Zero Emission Porto Tolle (ZEPT) Project

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Ricerca

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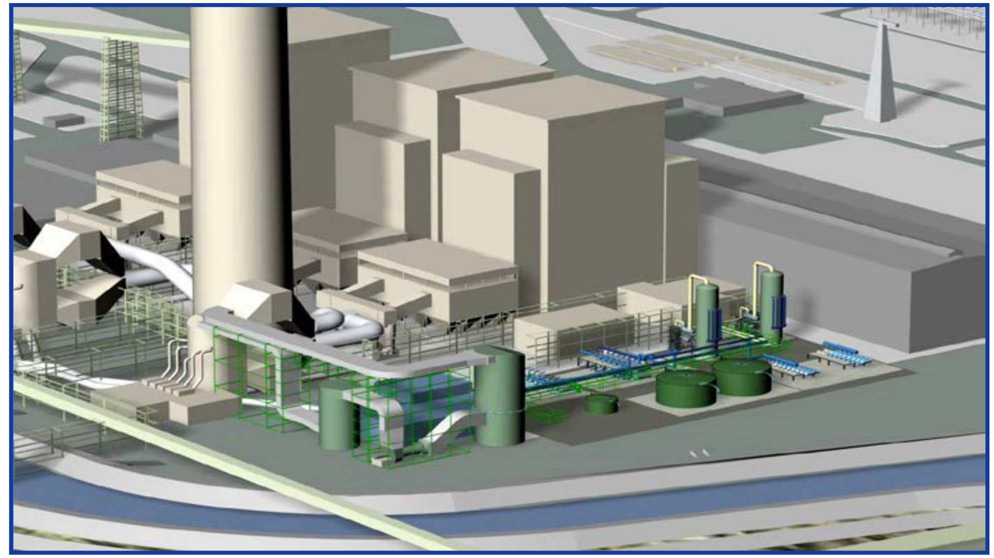
Porto Tolle CCS Demo Project



Project developer: ENEL

Power plant:

- Retrofit of oil-fired power plant to 3 USC coal-fired units of 660 MWe

Capture

- Retrofit of a stream of 660MW unit: 250MWe (net) post-combustion.

Transport

- 100-150km off-shore pipeline.

Storage

- Deep saline aquifer.
- 25 km offshore.
- ~1 $MtCO_2$/yr.

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1962 2012

Porto Tolle CCS Demo project update

Pilot in Brindisi has run over 5,000 hrs (promising results in the energy consumption and environmental results).

Capture: FEED Study – completed

Transport: Engineering – on going.

Injection: Feasibility studies for subsurface structure and injection system - completed.

Feed for platform and well(s) – to be started.

Storage: Site Selection – completed

- Modelling of storage site – completed
- Baseline area characterization – completed
- Environmental Impact studies for the appraisal well execution – completed

Transposition of Storage Directive accomplished; delays in technical decrees implementation

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Porto Tolle CCS Demo project

Permitting process update

In May 2011 the State Council of Italy decided to void the Environmental Authorization (EIA).

↓

new Environmental Impact Assessment to be submitted

↓

delays in the reconversion to coal and inevitable and inestimable delays in the commissioning of the CCS Demo Project

The monitoring: a transversal need

Site selection and characterization	Site preparation and well construction	Operation and performance assessment	Closure and post closure management
(~2-5 years) Site screening Site selection **Exploration permit** Site characterization	(~10-50 years) **Storage permit** Project develpment plan Site preparation Site construction Injection		(~100-1000 years) **Storage Closure permit** Decomissioning Site closure certificate Transfer of liability

Monitoring

Performance & Risk Assessment

Communication and Public Acceptance

Monitoring is one of the key activities to ensure the safety of geological storage as required by the CCS Directive and ETS Directive.

It is essential to assess whether injected CO2 is behaving as expected, whether any migration or leakage occurs, and whether any identified leakage is influencing the environment or human health

DIRECTIVE 2009/31/EC on the geological storage of carbon dioxide

art. 13 Monitoring e Annex II

The monitoring plan shall provide details of the monitoring to be deployed at the main stages of the project, including baseline, operational and post-closure monitoring. The following shall be specified for each phase:

(a) parameters monitored;

(b) monitoring technology employed and justification for technology choice;

(c) monitoring locations and spatial sampling rationale;

(d) frequency of application and temporal sampling rationale.

Baseline
Why?

Pre-injection measurements provide a general overview of the characteristics and peculiarities of the studied area.

The goal of this investigation is dual:

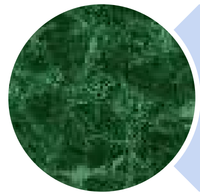
- ✓ identification of areas where it will be more likely to observe any leakage of CO2 and then planning of the continuous monitoring network where you will need to focus,
- ✓ obtain a database indicative of background values typical of the area and their natural variability.

The proper knowledge of the baseline is in fact important in the interpretation of data obtained from monitoring. The studied variables are characterized natural oscillations related to seasonality, but also by the periodic variation of intensity in the migration of endogenous gases.

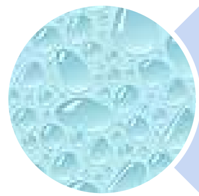
Baseline
Where?

Verify efficacy and safe of a CO2 storage site(**Environmental Monitoring**)

Atmosfere

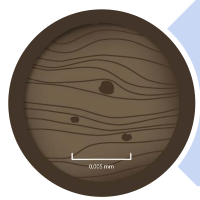


Surface

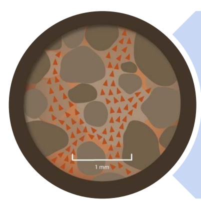


Ground water

Understanding the behavior of CO2 injected into the reservoir (**Operational Monitoring**)



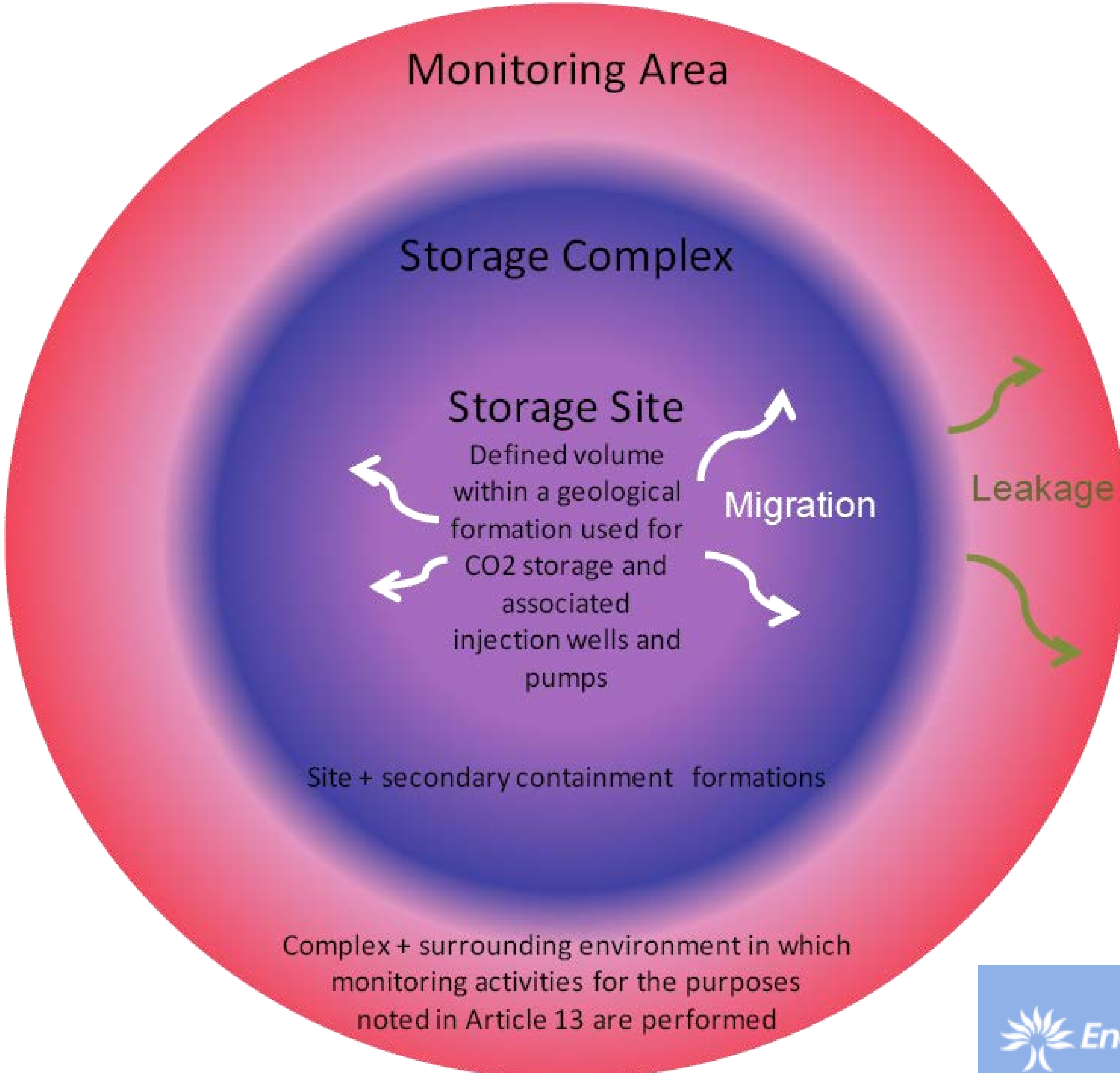
Caprock



Reservoir

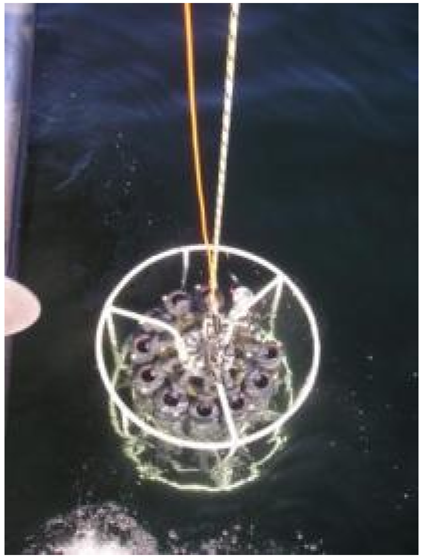
Baseline
Where?

Storage complex:
the storage site and surrounding geological domain which can have an effect on overall storage integrity and security; that is, secondary containment formations



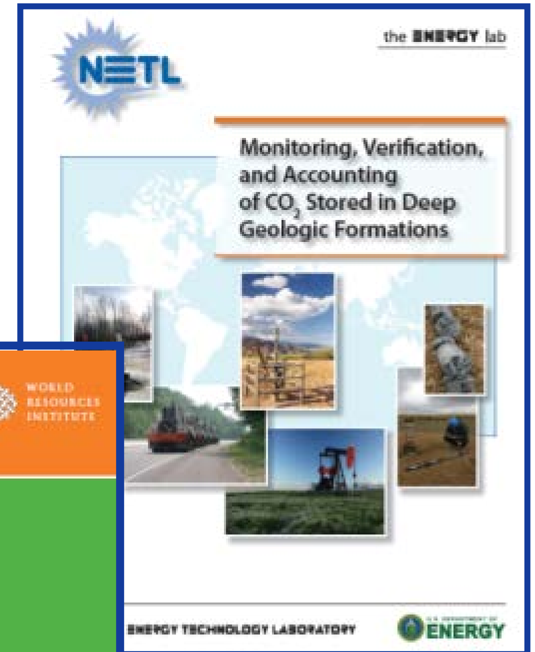
Baseline
What?

