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# BLACK SEA POLLUTION - CURRENT ENVIRONMENTAL PROBLEMS

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**Abstract**

*In respect to marine pollution, the Black Sea is one of the world's most vulnerable areas that environmental problems are serious. The Sea's shallow, mixed surface water, receive river discharges which are heavily loaded with nutrients containing nitrogen and phosphorus. In addition, a coastal industry appears to discharge wastes directly into the sea. Thus the water quality of the life-supporting surface layer has seriously deteriorated. Gas hydrates in the Black Sea are crystalline solids. Methane is the dominant component among other hydrocarbon gases in the sediments. Methane is important both as an energy resource and as a factor in global climate change.*

**Key words:** *Black Sea, environment, contamination, biological treatment, methane*

## INTRODUCTION

The Black Sea is the world's most isolated sea that has a surface area of 423 000 $km^2$, a volume of 5.45 x $10^5$ $km^3$ and a maximum depth of 2 212 m. It is a unique Sea shared between Bulgaria, Georgia, Romania, Russia, Turkey, and Ukraine. Its shallow, mixed surface layer has a relatively low salinity, maintained by a large influx of fresh water from two of Europe's largest rivers, the Danube and the Dnieper, as well as from the Dniester, Don, Kuban and a number of smaller rivers. The total drainage area extends more than 2 200 000 $km^2$. The total influx of fresh water is estimated to be 350 $km^3$ per year. A slightly smaller amount (230 $km^3$ per year) is derived from precipitation falling over the Black Sea area. The Mediterranean waters entering into the Black Sea through the Bosporus Strait in Turkey rapidly mix with cold waters on the continental shelf and sink to intermediate depth (500 meters), forming a series of cold intrusions spreading horizontally into the interior of the basin (Fabry K. et al. 1998). Unlike any other sea, the Black Sea is permanently anoxic (deficient in oxygen) below a depth of 150-200 m. 87% of the sea water is naturally anoxic.

This water brings a variety of products originated from the activity of more than 170 million people, who live in some of the most populated areas of the 17 different countries along river banks. The sea continues to suffer from a long list of ailments: pollution by land-based sources; losses of biodiversity as a consequence of pollution, invasive species, the destruction of habitats, overexploitation of marine living resources leading to a collapse of fisheries, etc, having a significant impact on the ecosystem health. In addition, there were and still are problems associated with coastal degradation, water borne diseases, the introduction of opportunistic exotic species, and maritime pollution caused by the transportation of oil and other hazardous substances

(http://www.globalpartnershipforoceans.org).

With regard to oxygen, the water is an extremely vulnerable environment. For the past thirty years, the major rivers that flow into the Black Sea have been dumping massive quantities of industrial waste into it, resulting in considerable damage to the ecosystem (DANUBS Project, 2002. 2001, DANUBS Project, 2005). The Black Sea is still the most popular tourist destination for people in nearby countries. Significant is the large volume of traffic passing through the area – both people and goods, including gas and oil on its way from the Caspian Sea - mostly transported on tankers. Major construction work is currently underway on pipelines. Co-operation is necessary between national authorities, responsible for water management, with a view to improving their ability to deal with challenges arising in a shared basin. Typical concerns include floods, drainages, construction and hydroelectric power plants, shipping and fishery. Water pollution is also an issue, with specific purpose of reducing the amount of pollution, discharged into the sea and protect water environment. However, although legislation on pollution exists, it is often not enforced (Dineva 2011).

Gas hydrates in the Black Sea are crystalline solids that form from mixtures of water and light natural gases such as methane, carbon dioxide, ethane, propane, and butane. Methane is the dominant component among other hydrocarbon gases in the sediments. Methane is important both as an energy resource and as a factor in global climate change. Methane gas hydrate is a solid combination of methane and ice. It is found under continental

shelves and on land under permafrost and can contain from 80–99.9 % of methane. Gas hydrate is found in sub-oceanic sediments and in continental slope sediments, where pressure and temperature conditions combine to make it stable. The difficulty with recovering this source of energy is that the fuel is in solid form and is not amenable to conventional gas and oil recovery techniques (Demirbas 2009).

