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Offshore and onshore seepage of thermogenic gas at Katakolo Bay (Western Greece)

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ABSTRACT

Considerable seepage of natural gas occurs throughout the Katakolo Bay, both at sea and on land, along the Ionian coast of Peloponnesus (Western Greece). Explosive levels of CH_4 and toxic concentrations of H_2S accumulating in the ground, pose a severe hazard for humans and tourist infrastructures. A wide offshore and onshore gas survey, including marine remote sensing, underwater exploration by a towed instrumented system, compositional and isotopic analyses, and flux measurements of gas, allowed us to assess that: (a) gas seepage takes place along two main normal faults; (b) offshore side-scan sonographs recorded at least 823 gas bubble plumes over an area of 94,200 m^2, at depths ranging from 5.5 to 16 m; (c) offshore and onshore seeps release the same type of thermogenic gas ($\delta^{13}C_{CH_4}$~−34 to −36‰); (d) offshore gas showed increased stable carbon isotopic ratio of CO_2 and propane, which suggests enhanced biodegradation of hydrocarbons; (e) isotopic data combined with thermogenic gas generation modeling and maturity plots, suggest that the gas is related to a deep Petroleum System with Jurassic carbonate reservoirs, Triassic source rocks, and Triassic evaporites; (f) H_2S ($\delta^{34}S$: +2.4‰) is produced by thermochemical sulfate reduction in deep anhydrites, in contact with hydrocarbon-rich carbonates; (g) due to the shallow depth, more than 90% of CH_4 released at the seabed enters the atmosphere, consistent with theoretical bubble dissolution models, with a mean plume output of 0.12 kg d^{-1}; total offshore CH_4 output was estimated in the range of 33 to 120 t y^{-1}; and (h) in the onshore area at least 50 gas vents in the harbor and a large seep on the adjacent Faros hill, emit in total about 89 t CH_4 y^{-1}. Katakolo results to be one of the biggest thermogenic gas seepage zones in Europe.

1. Introduction

Natural hydrocarbon seepage, either offshore or onshore, has for many years served petroleum exploration as a direct indicator of gas and/or oil subsurface accumulations (Link, 1952; Jones and Drozd, 1983). Surface macro-seeps (visible gas vents or oil leaks from the soil or rock outcrops) are generally an indication of a fault in an active Petroleum Seepage System (Abrams, 2005) belonging to a Total Petroleum System (Magoon and Schmoker, 2000; Etiope et al., 2009a). The assessment of the origin and flux of the seeping gas, is therefore a key task for understanding, without drilling, the subsurface hydrocarbon potential, genesis, and quality, e.g., the presence of shallow microbial gas, deeper thermogenic accumulations, oil, and non-hydrocarbon undesirable gases (CO_2, N_2, H_2S). The global number of seeps likely exceeds 10,000 (Etiope et al., 2008), but only a small number have been directly investigated. A global analysis of more than 200 onshore seeps worldwide, revealed that methane is thermogenic in about 80% of the cases, microbial gas is in only 4% of seeps, and mixed gas is in the remaining cases (Etiope et al., 2009a). Gas seeps can also indicate subsurface petroleum biodegradation (Etiope et al., 2009b), which has an important impact on hydrocarbon quality and it may influence exploration and production strategies.

Seeps can then represent a geo-hazard for humans, buildings, and industry: explosions and sudden flames may occur in gas-rich environments (boreholes, soil), if methane concentrations reach explosive levels of 5–10% in the presence of air. When methane is accompanied by hydrogen sulfide (H_2S, e.g., in salt diapirism zones), seeps can be toxic or even lethal under some circumstances (Etiope et al., 2006). Seeps plumbing can then damage buildings and infrastructures by a gas-pressure build-up in the subsoil or by general degradation of geotechnical properties of soil foundations. Finally, seeps represent a significant global natural source of greenhouse gas (methane; Etiope et al., 2008; US EPA, 2010), photochemical pollutants, and ozone precursors (ethane and propane; Etiope and Ciccioli, 2009). Onshore and offshore seeps (together with diffuse microseepage) are estimated to be the second most important natural source of atmospheric methane, after wetlands, both on a global and European scale (Etiope, 2009). While the global emission of methane from onshore seepage (~22–44 Tg y^{-1}; Etiope et al., 2008) was assessed on the basis of a wide experimental data-set, including direct flux measurements from many countries and different geologic settings, the global emission into the

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atmosphere from offshore submarine seeps is still based on a pure theoretical exercise (~10–30 Tg y^{-1}; Kvenvolden et al., 2001). Very few in fact, are the flux data from marine seeps referring to the actual amount of gas entering the atmosphere (Hornafius et al., 1999; Judd and Hovland, 2007; Zhou et al., 2009; Clark et al., 2010; Greinert et al., 2010; Yang et al., 2010; Brunskill et al., 2011; Jessen et al., 2011; Schneider von Deimling et al., 2011;) and they may include methane originated in recent, shallow sediments which is not completely "fossil" (radiocarbon-free) as defined by Etiope (2009). It is known, however, that significant amounts of methane can reach the atmosphere only for relatively big and shallow seeps, generally not deeper than 200–300 m (Schmale et al., 2005; Mc Ginnis et al., 2006) otherwise most of methane is dissolved and oxidized within the water column. A wide number of flux data are however needed to assess the marine seepage "emission factors", i.e., the basic element of the up-scaling procedures and greenhouse gas emission estimates on large scales (EMEP/EEA, 2009).