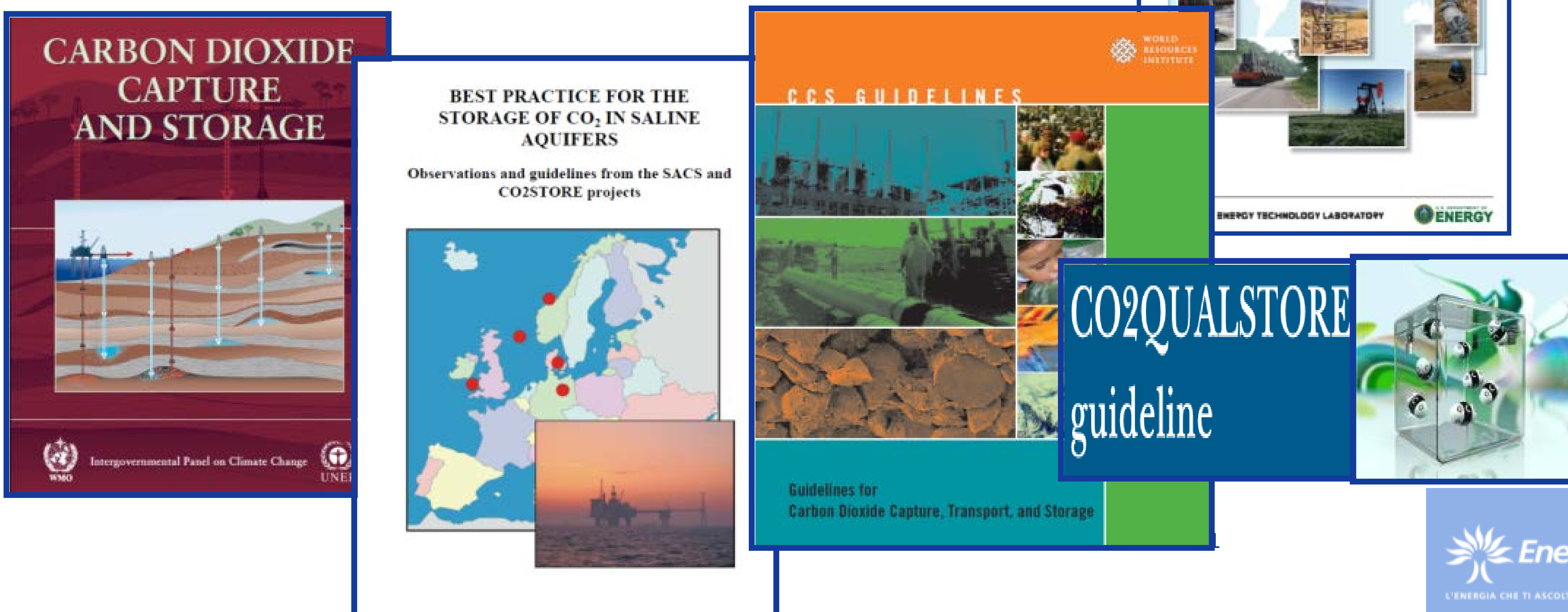
- ✓ Evaluation of formation gas and fluid characteristics in the storage reservoir and the surrounding area that might be affected by potential leakage, including aquifers;
- ✓ Measurements of background CO2 emissions at surface or sea floor;
- ✓ Surface and near surface environmental surveys;
- ✓ Seabed, surface or near surface baseline surveys to define any pre-existing leakage indicators such as pock marks;
- ✓ Ground surface surveying, where ground movement can be a risk




Best Practices

The "new" approach is to share a methodology in order to ensure a common work flow.





Design of an site monitoring program

1. Review all available proven and potential monitoring technologies.
2. Select which particular techniques are required to achieve the required objectives.
3. Design appropriate field deployment parameters to achieve effective monitoring.

This final step will in all likelihood require significant modeling work, including a comprehensive sensitivity analysis.

Potential monitoring tools

				acoustic imaging			well based		sonar bath.		grav.		Electric/o magnetic						downhole			marine		atmosphere				soil gas			remote sensing			Other		
																			Fuilds				gasses													
	Seismic																		Geochemical																	
	3D/4D surface seismic	Time lapse 2D surface seismic	Multicomponent seismic	Boomer / Sparker	High resolution acoustic imaging	Microseismic monitoring	4D cross-hole seismic	4D VSP	Sidescan sonar	Multibeam echo sounding	Time lapse srface gravimetry	Time lapse well gravimetry	Surface EM	Seabottom EM	Cross-hole EM	Permanent borehole EM	Cross-hole ERT	ESP	Downhole fluid chemistry	pH measurement	Tracers	Seawater chemistry	Bubble stream chemistry	Short closed path (NDIRs & IR)	Short open path (IR diode lasers)	Long open path (IR diode lasers)	Eddy covariance	Gas flux	Gas concentrations	Ecosystems studies	Airborne hyperspectral imaging	Satellite interferometry	Airborne EM	Geophysical logs	Pressure / temperature	Tiltmeters
on / off shore	on & off shore	on & off shore	on & off shore	off shore	off shore	on & off shore	on & off shore	on & off shore	off shore	off shore	on & off shore	on & off shore	on shore	off shore	on & off shore	on & off shore	on & off shore	on shore	on & off shore	on & off shore	on & off shore	off shore	off shore	on & off shore	on & off shore	on & off shore	on & off shore	on shore	on shore	on & off shore	on & off shore	on shore	on & off shore	on & off shore	on & off shore	on & off shore
deep	primary	primary	primary				primary	primary			primary	primary		primary	primary	primary	primary	primary	primary	primary	primary											primary		primary	primary	primary
shallow	secondary			primary	primary				primary	primary			primary	primary				secondary	primary	primary	primary	primary	primary	primary	primary	primary	primary	primary	primary	primary	primary		primary			secondary
plume location migration	primary	primary	primary	secondary	secondary	secondary	secondary	secondary			secondary		secondary	secondary				primary														primary				secondary
fine scale process	secondary	secondary	primary				primary	primary				secondary			secondary	secondary	secondary		secondary	secondary	secondary													primary		secondary
leakage	secondary			primary	primary				primary	primary			secondary					secondary	primary	primary	primary	primary	primary	primary	primary	primary	primary	primary	primary	primary	primary		primary		primary	
quantification	primary						secondary				secondary								secondary	secondary	secondary	secondary	secondary	secondary	secondary	secondary	secondary	secondary	secondary		secondary			secondary	secondary	

▇	on shore
▇	off shore
▇	on & off shore

▇	primary use
▇	secondary use

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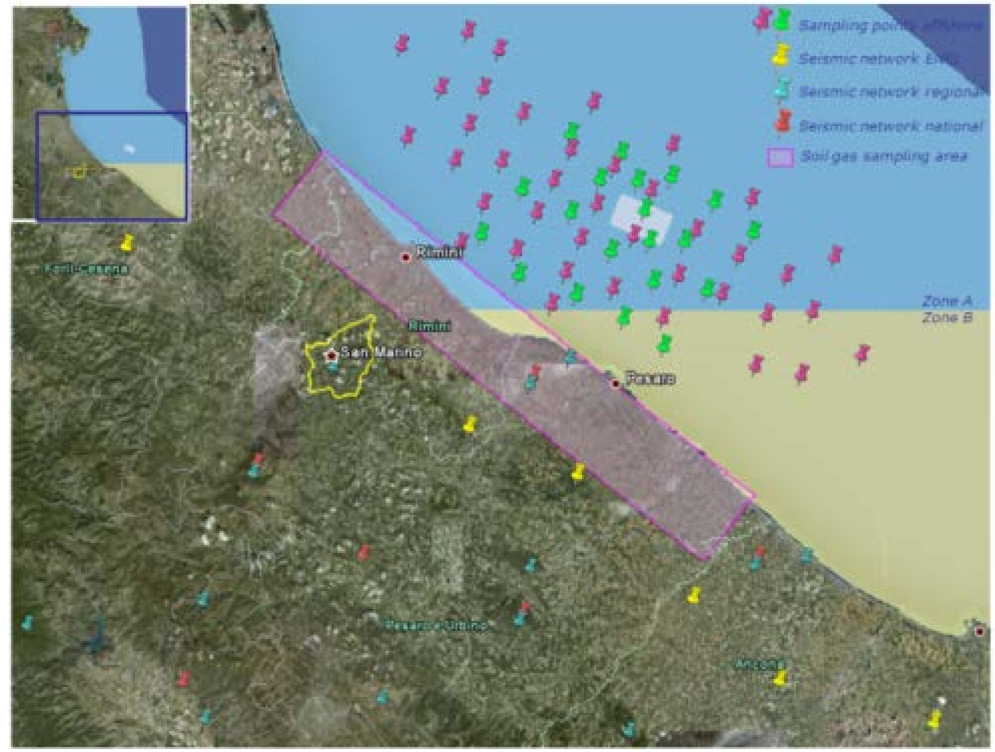
ZEPT Project approach

Site characterization: Pre-injection CO2 baseline

On-shore	soil gas and diffusive degassing
	Shallow aquifer and dissolved gas
	microseismicity
Off-shore	physical and chemical characterization of the column and dissolved gases
	characterization of sediment interface and water/sediment
	benthic communities
	oceanographic measurements
	chemical-physical parameter continuous monitoring

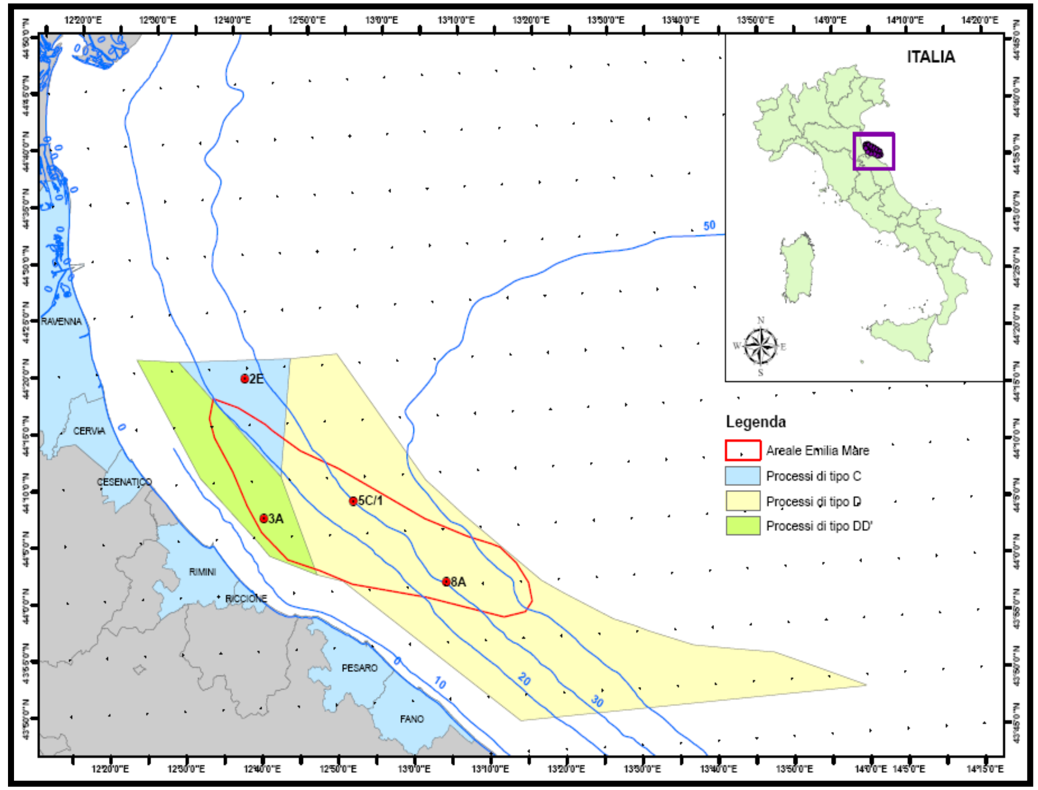


The activities are carried out in collaboration with **INGV, OGS, URS, RSE**

Pre-injection off-shore survey

The baseline study covers a ~ 400 km^2 area around the more probable injection locations in water depths ranging from 13 to 40 m.

Measurements include chemical, biological and physical analyses of both the water column and the near-surface sediments during four different periods of the year to define the ranges of baseline values in the area, both spatially and temporally.



