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# BLACK SEA GAS SEEPAGE AND VENTING STRUCTURES AND THEIR CONTRIBUTION TO ATMOSPHERIC METHANE

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ABSTRACT
Only recently the international scientific community started to pay more attention of such natural, geological sources as submarine gas seepages and mud volcanoes and realized that they are significant sources of atmospheric methane. In this work the Black Sea is considered to be one of the most prolific areas in the World. Here we present a detail overview of the gas seepage areas documented offshore along the Bulgarian coastline, on the Georgian, Russian, Ukrainian and Turkish shelves as well as seabed gas venting structures as pockmarks, mud volcanoes, methane derived carbonate chimneys etc. Some speculations about massive gas outburst due to destabilization of gas hydrates are commented. The attempt to evaluate the annual quantities of gas methane venting from the seafloor, passing trough the water column and entering the atmosphere from gas seepage and venting structures shows values form 1.5 to 5.5 Tg (2.0-6.0x$10^9$ $m^3$ ) released from the Black Sea area, an area no exceeding one percent of the World Ocean aquatory.

## INTRODUCTION

Greenland and especially Vostok (Antarctica) ice core records for the last few hundred thousands of years clearly show the saw-shaped character of changing in atmospheric methane concentrations with rapid increasing to peaks higher than today one and extend irregular restoring to about the initial values with similar but short lagging temperature curve (Chappellaz *et al.,* 1993; Petit *et al.,* 1999). These indicate that Global warming and Global cooling are mutually depended natural processes repeated already several times during the Late Quaternary, which unknown mechanisms are waiting to be revealed. The authors believe that the present ongoing Global warming is the subsequent climbing to the next fang of the saw, dramatically accelerated by the human activities since the industrial age.

The data also evidenced that the past changes of atmospheric methane concentrations of magnitude more than 400 ppbv happened without any anthropogenic influences, which force scientists to look for natural sources of not only methane but all the greenhouse gases and the pathways of their escape. Only recently the international scientific community started to pay more attention of such natural, geological sources as submarine gas seepages and mud volcanoes and realized that they are significant sources of atmospheric methane. The few existing estimations of global atmospheric methane flux from these "minor" sources vary from a few terra grams (1 Tg = 1x$10^{12}$ grams) (Lacroix, 1993; Cranston, 1994; Judd, 2000) to 65 Tg $CH_4$ (Hovland *et al.,* 1993) per year coming from submarine gas seepage and from 5.1 Tg (Dimitrov, 2002) to 30.5 Tg $CH_4$ (Milkov *et al*., 2002) from mud volcanoes world vide.

Among the great number of publications describing individual gas seep sites and related seabed features offshore the Black Sea countries, mud volcanoes in the deep basin and number of gas hydrate discovering there are only two of them devoted on quantification of methane flux in the Black Sea (Tkelashvili, *et al.,* 1998; Dimitrov, 2002). Both papers present regional estimations of the flux from gas seepage only for Georgian and Bulgarian shelves, respectively and do not include other gas venting features, as mud volcanoes etc.

The purpose of this paper is to evaluate the annual quantities of gas methane venting from the seafloor, passing trough the water column and entering the atmosphere from gas seepage and venting structures on the seabed from whole area of the Black Sea including some terrestrial mud volcano areas as Kerch and Taman peninsulas and wetlands in the mouth of Danube delta.

## GENERAL GEOLOGY OF THE BLACK SEA

The Black Sea is large semi - enclosed marine basin having area of 423,000 $km^2$, volume of 534,000 $km^3$, and maximum depth of 2,248 m. It is connected to the Mediterranean Sea via Bosporus, a narrow strait that has a sill depth of about 50 m. At the same time the Black Sea has a gigantic catchment basin which includes the river discharge of half of Europe and part of Asia, its drainage area of 2,290,200 $km^2$ exceeds by more than 5 times the area of the Black Sea basin itself.