In Sevastopol for example concentrations of dissolved methane in seawater and bottom sediments, as well as of methane emanating from gas seeps were measured at 18 stations including several small bays in the Sevastopol coastal area (Black Sea) during 2007– 2008 (Lyidmila et al. 2010). Methane concentrations in surface waters ranged from 10 to 2,970 nmol $l^{-1}$, and correlated well with values recorded for sediments. Methane concentrations in the water column were influenced by water depth, as well as by air and water temperatures.

As far back as the mid-1980s, local political leaders and environmental specialists began expressing concern about the worsening degradation. In the case of the Black Sea, the international community decided to act. The United Nations Development Programme (UNDP) led an international effort to identify the sources of degradation, invest in solutions, and strengthen the policies, regulations and institutions responsible for managing the Danube Basin into the future. The Global Environment Facilitymobilized funds. The project built on the Danube River Protection Convention which, in 1998, established the legal framework for cooperation among the Danube Basin countries. As a result of a UNDP-led effort, the flow of pollutants and urban wastewater into the northern Black Sea has abated, resulting in a healthier habitat with thriving marine life.

The aim is to analyze the current environmental setting related to discharges into the Bulgarian Black Sea and to focus on the most critical problems as to pollution. The survey ranges over a large number of discharges by rivers, municipal and industrial sources, agriculture, etc., linking to pollution of the Bulgarian Black Sea (BSERP Project 2003, BSERP Project 2007). On the other side the purpose of the study is to determine methane concentrations in the water column, bottom sediments and gas seepages, as well as to define potential methane sources.

## SUMMARY

*ANAEROBIC OXIDATION OF METHANE (AOM)*

Detailed historical overview of the last decades investigation of the Black Sea gas seeps are given in the most recent monograph "Methane seeps in the Black Sea: environment-forming and ecological role" (Egorov et al. 2011). The visual observation of gas bubble escapes from the seafloor in the Black Sea was firstly reported from the Bulgarian bay of Balchik and was treated as ordinary regional shallow gas indication (Dimitrov et al. 1979). However, in April 1989 methane seeps were discovered in the anoxic zone of the Black Sea during acoustic survey over the north-western shelf edge and the upper slope (Polikarpov and Egorov 1989). Afterwards, numerous seeps have been found by acoustic detection of plumes of emanating gas bubbles down to a water depth of 2070 m (Egorov et al. 2003, 2011). Most of these seeps are located along the shelf edge and on the upper slope, particularly at the paleo-deltas and canyons of the largest Black Sea rivers: Danube, Dnepr, Dniester and Don (Egorov et al. 2003). The deepest seeps have been discovered recently in association with faults and mud volcanoes in the central Black Sea basin (Egorov et al. 2003, Krastel et al. 2003). (Egorov et al. 2003) illustrated in their paper a distribution of methane seeps (dark spots) in the Black Sea. The beginning of this century was marked by a sharp increase in international multidisciplinary researches on Black Sea gas seeps, which were focused on: analysis of localization, spatial distribution and environmental role of seeps (Gevorkyan et al. 1991; Egorov et al. 2003; Shnukov et al. 1999; Egorov et al. 1998); study of geological conditions of gas hydrate generation (Shnukov et al. 1995; Naudts et al. 2006); studying the mechanism of bacterial oxidation of methane and formation of microbial build-ups in anoxic waters (Ivanov et al. 1991; Polikarpov et al. 1993; Michaelis et al. 2002); determination the age and genesis of methane in the Black Sea (Lein et al. 2002; Gulin et al. 2003), and quantification of emission of gaseous methane to the Black Sea water column and overlying atmosphere (Artemov et al. 2007; Egorov et al. 2003, 2011).