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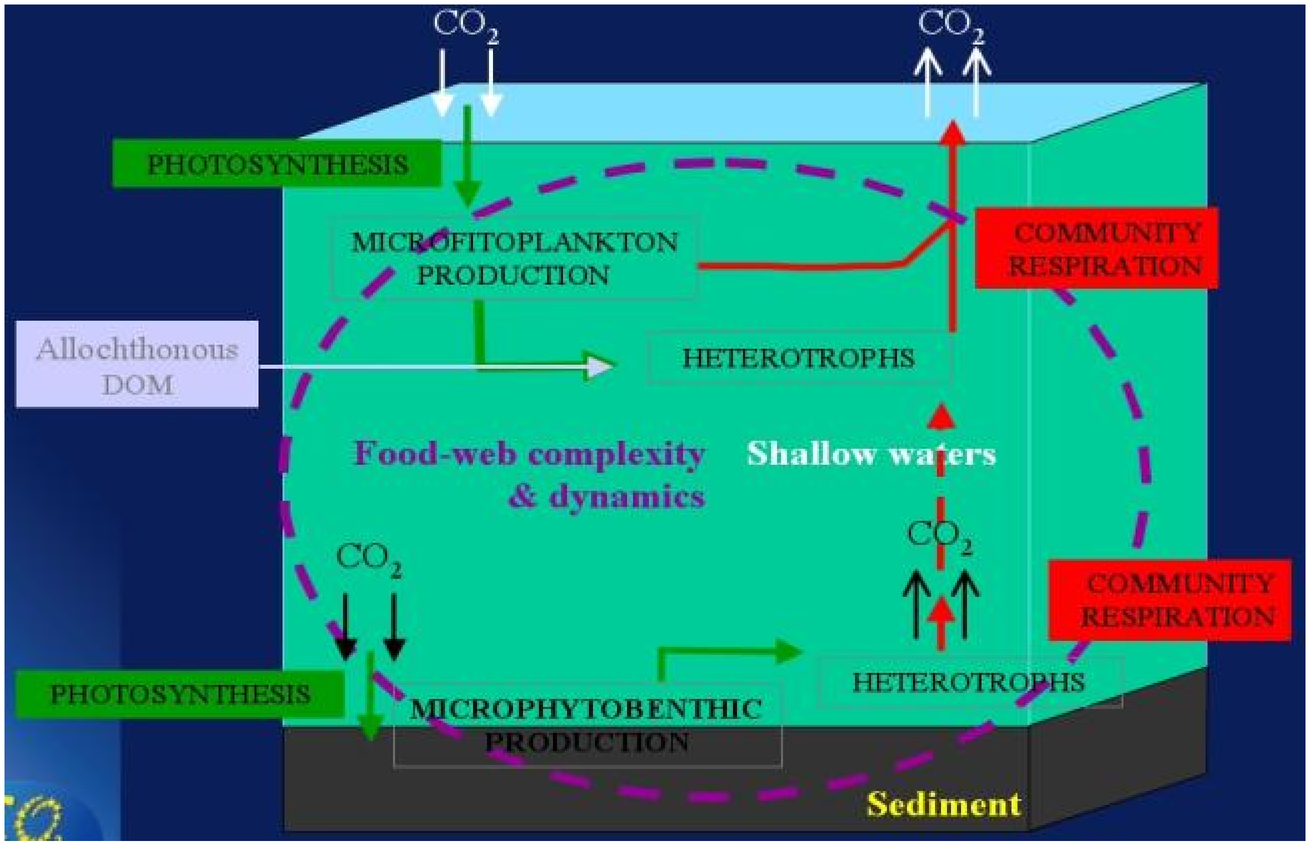
What effects on the marine ecosystem?



Courtesy of OGS-CO2GeoNet

- pH and pCO2
- biogeochemical carbon cycle
- diagenetic processes
- mobilization of pollutants in sediments deposited
- processes of production and respiration
- physiology
- calcification in different organisms
- ...

→ Effect on organism

The increase of CO2 in seawater reduces the availability of carbonate ions necessary for marine calcifying organisms such as corals, molluscs, echinoderms and crustaceans to produce their skeletons or shells of their CaCO3

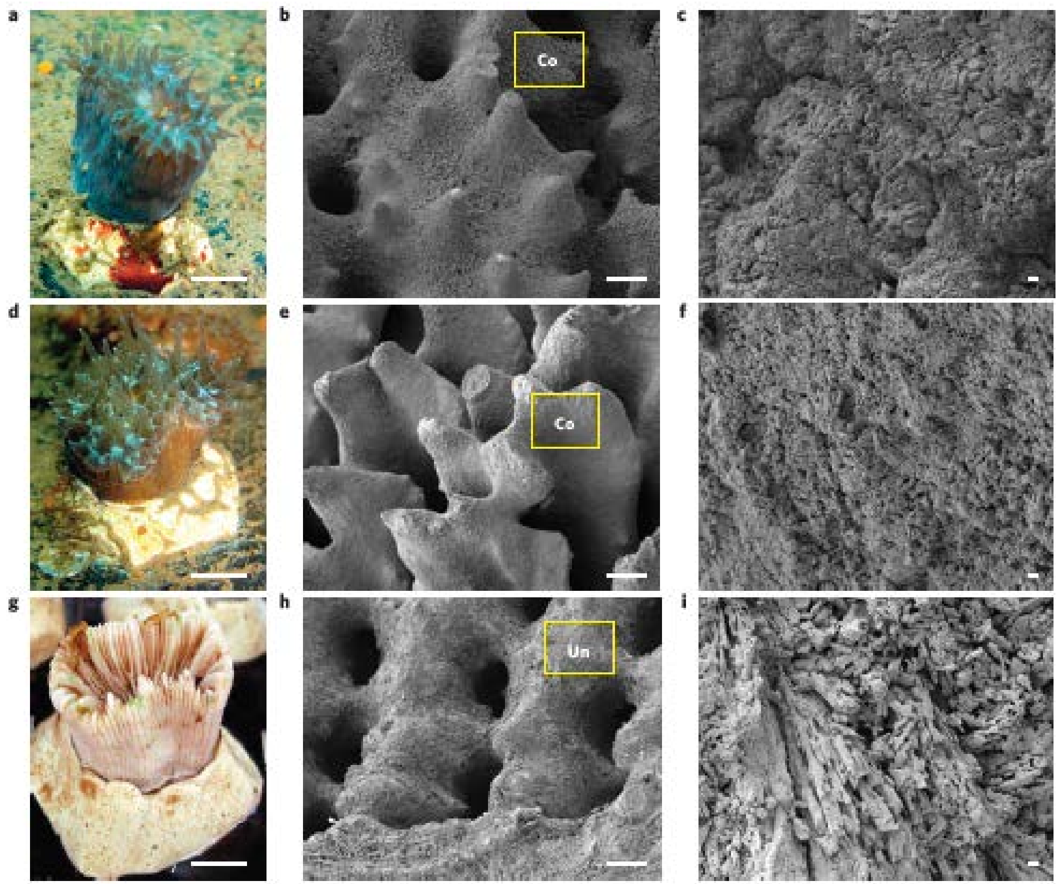


Figure 4 Underwater and scanning electron microscopy images of *B. europaea* transplanted along a CO_2 gradient off Ischia. a–f, Live coral after seven months at mean pHT 8.1 (a–c) and 7.3 (d–f). g–i, Dead coral after three months at mean pHT 7.3 (Supplementary Table S2a). Details of the outer corallite wall showing normal skeleton when covered (Co) in tissue (b,e) and dissolved skeleton when uncovered (Un) in tissue (h) . Enlargements (yellow boxes on b, e, h) show organized (c,f) and dissolved (i) bundles of aragonite crystals. Scale bars: 1 cm (a,d,g), 100 µm (b,e,h) and 1 µm (c,f,i).

Rodolfo-Metalpa *et al.* 2011

→ Examples of the response of marine fauna to acidification

Species	Description	CO_2 system parameters	Sensitivity
Planktonic foraminifera			
Orbulina universa	Symbiont-bearing	pCO_2 560–780 ppmv	8–14% reduction in shell mass
Globigerinoides sacculifer	Symbiont-bearing	pCO_2 560–780 ppmv	4–8% reduction in shell mass
Cnidaria			
Scyphozoa Hydrozoa	Jellyfish	North Sea seawater pH drop from 8.3 to 8.1	Increase in frequency as measured by CPR from 1958 to 2000
Mollusca			
Clio pyramidata	Shelled pteropod	Ω_{arag} <1	Shell dissolution
Haliotis laevigata	Greenlip abalone	pH 7.78; pH 7.39	5% and 50% growth reductions
Haliotis rubra	Blacklip abalone	pH 7.93; pH 7.37	5% and 50% growth reductions
Mytilus edulis	Mussel	pH 7.1 / 10 000 ppmv pCO_2 740 ppmv	Shell dissolution 25% decrease in calcification rate
Crassostrea gigas	Oyster	pCO_2 740 ppmv	10% decrease in calcification rate
Mytilus galloprovincialis	Mediterranean mussel	pH 7.3, ~5000 ppmv	Reduced metabolism, growth rate
Placopecten magellanicus	Giant scallop	pH < 8.0	Decrease in fertilization and emb development
Tivela stultorum	Pismo clam	pH <8.5	Decrease in fertilization rates
Pinctada fucada martensii	Japanese pearl oyster	pH 7.7 pH >7.4	Shell dissolution, reduced growth Increasing mortality
Mercenaria mercenaria	Clam	Ω_{arag} = 0.3	Juvenile shell dissolution leading t increased mortality
Illex illecebrosus	Epipelagic squid	2000 ppmv	Impaired oxygen transport
Dosidicus gigas	Epipelagic squid	0.1% CO_2, ~1000 ppmv	Reduced metabolism/scope for activity

V. J. Fabry et al. 2008

In addition to calcification, the increase of pCO2 influence a number of other physiological processes associated with adjustment mechanisms such as acid-base survival, growth, development, metabolism

Rome, April 18th 2013

Species	Description	CO_2 system parameters	Sensitivity
Sipuncula			
Sipunculus nudus	Peanut worm	1% CO_2, 10 000 ppmv	Metabolic suppression Pronounced mortality in 7-week exposure
Vertebrata			
Scyliorhinus canicula	Dogfish	pH 7.7 / 0.13%CO_2 7% CO_2, ~70 000 ppmv	Increased ventilation 100% mortality after 72 h
Sillago japonica	Japanese whiting	7% CO_2, ~70 000 ppmv	Rapid mortality in 1-step exposure
Paralichthys olivaceus	Japanese flounder	5% CO_2, ~50 000 ppmv	100% mortality within 48 h
Euthynnus affinis	Eastern little tuna	15%CO_2, ~150 000 ppmv	100% mortality of eggs after 24 h
Pagrus major	Red sea bream	5%CO_2, ~50 000 ppmv	>60% larval mortality after 24 h
Seriola quinqueradiata	Yellowtail/amberjack	5% CO_2, 50 000 ppmv	Reduced cardiac output; 100% mortality after 8 h
Sparus aurata	Mediterranean fish	pH 7.3, ~ 5000 ppmv	Reduced metabolic capacity
Dicentrarchus labrax	Sea bass	pH 7.25, 24 mg l^{-1} CO_2	Reduced feed intake
Arthropoda			
Acartia steueri	Copepod	0.2-1%CO_2,	Decrease in egg hatching success;
Acartia erythraea	Copepod	~2000–10 000 ppmv	increase in nauplius mortality rate
Copepods	Pacific, deep vs. shallow	860–22 000 ppmv CO_2	Increasing mortality with increasing CO_2 concentration and duration of exposure
Euphausia pacifica	Krill	pH < 7.6	Mortality increased with increasing exposure time and decreasing pH
Paraeuchaeta elongata	Mesopelagic copepod		
Conchoecia sp.	Ostracod		
Cancer pagurus	Crab	1% CO_2, ~10 000 ppmv	Reduced thermal tolerance, aerobic scope
Chaetognatha			
Sagitta elegans	Chaetognath	pH <7.6	Mortality increased with increasing exposure time and decreasing pH
Echinodermata			
Strongylocentrotus purpuratus	Sea urchin	pH ~6.2–7.3	High sensitivity inferred from lack of pH regulation and passive buffering via test dissolution during emersion
Psammechinus miliaris	Sea urchin		
Hemicentrotus pulcherrimus	Sea urchin	~500–10 000 ppmv	Decreased fertilization rates, impacts larval development
Echinometra mathaei	Sea urchin		
Cystechinus sp.	Deep-sea urchin	pH 7.8	80% mortality under simulated CO_2 sequestration

Benthos census

The abundance and biodiversity of the autotrophic and heterotrophic benthic communities was analysed on a subset of stations during 2 of the campaigns (winter and summer) in order to characterize the present status of the ecosystem and, possibly, to identify the most sensitive species.

