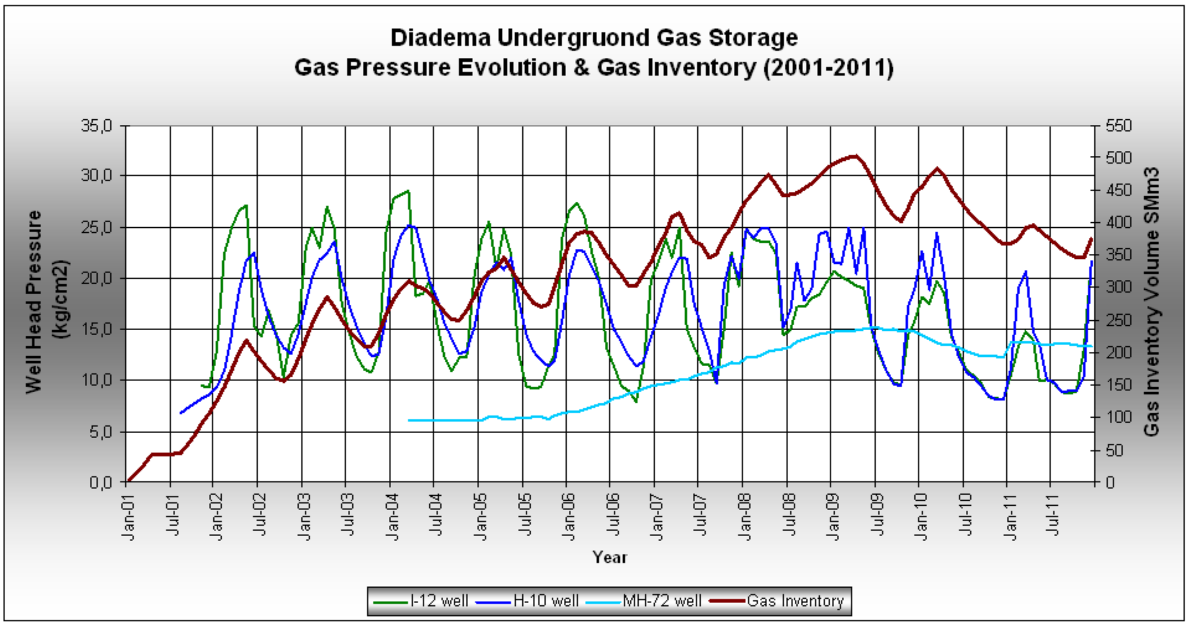



**Figure 9. -** Evolution of pressure per well and inventoried gas

### 4. - Geochemical and Isotopic Monitoring

Since 2004, an annual monitoring campaign has been conducted with the use of geochemical methods (molecular composition) and isotopic methods (C and H isotopes in hydrocarbons and C in CO2). The purpose of such monitoring is to determine the characteristics of the injection / extraction gas in the reservoir, the gas originally present therein, the gas associated to different development horizons in the area; the presence of gas in overlying aquifers, and eventually, determining any mixtures and possible leaks in the system, either for natural reasons or due to development operations. This technology has proved to be useful for a long time (i.e: Coleman, 1978; Schoell & Jenden, 1993, Ostera et al, 2006, 2008,2011 (unpub.); Rodriguez et al, 2009,)

### 4.1. - Sampling and Analysis

The sampling and analysis methods have observed recognized standards (IRAM-IAPG A 6858). Molecular compositions have been measured under GC-TCD/FID and isotopic relations by Combustion – IRMS, GC-IRMS and, Off Axis – ICOS).

The sampling is done on operating wells, in order to ensure the quality of the gas obtained and to avoid any samples from the casing or with abnormal residence times. Usually, two types of geochemical data are used to determine the source and destination of natural gas. The most usual is molecular composition, measured by gas chromatography or mass spectrometry and reported by percentage volume or equivalent units of mol per cent.

Main constituents usually measured are methane, ethane, propane, iso-butane, n-butane, nitrogen, carbon dioxide and hydrogen sulphide. The tracer constituents are the hydrocarbons with highest molecular weight, iso and normal pentane and hexanes + (hydrocarbons with 6 or more carbons), accompanied by oxygen (generally added by pollution during sampling), argon, helium and hydrogen. In many cases the tracer constituents are below the detection limits.

The second type of analysis are isotopic compositions of carbon and hydrogen, which can be measured in the hydrocarbons, usually up to C4. It is also possible to measure the isotopic composition of C in $CO_2$, which constitutes a further control item if there is any isotopic contrast. Nitrogen isotopes were used as a pilot test only once

**4.2. - Sampling points**

The sampling points were selected upon identifying various sources of gas, such as "local gas" (from inside), gas contributions injected into the reservoir (from outside), and mixtures produced, and also by learning about the migration direction of gas within the reservoir, presence of wells developing oil and gas in the area, and abnormal conditions in the development of wells operated by third parties.

We should note that in this document we define local gas as native gas existing in the differente stratigraphic horizons in the zone, i.e:

- Gas associated to oil development (associated gas)
- Original gas in place belonging to Banco Verde (BV) unit.
- Original gas from Río Chico Formation.