Anaerobic oxidation of methane (AOM) and sulfate reduction (SRR) were investigated in sediments of the western Black Sea, where upward methane transport is controlled by diffusion. To understand the regulation and dynamics of methane production and oxidation in the Black Sea, rates of methanogenesis, AOM, and SRR were determined using radiotracers in combination with pore water chemistry and stable isotopes. In the Danube Canyon and the Dnjepr palaeo-delta AOM did not consume methane effectively and upwards diffusing methane created an extended sulfate-methane transition zone (SMTZ) that spread over more than 2.5m and was located in brackish and limnic sediment. Measurable AOM rates occurred mainly in the lower part of the SMTZ,

sometimes even at depths where sulfate seemed to be unavailable. The inefficiency of methane oxidation appears to be linked to the paleoceanographic history of the sediment, since in all cores methane was completely oxidized at the transition from the formerly oxic brackish clays to marine anoxic sediments (Dineva 2011).

*ACOUSTIC DETECTION AND QUANTIFICATION OF GAS SEEPS*

*WATER EQUIPMENT*

It is well known that echo-sounding observation of the water column is an efficient method for the detection of bubble releases from the seafloor. Echo responses from numerous gas bubbles, rising towards the sea surface, combine on echograms into vertically elongated figures. This analogy is especially vivid if applied to color echograms where high levels of the echo-signal are coded with red hues. At the same time, "echographic gas flares are merely" “acoustic images” of real gas bubble streams, the physical size of which is difficult to estimate from echograms as illustrated echogram of the gas flare from seep site recorded at a ship speed of 1.9 km with the narrow beam 18 kHz Parasound parametric echosounder and photo of the same seep site obtained during the measurement of bubbling gas flux using the ROV QUEST-4000 (Egorov et al. 2003). Specialized software for acquisition and processing of acoustic data, accessible through the ETHERNET interface of the scientific echosounder SIMRAD EK-500, was developed (Artemov 2006) and regularly employed during a number of scientific cruises to obtain such data as: the area of a venting site; total number of bubbles, released per a time period; size spectrum and rise velocity of bubbles at different depths through the water column (Viktor et al. 2011).

The incomplete oxidation of methane in the major AOM zone and resulting methane tailing is a common feature of diffusion dominated methane rich sediments of the western Black Sea. The sluggish oxidation seems to be related to the location of the SMTZ in the sediment with a brackish or limnic history. Tailing of methane was less pronounced in core P824GC (Paleo-Dnjeper at 1014 m depth), where the SMTZ was located close to the sapropel and where the limnic sediment was covered by a thick layer of marine deposits.

Such methane cycling in the AOM zone might be based on higher levels of organic matter at the site of P824GC. In contrary, at the sites where the SMTZ is located in the originally limnic sediments it might be suggested that methanogenesis above the AOMzone could result in a tailing of the methane profile, which would be consisten with the data from P806GC ((Paleo-Dnjeper at 205 m depth) but could not be confirmed at P771GC (Paleo-Danube at 683 m depth). The importance of the brackish-marine transition was further indicated by the disappearance of methane at this transition in all cores, as well as the restriction of heterotrophic SRR to the marine deposits in P824GC. It was found that at the vast area of the Black Sea stretching from the Danube Canyon to the Kerch-Taman region only 1.6% of methane from gas bubble streams reaches the atmosphere in gas phase, while 98.4% dissolves in the water column (Viktor et al. 2011). Thus, the most part of methane carbon from gas bubble streams at this area transfers to the water column and enters into the biogeochemical cycles and bio-production process of the Black Sea.

