

# SOIL GAS ANALYSIS AND HELIUM FLUXES TO TRACE LEAK PATHS AT UGS DIADEMA – ARGENTINA. PRELIMINARY REPORT

Juan José Rodríguez<sup>1</sup>, Héctor Oстера<sup>2</sup>, Alejandro Simeoni<sup>3</sup>

- 1.- YPF – Argentina
- 2.- DTP Labs-INGEIS/FCEN(UBA) - Argentina
- 3.- Engaged by YPF – Argentina

Keywords: Migration, Soil gas, Helium Flux, Diadema

## Abstract

Diadema UGS started operation in 2001, when YPF decided to lease blocks, including the so-called *Banco Verde* horizon. This block had been a producer of natural gas, that started to develop the first underground gas storage in Argentina to partially provide for the winter demand in the central Patagonia area.

The Diadema field consists of monoclines in hydraulically-connected faulted blocks, which enables the stored gas to flow through the permeable faults. Such natural migration from the injection wells to the reservoir limits is monitored along the injection cycle (summer) and the gas extraction cycle (winter), to allow for a suitable recovery of gas inventory.

Because of the special features of the structural model, from the beginning of activities associated to underground gas storage, a number of measures were adopted to ensure reservoir water tightness, and various types of wells crossing the reservoir, in order to prevent any leaks of gas that could penetrate other hydrocarbon producing levels, and likewise the upper aquifers.

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.

Diadema's monitoring activities have included several campaigns of gas isotopic analysis. Recently, such activities have included a pilot test using soil gas surveys. These include *methane*, *T-VOCs*, *CO<sub>2</sub>* concentrations, *helium*, *radon* and *thoron* fluxes at specified underground locations. They test the ability of these techniques to trace likely migration paths for the gas stored into the reservoir.

Due to its geochemical properties (inert, biogenic and mobile), *He* is considered an ideal tracer. As *He* is more soluble in petroleum than in water, the mixture of water and petroleum will result in an enrichment of the *He* in the petroleum, and accordingly, in any anomalies associated with hydrocarbon accumulations. Methane anomalies in hydrocarbon accumulations have been proven; this constitutes the basis for geochemical prospection methods, and it is also used in environmental analyses. *Radon* and *thoron* have proven to be reliable indicators for fault zones.

Besides, *T-VOC* concentration studies enable the migration of molecules having a higher atomic weight, such as benzene and other aromatics. Such techniques are used in geochemical exploration, and eventually determine larger structures where they are associated to hydrocarbon leaks. *CO<sub>2</sub>* is also associated with preferential migration paths, the existence and migration of hydrocarbons to the surface, and biodegradation processes.

This work shows the results of this first pilot study at selected locations. The aim is to test the response of recognized structures and seek information on potential leaks of stored gas at specified locations.

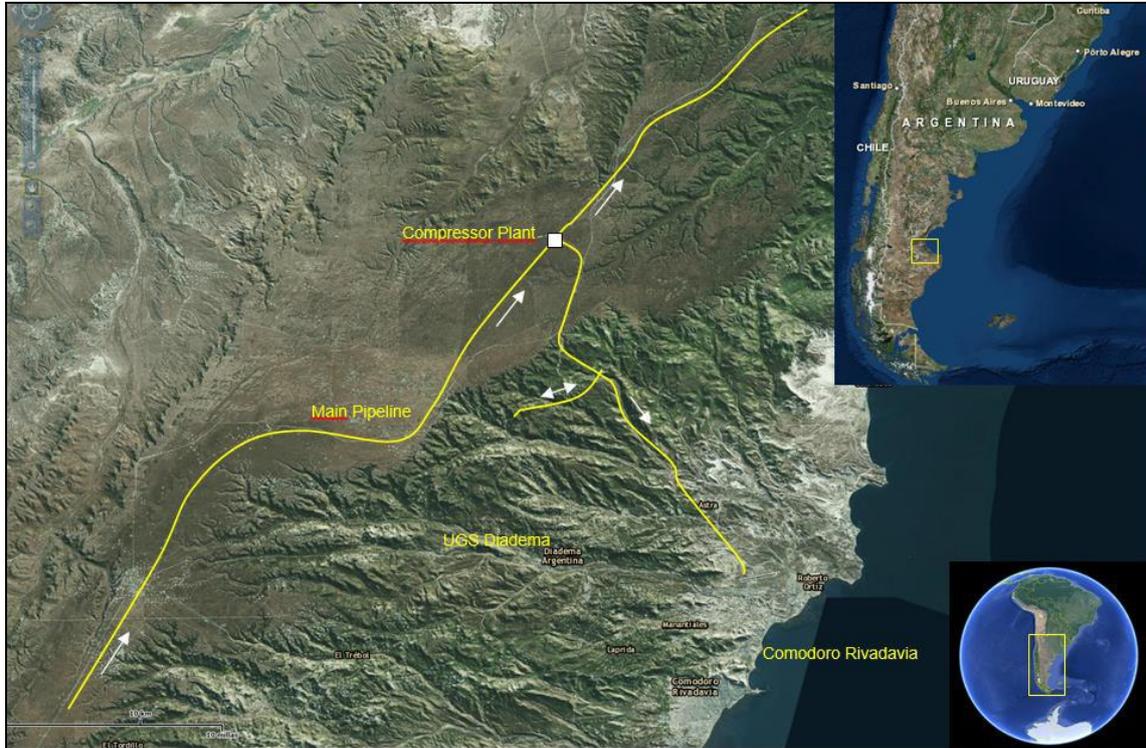
Our first conclusion is that significant anomalies in helium, radon, thoron fluxes and *CO<sub>2</sub>* concentration have been detected in the fault zones of the Diadema field, and significant methane

anomalies at the location of wells (associated with pipeline leaks). *T-VOCs* are not conclusive. This information allowed us to confirm the geological model used for reservoir numerical simulations.