In this work we show the results of a wide investigation, carried out in 2009 and 2010, of one of the biggest offshore–onshore gas seepage areas in Europe, located in the Katakolo Bay, along the Ionian coast of Peloponnesus (Greece) (Fig. 1). The origin of gas was preliminarily assessed in 2006 and partial flux measurements were done onshore (Etiope et al., 2006). Thermogenic CH_4-dominant gas (>80%) includes toxic and lethal amounts of H_2S (up to 0.5 vol.%), which induce a severe hazard for the local harbor and touristic activity. The origin of H_2S was suspected to be due to thermochemical sulfate reduction (TSR), based on the large H_2S amounts in Jurassic limestones (2500 m deep) and the wide presence of anhydrite. Here we extend the study by reporting: (a) side scan sonar and 3.5 kHz sub-bottom profile data, providing a complete "picture" of the offshore seepage area; (b) new molecular and isotopic data of the seeping gas including, for the first time, the isotopic composition of H_2S, CO_2, ethane (C_2H_6), and propane (C_3H_8); (c) extensive gas flux measurements, both onshore and offshore, based on a closed-chamber system. These data

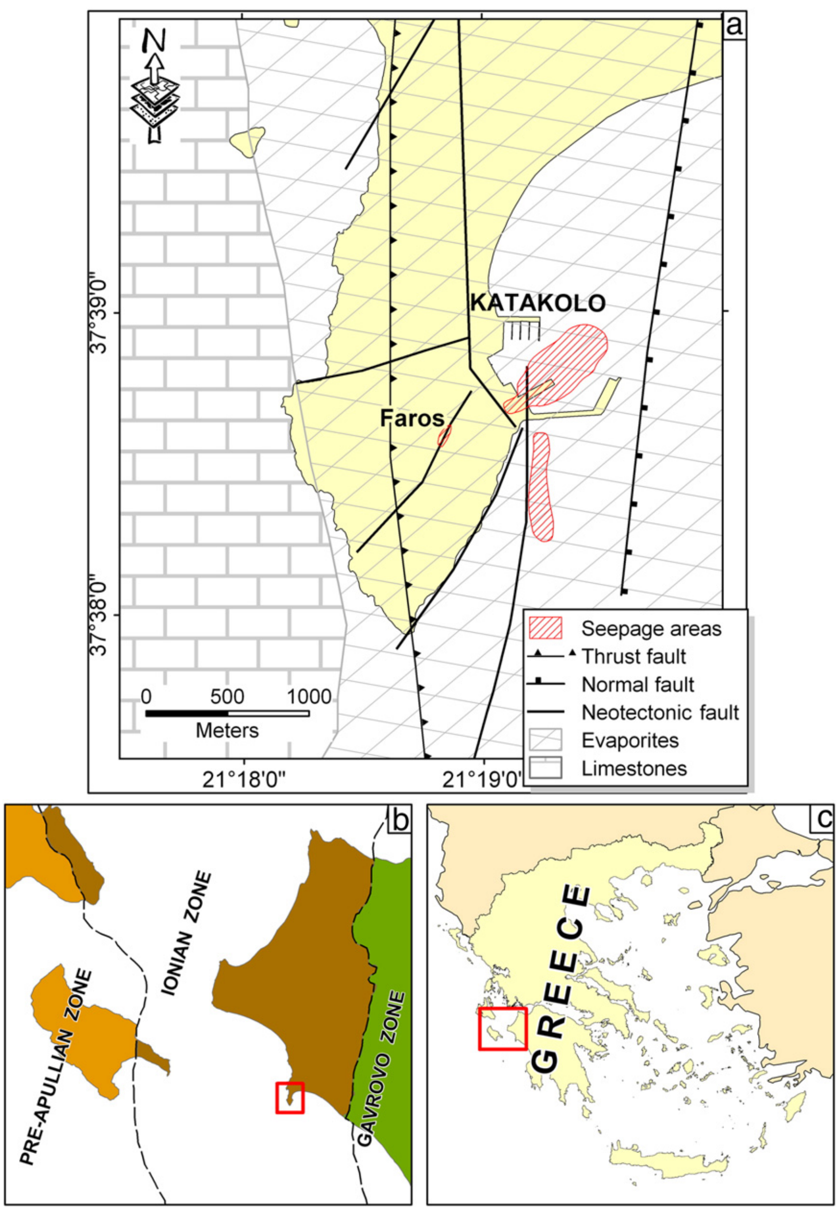

Fig. 1. (a) Structural map of Katakolo showing onshore and offshore seepage areas. Limestones and evaporites are present at the base of a 2000 m Neogene sequence. (b) General map showing the position of the study area in relation to the three tectono-stratigraphic zones of Western Greece. (c) Map of Greece with location of the study area.
Panel (a) was modified after Kamberis et al. (2000) and Etiope et al. (2006).