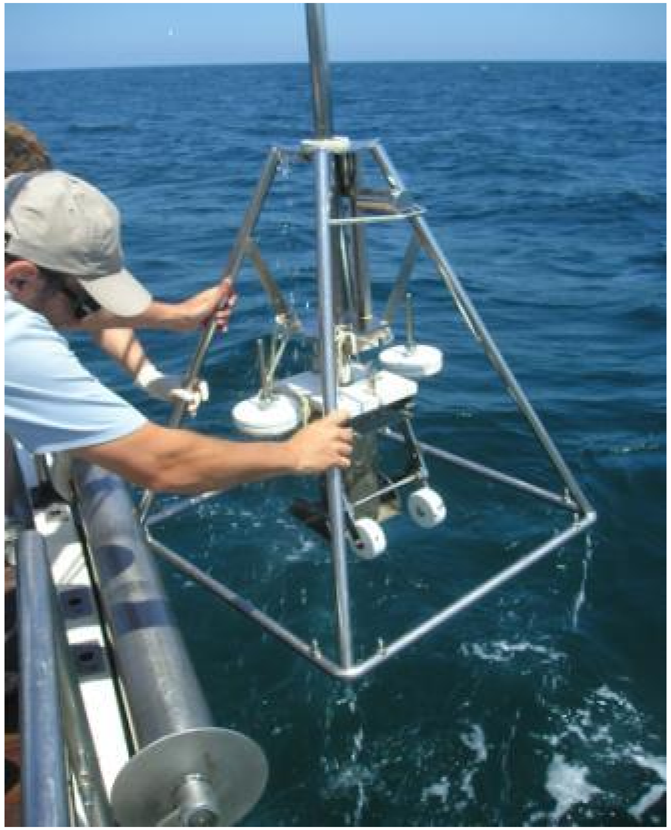
For macrobenthos determinations, three replicate samples will be collected in a grid of selected stations across the investigated area. Grab samples will be collected and all organisms retained in 1 mm mesh sieves will be fixed and preserved in formaldehyde-seawater solution until the successive determination. Other benthic communities will be subsampled from cores.

Box corer which was used to collect sediment samples for microphytobenthos and meiobenthos.

Macrozoobenthos

Discontinuous sediment cores sampling

19 to 20, 30 cm long box cores were collected during each cruise and 10-20 cm of the overlying bottom water (supernatant), with all cores being extruded and sub-sampled at the site.



Chemical / biochemical measurements in sediment cores

For the analyses of porewater components, sediment slices from the extruded core will be centrifuged, and the interstitial waters analysed for a series of parameters. Comparison of these results with the supernatant results will allow for the calculation of diffusive fluxes. Analyses will include DIC, DOC and inorganic nutrients, Eh and total organic carbon and nitrogen, chlorophyll a, major elements, and selected trace elements. Depending on sediment grain size, also H2S porewater analyses will be performed.
Moreover, selected samples will be analysed for δ13C on organic matter and DIC. The stable 13C isotopic composition of DIC (13CDIC), in fact, could be used as a sensitive indicator of processes affecting the production of DIC because the 13C composition of sedimentary organic matter differs significantly from that of carbonates and DIC in the bottom water layer. In general, dissolution of carbonates would add DIC enriched in 13C with respect to the sedimentary organic matter.

Water column sampling – discontinuous measurements

Bottom water samples were collected from 10 (or more) sampling stations using Niskin bottles mounted together with a CTD probe for conductivity, temperature, pressure, fluorescence, pH and dissolved O2 measurements.

Water samples were analyzed for pH, dissolved inorganic and organic carbon (DIC, DOC), alkalinity, dissolved O2, chlorophyll a (chl a), particulate organic carbon and nitrogen (POC, PON), inorganic nutrients (phosphate, nitrate, nitrite, ammonium, silicate), major elements and selected trace elements. Moreover, on selected samples δ13C analyses were performed on organic matter and carbonates, in order to investigate their origin.

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Bentic chamber

weight (in air) (kg)	67
Dimensioni (i.d. x h) (cm)	63 x 27
Volume (L)	~ 84-128
Surface (cm^2)	3116
Material	Plexiglas®
thickness DBL (μm)	400
Mixing Time (minuti)	5
Max. ΔP (Pa)	1
Cutting velocity (cm/s)	0,17

The implementation of an in-situ monitoring activity of the natural baseline levels of dissolved CO_2 at the sediment-water interface of aquatic ecosystems, requires the use of devoted sampling equipment and analytical instrumentation.

In this study, a BC equipped with an automatic and programmable system (VAMPIRONE) for the sampling of the aqueous samples and a multiparametric probe able to in-situ acquisition of the physico-chemical data of the inside water, was used.

Benthic fluxes at the sediment-water interface will be computed applying the following formulation:

$$\text{Flux} = (\delta C/\delta t)\ (V_{eff.}/A)$$

Where: $V_{eff.}$ is the volume of the water inside the BC (obtained from the addition of a CsCl tracer); A is the area of sediment covered by the BC, and $\delta C/\delta t$ is the temporal variation of the concentration of the considered parameter.

GD-FIA/Conductometry Analyser

In order to define the chemical speciation of the dissolved CO_2 in seawater, an analytical technique based on the Flow Injection Analysis (FIA) coupled with a gas diffusion semipermeable membrane (GD) and a conductometric micro detector, was developed.

This instrumentation is able to determine low levels of CO_2 both as dissolved (solvated) gaseous molecular form (CO_2aq) and as total Dissolved Inorganic Carbon (DIC) integrated parameter, simply injecting in the analyser the untreated and the acidified seawater sample.

Besides, the need for carrying out the measurements just after the recovery of the samples, in order to minimize their alterations, imposes that the analytical determinations must be performed on board.

This constraint, in his turn, imposes the availability of analytical instrumentation that, as well as assuring suitable analytical performance, has to be small sized, transportable and sturdy.

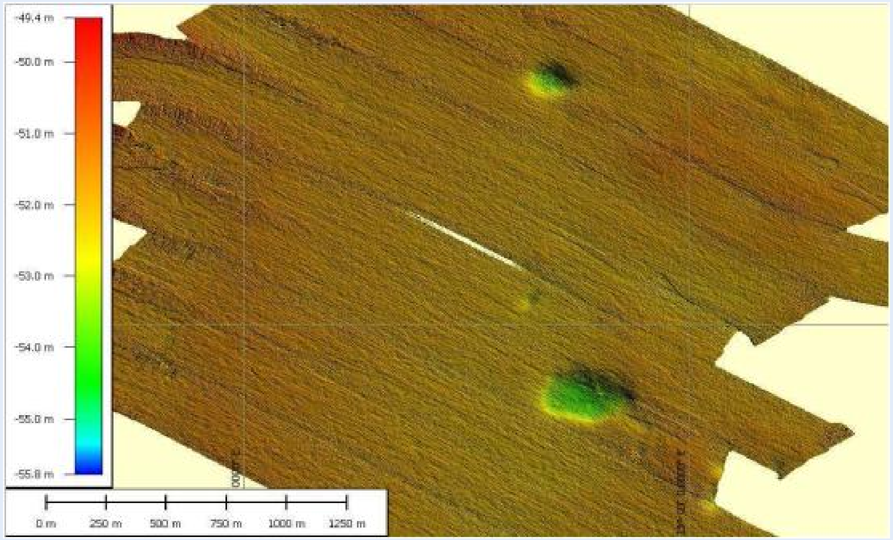
Analytical methodologies

The analytical techniques used for the measurements of the considered parameters were the following:

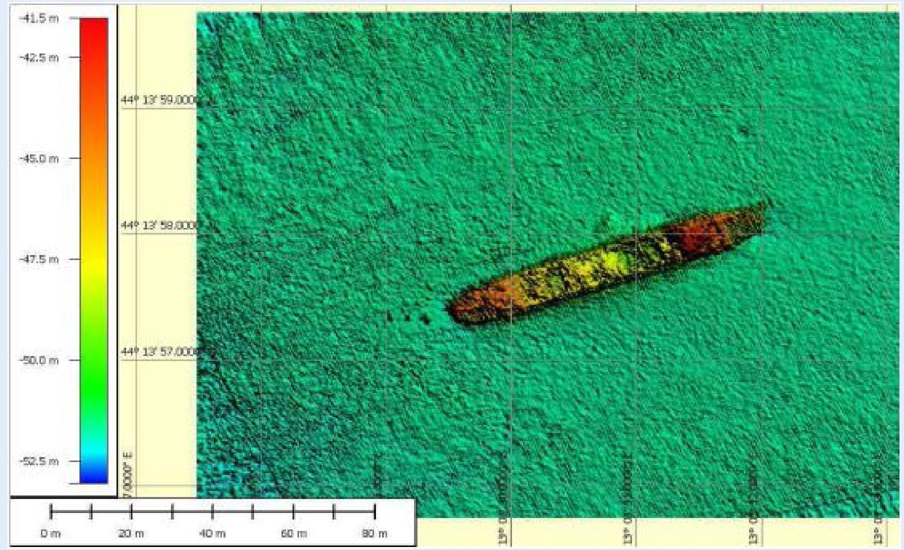
- ✓Potentiometric titration (TAlk)
- ✓Flame Emission Spectrometry (FES), Atomic Absorption Spectrometry (AAS), and Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) (metals)
- ✓CHN elemental analyser (TC, TH and TN)
- ✓Accelerator Mass Spectrometry (AMS) ($\delta^{13}C_{DIC}$ and $\Delta^{14}C_{DIC}$ in the DIC)
- ✓Continuous Flow - Isotope Ratio Mass Spectrometry (CF-IRMS) ($\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$, C_{org}tot (TOC) and TN in the SOM)
- ✓Automated UV-Vis Spectrophotometry (Autoanalyzer) (nutrients)
- ✓High Performance Liquid Chromatography (HPLC) (Cl, SO_4)
- ✓Sieves and X-rays sedigraph analyser (grain-size distribution)
- ✓Essication (porosity and water content)
- ✓GD-FIA/Conductometry and coulometry (DIC)
- ✓GD-FIA/Conductometry (dissolved CO_2)
- ✓Multiparametric probe and CTDOFT (physico-chemical parameters)

Site survey

Multibeam (echo-sounder)