## 1. Location and geology

### Location

Diadema UGS is located in the North Flank of the San Jorge Gulf basin, 40 km NW from the city of Comodoro Rivadavia (Figure 1).



**Figure 1.** Location of Diadema UGS

The site is a depleted natural gas field that was chosen for several reasons: the original gas properties, compatibility with the natural gas to be stored in the reservoir, a working gas volume in excess of 150 million Sm<sup>3</sup>, location near the main gas pipelines, and the city of Comodoro Rivadavia which is the destination of the storage services.

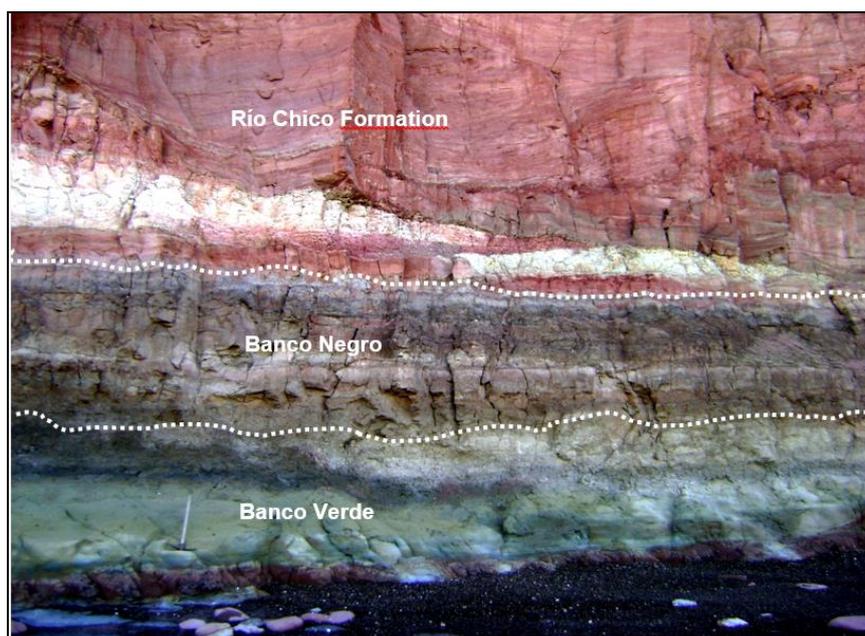
Table 1 shows the stratigraphic sequence of the Diadema area. The seal rock comprises basal shale levels of the Banco Negro, and the reservoir rock consists of the sandstones of Banco Verde horizon (red box).

Local Stratigraphic Chart								
Geo-chronological Units		Stratigraphic Unit					Geology	
Eratheon. Era	System period	Series Epoch	Formation	Member	Salamanca Fm. Levels	Thickness (Meters)	Facies	
Cenozoic	Quaternary	Holocene	Alluvial Deposit				Fluvial	
		Pleistocene	Patagonian Shingle			10-40	Fluvial-Glacial	
	Neogene	Pliocene	Upper					
			Lower	Discordance				
		Miocene	Upper					
			Medium	Santa Cruz			100	Continental
	Paleogene	Oligocene	Lower	Patagonia			200	Marine
			Upper					
		Eocene	Upper	Sarmiento			100	Continental
			Lower					
Paleocene		Upper	Rio Chico			(200-300)	Continental	
		Lower	Salamanca Fm.	Hansen	Banco Negro	20	Marine	
		Bustamante	Banco Verde	20				
				Fragmentosa (130-140)				
				Glaucónico Lignífero (10-30)				
Mesozoic	Cretaceous	Upper	Chubutian	Yacimiento El Trébol			Fluvio-Deltaic	
				Comodoro Rivadavia				Fluvial
	Lower		Mina el Carmen				Fluvial-Lagoon	