Materials and methods Gas seepages in the Sevastopol coastal area were observed sporadically in 1989–1999 with the acoustic fish-finder JFC-46 from a fishing boat, and with Simrad EK-400 and EK-500 echo-sounders installed onboard the RV Professor Vodyanitskiy. Since 2006, series of boat surveys have been conducted using a portable 50/200 kHz sonar/GPS+WAAS chart recorder SeaCharter 480 DF. Acoustic data were then analyzed by means of the postprocessing software WaveLens (Artemov 2006). Several small bays and the coastal area in the vicinity of the city of Sevastopol were chosen for assessments of dissolved methane in water and sediments, as numerous bubble gas seepages have been discovered there (Lyudmila et al. 2010). Concentrations of dissolved methane were measured during the springs and summers of 2007 and 2008. Surface water samples were collected at 18 stations and bottom sediments at nine stations. Also, two 20-cm-long sediment cores were taken in the Strelezkaya and Martynova bays (sts. 13 and 18 respectively). Water samples were collected into 25-cm3 glass vials and degassed using the headspace technique according to Bolshakov and Egorov (1987). Sediments were sampled with a tube corer, enabling collection of 50–60 cm long undisturbed cores that were then sliced onboard using an extruder: one core from Strelezkaya Bay at 1-cm intervals, and another from Martynova Bay at 5-cm intervals. Pore water methane measurements were done in sediments of varying porosity.

*UNDERWATER OBSERVATION AND BIOGEOCHEMISTRY OF THE SEEP-RELATED MICROBIAL STRUCTURES*

The Black Sea’s degradation-- in many respects a microcosm of ocean pollution worldwide-- results from contaminants flowing from the Danube River, which courses some 2800 kilometers from southern Germany,

through farms, factories and crowded cities. Over a half century, nutrient-rich runoff from farms, plus urban wastewater, has led to eutrophication in the northwestern shelf of the Black Sea, with low-oxygen dead zones expanding. The resulting loss of fisheries and marine habitats disrupted livelihoods and diminished tourism.

A peculiar type of methane-driven microbial habitat is the large gas seepage area in the anoxic part of the northwestern slope of the Crimean Peninsula in the Black Sea (Michaelis et al. 2002). The deep anoxic shelf of the northwestern Black Sea has numerous gas seeps, which are populated by methanotrophic microbial mats in and above the seafloor (Demirbas 2009). Above the seafloor, the mats can form tall reef-like structures composed of porous carbonate and microbial biomass (Mahajan et al., 2007). Carbon dioxide ($CO_2$) reduction to methane was investigated in the presence or absence of methane, sulfate, and hydrogen. The level of $CO_2$ reduction was about 10% of the level of anaerobic oxidation of methane. However, since considerable methane formation was observed only in the presence of methane and sulfate, the process appeared to be a rereaction of anaerobic oxidation of methane rather than net methanogenesis (Treude et al., 2007).

The first underwater observations were carried out in 1990 with the scientific submarine “Benthos-300” and in 2001 with the submersible “Jago” (Germany). It was shown underwater photos of the methane-seep-related microbial buildups growing at the upper slope of the NW Black Sea. Recent microbiological, isotopic, molecular and petrographic analyses showed that such microbial build-ups were formed as a result of anaerobic oxidation of methane seeping from the bottom sediments, which was operated by a consortium of archaea and sulphate-reducing bacteria (Polikarpov et al. 1993; Boetius et al. 2000; Thiel et al. 2001; Michaelis et al. 2002). Stable carbon isotope analysis of the taken samples showed that carbonates of the buildups were isotopically light, indicating a high presence of the 13C-depleted methane carbon in the carbonates (Ivanov et al. 1991; Polikarpov et al. 1993; Michaelis et al. 2002). As no carbonate structures in the form of chimneys were found in the oxic waters, it was assumed that the Black Sea microbial buildups are formed as a result of anaerobic bacterial oxidation of methane seeping from the bottom sediments (Ivanov et al. 1991; Polikarpov et al. 1992). This has been argued recently by radiotracer, molecular and petrographic analyses of the Black Sea carbonate buildups, showing that anaerobic oxidation of methane is mediated by methanotrophic archaea in syntrophy with sulfate reducing bacteria (Thiel et al. 2001; Michaelis et al. 2002). The earlier 14C-dating has showed that age of carbonates in the base part of the Black Sea microbial buildups is in the range of 5100 years at water depth of 230 m (Ivanov et al. 1991) to 17500 years at depth of 1738 m (Shnukov et al. 1995, 2003). This dating, however, combines the age of both methane-derived carbon and carbon of bicarbonates dissolved in seawater (Gulin et al. 2003). Thus, the given ages may be considerably differernt from the actual time of origin of the Black Sea microbial buildups.

