2019 IMEKO TC-19 International Workshop on
Metrology for the Sea
Genoa, Italy, October 3-5, 2019

Cost-effective and relocatable monitoring of hydrocarbon seepage in offshore environments

Rovere M.[1], Mercorella A.[1], Spagnoli F.[2], Frapiccini E.[2,3], Funari V.[1,7], Pellegrini C.[1], Bonetti A.S.[4,6], Dell'Orso M.[4], Mastroianni, M.[4], Veneruso, T.[4], Ciccone F.[1,4], Antoncecchi I.[4,5], Tassetti A.N.[2], Giuliani G.[2], De Marco R.[2], Fabi G.[2]

[1] *Istituto di Scienze Marine del Consiglio Nazionale delle Ricerche, Via P. Gobetti 101 – 40129 Bologna*
[2] *Istituto per le Risorse Biologiche e le Biotecnologie Marine del Consiglio Nazionale delle Ricerche, Largo Fiera della Pesca 2 – 60125 Ancona*
[3] *Dipartimento di Scienze della Vita e dell'Ambiente, UNIVPM – DISVA, Via Brecce Bianche – 60121 Ancona*
[4] *Divisione V della DGS UNMIG Ministero dello Sviluppo Economico, Via A. Bosio 13B – 00161 Roma*
[5] *Ricerca sul Sistema Energetico - Sicurezza e sostenibilità delle fonti energetiche, Via Rubattino 54 – 20134 Milano*
[6] *ENVIRONMENT PARK S.P.A. Parco Scientifico Tecnologico per lAmbiente, Via Livorno 60 – 10144 Torino*
[7] *BiGeA, Università di Bologna, Piazza di Porta San Donato 1 – 40126 Bologna*

Hydrocarbon seepage is overlooked in the marine environment, mostly due to the lack of high-resolution exploration data.

This contribution is about the geophysical and geochemical investigation of two seepage sites on the shelf of the Adriatic Sea: an oil spill off Civitanova Marche, at water depth of 10 m; scattered biogenic seeps offshore Mt. Conero, at water depth of 84 m. The accurate detection of gas plumes was achieved with a multibeam system acquisition of the water column reflectivity. Dissolved benthic fluxes of nutrients, metals and DIC were measured by in situ deployment of a benthic chamber, which was used also for the first time as water samples collector for hydrocarbons gas characterization. In addition, concentration of Polycyclic Aromatic Hydrocarbons and major and trace elements was analyzed to provide an estimate of hydrocarbon contamination in the surrounding sediment.

I. INTRODUCTION

Hydrocarbon seepages are often present on the seafloor bottom in shelf and deep marine environments.

Shallow marine environments, such as the north and the central Adriatic Sea, are ideal for the formation of hydrocarbons, because organic matter sinks to the sea bottom where undergoes rapid burial and anaerobic degradation. On the other hand, deeply-trapped hydrocarbons tend to migrate to shallower sedimentary horizons, they may pierce the seabed, giving rise to peculiar seafloor morphology, and, under particular conditions, fluids escape the seabed to form gas plumes in the water column. The latter can be accurately detected by modern multibeam sonar systems as 3D density anomalies, which sometimes can reach high at the sea surface.

This contribution regards the setup of a new cost-effective and relocatable integrated monitoring system able to detect and monitor offshore hydrocarbon seepage and water column plumes of natural or anthropic origin, by means of techniques and know-how developed at CNR and the Ministry of Economic Development. The aim of this study is to determine and understand the transport processes of hydrocarbon gas from the sub-seabed to the seabed and the water column and potentially to the atmosphere, where they might increase the global carbon budget. Furthermore, understanding the migration of hydrocarbons in the subsurface is of primary importance for oil and gas exploration. Fluid migration structures on reflection seismic data are difficult to map manually and subtle features that are related to hydrocarbon migration are often overlooked. Finally, monitoring natural or human-induced gas seepage is important to mitigate the adverse effects of hydrocarbon spill and discharge, especially if located near the coast or nearby human activities.