**Table 1.** Simplified stratigraphy of Diadema area.

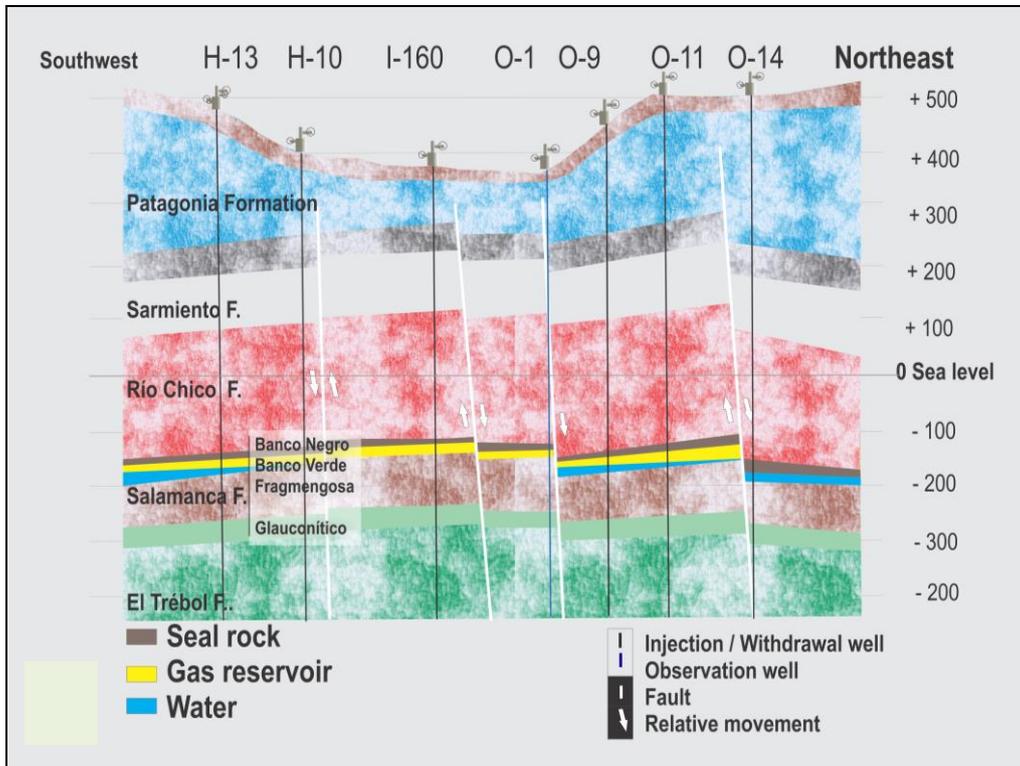
The geological level used by the UGS is a lithostratigraphic unit called “Banco Verde”, part of the Hansen Member in the Salamanca Formation. It is located at an average depth of 650 meters below ground. Banco Verde consists of sandstones of medium to coarse grains, originally sea material, covered with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

A Banco Verde outcrop is shown in Figure 2, with the overlying horizons.



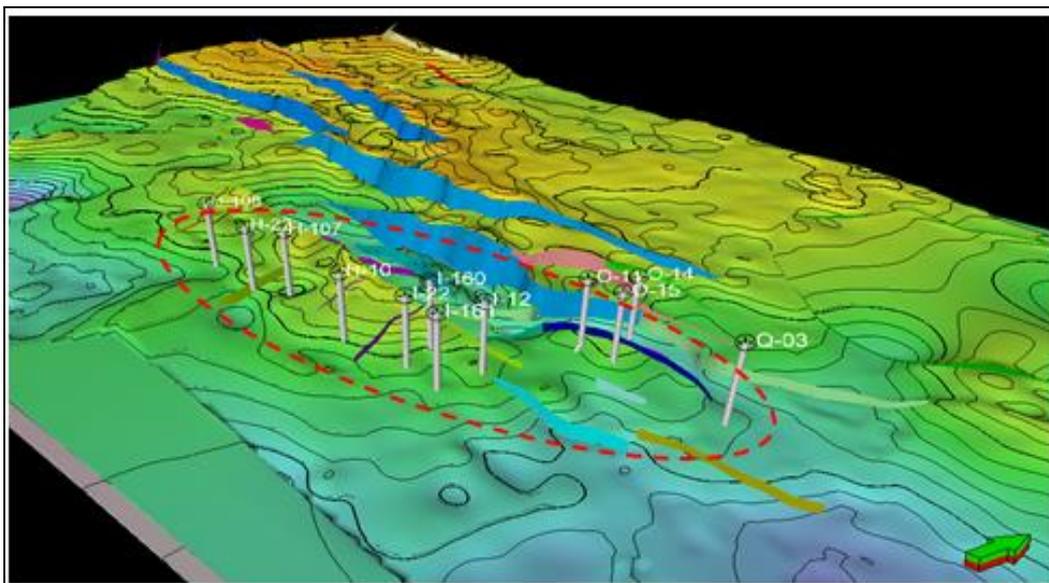
**Figure 2.** Banco Verde outcrop

Banco Verde is structurally divided into blocks, that arise from direct faults with regional length and E-W NE-SW direction, with over 40 meters of vertical displacement. These faults are permeable, so they permit hydraulic communication among adjacent blocks, and as a result, the system functions as one reservoir (Figure 3).



**Figure 3.** Structural cross-section of the gas storage

The geological structures associated with the gas storage, which include the main faults in E-W direction that cross the reservoir, are shown in Figure 4. The 3D model shows the area where the gas bubble was formed.