Carbonate structures at different depths of the continental slope may reflect dynamics of the long-term rising of the oxic/anoxic interface in the water column. This resulted in a change from aerobic to anaerobic oxidation of the seeping methane when oxygen has depleted at the respective depth. This suggestion allows for the consideration that the methane-derived microbial buildups are unique objects for further detailed tracing of the evolution of anoxic conditions in the Black Sea (Viktor et al. 2011).

*CLATHRATES AS UNCONVENTIONAL GAS SOURCES*

Gas hydrates were discovered in 1810 by Sir Humphrey Davy, and were considered to be a laboratory curiosity. In the 1930s, clathrate formation turned out to be a major problem, clogging pipelines during transportation of gas under cold conditions. Thermodynamic conditions favoring hydrate formation are often found in pipelines. Clathrates are crystalline solids which look like ice, and which occur when water molecules form a cage-like structure around smaller “guest molecules.” (Demirbas 2009). The most common guest molecules are methane, ethane, propane, isobutane, normal butane, nitrogen, carbon dioxide, and hydrogen sulfide, of which methane occurs most abundantly in natural hydrates (Mahajan et al. 2007). Water crystallizes in the cubic system in clathrates, rather than in the hexagonal structure of normal ice. In this structure, the cages are arranged in bodycentered packing; the unit cell contains 46 molecules of water and up to eight molecules of methane ($CH_4$). $5.75(H_2O)$], but not all cages are occupied. Methane is formed from the microbiological decay of organic matter in the absence of oxygen and can also be of thermogenic origin (Gupta 2004). The methane in gas hydrates is dominantly generated by bacterial anaerobic degradation of organic matter in low oxygen environments. Organic matter in the uppermost few cm of sediments is first attacked by aerobic bacteria, generating $CO_2$, which escapes from the sediments into the water column. In this region of aerobic bacterial activity, sulfates are reduced to sulfides. Below the zone of solid clathrates, large volumes of methane may occur as bubbles of free gas in the sediments. Clathrates occur wherever the conditions within the sediments are in the methaneclathrate stability field, and where methane and water are available. This stability is limited by temperature and pressure: gas hydrates are stable at low temperatures and/or high pressures. The average thickness of the clathrate stability

zone along continental margins is about 500 m. The depth of its lower boundary is determined by the geothermal gradient: at greater depths in the sediment, the temperature becomes too high for gas hydrates. The thickest clathrate zones occur in regions of low geothermal gradients; most clathrates occur within 2,000 m of the earth's surface.

The Black Sea is a unique energy-rich sea. It abundantly contains gas hydrates and hydrogen sulfide ($H_2S$) as methane ($CH_4$) and hydrogen source, respectively. The Black Sea is the world largest water body containing hydrogen sulfide and its hydrogen sulfide layer that begins about 200 meters below the surface. The concentrations of $H_2S$ differ from 1.5 to 2.3 mL/L in the Black Sea at depths of 200–1,500 m (Eremeev et al. 1998). Methane seepage is extremely intense on the shelf and on the slope of the Black Sea. Methane hydrates can form in the Black Sea at water depths exceeding 580 to 700 meters. One of the first reported observations of gas hydrates in marine sediments was from the Black Sea (Yefremova and Zhizhchenko 1974). The area of the Black Sea that is suitable for gas hydrate formation is evaluated at 288,100 $km^2$, representing about 68% of the total Black Sea or almost 91% of the deep-water basin. Methane has discharged into the Black Sea and the global ocean via fluid flow through submarine mud volcanoes. The areas of active fluid venting and mud volcanism were investigated in the Black Sea below the oxic zone at depths varying between 800 and 2,200 m. The presence of gas hydrates in oceanic sediments was first postulated on the basis of seismic observations (Tucholke et al. 1977). It soon appeared that vast amounts of gas hydrates must occur in sediments of continental slopes and rises, if the bottom-simulating reflector and the commonly underlying acoustic transparent layer were to be attributed to gas hydrates and underlying gas charged sediments (Shipley et al. 1979).