Geologically, the Black Sea is located to the south of the European craton and occupies a complex position on several structural zones. It is surrounded to the north, north-east, south and south-west by Alpine folded systems of Crimea, Caucasus, East and West Pontides and Southern Balkans. To the north and north-west it is bordered by the epihercynian, Mesozoic and Cenozoic formations, the Moesian and Scytian platforms. The deep Black Sea basin itself is formed by two basins separated by a ridge (the Mid-Black Sea Ridge) andrepresents a large depression infilled by up to 16 km thick, sedimentary series burying the pre-existing relief (Finetti *et al.*, 1988). The little-disturbed sedimentary strata lie almost horizontally in the whole deep basin. The basin fill consists of very thick from (3 to 5 km) Paleogene, mainly Eocene sediments, followed by Oligocene (about 3.5-4 km thick), covered by more than 2 km Miocene sediments. Pliocene and Quaternary are characterized by thick Danube fan deposits. The present sediment distribution pattern is a mixture of terrigenous sediments along the shelf and flanks of the basin, turbidites in the basin apron, and biogenic carbonates in the deep portion of the basin.

There are various views on the reason and timing of the formation of the Black Sea; area of resent oceanization, remnant part of Paleo Thetis ocean etc. From the view of plate tectonics the Black Sea may represent a remnant of back-arc marginal basin (Finneti *et al.,* 1988). According to this, during the geodynamic process, initiated in the upper part of Lower Cretaceous and terminated at the end of Paleocene (110-55 million years BP.), the opening of the Black Sea took place as a consequence of the formation of two back-arc basins behind the W and E - Pontides. The W-basin evolved to the stage of complete crustal opening with a basaltic basement, while E-basin evolved to the stage of a very thin continental crust affected by numerous listric faults and tilted blocks. In the Middle Eocene, the first compressive tectonic phase occurred and generated most of the orogenic belts surrounding the Black Sea. These compressive movements with overthrust deformation continue to the present day on the offshore Caucasus, and in the Crimea.

With respect to the water body, until the late Miocene the Black Sea was a shallow marine basin which, but subsidence during the latest Miocene to earliest Pliocene time (5 million years BP) transformed it into a deep marine basin. Since then, during the eustatic sea-level changes and because of the very narrow and shallow sill, the Black Sea became connected with or disconnected from its marine source. Thus it changed back and forth from marine to brackish to freshwater environment. During the last glacial period the Black Sea was a deep isolated fresh water lake. As the sea level rose at the end of the glacial the high salinity and dense waters from Marmara Sea were introduced into the Black Sea (about 7,000 years ago). Thus stratified the water column which caused the bottom waters to became anoxic.

## GAS SEEPAGE AND VENTING STRUCTURES

Data on shallow gas, mud volcanoes, gas seepage and related seabed features suggest that the Black Sea may be is one of the most prolific areas in the World. Here we will present a short review on all these features based on published information and own data. Most of the information is summarized on figure two illustrated with the major and most spectacular findings in the Black Sea area.

Evidences of shallow gas occurrences have been found almost everywhere within the Black Sea basin: from around the nearshore, shelf, especially the shelf breaks, continental slopes and abyssal plain. They include both geophysical (echo-sounder, seismic, subbottom profilers and side-scan sonar records) and (geo) chemical data.

The huge terigenous flux with relatively high content of fresh organic matter derived in the Black Sea is an excellent source for methane generation. There are two main patterns for discharging of this material. The first one, working in the largest NW and Western Black Sea shelf is the South density current - the major lythodinamic factor in this part of the sea. This anti clockwise current carry the terigenous material derived from Danube, Dneper and Dnester rivers (almost 80% of the total Black Sea flux) and discharge it mainly on the Bulgarian shelf. The second way is the discharging of the material derived from all other rivers. Because of very narrow shelf as in the southern par (all Turkish shelf), as in the Crimea region, as well as whole eastern part of the sea, the sediments are loaded directly at the slope base and abyssal plain passing the shelf and slope. This pattern have been valid many times for all Black Sea basin in the past, when the sea level have been about 100 m below present, because of eustatic changes. During that times have been deposited a series of organic rich sapropel layers, because of dramatic, sharp change of the living environment. Because of these, the scale of generating and retaining of "shallow gas" are larger in the Holocene muds of the shelf due to the relatively high content of fresh organic matter, and in the Pleistocene sediments in the deep waters.

**Gas seepages**

The seepage of natural gas is known to be widespread in both land and marine environments (Hovland & Judd, 1988). Gas seeps are known to be associated with leakage from gas reservoirs and shallow gas accumulations, and from gas hydrates; consequently, they occur in all the oceanic environments: coastal environments of deposition (bays, estuaries etc.); major deltas; hydrocarbon-bearing sedimentary basins on the continental shelf and slope etc.