Area with "pockmark"-like structures

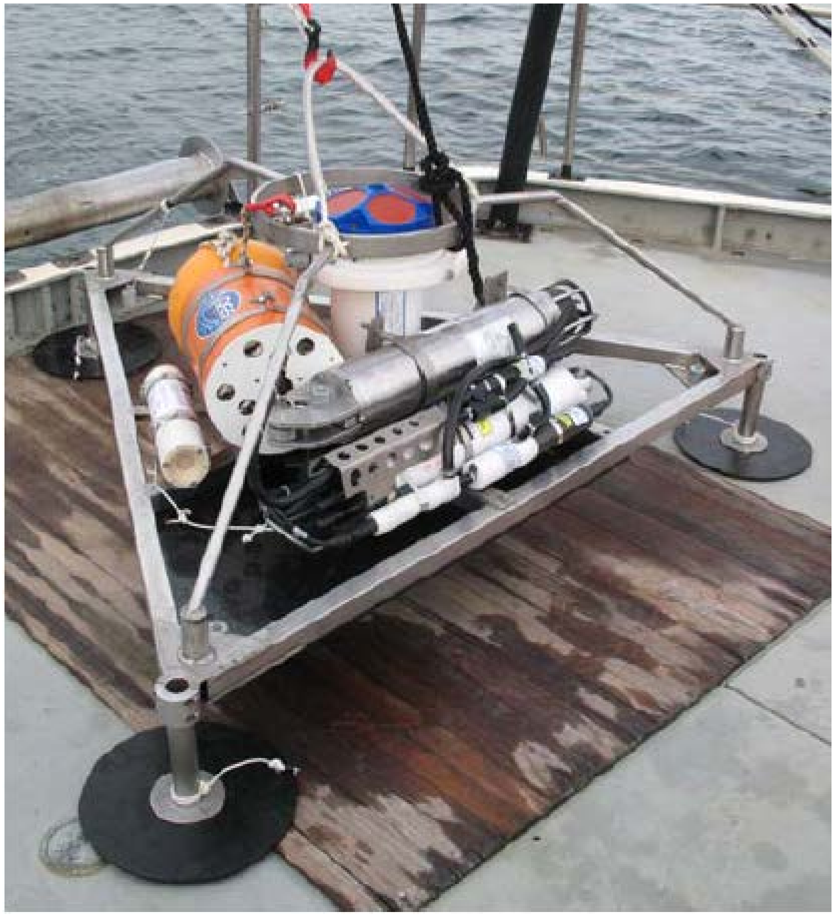


"Anni" ship wreck

Chirp SBS
(Sub Bottom Profiling)

Sedimentary structures under the seafloor and profile of the M/n "Anni" ship wreck

Continuous monitoring: Deep lab station

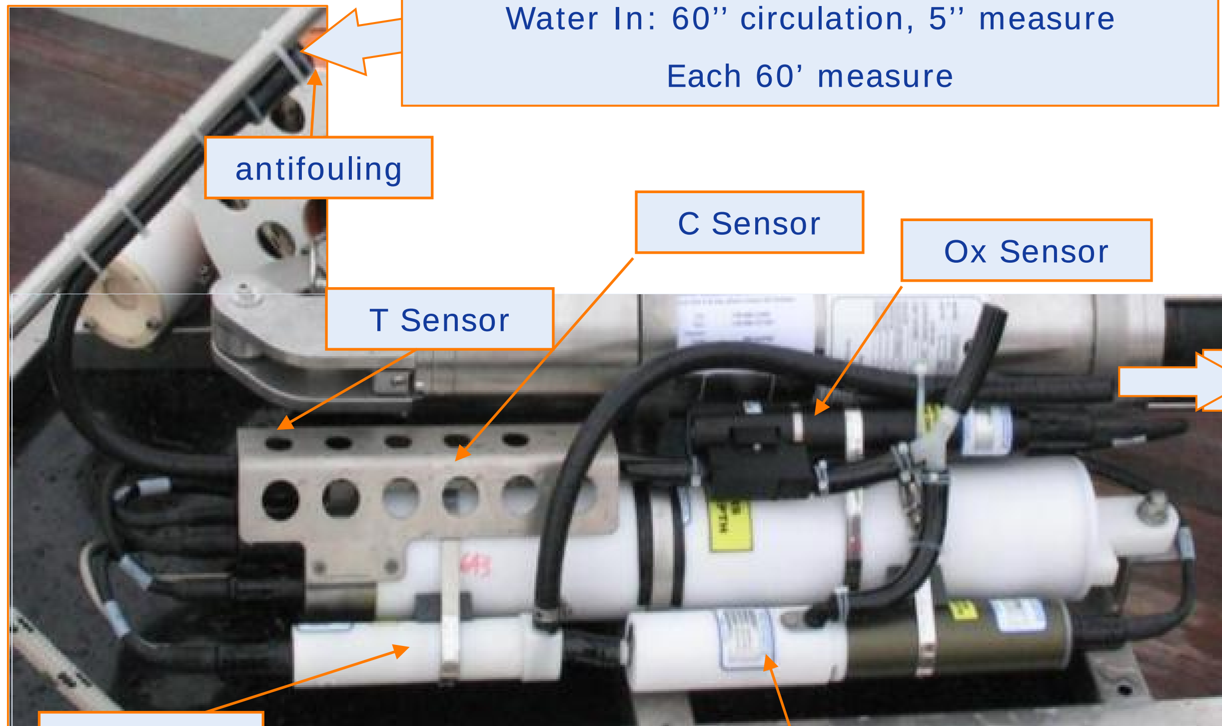


The two stations record time series of physical-oceanographic and chemical parameters of the bottom water and of the water column by using the following self recording instruments:

- a CTD probe SeaBird 16 Plus for temperature, conductivity, pressure and dissolved oxygen measurements.
- an upward facing Acoustic Doppler Current Profiler RDI 600 kHz Self-Contained Sentinel for current direction and speed measurements at several depths, directional wave, temperature and sea level measurements.
- a CO_2/CH_4 probe.
- an acoustic transponder-releaser for position detection (acoustic telemetry) and retrieval of the station.

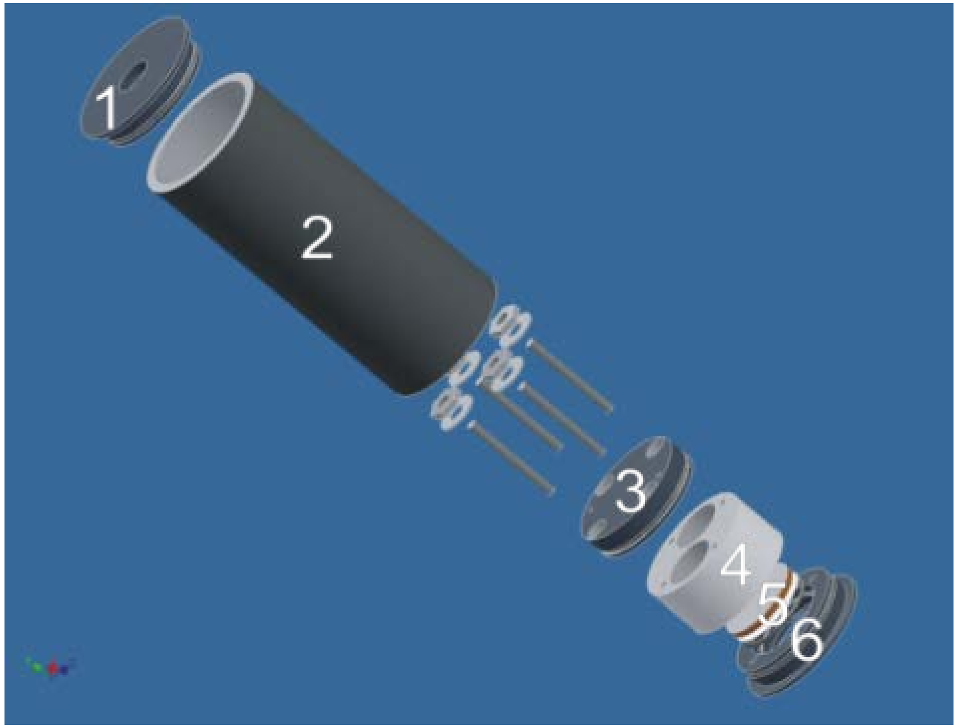
Deep lab station

Each station is constituted of a stainless steel pyramidal with triangular base frame (of about 1.6 m of leg) which holds the instruments and the sensors. Using acoustic commands sent from a deck unit and a transducer on board, a releaser-transponder fixed to the station permits to locate it by calculating the distance from the ship, and to release a buoy for its recover without the need of divers.



PARAMETER	RANGE	ACCURACY	RESOLUTION
Temperature (°C)	-5 to 35	0.005	0.0001
Conductivity (S/m)	0 to 9	0.0005	0.00005 S/m typical
Pressure (strain gauge)	0 to 100	0.1% of full scale range	0.002% of full scale range
PH	0-14 pH	0.1 pH	
Dissolved Oxygen	120% of surface saturation	2% of saturation	

Dissolved gas sensor stations



1. Top cap, USB connection and T sensor;
2. PVC cylinder hosts battery and electronics
3. Electronic support for NDIR sensor;
4. sensor support;
5. Teflon AF membrane (diameter 35 mm) and supporting porous metallic disk;
6. Bottom cup.

Type	Parameter	Range
NDIR-1	CH_4 CO_2	0-5% 0-5%
NDIR-2	CO_2	0-100%
Digital sensor	Temperature	-20°+80°

The configuration allows the system to record up to 5000 measurements and to have autonomy of 500 acquisition cycles with a warm-up time of 10 minutes

Laboratory tests

The sealing capacity of the probe has been tested up to a pressure of 5.5 bars using a custom built pressure chamber. During the test the chamber was filled with water and the pressure was incrementally increased using a compressor. The mounted IR sensors have a non linear response and vary as a function of temperature, and thus several tests were performed to determine the appropriate linearization parameters and to evaluate the temperature compensation coefficients

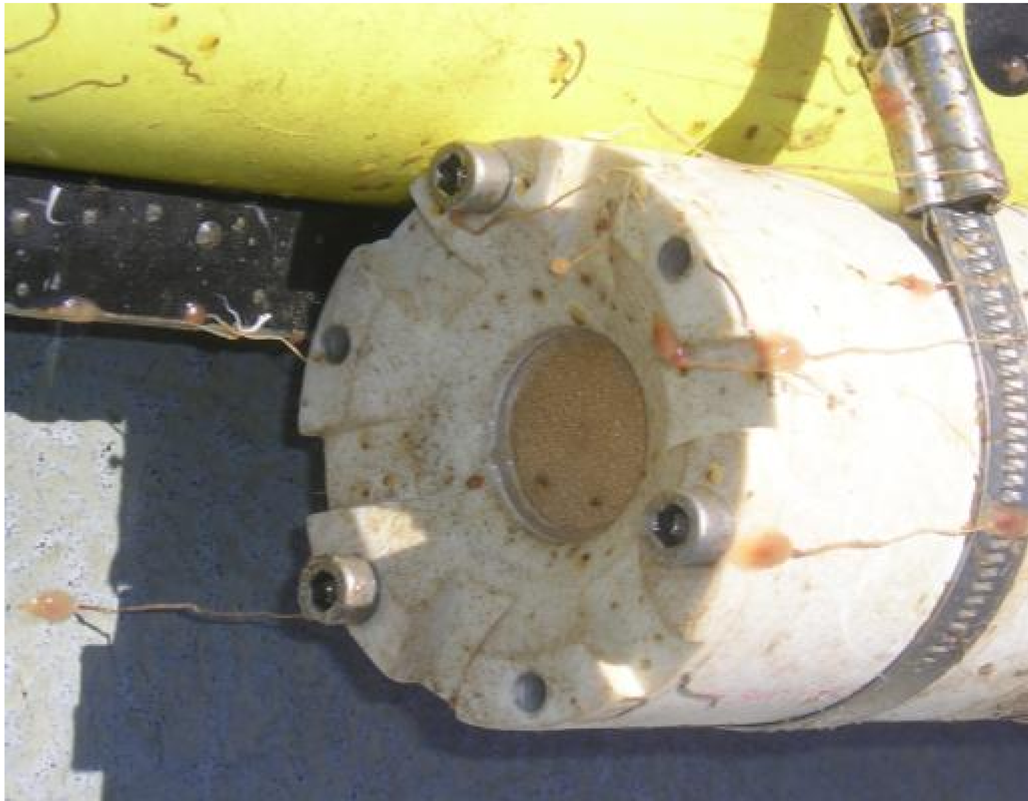
Standard calibration (zero and span) can be rapidly performed by connecting the probe to the computer and applying a flux of gas of known concentration, in this case pure nitrogen for the zero and then 5% CO_2, 100% CO_2, or 5% CH_4 for the span. By connecting the probe to the computer it is also possible to set the frequency of the daily measurements, the warm-up time of the sensors, the time of the real time clock, or to cancel the eeprom memory