Methane gas hydrate is a solid combination of methane and ice that can be found under continental shelves and on land under permafrost and can contain from 80–99.9% of methane. Gas hydrates are also called clathrates. The word "clathrate" is derived from the Latin word "clatratus" meaning with bars or a lattice. A clathrate, therefore, is a material which is a weak composite with molecules of suitable size captured in spaces that are left by the other compounds. Considerable knowledge has been developed about their occurrence in nature and properties. However, the issues of technology and economics of natural gas production from gas hydrates are less well understood. Gas hydrate is an ice-like crystalline lattice of water molecules with gas molecules trapped inside. Given the favorable combination of pressure and temperature, and the availability of free methane and water, gas hydrates can form and remain stable (Sloan, 1990). Such conditions can exist in ocean-bottom sediments at water depths below 500 m (Kvenvolden 1993).

In the last few years, many governments (including those of the U.S., Canada, Russia, India, and Japan) have become very interested in possibilities of methane hydrates. Gas hydrates represent one of the world's largest untapped reservoirs of energy and, according to some estimates, have the potential to meet global energy needs for the next thousand years. Gas hydrates are potentially one of the most important energy resources for the future. Methane gas hydrates are increasingly considered to be a potential energy resource (Demirbas 2009). Considerable knowledge has been developed about their occurrence in nature and properties. However, the issues of technology and economics of natural gas production from gas hydrates are less well understood. Gas hydrates are increasingly recognized as a potential future energy resource, based on the vast amounts of methane trapped within them (Kvenvolden 1993). Gas hydrates are of considerable interest for their potential as an energy resource and for their potential role in global climate change. From an energy resource point of view, the enormous amounts of gas hydrate under the ocean and beneath arctic permafrost represent an estimated 53% of all fossil fuel (coal, oil, natural gas) reserves on earth, about 10,000 gigatons (Lee and Holder 2001). The worldwide amounts of organic carbon bound in gas hydrates is conservatively estimated to total twice the amount of carbon to be found in all known fossil fuels on Earth (Kvenvolden 1998; Collett 2002).

The difficulty with recovering this source of energy is that the fuel is in solid form and is not amenable to conventional gas and oil recovery techniques (Lee and Holder 2001). Proposed methods of gas recovery from hydrates generally deal with dissociating or melting in situ gas hydrates by heating the reservoir beyond the temperature of hydrate formation, or decreasing the reservoir pressure below hydrate equilibrium. The models have been developed to evaluate natural gas production from hydrates by both depressurization and heating methods. The depressurization method is lowering the pressure inside the well and encouraging the methane hydrate to dissociate. Its objective is to lower the pressure in the free-gas zone immediately beneath the hydrate stability zone, causing the hydrate at the base of the hydrate stability zone to decompose. Natural gas production from the dissociation of methane hydrate in a confined reservoir by a depressurizing down-hole well was studied. The case that the well pressure was kept constant was treated, and two different linearization schemes in an axi-symmetric configuration were used in the analysis. It was shown that the gas production rate was a sensitive function of well pressure and reservoir temperature (Ahmadi et al. 2007). The thermal stimulation method is applied to the hydrate stability zone to raise its temperature, causing the hydrate to decompose. In this