Table 3 shows sampling points at Diadema UGS that were used in different campaigns. Their location can be seen on the map in Figure 10.

| **Diadema UGS** | | | |
|---|---|---|---|
| | **Sampling** | **Pozo** | **Nivel** |
| 1 | SAMPLING O | O-14 | Salamanca Fm. – Banco Verde Mb.. Pressure 7.8 $kg/cm^2$ |
| 2 | SAMPLING O | O-15 | Salamanca Fm.- Banco Verde Mb.- Pressure 8.5 kg |
| 3 | SAMPLING O | 0-16 | Salamanca Fm. – Banco Verde Mb. Pressure 2-3 kg. |
| 4 | SAMPLING H | H-21 | Salamanca Fm. – Banco Verde Mb. – Monitoring well Pressure 7 $kg/cm^2$ |
| 5 | SAMPLING H | H-107 | Salamanca Fm. – Banco Verde Mb.. Injection well. Pressure 10.5 $kg/cm^2$ |
| 6 | SAMPLING H | H-32 | Salamanca Fm. – Banco Verde Mb.. Injection well. Pressure 10.5 $kg/cm^2$ |
| 7 | WEST ZONE | MH-72 | Salamanca Fm. – Banco Verde Mb.. Monitoring well. Pressure 2.5 $kg/cm^2$ |
| 8 | SAMPLING I | I-22 | Salamanca Fm. – Banco Verde Mb. Injection / Development well. Pressure 8.8 $kg/cm^2$ |
| 9 | SAMPLING I | I-134 | Salamanca Fm. – Banco Verde Mb. Injection / Development well. Pressure 5 $kg/cm^2$ |
| **Aquifers** | | | |
| 10 | SAMPLING I | I-162 | Río Chico Fm. Gas level |
| 11 | SAMPLING C | C-38 | Patagonia Fm. |
| 12 | SAMPLING O | 0-27 | Patagonia Fm. |
| **Other** | | | |
| 13 | La Begonia | LB - 69 | Salamanca Fm – Glauconitic Mb |
| 14 | La Begonia | LBK-39 | Salamanca Fm - Glauconitic Mb |
| 15 | Separator | I-32 | Bajo Barreal Fm |
| 16 | Diadema Plant | | Injection gas sample |
| 17 | Compressor | L - 85 | Development well |
| 18 | Compressor | I - 50 | Development well |
| 19 | San Diego II Plant | | Plant |