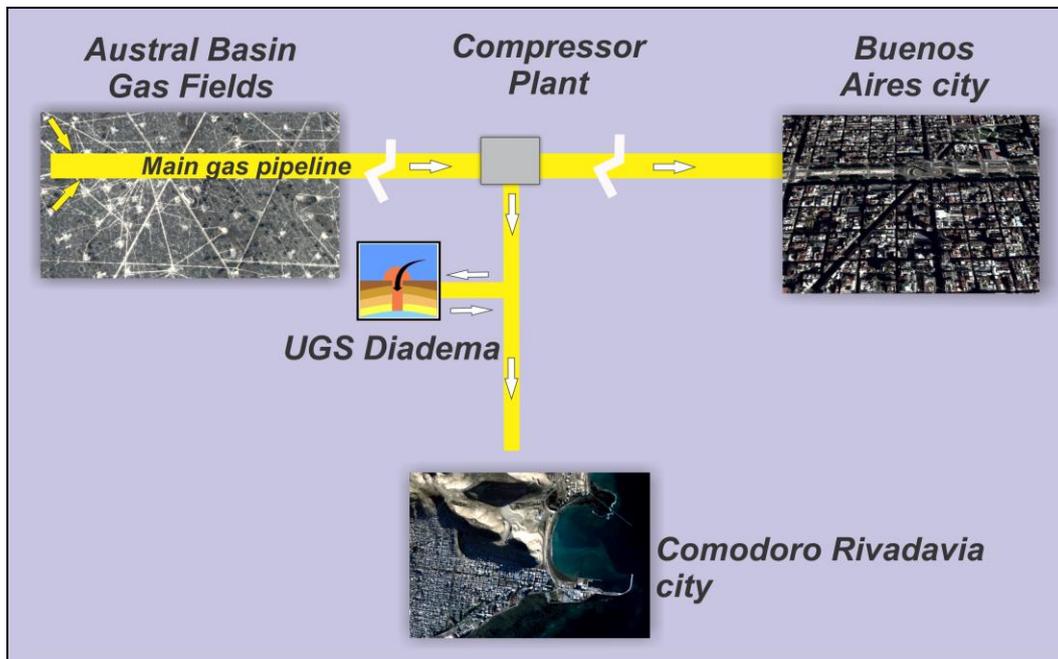


**Figure 4.** 3D model at the top of Banco Verde horizon, and the UGS wells location

## 2. Operation

Diadema UGS has been operating since 2001, together with the trunk gas pipeline called General San Martín (TGS) and the local distribution company (LCD - Camuzzi Gas del Sur S.A), as shown in Figure 5.

The stored gas at Diadema UGS is produced in gas fields located in the Austral basin, in the provinces of Santa Cruz and Tierra del Fuego, in the southern Patagonia.



**Figure 5.** Gas pipelines interconnection system

The operation consists of injecting natural gas into the reservoir in summer and extracting it in winter (southern hemisphere). The injection and withdrawal gas capacity is approximately 1.5 million Sm<sup>3</sup>/day, using 18 operation wells.

The reservoir operates at the pressure range of 10 kg/cm<sup>2</sup> (minimum) to 26 kg/cm<sup>2</sup> (maximum), at the end of winter and the end of summer, respectively.

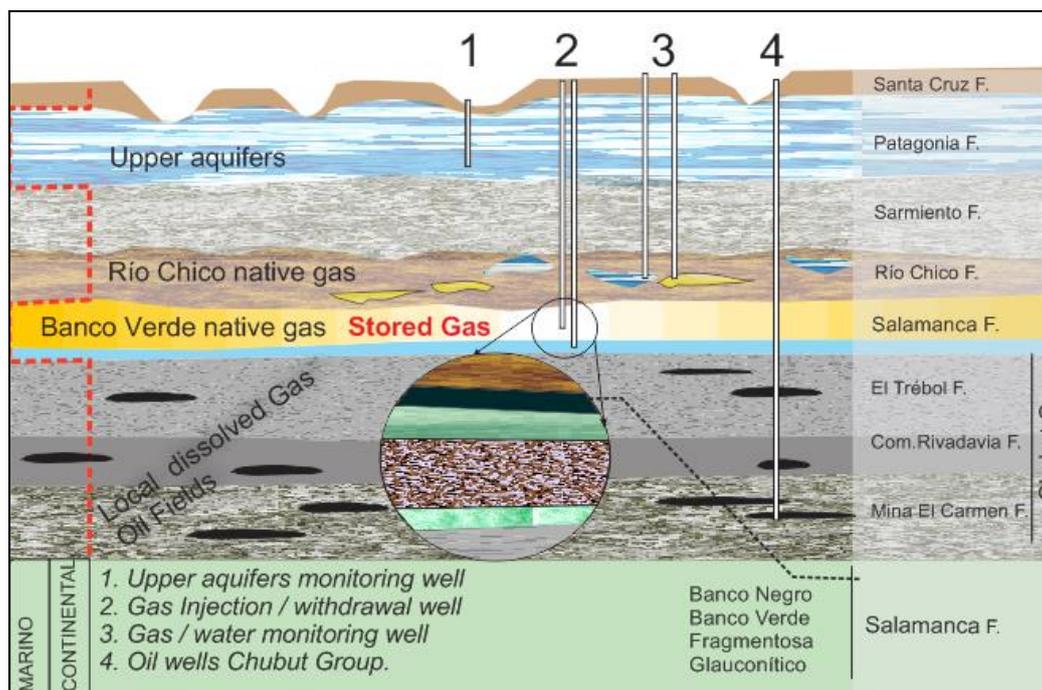
The extracted gas from the reservoir is first conditioned at a plant which can process 1.5 million Sm<sup>3</sup>/day, and which is made up of 3 gas-liquid separators, 4 motor compressors, 2 coalescent filters to withhold liquid and solid particles and 2 dehydrating towers with (TEG) tri-ethylenglycol. The gas is then delivered to the LDC for consumption in the city of Comodoro Rivadavia.

## 3. Monitoring process

This process consists of regularly controlling pressure at the well head on a daily basis, determining other physical and chemical parameters to monitor the gas bubble evolution in the reservoir, such as static pressure gradients, molar composition, isotopic analysis, etc.

As the Diadema UGS area is used to extract 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 these development and non-development (to be abandoned) wells.

Figure 6 shows a general depiction of monitoring activities in the wells of the area, including overlying aquifers. Each well is monitored on a daily basis (pressure, gas flow rates, molar composition, gas inventory, etc.).



**Figure 6.** Monitoring wells at Diadema UGS area

### 3.1. Geochemical and Isotopic monitoring

An annual monitoring campaign was conducted with the use of geochemical methods (molecular composition) and isotopic methods ( $C$  and  $H$  isotopes in hydrocarbons and  $C$  in  $CO_2$ ), since 2004 at present.