II. STUDY AREA

The method has been tested in two sites selected on the basis of a comprehensive mapping of natural hydrocarbons at the seabed and in the water column in the Italian seas (Fig. 1) [1].

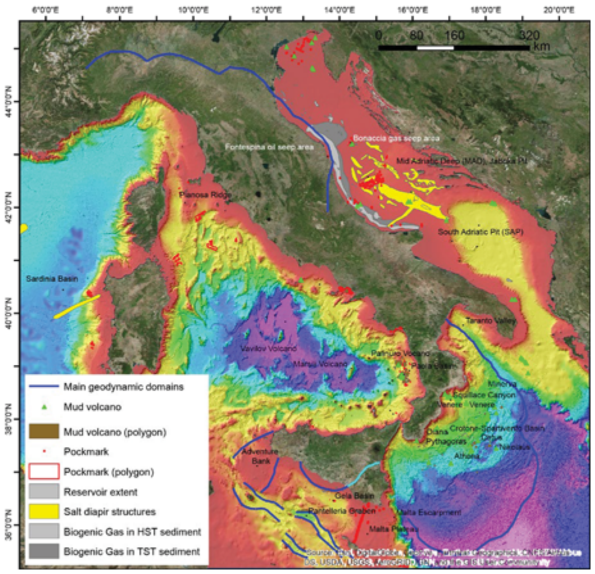

Fig. 1. Map of the natural seepage in the Italian offshore.

The map has been realized using high-resolution seismic reflection data, bathymetric and reflectivity data of the sea-bottom and water column acquired by CNR-ISMAR. Where no CNR-ISMAR data were available, information from literature was gathered (e.g. [2], [3]).

The two sites investigated for this study are located at water depth of 10 m and about 1 mile off Fontespina village (Fontespina site) and offshore Mt. Conero, at water depth of 84 m near the Bonaccia cluster of gas exploitation plants (Bonaccia site) (Fig. 2).

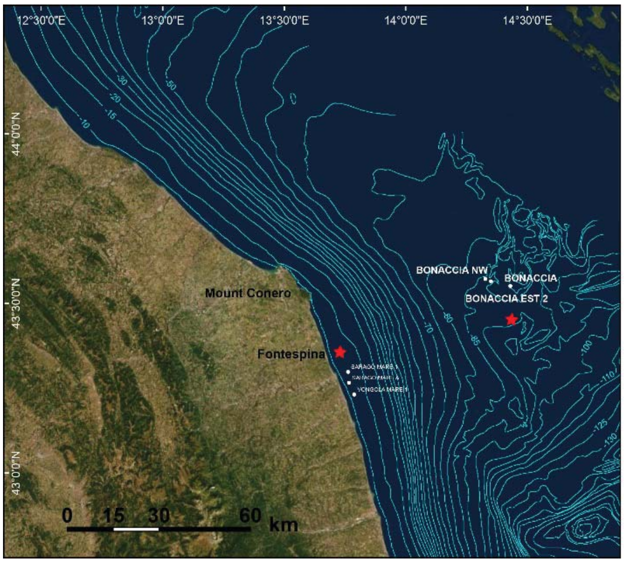

Fig. 2. The Fontespina and Bonaccia sites (red stars).

The two sites have been selected on the basis of a few considerations: Fontespina is inferred to have a thermogenic origin, while Bonaccia most probably releases biogenic gas; water depth is compatible with devices operability and ship-availability; presence of baseline information; proximity to the coast in the case of Fontespina, where seeps may interfere with tourism and leisure activities, thus being of concern for public health.

III. MATERIALS AND METHODS

The two tests have been carried out on board the R/V Tecnopesca II, in August 2018. During the survey three kinds of data have been acquired: acoustic backscatter of the water column by a multibeam sonar system; water samples and benthic fluxes at the sediment-water interface, measured by an automatic benthic chamber; sediment samples collected nearby seepage sites by a box corer for geochemical laboratory analyses.