**Table 3. -** Sampling points for geochemical and isotopic analysis

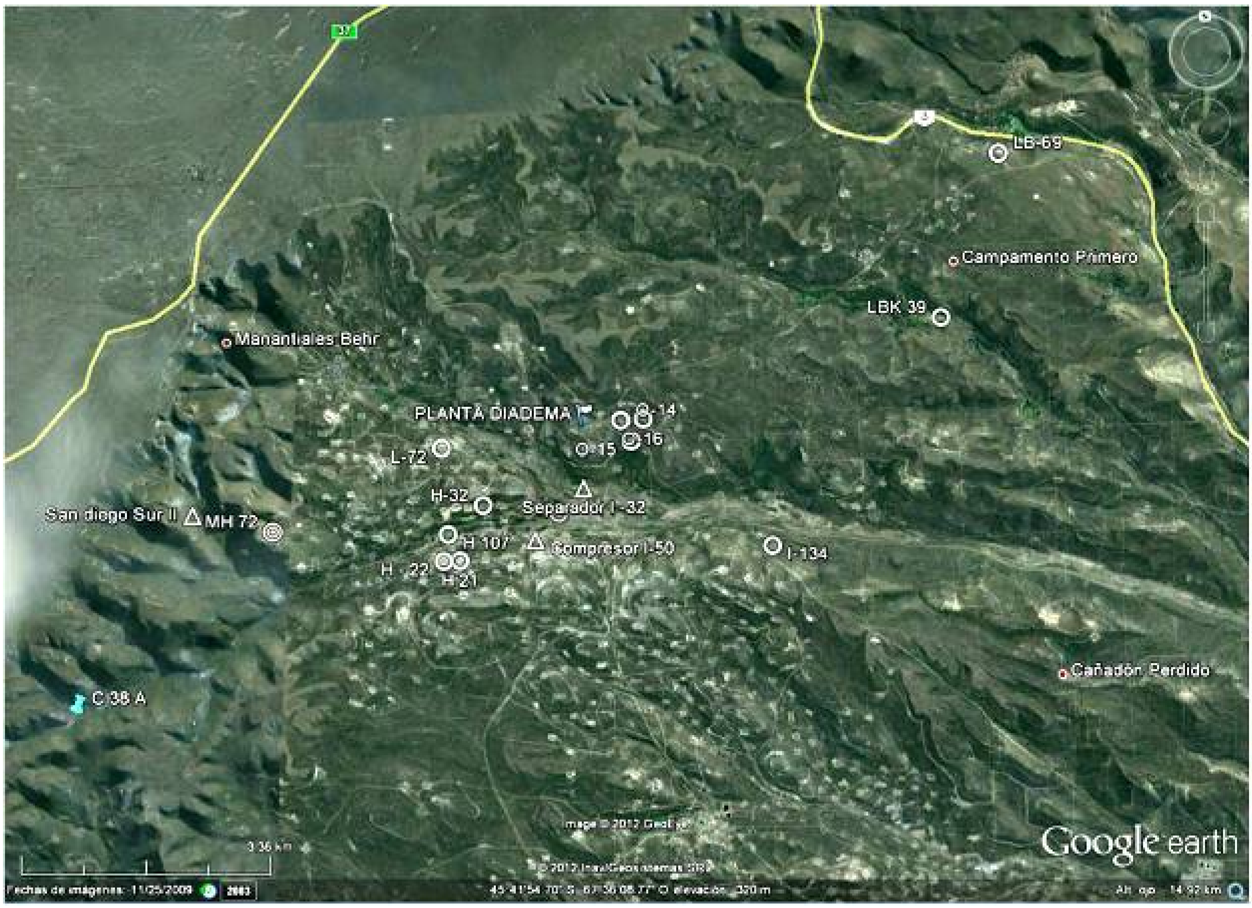



**Figure 10. -** Location of sampling points

### 4.3. - Expression showing the results

The expression for the isotopic results is shown with the usual notation:

$$\mathrm{d}_{0/00} = 1000 \times \frac{R_M - R_E}{R_E}$$

Wherein $R_M$ is the isotopic ratio of the sample and $R_E$ is the isotopic ratio of the standard, in this case V-PDB for the C isotopes and V-SMOW for hydrogen.

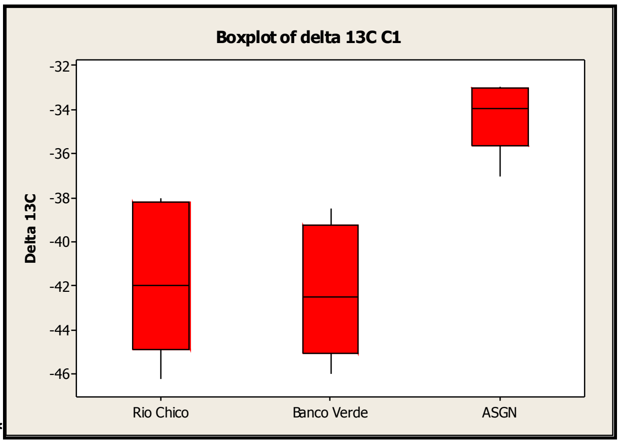
## 5.- Results Obtained

### 5.1.- Results

The results of molecular and isotopic analysis performed on the different samples of natural gas are summarized below.

Isotopic compositions of $C_1$ for local gas have relatively lower values, ranging from -46 to -38. The gas injected into the storage, on the contrary, shows higher values of the delta 13C ratio (-32/-37 per thousand) (Figure 11).

The value of Delta Deuterium in local gas is lower than Delta Deuterium on average (-174/-217) and lower than in the storage gas (-158/-176), and is within a much narrower range (Figure 12).



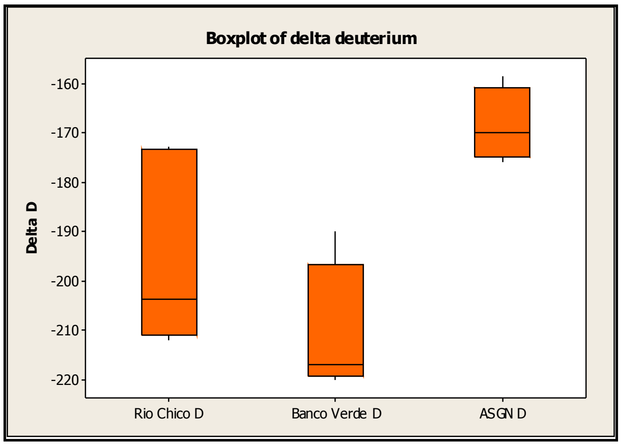




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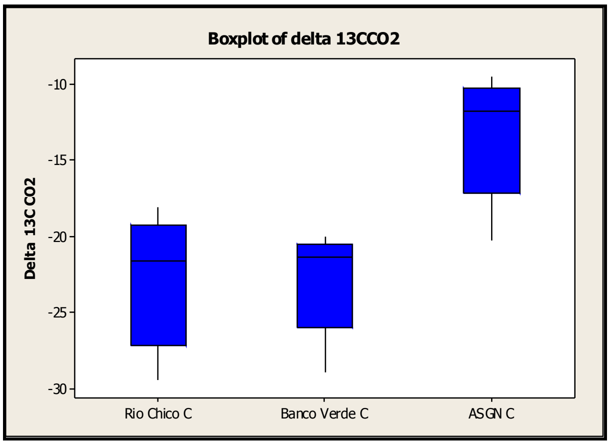
**Figure 11. -** Boxplot showing d13C CH4 ratios

**Figure 12. -** Boxplot showing CH4 ratios.

Besides, the isotopic composition of C for the $CO_2$ is isotopically lighter (-18/-29) at the Rio Chico and Banco Verde Formations (Native Gas), than the average for the storage (-9.6/-20,Figure 13). Locally, in development wells near the UGS, these values can be higher (up to 4.8 per thousand).