Dissolved gas sensor stations

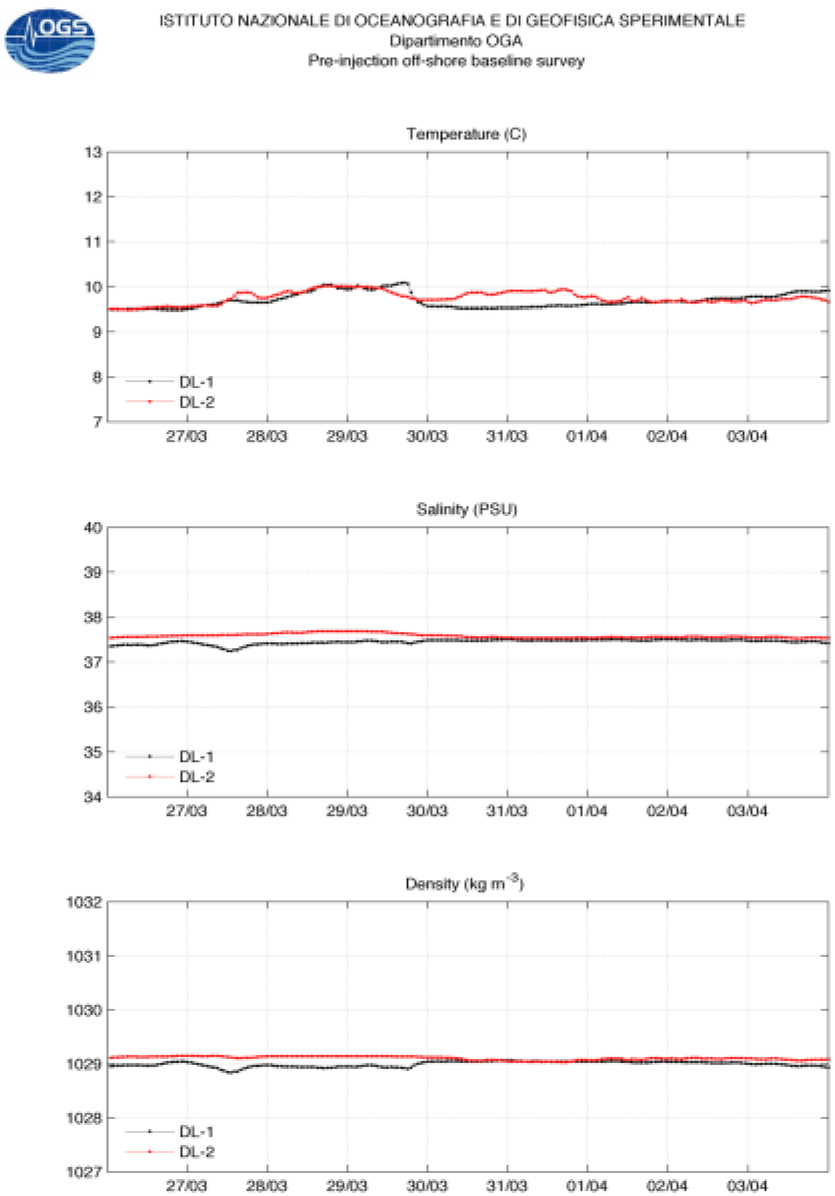
The acoustic release has a diameter of 102 mm and a length of 840 mm.

Thanks to this configuration the system is maintained in a vertical position during the acquisition period.
The system can be interrogated from the surface in order to verify the presence and distance.
The release command releases the ballast and sensor-blocking release pushed back to the surface by the buoy.

Some problem: fouling



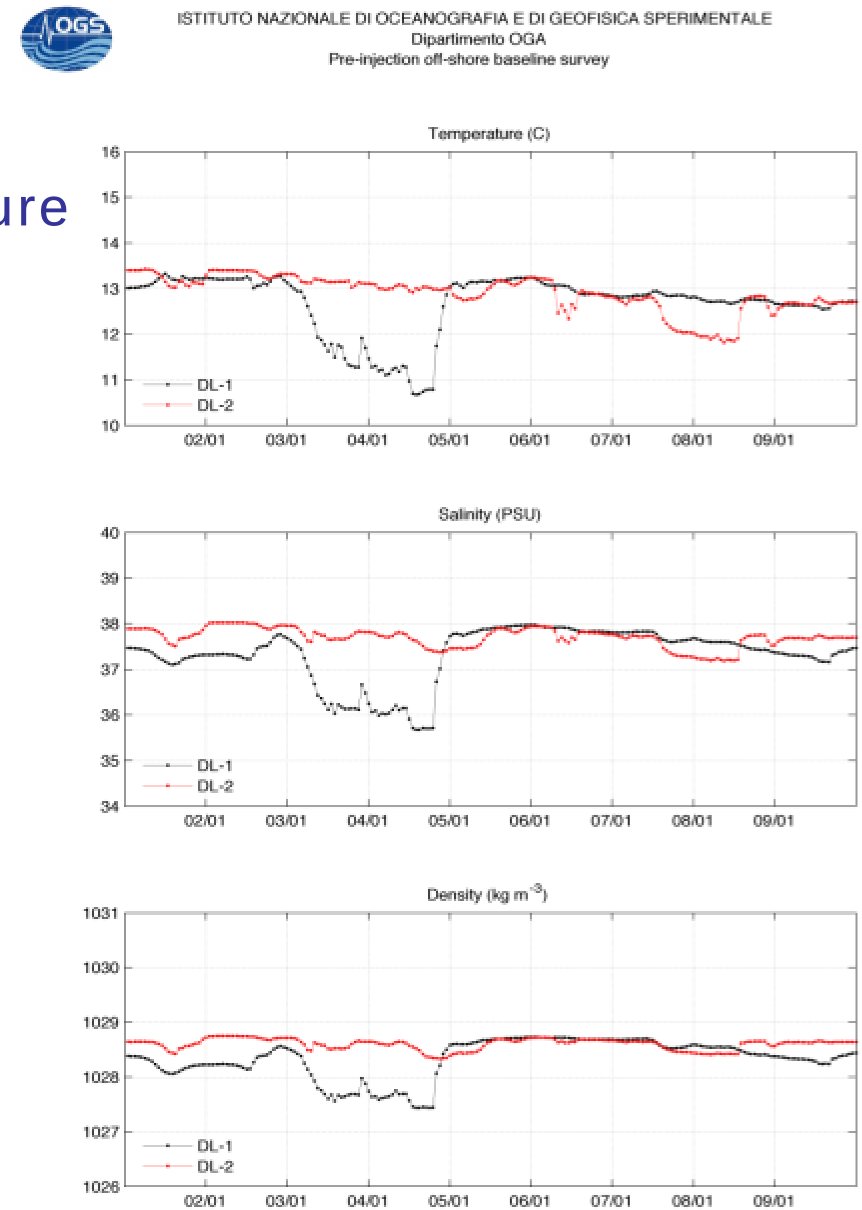
Time and space variability



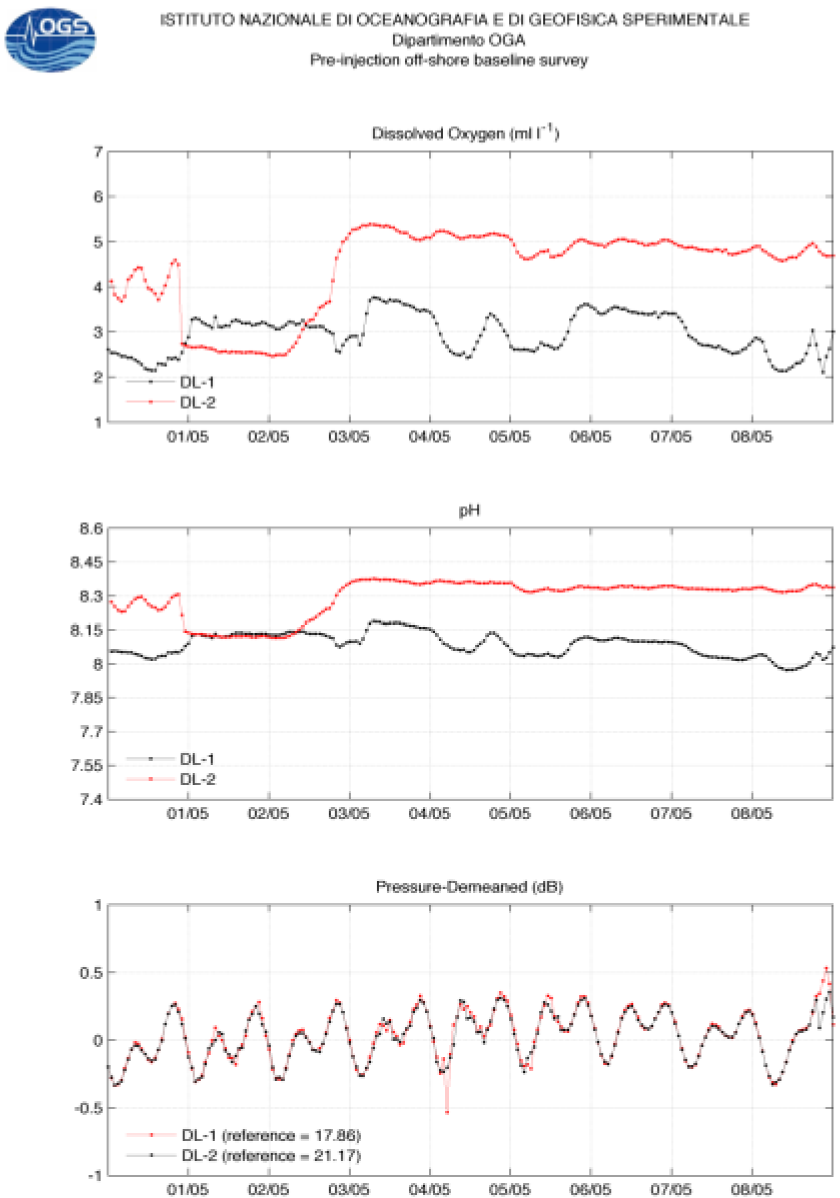
temperature

salinity

density



Variability intrinsic or induced?

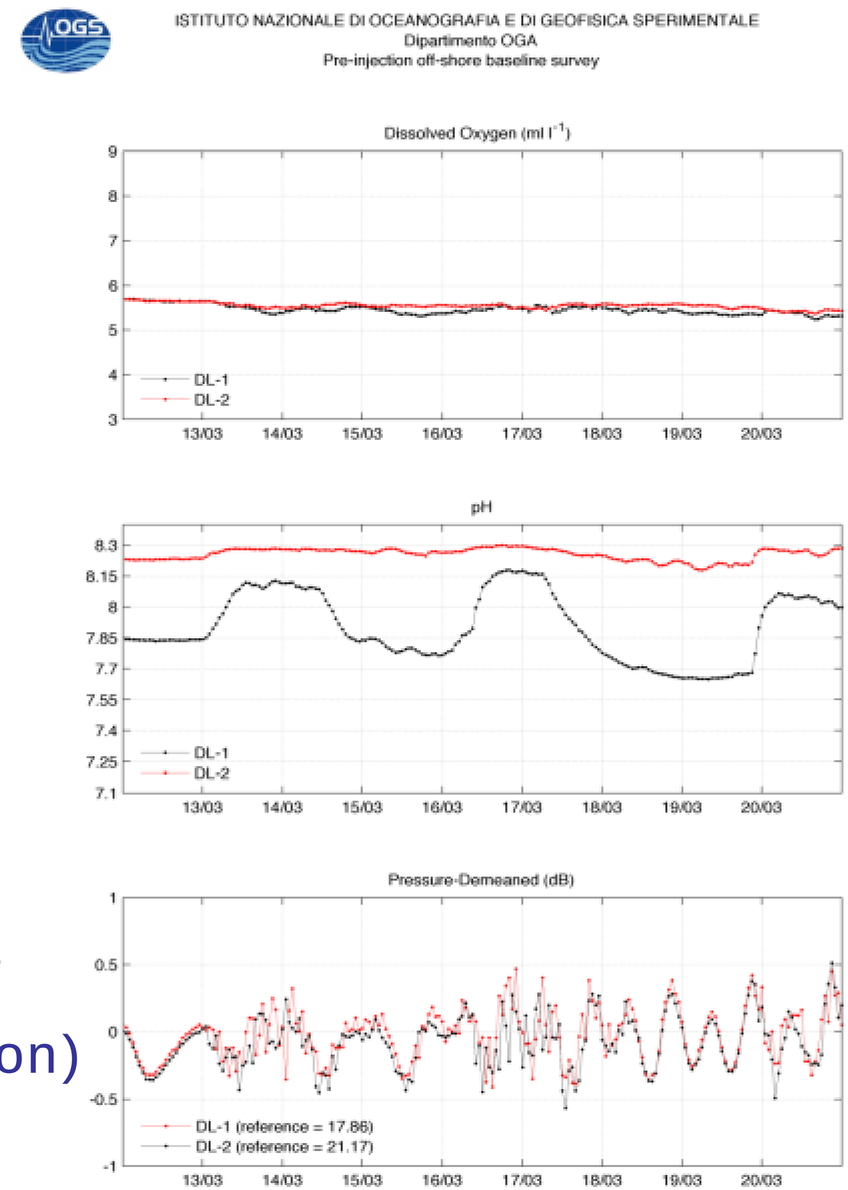


Oxigen

pH

Pressure

(wave motion)



Pre-injection on-shore survey

The development of the pre-injection grid was carried out through

- soil geo-gas measurements (CO_2 and CH_4 fluxes)
- geo-gas concentrations (CO_2, CH_4, He, ^{222}Rn, H_2S, CO, H_2, N_2, O_2, and light hydrocarbons)
- shallow and deep aquifer fluids in terms of physico-chemical parameters (temperature, salinity, pH, redox conditions), chemical composition (major, minor and trace elements) and dissolved gases content.