A. Multibeam sonar systems

A multibeam Kongsberg EM2040 has been used to detect and record gas plumes in the water column. The EM2040 system is an hull-mounted dual-head large swath coverage [140-200°] shallow water multibeam echo sounder with operating frequency range 200-400 kHz. For this specific water column survey, an optimized frequency between 250 and 300 kHz has been used.

B. Automatic Benthic Chamber

The measurements of dissolved benthic fluxes at the sediment-water interface are fundamental to better understand the marine biogeochemical cycles and alterations of aquatic ecosystems as a consequence of human activities or natural processes. Benthic fluxes are the dissolved chemical substances released or absorbed by the seabed as result of early diagenesis processes or volcanic and hydrothermal/hydrocarbon release processes. The Automatic Benthic Chamber “Ada_N:” is a tool for measuring the flux of dissolved substances at the water-sediment interface, through a multi-parameter probe and water sampling, the latter to be analysed for nutrients, metals, DIC, dissolved gases, isotopes of the C and other dissolved pollutants [4].

During the Spinaccia survey, Ada_N. (Fig. 3) has been deployed on the seabed at the Fontespina site at 11 m water depth for 9 hours, in order to evaluate if this device could sample liquid and gaseous substances related to hydrocarbon seepage at the seabed for subsequent headspace and trace metal analysis, which have been conducted at the Ministry of Economic Development (DGS UNMIG Division V laboratories). Furthermore, dissolved benthic fluxes have been measured for total dissolved inorganic carbon (DIC), oxygen and pH, while salinity, temperature and depth have been monitored during all the test. DIC content has measured by coulometric analysis with an in house acidifier [5]. Oxygen, pH, salinity, temperature and depth have been measured by an inside chamber multiparametric probe (Hydrolab MS5).

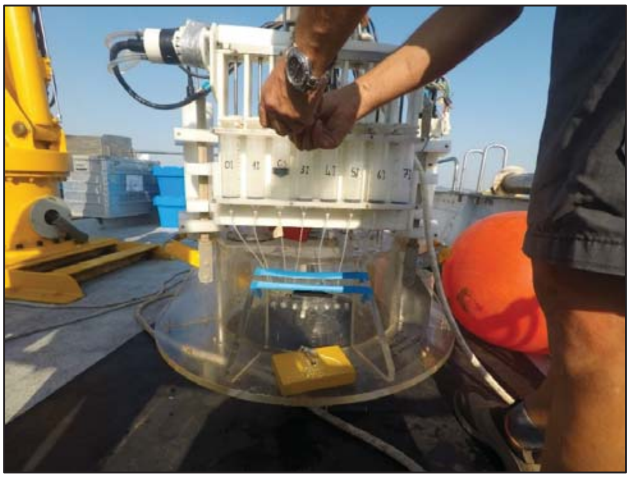

Fig. 3. Set up of Ada_N on board Tecnopesca II.

C. Biogeochemical analyses of water and sediment samples

Water samples collected by Ada_N were refrigerated and transferred to the DGS-UNMIG laboratories, where they were analysed by headspace gas chromatography - thermal conductivity detector for the quantitative determination of the gas compounds dissolved in the sample and by inductively coupled plasma optical emission for the determination of metal composition. The analytical techniques included: 1. determination of gas compounds by headspace gas chromatography using a thermal conductivity detector (GC-TCD); 2. Determination of metal composition by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) analysis (APAT IRSA-CNR 29/2003 – 3020). The ICP source consists of a flowing stream of argon inductively (radio frequency field 40 MHz) ionized by a cooled coil surrounding a quartz “torch” that supports and confines the plasma, with temperatures range 6000 – 10000 K. Double-monochromator optical system scanning of each element’s typical wavelengths usually permits to achieve quantification linear dynamic ranges of four to six orders of magnitude for many elements. The method includes the preventive filtration and subsequent acidification of the solution with concentrated nitric acid up to pH $\leqslant$ 2, aimed to prevent or in any case delaying effects of precipitation, adsorption effects or even the formation of metal complexes.