C1/C2+ ratios for injected / extracted gas have varied between restricted limits of 9/15, differing from the relatively dryer values of the original gas and the gas associated to oil in the zone (41/1200, Figure 14).



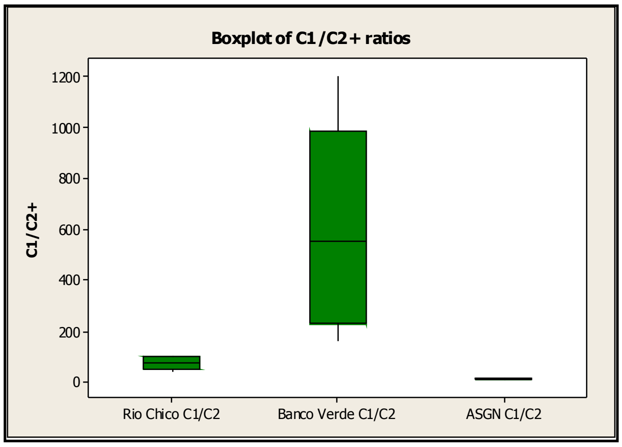




**Figure 13. -** Boxplot showing $C1/C2_+$ ratios

**Figure 14. -** Boxplot showing d13C ratios for $CO_2$.

As we can see, the geochemical and isotopic fingerprint of the Diadema UGS has remained within a limited range in the period under review, and is clearly different from the gas fingerprint developed locally, and even from the gas originally present in the reservoir.

A review of the information has shown that there is a number of usual graphs that can properly display the Diadema UGS fingerprint. These include the conventional correlation diagram $^{13}CCH_4$ – $DCH_4$ ( UGS, local gas and mixing line shown,Figure 15); Bernard's diagram (Figure 16), the Natural Gas Plot (Figure 17) and the binary diagrams d13CC1-d13CC2 or d13C2-d13CC3 (see example in Figure 18).

Likewise, the correlation d13CC1 vs. d13CCO2 clearly shows the relevant fields (Figure 19), where the elevated local abnormal values are noticeable.