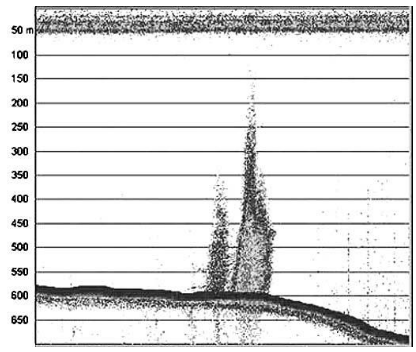


*Figure 1. A SIMRAD EK - 500 echogramm of double-seep, nicknamed "Two Captains" in the NW Black Sea at a depth of 593.5 m. The plume rises some 400 m into the water column (courtesy of V. Egorov/S. Gulin, Sevastopol, Ukraine)*

50 long existing gas seepage areas are described in Bulgarian coastal waters with more than 6,000 individual seeps and 482 water column targets representing gas seeps are identified offshore Bulgaria (Dimitrov, 2002a). Some ten thousand of seepage are reported to exist within the Georgian shelf (Tkelashvili *et al.,* 1998). Several areas of active gas venting are also known in Romanian (modern Danube delta preferably), Ukrainian (Geodekyan *et al.,* 1991) and Turkish waters as well as oil seeps (Iztan, 1996). More than 500 gas

plumes are documented by echo-sounding (fig. 1) along the shelf break of the Western and North-Western part of the Black Sea (Shnukov *et al*., 1999). Abundant gas seepage have been found around the edge of the basin in water depth down to 800 m along the shelf break and active faults in the shelf areas, especially along the frontal lines of Balkanides, Crimea and Great Caucasus, in the NW shelf where several oil and gas fields in the Ukrainian and Romanian shelves are exploiting, in the area of the Danube, as well as other delta and submarine fan complexes.