Marine sediments have been collected by a box-corer (BC) in 12 stations (6 for each site, including reference sites collected away from the seepages). Each BC has been subsampled at different depths (sediment layers) for the biogeochemical analyses (Fig. 4)

Representative samples from BC were analysed using an X-Ray Fluorescence (XRF) spectrometer (PANAlytical AXIOS) to determine the chemical composition of the sediments surrounding the seepage sites.

Marine sediment collected in proximity of gas and oil seepage were also analysed for the presence of pollutants, such as polycyclic aromatic hydrocarbons (PAHs) because the submarine seeps can be a natural source of them and other pollutants for the marine environments.

PAHs have been extracted from sediment layer by an ultrasonic bath. PAH identification and quantification have been performed using an HPLC system (Ultimate 3000, Thermo Scientific, Waltham, MA, USA) equipped with a fluorescence detector (RF-2000, Thermo Scientific).

Fig. 4. Box corer and sample collection procedure on board Tecnopesca II.

IV. RESULTS AND DISCUSSIONS

In the Fontespina site, about 24 km of lines have been acquired for a total of 50 track lines and about 8 working hours. In Bonaccia site, about 43 km of lines have been acquired for a total 33 track lines and about 7 working hours. Caris Hips and Sips software has been used to process bathymetric data while the software QPS-FMMidwater and QPS-Fledermaus was used to process and visualize 3D plumes. Preliminary data processing allowed to identify 31 plumes in the Bonaccia site and 110 plumes in the Fontespina site (Fig. 5). The heights of the plumes in Bonaccia can reach up to 70 m from the seafloor.

Data collected by Ada_N. shows that the benthic chamber worked at an average depth of about 11 m with weak variations due to tidal oscillations (11.04±0.05), temperature during the deployment was stable (27.7±0.01 °C) and represents the water column temperature of the bottom layer, also salinity showed stable (37.4 ±0.01 °C).

The fluxes at the sediment-water interface, at the Fontespina site, have been measured by Ada_N for oxygen, Dissolved Inorganic Carbon (DIC) and H^+ (pH) (Table 1). Oxygen showed a constant decrease, corresponding to a medium flux of -51.53 mmol/m^2*d. The negative oxygen flux is due to the microbic mineralization of the fresh organic matter deposited on the sea bed in the days before the test.

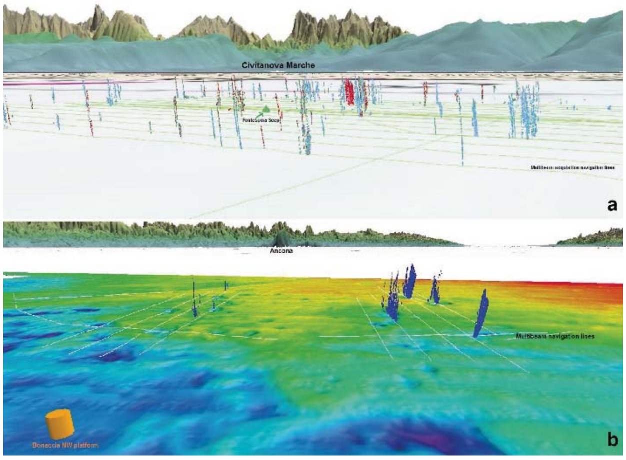

Fig. 5. 3D visualization (Fledermaus) of processed gas plumes in the water column in the two sites (Fontespina site, a, and Bonaccia site, b).

Dissolved benthic fluxes (mmol/m2*d)			
	Oxygen	DIC	H^+
Fontespina site	-51.53	42	$2e^{-0.7}$
Central Adriatic Sea*	-39	9.38	n.d.

*average of fluxes measured in summer and fall on the pelitic Holocene wedge between Ancona and S. Benedetto del Tronto [7].