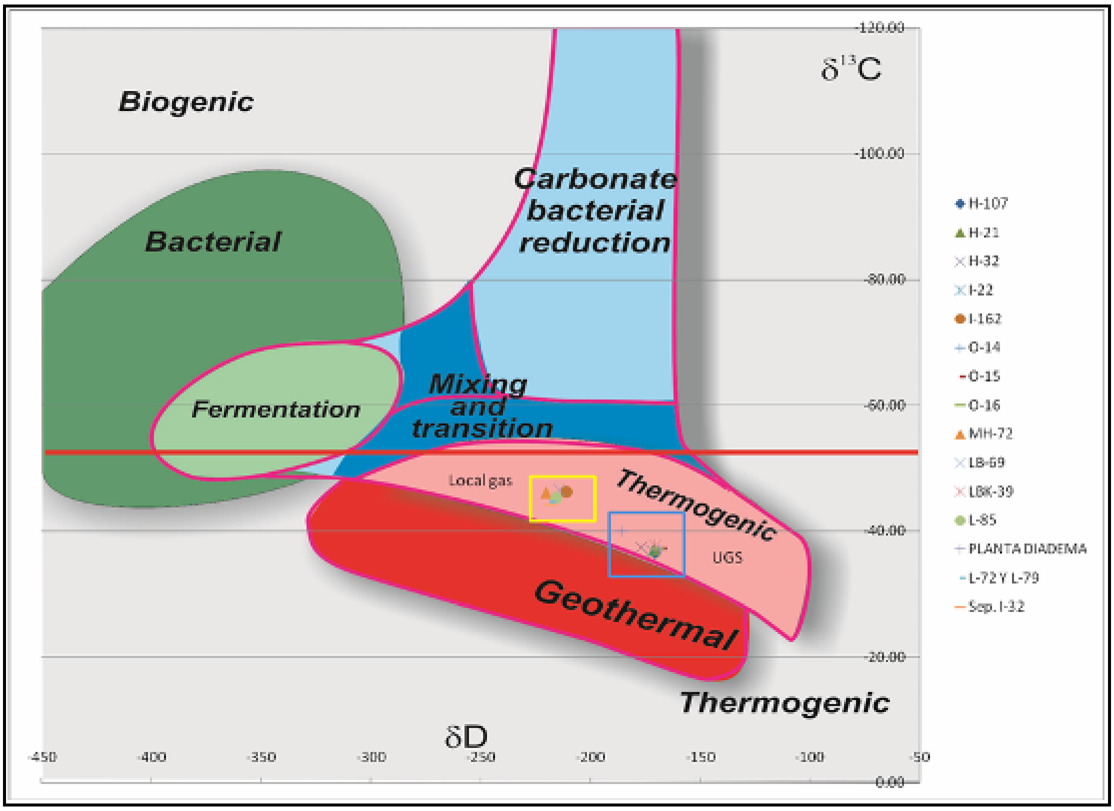



**Figure 15. -** Correlation diagram δ $^{13}CCH_4$ –d$CH_4$. UGS, local gas and mixing line shown.

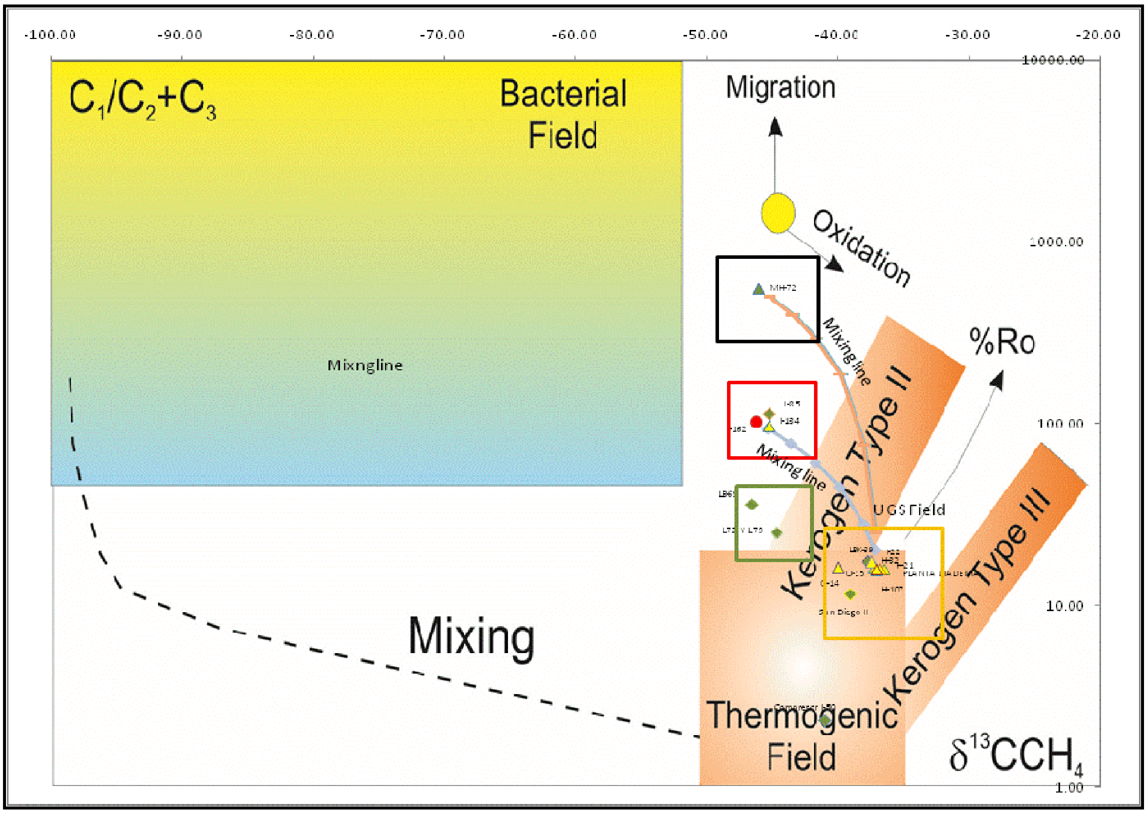



**Figure 16. -** Diagram of Bernard. Highlighted in orange; Diadema UGS Field. Green: Natural gas field associated to co-developed oil. Red: Local thermogenic gas field, Rio Chico Fm. Black: Original thermogenic gas field, Banco Verde Fm.