Flux measurements

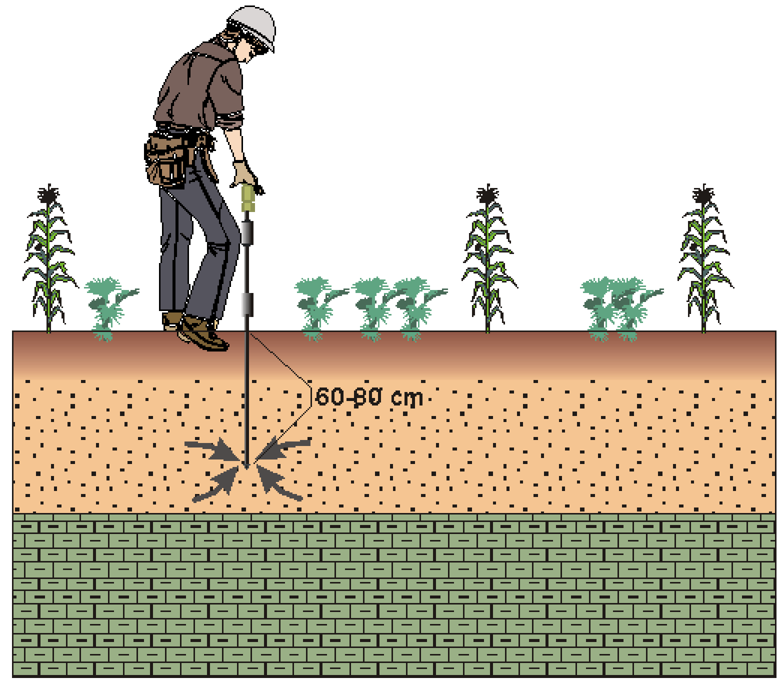
Probes or accumulation chambers are placed in a grid configuration over the expected leakage ‘footprint’, in or on the soil, and samples analysed periodically to determine CO_2 concentrations and flux.

West System® instrument is equipped with two sensors, a pump, alkaline battery, two pipes to connect the accumulation chamber to the instrument, and a mixing device that allows a optimal mixing of the gas inside the chamber to increase the measurement accuracy. This instrument is also supplied with a small, pocket size, computer (PDA) to manage the data, to show the results of measurement in real time and connected to the instrument by Bluetooth connection.

PARAMETER	TYPE	RANGE	ACCURACY	REPEATABILITY
CO2	LICOR - LI820	0 to 300 moles/m^{2}day	2%	± 5 ppm
CH4	IR spectrometer	60 ppm	5%	2%

Soil Gas Measurements

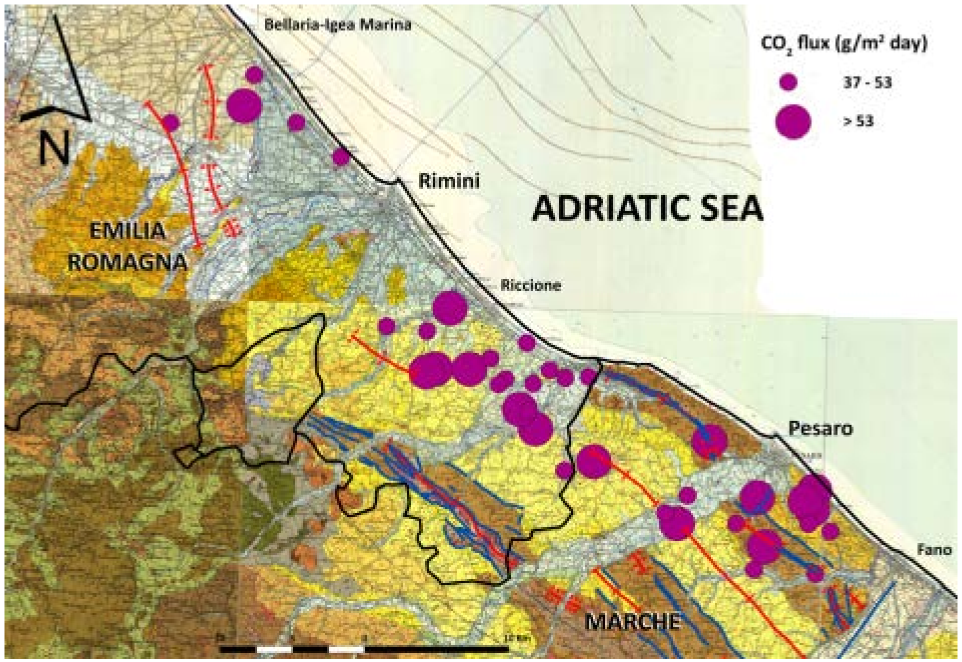
The main task of this survey is to characterize geo-gas (CH_4, Rn, He, CO_2, H_2, etc…) background, in terms of concentration and fluxes, and define their origin, potential pathways in permeable zones, migration mechanisms and carrier-gas role in the geological layers closer to the surface.

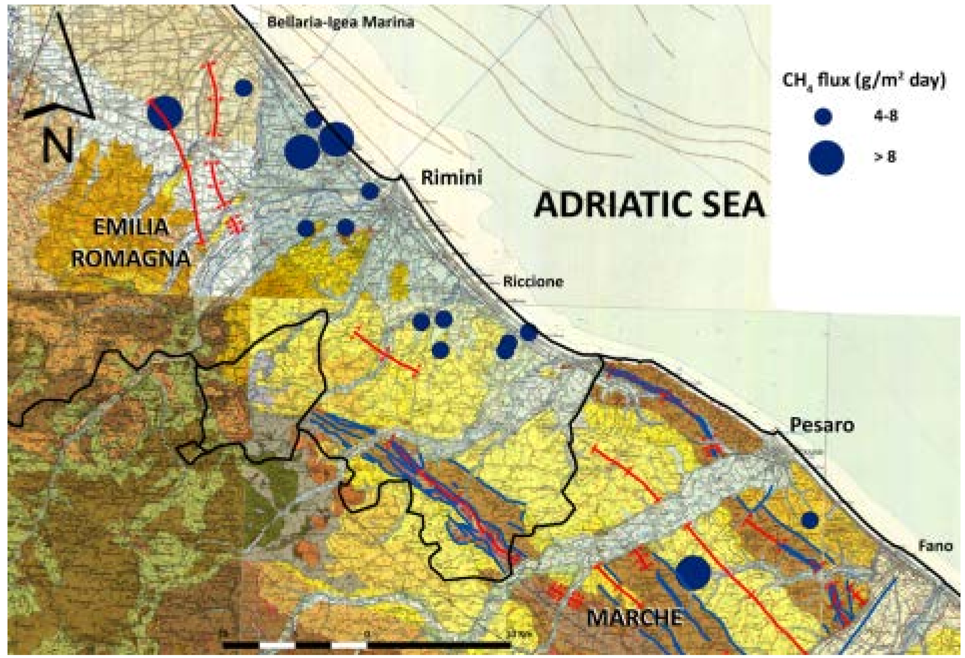


Radon is used as a tracer gas to provide a qualitative idea of gas transport processes toward the surface (velocity and flux, hints of convections, etc…); carbon dioxide and methane are believed to act as carriers for other gases (i.e., Rn and He); helium and hydrogen are used as shallow signals of crustal leaks along faults. Methane is also considered both a characteristic biogenic indicator of organic matter deposits and a tracer of major crustal discontinuities.

Role of the structural settings

To investigate the role of the structural settings on the distribution of flux data, the spatial distribution of CO_2 and CH_4 fluxes have been plotted on the geological map of the study area.





The classed post map of methane fluxes overlapped to the geological-structural map of the study area highlights the absence of a correspondence with the structural elements of the study area as well as lack of correlation with CO_2 fluxes, confirming the hypothesis of a shallow and biogenic source of these gas species

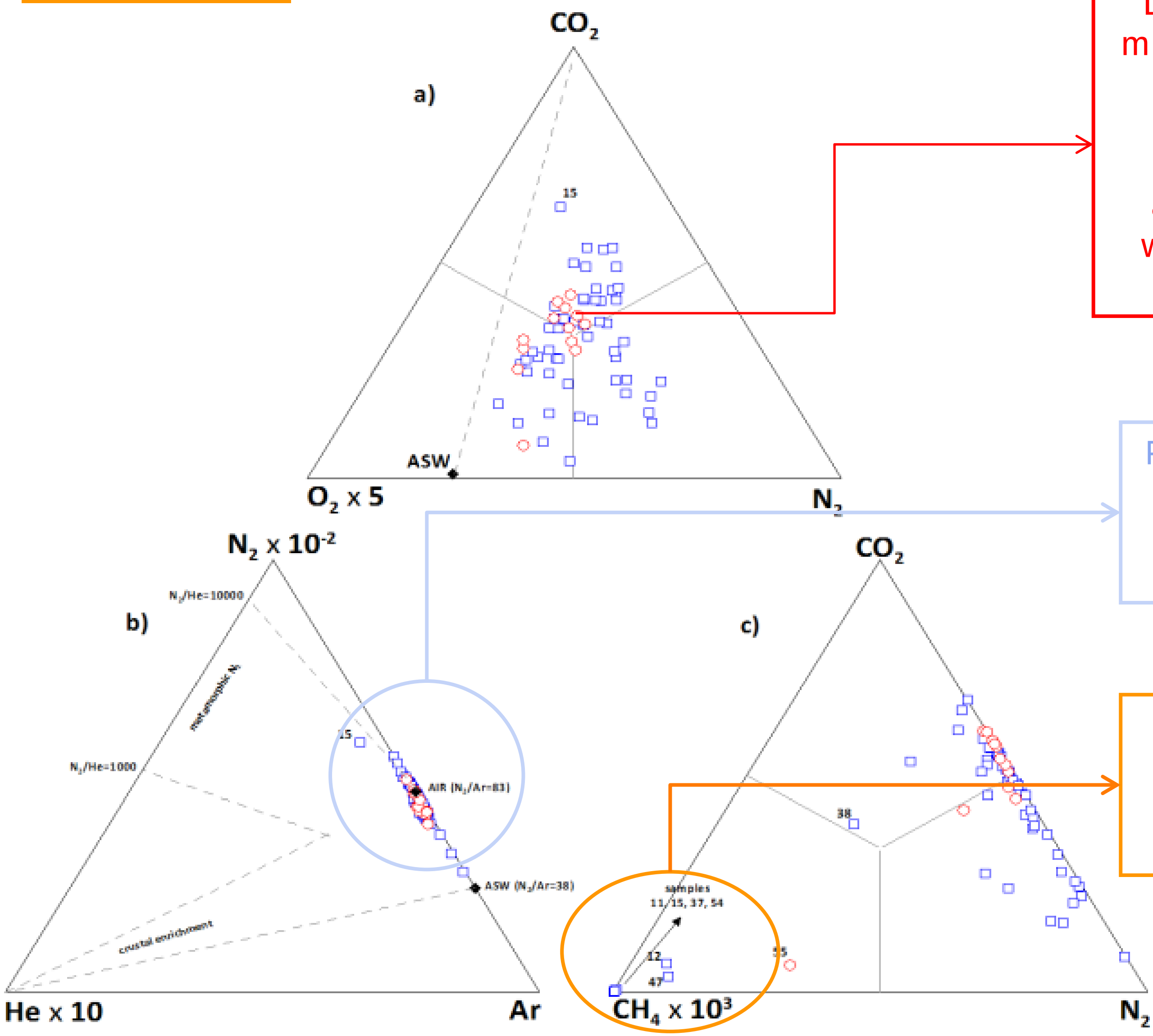
On-shore baseline shallow aquifers & dissolved gases survey

The monitoring plan for a selected CO_2 geological storage site comprises, during the pre-injection phase, the evaluation of the background conditions of the most significant circulating fluids, including shallow aquifers in terms of physico-chemical parameters (temperature, salinity, pH, redox conditions), chemical composition (major, minor and trace elements), dissolved gases content and isotopic composition (mailnly for the C-O-H-He elements).

