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# First high-accuracy temperature measurements of underwater methane seeps Zelenka, Black Sea

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## Първи високоточни температурни измервания на подводни метанови извори Зеленка, Черно море

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Abstract. We report the first high-precision temperature measurements of individual methane seeps in the Zelenka methane seep field, achieved with an accuracy of 0.003 °C, a sensitivity of 0.001 °C, and a sampling interval of 2 seconds. This paper reviews previous Bulgarian research on underwater gas seeps, with a particular focus on the extensively studied shallow methane seep field at Zelenka, located west of Cape Kaliakra. We discuss the feasibility of temperature-based monitoring and emphasize the necessity of temperature measurements as an integral component of underwater methane seep surveillance

Keywords: temperature, methane, seeps, Zelenka, precursor.

### Introduction

More than 50 shallow-water methane seep (MS) fields have been documented along the Bulgarian coast (Dimitrov, 2002), with over a half located within the Balchik region. Zelenka and Aladja Bank (Golden Sands) are the only fields where gas flux, seep field areas, and gas composition have been measured. The absence of systematic methane emission monitoring complicates the understanding of their role as greenhouse gas sources, contributors to seafloor instability, potential energy reserves, and indicators of active faulting, pockmarks, mud volcanoes, and unique marine ecosystems.

The increasing global concern about methane's contribution to climate change, particularly its growing atmospheric concentration, suggests it may surpass carbon dioxide ( $CO_2$ ) as the dominant greenhouse gas by the mid-21st century (Methane, 2024). Approximately 60% of methane emissions stem from anthropogenic activities. Given methane's relatively short atmospheric lifetime compared to  $CO_2$ , efforts to reduce emissions could result in measurable decreases within a decade (Trio of Sentinel satellites, 2023).

Several studies have explored the connection between seismic activity and underwater gas seepage (Nikonov, 2002; Gasperini et al., 2012; Fischer et al., 2013; Géli et al., 2018; Bonini, 2019). In the Bulgarian context, this relationship is particularly relevant due to the Shabla-Kaliakra Seismic Zone, known for historical earthquakes, and the active fault systems in the Balchik Bay, manifesting in the Zelenka and Aladja Bank methane seep fields. Gas eruptions, sometimes ignited, were reported before the 1901 Balchik earthquake (M = 7), indi-

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cating a potential earthquake precursor (Vasilev et al., 2021). Patented technologies for methane capture, monitoring, and the study of its connection to seismicity (Parlichev et al., 1986, 2024) have been proposed.

Current methane detection techniques in seawater include electrochemical sensors, optical methods, mass spectrometry, and biosensors, but these methods require further optimization in durability, cost, or precision (Liu et al., 2023). Acoustic methods remain the most widely applied technique for bubble detection. Here, we present high-accuracy temperature measurements taken near methane seeps and explore their potential for monitoring seep activity. The area of interest is the shallow Zelenka MS field.

## Zelenka Methane Seeps (MSs)

The Zelenka MS field is situated approximately 3 km west of Cape Kaliakra and 150–300 meters offshore from the fisherman's hut at Zelenka. Geophysical surveys using side-scan sonar and infrared imagery from the adjacent cliffs reveal two parallel lines of intense methane emissions. Most of seeps occur at depths of 6–9 m, though some are found between 3 and 12 m.

The seabed consists of sandy deposits and white clay silts, with outcrops of a Sarmatian limestone. The gas composition is primarily methane (CH<sub>4</sub>) at 95%, with nitrogen (N<sub>2</sub>) at 4% and trace amounts of oxygen (O<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), and ethane (C<sub>2</sub>H<sub>6</sub>). Methane is of biogenic origin (Vasilev et al., 2021). Similar gas compositions at both Zelenka and Aladja Bank suggest a common deep methane source. Previous temperature-salinity measurements in Balchik Bay have detected multiple freshwater sources, which may also exist in the Zelenka and Aladja Bank areas.

## Methods

The temperature data presented here were collected during short-term monitoring of methane seeps as part of the METZE3 Bulgarian-French campaign, focused on methane emissions at Zelenka. The data were analyzed within the framework of the EC project "DOORS: Developing Optimal and Open Research Support for the Black Sea."

The study follows initial observations from infrared thermal imaging conducted by IO-BAS and the Technical University of Varna, which identified two distinct linear temperature anomalies parallel to the coastline. Temperature, a critical parameter for gas monitoring, was measured to assess its potential as a rapid and integral method for estimating methane seep emissions. Thermal anomalies observed on the seafloor may provide key data for modeling subsurface heat sources.

## Results

Temperature measurements were conducted during the METZE3 cruise (September 27–28, 2024), using two autonomous temperature loggers (MTL 1854C, Antares GmbH, Germany). These loggers, designed for autonomous operation at depths of up to 6,000 meters, were calibrated in Varna in 2024, achieving a measurement accuracy of 0.003 °C.

Each morning, the MTLs were programmed with the start and end times for data recording and set to a measurement interval, primarily at 2-second intervals (with one exception on 64 – 27.09.2024, set at 10 seconds). The boat journey from Kavarna to Zelenka takes approximately 20 minutes (see Fig. 1a), following the trip from Balgarevo to Kavarna Port to launch the boat. Three scientists/divers from Ifremer in Brest installed the MTLs directly above active seeps within a  $10 \times 10$  m micro-polygon – the study area for METZE3/2024, at a water depth of approximately 6 m. The devices were secured using three stainless-steel mini-pilots, each 60 cm in length and 6 mm in diameter, gently fastened at one end of each device (see Fig. 1b). Due to the small boat size and an unfavorable weather forecast, the data collection period was reduced to roughly 2 hours instead of the initially planned 24 hours. Figures 1c-f display only the segments of each record that begin and end with the MTL deployment in the Zelenka area.

## Discussion

Our preliminary temperature measurements confirm the viability of using temperature sensors for methane seep detection and monitoring. Key findings include:

- Temperature is essential for quantifying fluid flow.
- The recorded temperature curves exhibit distinct day-specific patterns.
- Multiple groups of temperature anomalies were identified, warranting further investigation.
- The data provide potential evidence of freshwater seepage at Zelenka.
- These initial results establish the baseline requirements for developing low-cost temperature sensors for methane seep studies.

However, challenges remain, such as the need for additional calibration and supplementary monitoring tools to ensure accurate fluid flow estimates.



**Fig. 1.** EC project DOORS METZE3 campaign: temperature measurements at the Zelenka methane seep (MS) area 27–28.09.2024 with miniature temperature loggers MTL 1854C (Antares GmbH<sup>©</sup>). *a*) Photo: The working group in the boat travel from Kavarna; *b*) Photo: MTL logger fixed above an active MS; *c*–*f*) Graphics of temperature measurements with discretization 0.001 °C – vertical axis: temperature in °C, horizontal gridlines step 0.01 °C; horizontal axis: time, vertical gridlines step 5 min, period between main vertical gridlines (thicker black lines) is 1 hour. Red curves (Fig. *1c, e*): registration at 27.09.2024; blue curves (Fig. *1d, f*): registration at 28.09.2024. Fig. 1*c, d* are registered with MTL 185464C; Fig. 1*e, f* are registered with MTL 185465C.

#### Conclusions

Our findings highlight the potential of temperaturebased methods for the detection and monitoring of underwater methane seeps. The Zelenka methane seep field provides a unique and accessible site for further studies on gas emissions and their connections to tectonic activity.

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