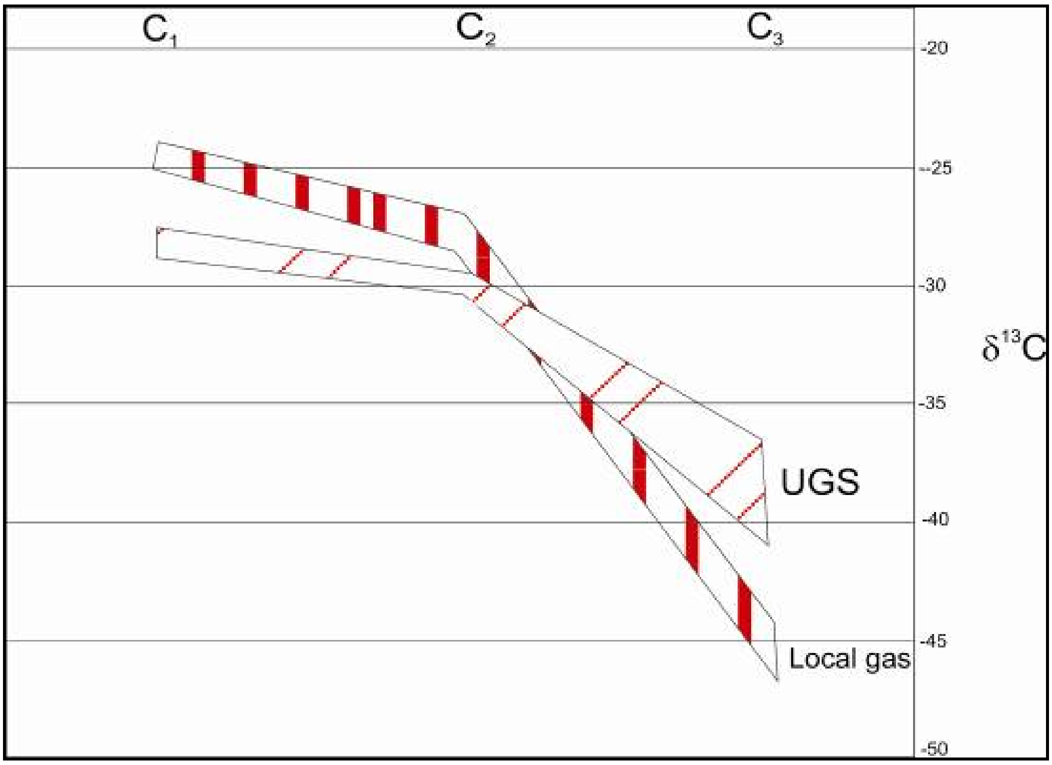



**Figure 17. -** Diagram of Chung (NGP).

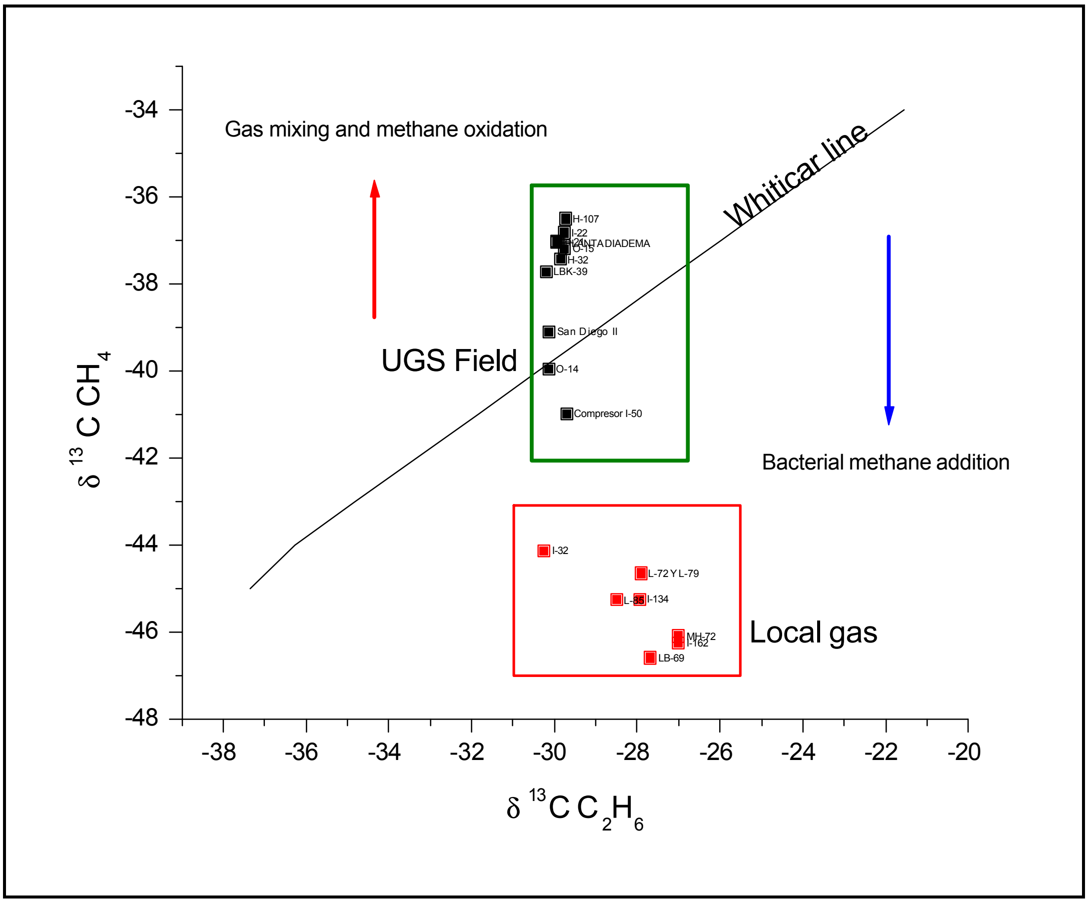



**Figure 18. -** $\delta\ ^{13}CC_1$- $^{13}C^2$ Correlation Diagram. UGS and local gas (Rio Chico, Banco Verde and local development wells).