The main tasks of this study are:

- ✓ to define the origin of shallow and deep fluids and the relationships between them on the basis of their physical-chemical, chemical and isotopic features;
- ✓ to investigate the role of water-gas-rock interaction and the buffer capacity of the shallow aquifers relative to dissolving gases, both of shallow and deep (including the injected one)
- ✓ to establish the presence of preferential migration pathways (i.e., fractures and faults) for the faster ascent of deep-originated fluids toward the surface.

Origin of dissolved Gases in groundwater



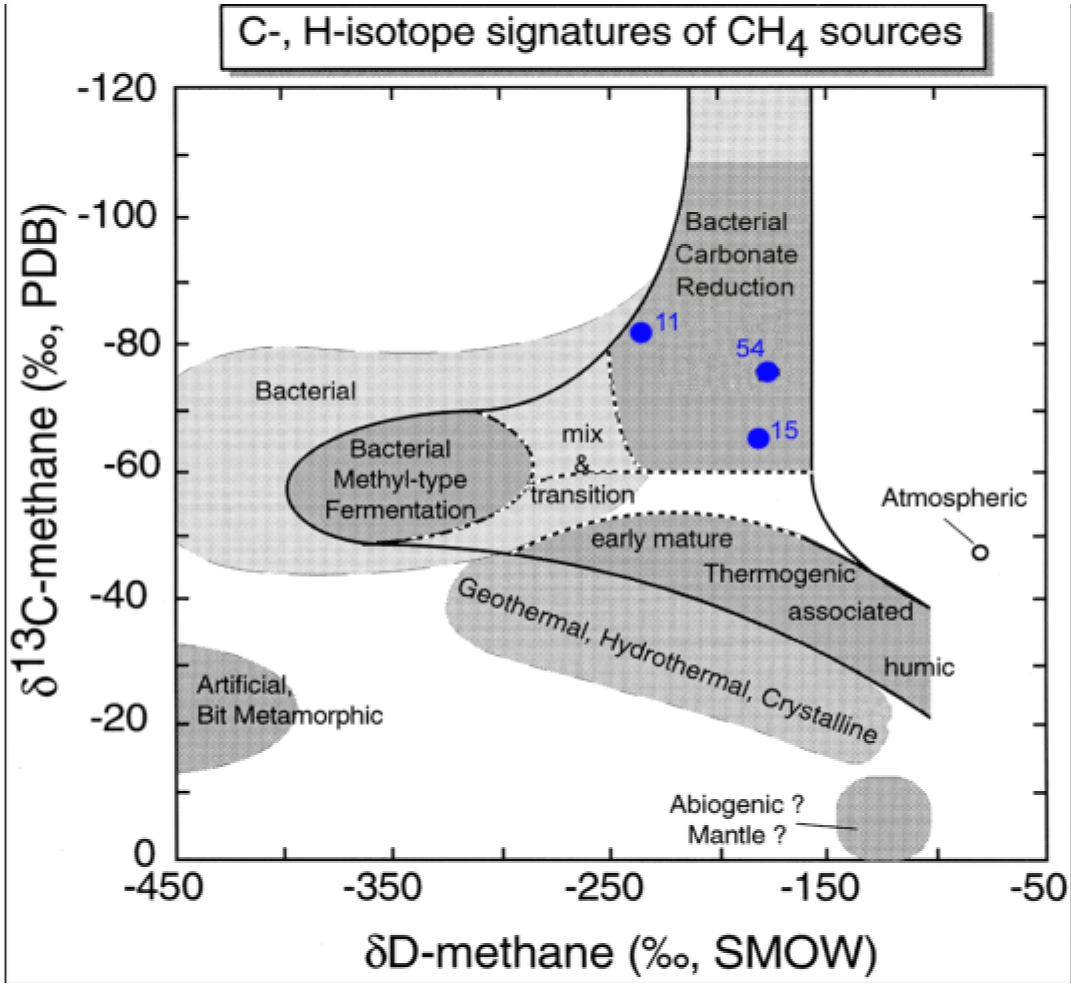
Dissolved gases result from a two-component mixing between air-derived components (N_2 and O_2) and carbon dioxide. The increase in the N_2/O_2 ratio compared to that of air saturated water (1.88) observed at all sites can be ascribed both to O_2 consumption during gas-water-rock reactions occurring in sedimentary settings and to N_2 excess relative to air

Part of the samples have N2/Ar ratios higher than that of air (N2/Ar=83) indicating a secondary, crustal, non-atmospheric source of nitrogen

Methane production is compatible with a shallow and biogenic source originating from decomposition of swamp peat and/or lignite layers

ASW = air saturated water

Origin of dissolved Gases in groundwater



from Whiticar, 1999

Isotopic analyses of C and H of methane have been performed on gases extracted from some representative CH_4-rich waters

The $\delta^{13}C$-CH_4 and δD-CH_4 values confirm that methane is likely produced from a shallow and biogenic source through CO_2 reduction processes

Evaluation of pre-injection micro-seismicity

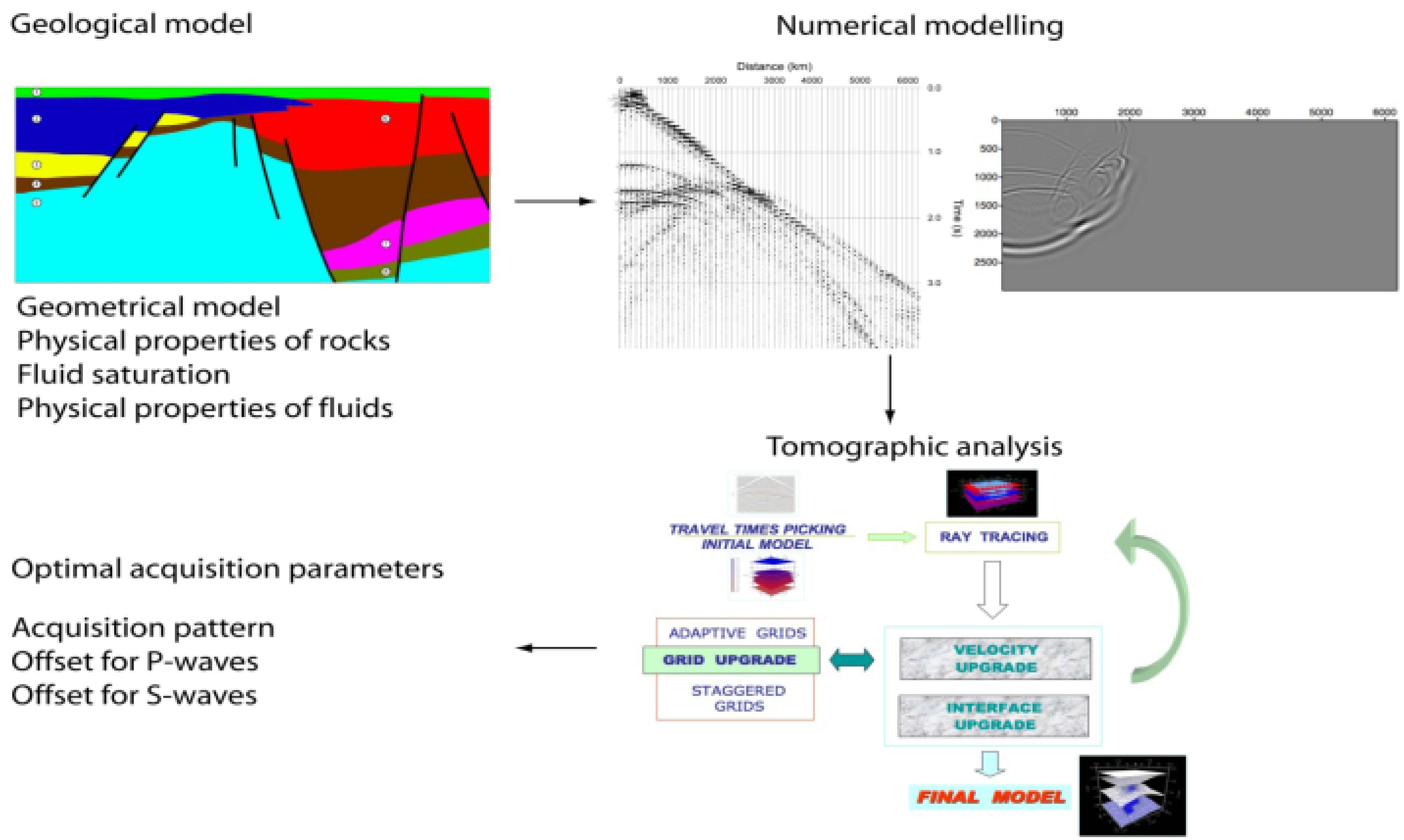
Study of historical seismicity of interesting areas.

The goal of the feasibility studies is the collection of a new passive seismic dataset, in order to increase both the seismic behavior and the deep geological and tectonic setting of the area.

The aim of the seismic experiment is to increase the grid of the permanent seismic networks already available (Italian National Seismic Network and Marche Seismic Network) in order to increase the sensitivity of the networks and locate earthquake with ML <2.

Design of an seismic monitoring plan

Studies on the rock and fluid physical properties constitute the base to understand the sensitivity of seismic properties to small variations in the fluid content within the rock. Moreover, they are the bases for a numerical modelling, aimed to calculate synthetic seismograms. From the tomographic analysis of them, it is possible to test the feasibility of a monitoring on a CO_2 storage site and the optimal acquisition parameters to guarantee a successful monitoring.



Key notes

- In the perspective of monitoring for a hypothetical CO_2 leakage from a sub-seabed storage site at least one multi-parameter continuous montoring station should be deployed near the injection well. In addition, to provide greater spatial coverage (as leakage could potentially occur away from the well and to capture any bottom water CO_2 anomalies transported away from a potentially small leakage site), **low-cost CO_2 monitoring sensors** could also be deployed at a larger number of points throughout the area.

- For non-continuous data measurements, some **sampling campaigns** (to be repeated for at least three consecutive years) should be planned, where both seawater and sediment samples should be collected. The location of the sampling stations must consider the critical points (old wells, “pockmarks”, faults or geological discontinuities, etc.) and/or the diagenetic features of the seabed.

- **Integrated interpretation of results:** the comparison and integration of the results with all the other physical, geochemical and biological data that have been acquired in the area, improves the reliability and usefulness of the monitoring

Thanks for the attention

Rome, April 18th 2013