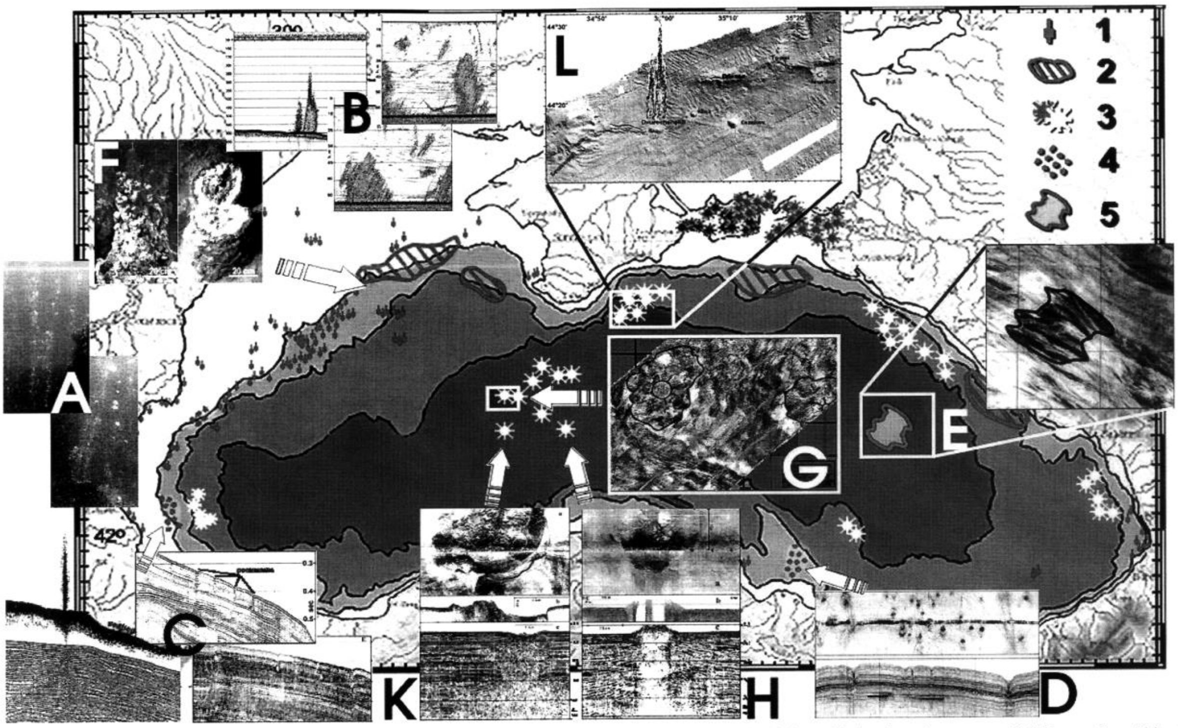


*Figure 2. Map of the documented Black Sea gas seepage, seabed venting structures and mud volcanoes. 1. Gas seepage or venting sites; 2. Areas with abundance of gas seepage; 3. Offshore and terrestrial mud volcanoes; 4. Seabed pockmarks; 5. Area of seafloor gas boiling swamp. A – Pictures of gas seepages offshore Bulgaria; B – Echograms of gas plumes from shelf break in the NW part of the Black Sea; C – Sparker profiles showing seabed pockmarks offshore Southern Bulgaria; D – Side-scan sonar image and corresponding subbottom profiler section with pockmarks on the uppermost Turkish slope; E – Deep tow side-scan sonar mosaic with the area of seafloor gas boiling swamp; F – Methane derived carbonate chimneys at water depth of about 250 m in the Northern Danube deep sea fan; G - Deep tow side-scan sonar mosaic of the MSU and Yuzhmorgeologia mud volcanoes; H – Composite Image (sonogram above, profiler and seismic sections bellow) of the Malishev mud volcano in the Black Sea abyssal plain; K – The same of the TREDMAR mud volcano; L – Swath bathymetry of the seafloor in the Sorokin trough wit several mud volcanoes and high intensity double vents on Dvurechenski mud volcano*

**Seabed gas venting structures**

Except, plumes from free gas bubbles in the water column, there are prominent features on the seafloor originated by the escape of the gas from seabed, i.e. pockmarks, carbonate chimneys, cold reefs, "boiling seafloor swamp" etc.

Pockmarks include isometric cone to saucer shaped depressions on the seafloor varying in size from a meter to more than a few hundred meters across with depths of less than one to more than ten meters. They were described and named for the first time in 1970 as morphological features formed on the continental shelf off Nova Scotia, Canada, (King & MacLean, 1970) and then observed and reported in many places all over the world ocean (e.g. Hovland & Judd, 1988). They occur in areas of fluid discharge, and need fine-grained sediments to support their structure and long existence. Nowadays it is widely accepted that pockmarks originated by expulsion of gas from over-pressured shallow gas pockets, dispersing the sediment into the water column (Hovland and Judd, 1988) or by intensive continuous fluid discharge hindering sediment deposition around the seep. Pockmarks may stay active, calmly seeping gas for long periods, or lie dormant between episodic eruptions.

In 1988 pockmarks were discovered for first time in the Black Sea along the Southern Bulgarian shelf break described by Dimitrov and Doncheva (1994). After then other two pockmark areas have been found in the peripheral shelf terrace south-east of cape Kaliakra (Dimitrov, 1998) and on the uppermost eastern Turkish continental slope (Kruglaykova *et al*., 2002)

The first area embraces about 100 km$^2$ zone with length of more than 41 km and wide from 2 to 5 km at water depths from 160-240 m to 230-350 m (fig. 2C). There are 305 documented pockmarks within it part of which active.

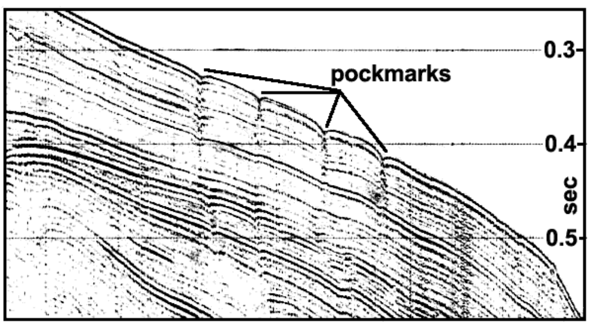


*Figure 3. A high-resolution sparker section from the upper part of southern Bulgarian continental slope on which V-shaped pockmarks are clearly visible*

The second one near cape Kaliakra is also elongated along the shelf break and more then 160 pockmarks are observed (fig. 3). The last one were localized during pipeline survey on the "Blue Stream" project in 1996. It is situated at water depths of 220-400 m (fig. 2D) and a lot of gas jets are observed coming out from the mouths of the pockmarks suggesting their present high activity.

Other evidences for gas leaking from the seabed are so called methane derived carbonate buildups. These are formed around gas migration path where occurs methane oxidation by methanotrophic bacteria inducing precipitation of carbonate which litifies the sediment. Cementation goes on around the methane pathway, fills channel and the pillar structure grows from outside.