method, a source of heat provided directly in the form of injected steam or hot water or another heated liquid, or indirectly via electric or sonic means. This causes methane hydrate to decompose and generates methane gas. The methane gas mixes with the hot water and returns to the surface, where the gas and hot water are separated. The chemical inhibition method seeks to displace the natural gas hydrate equilibrium condition beyond the hydrate stability zone's thermodynamic conditions through injection of a liquid inhibitor chemical adjacent to the hydrate. In this method, inhibitor such as methanol is injected from the surface down to methane hydrate-bearing layers. The thermal stimulation method is quite expensive. The chemical inhibitor injection method is also expensive. The depressurization method may prove useful to apply more than one production. Carbon dioxide emission of methane is lower than all other petroleum derivates fuels in which it makes engine favorable also in terms of the greenhouse effect. Very positive contribution of natural gas on the environmental pollution must also be considered in economical aspects (Davies, 2001; Demirbas 2009).

## CONCLUSION

Studies in the Black Sea conducted from 1989 to present days revealed a previously unknown chemoecological and resource factor in the Black Sea – numerous methane-emitting gas bubble streams. At gas bubble outlets various biogeochemical and hydrodynamic effects are originated including gas exchange between gas bubbles and the water environment, the creation of zones of upwelling and vertical mixing of water, transferring from the bottom to the water column bacteria, sediment particles, as well as oil. Depending on water depth, initial size, rising speed, as well as some other parameters, gas bubbles can completely dissolve in the water column or reach the sea surface releasing to the atmosphere methane, one of the most important greenhouse gas.

Gas hydrates trapped in the marine sediments require multifaceted, extensive efforts to bring them into world energy balance. Gas hydrates exist in huge quantities in marine sediments below the sea floor and are found in association with permafrost in the Arctic. The volume of carbon contained in methane hydrates worldwide is estimated to be twice the amount contained in all fossil fuels on Earth. With increasing energy demand and depleting energy resources, gas hydrates may serve as a potentially important resource of future energy requirements. There are big gas hydrate reserves in the Black Sea. The Black Sea is a unique energy-rich sea. It abundantly contains gas hydrates as methane ($CH_4$) source. Methane can be recovered from the gas hydrates by the depressurization, thermal stimulation, and chemical inhibitor injection methods. The thermal stimulation and chemical inhibitor injection methods are quite expensive. The depressurization method is considered to be the most economically promising method for the production of methane gas from gas hydrates.

In Sevastopol coastal area, considerable amounts of methane reach the water and atmosphere from sporadically discharging gas seepages located along geological faults, and also from sediments due to the activity of methanogenic bacteria. Gas emitted by coastal seeps located beyond the area of geological faults contains 57 vol % methane. Radiocarbon dating suggests that the age of the seeping methane is less than 150 years, implying a biogenic origin. Concentrations of dissolved methane in bays of the Sevastopol area in 2007–2008 ranged from 10 to 2,100 nmol $l^{-1}$. Methane saturation in the surface waters varied between 960% and 71,900% during 2008, with maximum levels in summer in shallower waters. Estimated $CH_4$ atmospheric fluxes from surface waters ranged from 190 μmol $m^{-2}$ $day^{-1}$ in relatively deep coastal waters (depth of 5 m) to 1,550 μmol $m^{-2}$ $day^{-1}$ in shallower waters. $CH_4$ concentrations in sediments in the coastal seep area were higher than those recorded further offshore.

Major environmental threats for the Bulgarian Black Sea are untreated or not adequately treated waste waters, eutrophication (excess of nutrients), chemical pollution (toxic substances), oil spills, etc. The research about water discharges into the Bulgarian Black Sea found out that actions are needed by governmental institutions to approach efficient water management, including on these lines: implementing the best practices of water discharge management; developing an effective pollution defense strategy; efficient management of Bulgarian Black Sea watershed; new solutions on municipal water discharge and installation of the necessary infrastructure related to appropriate treatment facilities; action to prevent illegal untreated waste discharges; adapting techniques to meet industry challenges; involving in decision making process researchers, industry leaders and leading panel of shipowners and managers.

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