Table 1. Oxygen, DIC and H^+ dissolved benthic fluxes measured by Ada_N in Fontespina and on pelitic sediments of the Central Adriatic Sea.

The DIC fluxes showed positive values of 42 mmol/m^2*d (Table 1). Also in this case the positive flux is due to the aerobic and anaerobic mineralization of fresh and reactive organic matter deposited on the sea bed in the days before the experiment [6].

pH shows weak decreasing values around 8.20 (±0.007) corresponding to a flux towards the water column (or an increase inside the chamber) of $2e^{-0.7}$ H^+ (Table 1). The pH decrease and then the H+ increase, is a consequence of the DIC increase that acidifies the water inside the chamber.

Moreover, the comparison of Fontespina oxygen and DIC flux with fluxes previously measured in Central Adriatic Sea highlights stronger positive (DIC) and negative (oxygen) fluxes in the Fontespina site (Table 1) [7]. This differences of DIC and oxygen fluxes between two areas with similar early diagenesis processes suggest the presence of greater contents of local and temporal fresh and reactive organic matter and/or older and thermogenic organic substances possibly due to hydrocarbons seepage contributions. This supports the capability of the benthic chamber system to record the contribution of hydrocarbon seeps to sediment-water fluxes. The hydrocarbons indeed undergo a partial mineralization that consume oxygen and produce excess of DIC flowing upwards.

The test carried out in the Fontespina site shows that the comparison between dissolved fluxes measured in an affected seepage site and in a blank site is able to detect the presence of the seepage and diagenetic components of the benthic fluxes and their contribution. For these reasons, the benthic chamber may be considered a promising tool to evaluate the contribution of the hydrocarbon seeps to the local whole dissolved benthic fluxes.

However, a more exhaustive set of chemical analysis such as carbon isotopic composition and hydrocarbon species, as well as nutrients, Fe and Mn, giving information on the early diagenetic processes, would obviously give a more precise definition of the hydrocarbon seep contribution on the marine chemistry of the environment. Furthermore, the dissolved benthic fluxes could be investigated more in depth by the study of the early diagenesis processes. The analysis of pore waters at the sediment-water interface could explain the role of the final electron acceptors (O_2, NO_3, Fe, Mn, SO_4, CH_2O), of organic matter and of thermogenic components in producing the benthic fluxes [6].

Preliminary results of the analysis on seven water samples, collected with the benthic chamber in Fontespina, show that major gas compounds are: nitrogen, oxygen and only in some samples, traces of carbon dioxide and methane. Regarding the metal composition, the results show a typical sea water composition (Table 2). The high salinity content of the samples made it necessary to apply a dilution. A "simulated" matrix (salinity similar to sea water) was used both for the preparation of the standards and the "blank" solution, which reproduces the salinity of the diluted samples. The concentration of the metal elements is thus determined by constructing a calibration curve with a series of reference standards at different concentrations. The calibration curve was built on 3 points using a solution of NaCl (16.45 g/L) with multi-element standard solutions at different and increasing concentrations. The lowest concentrations of the curve were taken as a reference for determining the "Detection limits" (D.L., Table 2) such as the lowest concentration of the analytes in a sample that can be detected in the method experimental conditions.

In both sites, spatial and vertical distributions of PAHs have been analyzed in the sediment layers (Fig. 6). Total PAH concentrations (ng/g, d.w.) are reported for each sediment samples and references sites. The average of the PAH concentrations was slightly higher in the Fontespina site (61 ng g^{-1}, d.w.) compared to Bonaccia site (51 ng g^{-1}, d.w.). Preliminary results show high variability of the PAH concentrations in the subsampled sediment layers (maximum at -2 and -4 cm depths), for both sites, with greater concentration of the high molecular weight (HMW)-PAH concentrations.