Some areas with number of methane derived carbonate buildups big up to 3.5 m in height are discovered on the seafloor in the upper parts of north and north-western continental slopes – fig. 2F (Gevorkyan *et al.,* 1991; Treude *et al.,* 2002) as well as carbonate crusts in several places in the Sorokin Trough.

Recently a very interesting phenomenon named seafloor "boiling sediment swamp" was discovered in the Eastern Deep Black Sea Basin by the Russian team form Yuzhmorgeologiya, Gelendzhik (Kruglyakova *et al*., 2002). A large spot of high intensity backscattering is observed on the swath bathymetry mosaic of about 3,600 km$^2$ (fig. 2E). The more detail look on the area by deep towed side-scan sonar MAK-1 with profiler system shows that the seabed sediment in the area is highly gas charged and seafloor is very hummocky by abundance of small griphones – isometric hills about 5-6 m in diameter and near two metres of height, continuously venting gas.

**Mud volcanoes**

Mud volcanoes are geological structures formed as a result of the emission of argillaceous material on the Earth's surface or the sea floor. Sufficient water and gas is incorporated within this fine-grain muddy sediment to make it semi-liquid and to force it up through long narrow openings or fissures in the crust to produce an outflowing mass of so called mud breccia on the surface. The main driving force for mud volcano formation, discussed in detail by Hedberg (1980), Brown (1990) and Dimitrov (2002), is abnormally high-pore fluid pressure caused by a combination of rapid sedimentation, *in situ* gas generation and structural or tectonic compression. Depending of the activity of the mud volcanoes, they sporadically or continuously emit considerable volumes of gas to the atmosphere and it is mainly methane – up to 99% (Dimitrov, 2002).

There are 46 mud volcanoes on the easternmost part of Kerch peninsula and 42 on the Taman peninsula and more than 50 in adjacent shallow waters of Azov and Black Seas (Dimitrov, 2002) many of them presently active.

The presence of mud volcanoes in the central Black Sea abyssal plain has been supposed since the end of 1970s, when a set of multichannel seismic data was obtained by "Yuzhmorgeologia" - Gelendzhik, Russia.

The Black Sea mud volcanoes are randomly distributed at water depths below 2 km in an area of 6,500 km$^2$ south of Crimean Peninsula known as Central abyssal mud volcano area. Since 1988 to several expeditions was carried out by international teams in this area and 9 large mud volcanoes were studied in detail (Ivanov *et al.,* 1989)

Belts of clay diapirs and mud volcanoes are situated along the continental slope south-east of East Crimea in the Sorokin Trough where 11 exposed on the seafloor mud volcanoes are localized (Bouriak & Akhmetjanov, 1998; Bhorman *et al*., 2002). Several mud volcanoes have been found on the continental slope in the north-west Caucasian margin (Korsakov *et al.,* 1989.), southern Bulgaria part and in eastern Turkish continental slope. All these belts are connected with overthrust zones and with the development of Oligocene-Miocene basins in which 2 – 5 km thick fine-grained sediments of Maicopian Formation have been deposited. These sediments are believed to be the root of mud volcanoes, just as in the Kerch and Taman mud volcano areas.

Recently, tow big gas flares have been recorded by echo-sounder at the vicinity of Dvurechenski mud volcano in the Sorokin Trough rising some 700 m above the seafloor (fig. 2L). Judging by the measured high geothermal gradients and presence of gas hydrates in the bottom sediments other mud volcanoes are inferred to be active today as TREDMAR, Odessa, Vassoevich, Malishev (fig. 4) etc.