The purpose of such monitoring is to determine the characteristics of the gas injection / withdrawal in the reservoir, the gas originally present, the gas associated to different development horizons in the area, the presence of gas in overlying aquifers, and eventually, to determine any mixtures and possible leaks in the system, that are due to natural occurrences or development operations. This technology has proven to be useful over many years (i.e: Schoell & Jenden, 1993, Oстера et al, 2006, 2008, 2011 (unpub.); Rodriguez et al, 2009, 2012).

#### Sampling and Analysis

The sampling and analysis methods have recognized standards (IRAM-IAPG A 6858). Molecular compositions were 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 type is molecular composition, measured by gas chromatography or mass spectrometry, and reported by percentage volume or equivalent units of mol percent.

The main constituents usually measured are methane, ethane, propane, iso-butane, n-butane, nitrogen, carbon dioxide and hydrogen sulphide. The tracer constituents are the hydrocarbons of 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.

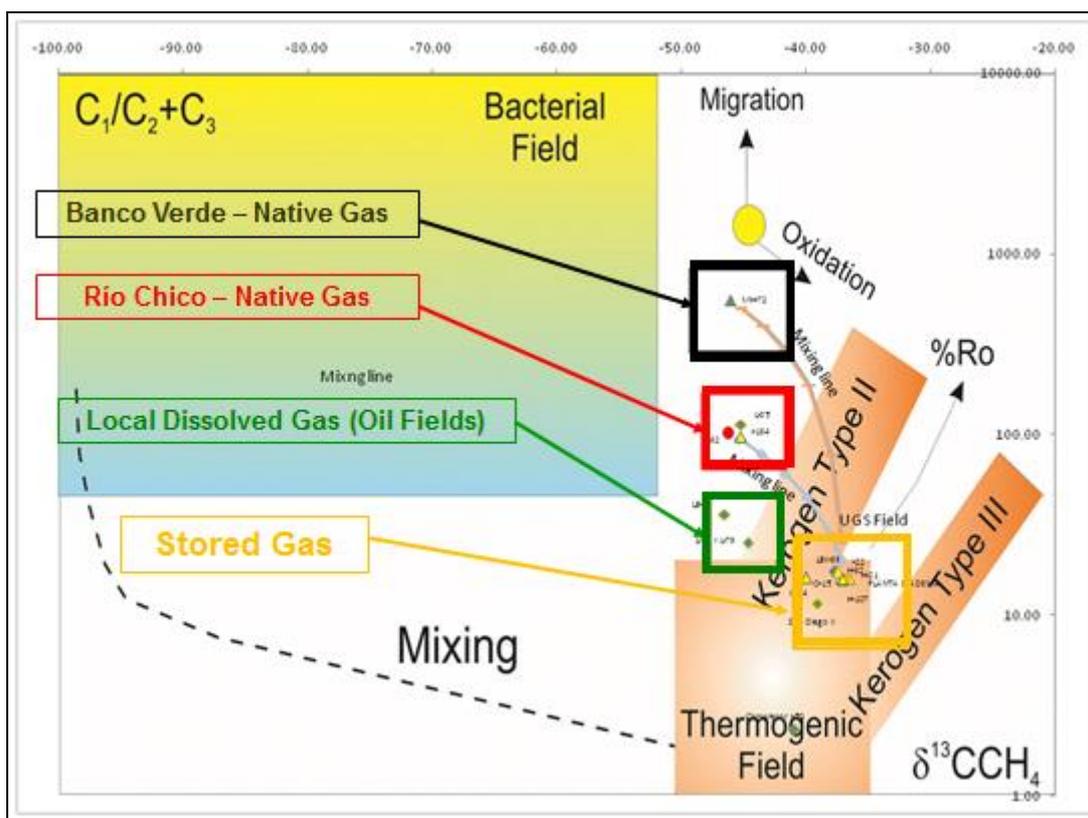
The second type of analysis is the isotopic compositions of carbon and hydrogen, which can be measured in the hydrocarbons, usually up to  $C_4$ . It is also possible to measure the isotopic composition of C in  $CO_2$ , which constitutes a further control item in the case of any isotopic contrast. Nitrogen isotopes were used as a pilot test only once

The sampling points were selected from identifying various sources of gas, such as “local gas” (from inside), gas contributions injected into the reservoir (from outside), and mixtures produced. Others were selected by learning about the migration direction of gas within the reservoir, the 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 different stratigraphic horizons in the zone, i.e:

- Associated gas to oil development (dissolved gas)
- Native gas in Banco Verde horizon
- Native gas in Río Chico horizon

The results of representative molecular and isotopic analysis performed on the different samples of natural gas are in Figure 7.



**Figure 7.** Gas families at the Diadema UGS area (Diagram of Bernard)

### 3.2. Helium, radon and thoron fluxes and soil gas analysis

#### Soil gas analysis and He

Soil gas analysis is widely used in several research fields such as volcanology, geothermal research, earthquakes forecasting, gas hazard and geochemical explorations of active faults. Changes in the amount of fluids discharged can be related to zones of seismicity and high tectonic stress.

Fluids often play an important role in fault mechanisms and in the triggering of earthquakes. Over-pressurized fluids stored in deep reservoirs can cause additional stress to host rocks and trigger seismicity (Yang et al, 2005; Salazar et al., 2002).