Metal	0 l	1 l	3 l	4 l	5 l	6 l	7 l
Al	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Cd	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Cr	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Cu	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Pb	< D.L.	< D.L.	0.047	< D.L.	0.019	0.023	< D.L.
Mn	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
As	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
B	4.174	5.318	4.572	3.847	5.265	5.382	4.148
Ba	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Be	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Co	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Fe	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Ni	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Se	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Sn	0.063	0.063	0.063	0.063	0.063	0.063	0.063
V	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
Zn	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	0.012	< D.L.

Table 2. Metal concentrations in water samples at Fontespina (mg/l). D.L. detection limit. Accuracy within the 95% confidence interval of the certified values.

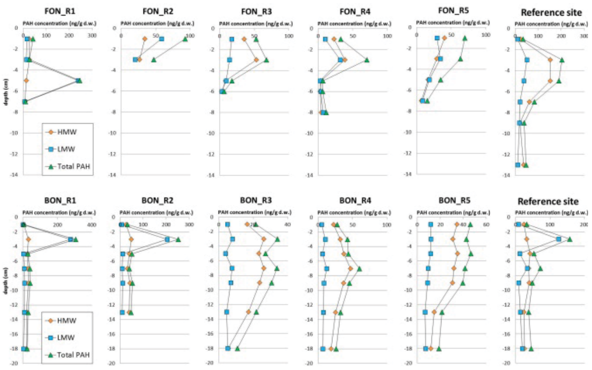

Fig. 6. Total PAH concentrations (Total PAH), PAHs with high molecular weight (HMW) and PAHs with low molecular weight (LMW) recorded in Fontespina (a) and Bonaccia (b) sites.

However, Fontespina site recorded a presence of low molecular weight (LMW)-PAH greater than Bonaccia one, underling a presence of compounds likely derive from the oil seepage. For a better understanding of the origin of investigated PAHs, a PAH diagnostic ratios commonly used to identify origin of PAHs in environment have been applied [8, 9]. Therefore, Fig. 7 shows that for both investigated sites, PAHs come mainly from petrogenic source, unlike the references site collected away from the seepages, confirming the natural origin of these chemicals.

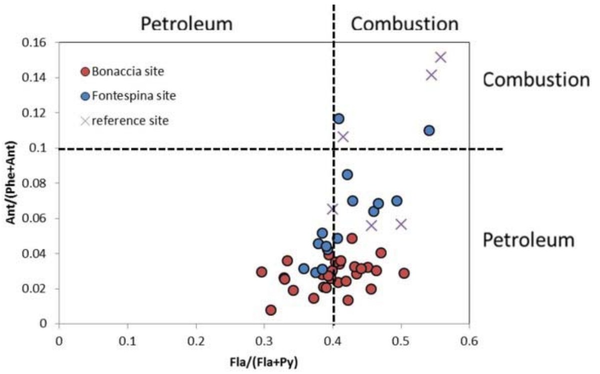

Fig. 7. Cross plots of PAH diagnostic ratios Ant/(Phe+Ant) vs (Fla/(Fla+Py) identifying sources of PAHs in all sediments layers and in reference site.

The XRF results showed distinct chemical compositions for Bonaccia and Fontespina sites, respectively. While Si and Ca were high in both sites, Al was lower in Fontespina than in Bonaccia. The range of concentration of Cl, S (and Br) was elevated in Fontespina, likely substantiating the hypothesis of higher levels of PAHs. Metals like Fe, Co, Ni, V and Zn are comparably higher in Bonaccia suggesting potential mineralization taking place at the sediments surrounding the sampling site, which likely recorded a more complex diagenetic process. Trace elements concentrations in both seepage sites were different from the reference sediment sample as a likely consequence of hydrocarbon contamination.