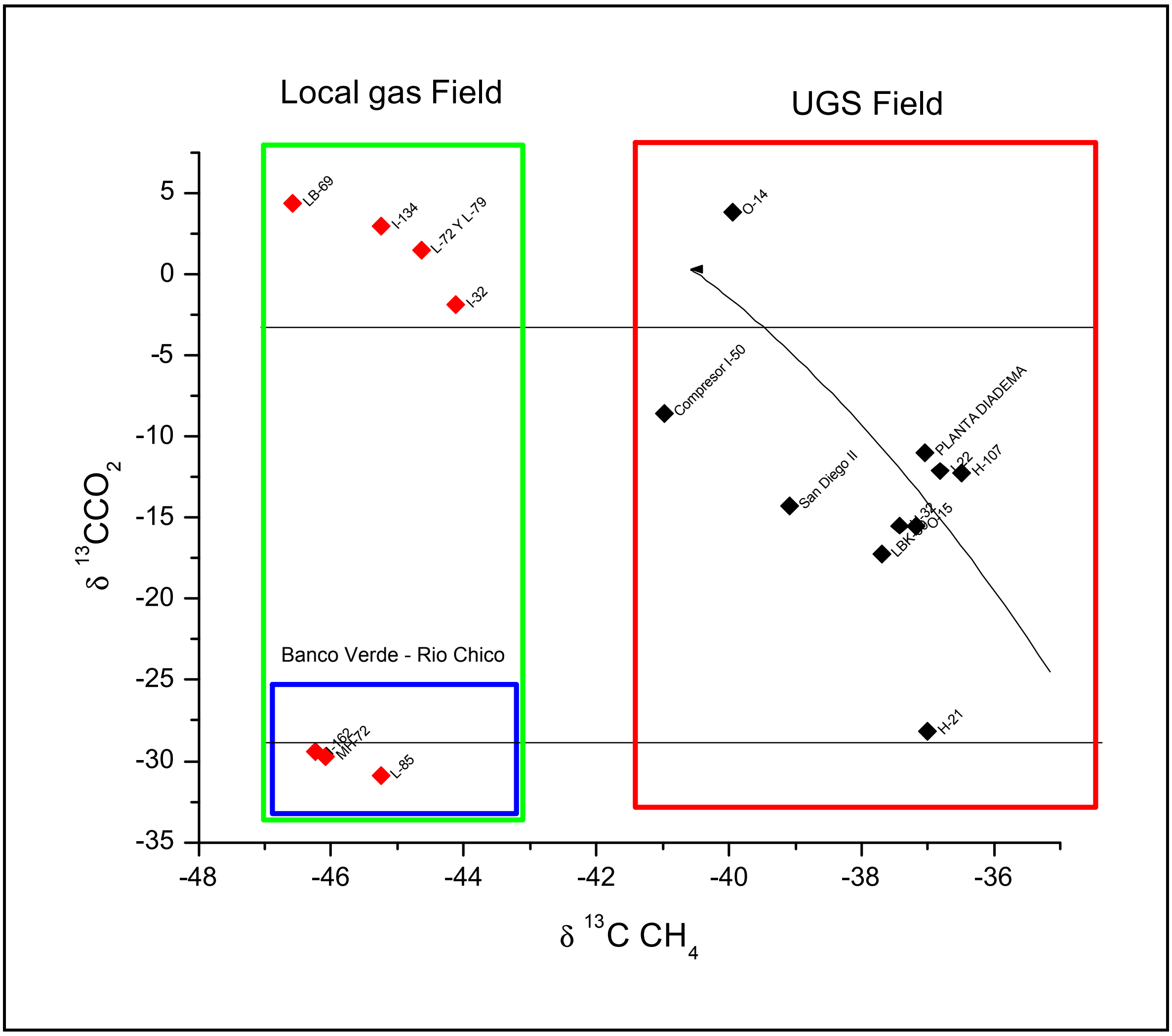



**Figure 19. -** Correlation diagram $\delta\ ^{13}CC_1$-$d^{13}CCO_2$ . UGS and Local gas.(Gas from Rio Chico - Banco Verde highlighted in a blue box) .

## 6. - Applicability of the technique

In order to demonstrate the applicability of the technique, we can recall the case shown in Figure 19, where we can see a pair of wells not operated for the UGS, which showed a mixing fingerprint that reflected the contribution by UGS.

In the first case, an oil well operated by third company at the Diadema area began to increase its GOR during several weeks, up to the point that, for operating reasons, the surface facilities had to be modified. In this case, a mixture of gas from the storage was detected in a gas/oil separation unit by systematic sampling, and subsequently it was found that one well's casing was broken.
In the second case, a gas well belonging to YPF themselves, in the area adjacent to the storage, improved its gas production and maintained it without loss of pressure in time. Again, the technique confirmed a mixture of native gas with gas from UGS.

A comparison with other previously mentioned isotopic data confirmed these evaluation for both cases. With this information, and upon verifying developments in flows and pressures at the well head, we were able to establish the magnitude of the extracted volume, proceed to make the relevant claim and the related repairs.