#### He

Noble gas chemistry has proven useful in many different fields of geology, as a tracer and a geochronological tool. The noble gases have also been employed in the study of mantle degassing and atmospheric evolution. Noble gases are not chemically modified in solution, so they can be employed extensively in different studies (i.e: groundwaters, flow regimes, palaeotemperatures, etc; Ozima & Podosek, 1983; Ballentine et al, 1996; Porcelli et al., 2002).

The principal isotope of helium,  $^4\text{He}$ , is generated during the radioactive decay of isotopes of uranium, thorium and a few other elements; it is an inert gas, and has been used as a pathfinder for deposits containing these elements (Hale, 2000).

Basement-derived helium may also appear along faults, including active ones, and its detection may be applied to locating faults in areas of poor outcrop (Ciotoli et al., 2004). Additionally to Rn, short-term fluctuations of the helium flux have been suggested as possible predictors of earthquake activity.

#### Radon and thoron

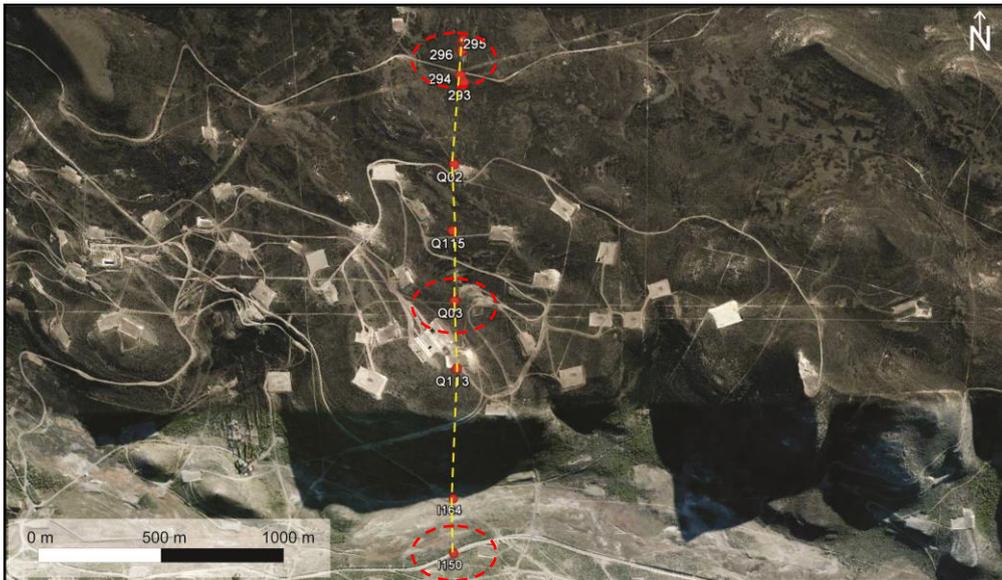
Radon ( $^{222}\text{Rn}$ ) concentration and radon flux anomalies have been proposed as a way to detect hidden faults (Richon et al, 2010, Burton et al., 2004, King et al, 1996, among others). Radon and thoron ( $^{220}\text{Rn}$ ) anomalies were found in many cases associated with major structures and seismic activity (IAEA, 1993).

#### CO<sub>2</sub>

Most of the studies on diffuse soil gas emissions in geothermal and volcanic areas have focused on CO<sub>2</sub> because it is usually the most abundant volatile species in magma, that is only second to water, and it is the first species that exsolves. The gas is usually generated by degassing intrusives. CO<sub>2</sub> travels upward by advective - diffusive transport mechanisms and appears on the ground surface. The information on changes over time in the CO<sub>2</sub> soil gas concentration and flux pattern provides criteria for evaluating volcanic activity (Baubron et al, 1991; Chiodini et al, 1998, between others).

However, in this case we expected that the CO<sub>2</sub> could serve as fault pathfinder and carrier gas, associated with migration from the deeper crust (Richon et al, 2010, Toutain & Baubron, 1999).

In order to establish the relationship between well recognized faults (seismic surveys) and its surficial expression, a pilot survey was carried out in a cross section of the Diadema field. Figure 8 shows its location and detected anomalies (red circles).



**Figure 8.** Cross section location

## **CH<sub>4</sub>**

Anomalies in methane concentrations can be associated with oil and gas accumulations in subsurface. These anomalies can often trace leaks of reservoirs or wells (Schumacher & Abrams, 1996). Methane anomalies are used in geochemical exploration, although some constraints (daily and seasonal variations) have limited its use up to the present.

## **T-VOCs**

Aromatic compounds (included in T-VOCs) have been found in many cases associated with seeps and micro seeps; the relationship with major structures has been noted as well (Schumacher & Abrams, *op.cit.*).

## **Methodology**

For *He* analysis, many studies have utilized modified vacuum leak-detectors (Friedman & Reimer, 1986; Reimer, 1976; Dyck and Pelchat, 1977). These are not expensive, are relatively robust and can be adapted for use in the field. In this case, the He Mass spectrometer MKS PICO was used. It has the advantage of miniaturization and maximum integration of the pumping system. A turbo molecular pump together with a two-stage scroll pump is integrated within a compact block without further vacuum tubing. The core of the detection principle is based on Paul trap principle as used in mass spectrometers, which requires mass selectivity and sensibility in a small volume.

For CO<sub>2</sub> analysis, a non-dispersive, infrared gas analyzer PP Systems EGM-4 CO<sub>2</sub> instrument was used. CH<sub>4</sub> analysis was done with a Microgas 3 methane analyzer (TCD). T-VOCs were analyzed using a portable gas chromatograph Photovac Voyager, with PID detector.