	BON RIF	FONR1	FONR4	FONR5	BON R3	BON R4	BON R5	BON R6
wt.%								
Al2O3	8.24	5.46	5.29	6.12	8.98	10.81	10.22	10.67
CaO	25.41	29.34	29.37	28.22	22.99	19.31	21.85	20.14
Fe2O3	3.36	2.25	2.2	2.34	3.67	4.47	4.15	4.5
K2O	1.56	1.15	1.13	1.17	1.62	2.13	1.87	1.98
MgO	2.57	2.16	2.11	2.33	4.33	4.64	3.89	4.7
MnO	0.1	0.1	0.11	0.1	0.09	0.1	0.09	0.16
NaO	1.58	0.96	0.76	1.78	1.76	0.94	2.95	1.91
P2O5	0.13	0.13	0.13	0.12	0.11	0.13	0.11	0.12
SiO2	36.89	33	32.46	32.25	34.54	38.95	36.97	39.55
TiO2	0.43	0.33	0.32	0.37	0.47	0.52	0.55	0.55
LOI	21.08	22.18	22.18	22.38	22.98	20.87	21.82	20.39
mg/kg								
As	9.6	9.4	8.8	8.9	10.6	10.5	8	15.5
Ba	277	253	267	258	188	240	215	224
Bi	0.4	0.5	0.4	0.5	0.5	0.5	0.5	0.5
Br	15.1	18.1	12.1	44.4	25.7	23.8	28.9	29
Ce	26.9	40.7	43.9	33.2	34	53.2	48.8	59.8
Cl	4948	3880	2015	9224	4828	1716	8378	4724
Co	9.8	6.1	9.2	5.5	11.1	13.5	13.1	12
Cr	158	170	183	177	160	170	155	187
Cu	16	10.1	9.2	10.7	11.7	19.4	16.7	17.4
Ga	8.8	6.6	6.4	5.8	8.8	11.4	10.7	11.2
La	18.2	20	14.1	17.3	17.2	20.7	15.2	14.5
Nb	8	6.4	6.7	6.8	8.1	9.5	9.7	9
Nd	24.1	19.2	20.3	13.5	11.2	24	25	29.7
Ni	39.6	23.2	22.6	21.9	47.9	68	58.6	64.3
Pb	13.2	10.9	12.7	9.5	16.7	19.5	19.1	21.8
Rb	70.9	47.7	47.4	48.6	58.8	80.7	78.5	79.8
S	1047	904	778	1747	752	596	809	574
Sc	12.6	15.7	5.5	10.4	1	17.6	23.1	16.5
Sm	4.6	3.3	3.2	2.9	5	6.5	6.2	6.4
Sr	424	462	453	446	547	453	527	451
Th	3.5	4	3.3	3.4	2.7	3.4	5.3	4.9
U	3	2.7	1.5	2.2	1.4	1.5	2	2.4
V	86.9	59.2	60.1	70.7	96.3	126	113	124
Y	19.1	20.1	20.3	20.1	18.2	20.5	20.9	18.8
Zn	52.1	32.5	31.1	33.9	44.9	67.2	61.2	62.5
Zr	138	186	206	231	120	115	131	105

Table 3. major and trace elements of the sediment samples collected at Bonaccia and Fontespina sites (BON, FON). RIF stands for reference site.

Comparing samples FON-R1 and BON-R3 collected at the sediment-water interface (Table 3), significant variation of extractable/exchangeable ions like Sr, Rb, Ce, and V can be noted. Further insight into the diagenetic processes and rock-sourcing shall be taken from isotopic analysis that will be carried out as a next step.

V. CONCLUSIONS

This new multidisciplinary and multi instrumental method (REMO; Relocatable Monitoring) proved to be effective for a fast detection of water column anomalies by geophysical equipment which provided the exact location for water and sediment sampling.

The benthic chamber is a promising tool to identify hydrocarbon seeps and to evaluate their contribution to the local dissolved benthic fluxes. Additionally, dissolved benthic fluxes could be supported by the study of the early diagenesis processes. That are able to explain the genesis of the fluxes and the role of other chemical such as trace elements and organic matter components. A more exhaustive set of chemical analysis such as carbon isotopic composition and hydrocarbon species, as well as nutrients, Fe and Mn, would obviously give a more precise definition of the hydrocarbon seep involvement.