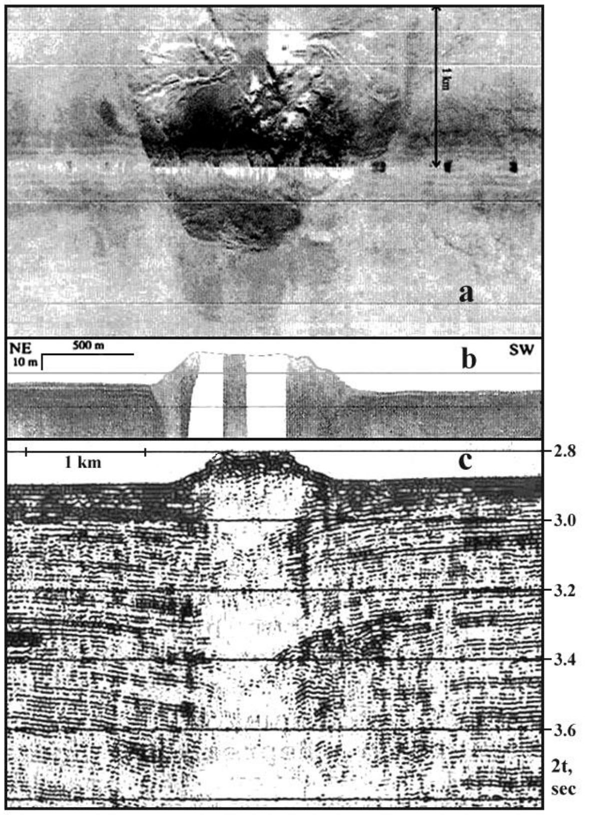


*Figure 4. The Malishev mud volcano (fig. 2F). a) MAK-1 deep tow sidescan sonar image with its corresponding subbottom profiler line (b) and seismic section (c). The well developed dome-like structure of the mud volcano is clearly seen as well as mud flow patches on the sonogram and several bright spots around the well delineated feeder channel on the seismic section*

## CONTRIBUTION TO ATMOSPHERIC METHANE

The previous estimations made by L. Dimitrov (2002) for the Bulgarian continental shelf suggest an annual gas flux at the sea-surface running from about 3,600 $m^3$ per $km^2$ to more than 18,000 $m^3/km^2$; the evaluation of Egorov and co-workers (2002) for an area abundance of high-intensity gas seepage set up these values between 9,100 $m^3/km^2$ and 630,000 $m^3/km^2$ (about 90,000 $m^3/km^2$ on average); and the extreme values form about 400,000 $m^3/km^2$ to 1,225,000 $m^3/km^2$ calculated for the Georgian shelf (Tkeshelashvili *et al*., 1997). If take an average conservative flux of about 10,000 $m^3/km^2$ than the quantity escaping to the atmosphere from the whole shelf area of the Black Sea (about 132,200 $km^2$) can be estimated on about $1.3x10^9$ $m^3$ or near one Tg.

The diffusive flux and low intensity gas venting from mud volcanoes in deep water environments are not taken into account also because gas is partially converted into hydrate (as much as 10 %), partially consumed by bacteria or oxidized in the near bottom sediments, other parts are captured in a hydrate form directly on the seafloor or consumed by diversity of species in a chemosynthetic communities, and the amount of the gases left dissolve totally in the sea water. The only gas able to enter the atmosphere from deep water environment is from very high-intensity plumes or blow-outs during the eruption of mud volcanoes.

The total contribution to atmospheric methane by mud volcanoes have been evaluated to be from 5.1 - 30.5 Tg per year commimg from near 1,900 individuals (Dimitrov 2002; Milkov *et al.*, 2002). There are about 200 mud volcanoes in the Black Sea and surrounding land areas, hence they should emit 10% of the world total as a minimum which give about 0.5 – 3.0 Tg ($0.7\text{-}4.2x10^9$ $m^3$) of methane annually.

## CONCLUSIONS

This short review evidenced that shallow gas, gas seepage and seabed gas venting structures are very common in the whole Black Sea area, which add another unique characteristic of the basin - the diversity and abundance of the shallow gas events.

The evaluation of the quantity of the gas released trough all these features shows that they are one of the significant natural, geological sources of atmospheric carbon and particularly gas methane. The total annual amount emitted trough them is estimated in the range 1.5 to 5.5 Tg ($2.0\text{-}6.0x10^9$ $m^3$) methane enter the atmosphere every year from gas vents of the Black Sea – an area no exceeding one percent of the World Ocean aquatory shelves and what about inland gas seepage and venting structures?

The released methane from the Black Sea area is comparable with the totals of other “minor” natural sources (Judd *et al.*, 1993) as natural coal seam fires (~1 Tg $CH_4$ $yr^{-1}$), hydrothermal sources ($2.3\pm1.4$ Tg $CH_4$ $yr^{-1}$) and are as significant as the anthropogenic emissions from total Industrial sources (9.1 Tg $CH_4$ $yr^{-1}$) (Judd *et al.*, 1993) or petrochemicals, petroleum refining and combustion of fossil fuels all together ($11.1\pm1.9$ Tg $CH_4$ $yr^{-1}$) (Lacroix, 1993).

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