Rn measurements were carried out with a Rad 7 radon monitor, which measures radon and thoron activities, and an accumulation chamber. The acquisition of the data is “*in situ*” -real time. Calibration is performed with certified standards. Except for radon and thoron, which use an accumulation chamber, the instruments are coupled with tubing to a direct push probe (1 m depth).

## **Results**

The main results of the survey indicated in Figure 8, are shown in Table 2 and Figure 9.

ID	Surficial emission of radon (Bq/min.m2)	Surficial emission of thoron (Bq/min.m2)	He (mol/s@0°C)	CO2 (ppmV)	CH4 (ppmV)	T-VOCs (ppmV)
Q03	0,24	36,14	10*10 <sup>-11</sup>	2837	12500	0,22
Q106	0,31	24,56	3.09*10 <sup>-11</sup>	1944	20	0,18
Q113	0,03	19,55	2.25*10 <sup>-11</sup>	1440	10	0,16
290	0,25	29,35	5.97*10 <sup>-11</sup>	2427	20	0,21
Q02	0,31	23,56	7.1*10 <sup>-11</sup>	1045	30	0,2
Q115	0,25	28,96	8.9*10 <sup>-11</sup>	2386	30	0,24
293	0,21	26,36	8.7*10 <sup>-11</sup>	2125	20	0,2
294	0,32	31,35	6.8*10 <sup>-11</sup>	2628	40	0,24
295	0,21	17,13	1.51*10 <sup>-11</sup>	1196	20	0,16
296	0,27	23,96	2.73*10 <sup>-11</sup>	1884	30	0,15
297	0,57	34,35	8.96*10 <sup>-11</sup>	2929	60	0,2
I164	0,20	20,17	0.45*10 <sup>-11</sup>	1820	1000	0,18

Table 2. Results of the survey

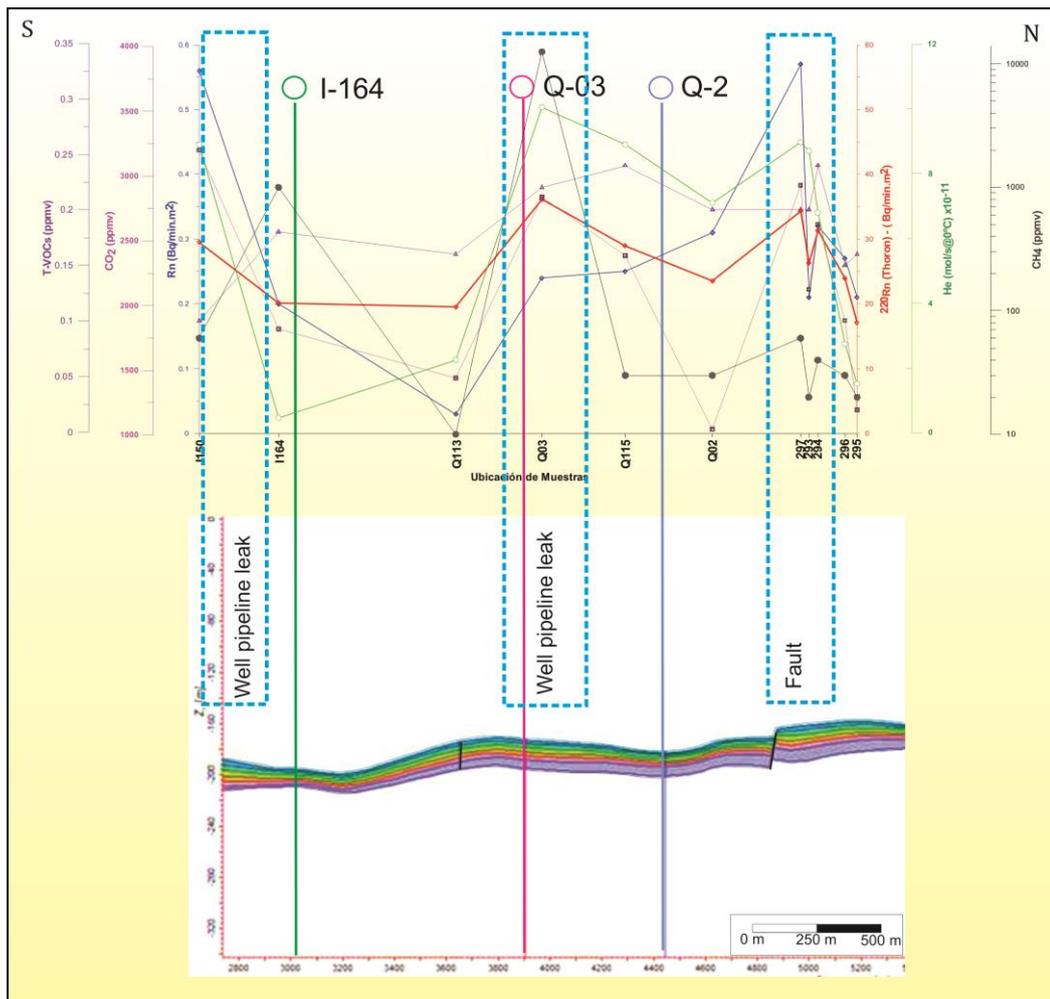


Figure 9. Cross section and results

## Discussion

All the data was plotted in a geological cross-section that show the main structures. As it can be seen, radon, thoron, helium fluxes and carbon dioxide concentration follow a similar trend to what was expected. To the contrary, methane and *T*-VOCs do not show a clear relationship with the inferred faults.