Some of the analysis are still undergoing but we can confirm that surface geochemical exploration and hydro-acoustic methods combined together are effective in detecting and measuring seeps and gas bubbles in the water column. Real time measurements at gas and methane leakage sites provide geophysical, benthic fluxes and chemical measurements taken directly from the source.

On the whole the combination of the geophysical, geochemical and sedimentological methods proposed in this study has proved to be an excellent method to localize and characterize bottom seepages. The use of this technology is easy and cost-effective since it avoids the use of divers, it is applicable in different sites due to its easy transport, assembly, set-up and use as well as it presents limited costs as regard hosting vessel, instruments and analyzes. The only present restriction is the limitation to the shelf environment that can in any case overcame by the employment of more complex instrumentation and ships.

This relocatable system may be used for several applications such as: 1. monitoring of coastal areas, i.e. continuously shifting water dynamics due to changing seasons and other factors can limit and modify vertical methane and oil migration affecting the variable intensity of discharge on the coast (*e.g.* Fontespina oil spill). 2. Fast detection of upward migrating biogenic methane along the boreholes, originating for example from shallow gas accumulations that are penetrated when drilling into the underlying deep hydrocarbon reservoirs. 3. Monitoring leakage from abandoned or decommissioned wells. 4. Detecting reservoir leakage through sand injectites, fractures and faults, without expensive seismic acquisition or tailored re-processing.

REFERENCES

[1] Rovere, M., E. Campiani, E. Leidi, A. Mercorella, 2017. Natural hydrocarbon seepage in the Italian offshore. Geoingegneria Ambientale e Mineraria, Anno LIV, 3, 35-40.

[2] Etiope, G., Panieri, G., Fattorini, D., Regoli, F., Vannoli, P., Italiano, F., Locritani, M., Carmisciano, C., 2014. A thermogenic hydrocarbon seep in shallow Adriatic Sea (Italy): Gas origin, sediment contamination and benthic foraminifera. Mar. Pet. Geol. 57, 283–293.

[3] Capozzi, R., Guido, F.L., Oppo, D., Gabbianelli, G., 2012. Methane-Derived Authigenic Carbonates (MDAC) in northern-central Adriatic Sea: Relationships between reservoir and methane seepages. Marine Geology 332-334: 174-188.

[4] Spagnoli, F., Penna, P., Giuliani, G., Masini, L., Martinotti, V. (2019). The AMERIGO Lander and the Automatic Benthic Chamber (CBA): Two New Instruments to Measure Benthic Fluxes of Dissolved Chemical Species. Sensors, 19(11).

[5] Spagnoli F., 2018. Dispositivo di estrazione del carbonio inorganico disciolto totale da una soluzione acquosa e sistema di analisi comprendente tale dispositivo. Total dissolved inorganic carbon extraction device from aqueous solutions and analysis system comprising such device. Consiglio Nazionale delle Ricerche. Industrial patent n. 102016000048914 of 3 December 2018, Rome, Italy.

[6] Hammond D. E., Cummins K. M., McManus J., Berelson W. M., Smith G., Spagnoli F., 2004. A Comparison of Method for Benthic Flux Measurement Along the California Margin. Limnology & Oceanography: Methods, 2, 146-159. WOS:000227420000001

[7] Spagnoli F., DellAnno A., De Marco A., Dinelli E., Fabiano M., Gadaleta M. V., Ianni C., Loiacono F., Manini E., Marini M., Mongelli G., Rampazzo G., Rivaro P. and Vezzulli L., 2010. Biogeochemistry, grain size and mineralogy of the central and southern Adriatic Sea sediments: a review, Chemistry and Ecology, 26: 1, 19—44. DOI: 10.1080/02757541003689829

[8] Marini, M., Frapiccini, E., 2013. Persistence of polycyclic aromatic hydrocarbons in sediments in the deeper area of the Northern Adriatic Sea (Mediterranean Sea). Chemosphere 90, 1839-1846.

[9] Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110-119.