In the latest campaign, the presence of gas from UGS was also discarded in two other suspicious wells located near storage, which had several vents between columns.

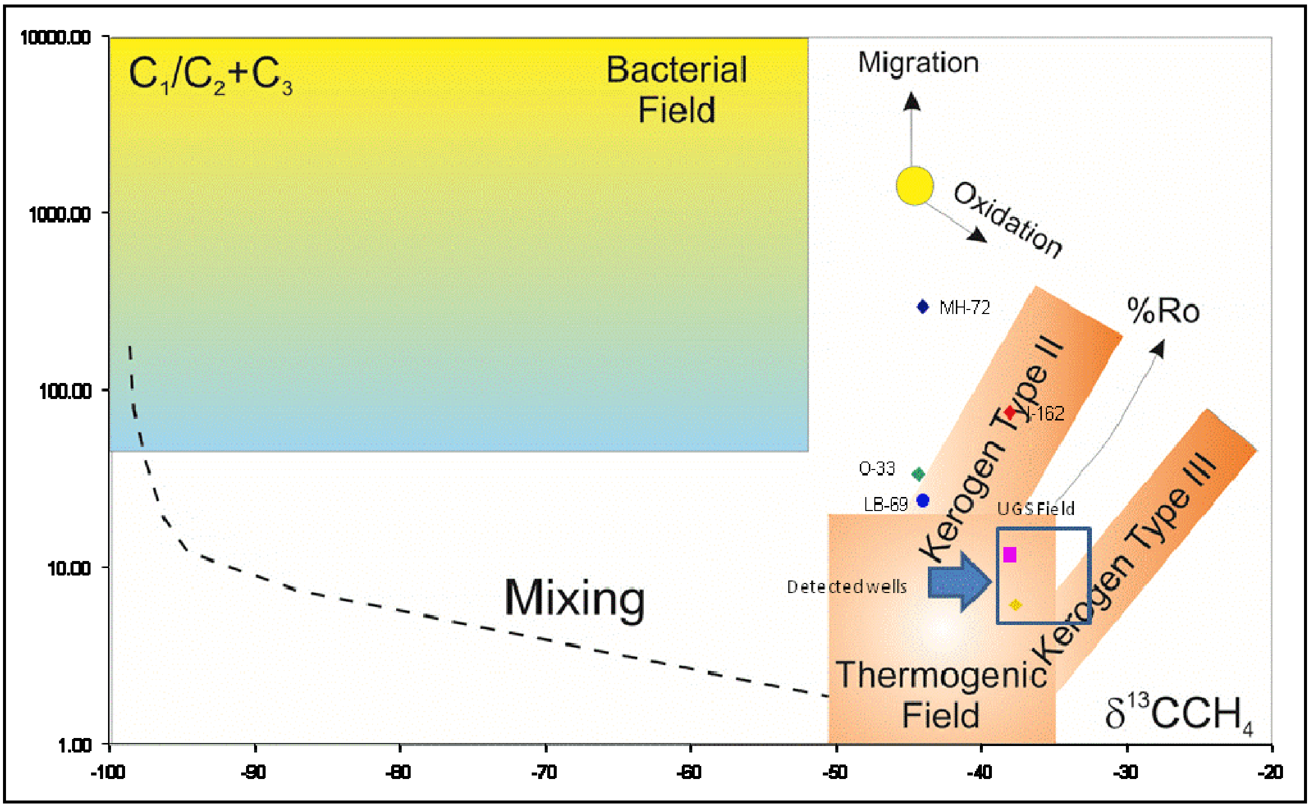



**Figure 20. -** Detection of releases by correlation between isotopes – dryness

**CONCLUSIONS**

We conclude that the geochemical and isotopic tools used to monitor the Diadema UGS have proved to be valid and useful in the time elapsed since the beginning of operations. This has ensured that the reservoir is watertight and also enabled gas extraction from the reservoir by third parties to be stated for record.

These analyses over 19 samples from different objectives (aquifers, Banco Verde, the Río Chico Formation, the Bajo Barreal Formation, gas separators and batteries, injection gas, taken during 6 annual campaigns, have so far detected two gas releases in outside wells, and two were discarded.

The obvious benefits from the method indicate that it should be used regularly as a monitoring tool for this type of operations, as its accuracy has been shown by being able to distinguish the mixture of gases with infinitesimal proportions, which can increase knowledge of gas migration within the reservoir, the development of mixtures with native gas, separate the reservoir into compartments, determine the permeability of faults serving as boundaries to certain blocks, identifying gas releases, and so forth.

A practical use of this method was to be able to claim a financial indemnity in cases where storage gas was found to have been unduly extracted, by wells not belonging to the Storage.

The monitoring program is still in progress, with the addition of new toos to control developments in the gas bubble in the reservoir.

As a final comment, we should note that the results of the isotopic and geochemical analyses have indicated that, for the time being, there is no evidence of natural gas migration from Diadema UGS to the overlying aquifers in the Patagonia and Rio Chico Formations.

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