The pattern of radon and thoron fluxes close to the Q-2 well resembles examples from the literature (i.e.: Dubinchuk, 1991, King, 1991, in IAEA, 1993).

Other sites (not shown in the cross section) like at the I-150 well, located close to faults, also show evidence of helium, radon, thoron and carbon dioxide anomalies. The ability of this kind of surveys to identify well and pipeline leaks was noted in the Q-3 well location, where local gas anomalies (unrelated to the structure) were found and led to well inspection and pipeline repair (Figure 8 y 9).

## 4. Conclusions

Monitoring of Diadema UGS is carried out with different tools, which allow for an adequate control of operating activities. The use of new techniques related to soil gas analysis and fluxes contribute to enhancing knowledge and preventing risks. The results of the pilot study suggest that helium, radon, thoron fluxes and carbon dioxide soil gas concentrations seem to be the most promising techniques to be used in these activities.

The monitoring program is ongoing, with the addition of new tools to control developments in the gas bubble in the reservoir.

The results of the isotopic and geochemical analyses have indicated that, at present, there is no evidence of natural gas migration from Diadema UGS to the overlying aquifers.

## References

- Oстера, Héctor A. (2011). "Aplicación de Isótopos en Almacenamientos Subterráneos de Gas Natural – ASGN Diadema, Etapa 6" – Internal Report.
- Oстера, H., Fasola, M., Rodríguez, J.J. et. al. (2008). "Diadema - Underground Gas Storage Monitoring". South American Symposium on Isotope Geology. CD-ROM Edition 5 - San Carlos de Bariloche.
- IAEA, 1993. Isotopic and geochemical precursors of earthquakes and volcanic eruptions. Proceedings of an Advisory Group meeting, Vienna, 9-12 September 1991. IAEA TECDOC 726.
- Ozima M. and Podosek F. A. (1983) Noble Gas Geochemistry. Cambridge University Press.
- Ballentine C. J., O'Nions R. K., and Coleman M. (1996) A Magnus opus: He, Ne and Ar isotopes in a North Sea oil field. *Geochim. Cosmochim. Acta* 60, 831–849.
- Hale, M. 2000. Handbook of exploration geochemistry. Volume 7. Springer, Berlin.
- Salazar, J.M.L., Pérez, N.M., Hernández, P.A., Soriano, T., Barahona, F., Olmos, R., Cartagena, R., López, D.L., Lima, R.N., Melian, G., 2002. Precursory diffuse carbon dioxide degassing signature related to a 5.1 magnitude earthquake in El Salvador, Central America. *Earth Planet. Sci. Lett.* 205 (1–2), 81–89.

- Yang TF, Italiano F, Heinicke J (2005b) Special issue on Recent Progress in Gas Geochemistry – Preface. *Geochemical Journal*, 39, 395.
- Burton, M., Neri, M., Condarelli, D., 2004. High spatial resolution radon measurements reveal hidden active faults on Mt. Etna. *Geophys. Res. Lett.* 31 (7), 1–4.
- King, C.-Y., King, B.-S., Evans, W.C., Zhang, W., 1996. Spatial radon anomalies on active faults in California. *Appl. Geochem.* 11 (4), 497–510.
- Reimer, G. M., 1976. Design and assembly of a portable helium detector for evaluation as a uranium exploration instrument, U.S. Geol. Surv. Open File Rep. 76-398, 18.
- Reimer, G. M., Design and assembly of a portable helium detector for evaluation as a uranium exploration instrument, U.S. Geol. Survey. Open File Rep. 76-398, 18, 1976.
- Dyck, W., and J. C. Pelchat, A semi-portable helium analysis facility, Report of Activities, Part C, *Geol. Surv. Can. Pap.* 77-1C, 85-87, 1977.
- Baubron, J.-C., Allard, P., Sabroux, J.-C., Tedesco, D., Toutain, J.-P., 1991. Soil gas emanations as precursory indicators of volcanic eruptions. *J. Geol. Soc. Lond.* 148, 571–576.
- Toutain, J.-P., Baubron, J.-C., 1999. Gas geochemistry and seismotectonics: a review. *Tectonophysics* 304 (1–2), 1–27.
- Chiodini, G., Cioni, R., Guidi, M., Raco, B., Marini, L., 1998. Soil CO<sub>2</sub> flux measurements in volcanic and geothermal areas. *Appl. Geochem.* 13 (5), 543–552.
- Rodríguez, J.J., Osters H., Simeoni, A., Santistevan, P. y Buitrago, H. (2012). “Isotopic Techniques to Monitor Gas Releases at Underground Gas Storage Diadema – Argentina”. World Gas Conference 25th Kuala Lumpur. CD-ROM.
- Rodríguez, J.J., Osters, H. y Fasola, M. (2009) “Integrated Monitoring Tools in Diadema UGS – World Gas Conference 24th”. Buenos Aires. CD-ROM.
- Rodríguez, J.J. and Morisseau, J.M. (2003). “Diadema. The First Underground Storage Facility For Natural Gas in Argentina. World Gas Conference 23rd. Tokio. CD-ROM
- Rodríguez, J. J. and Santistevan, P. (2001). “Diadema Project – Underground Gas Storage in a Depleted Field in Patagonia”. SPE 69522.
- Schoell, M. and P.D. Jenden. (1993). “Isotope Analyses of Gases in Gas Field and Gas Storage Operations”. SPE 26171.