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ENVIRONMENTAL MANAGEMENT OF TRANSBORDER CORRIDOR PORTS

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Final report
/Executive Summary/

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The present report of environmental pilot monitoring of Port Bourgas - stage 1 *Preliminary Monitoring* is prepared in relation to the Project Environmental Management of Trans-border Corridor Ports /ECOPORT 8/ under Operative Programme for Trans-National Cooperation in South-East Europe by department “Water Use and Management” of the National Institute of Meteorology and Hydrology at Bulgarian Academy of Sciences, NIMH-BAS (previous Institute of Water Problems – BAS). The report is based on collective activities of the project team of NIMH and subcontractor-research groups.

This monitoring is an implementation of the first stage of the Pilot Monitoring Plan of Port Bourgas.
Implementation of Pilot Monitoring Plan of the Bourgas port,  
(Stage 1)  

Final report  
(Executive Summary)  

Introduction  
The environmental monitoring is one of the main concerns and tasks of the ECOPORT 8 project. The purpose of the monitoring stems from the first strategic goal of the common ECOPORT8 strategic environmental approach (see Final report WP4 Ch.8) - to assess the current environmental status of the port waters, air, sediments and maritime habitats and to identify in detail significant environmental impacts from the activities of the ports and ships in the ports and the activities in the port regions. It is essential for detecting in advance the environmental pollution caused by port activities and planning and implementing anti-pollution measures and activities. The pilot monitoring in the ports of Corridor 8 aims at gathering of current information about the main parameters, determining the port water and air quality, and any possible impact on them by the activities in the port. Such approach will allow initiating corrections in the technological operations for environmental protection and will support port management.  
Corridor 8 ports are different in type. They vary in size, location to the coastline and the city, the type of handled cargoes, with different approach to their historical development. This reflects in the choice of means of monitoring. When the harbor has no clearly defined boundaries of a protected marine area as the port of Bourgas, then the monitoring of waters and sediments becomes more complex and elaborate task. To substantiate the proposed research monitoring approach and methodology it is necessary to make a brief analysis of the existing conditions and prerequisites.  

Analysis of the existing conditions and formulation of the research assignment  
The port is located in the western part of the small Bourgas bay which is a part of the Bourgas bay- the largest bay along the Bulgarian coast line. Four Bourgas port terminals – the terminal “East” (the old harbor), the Bulk cargo terminal (or the terminal 2A), terminal “Ro-Ro” (future expansion) and the terminal “West” (or the Container terminal) are located in the small Bourgas bay. The Oil terminal “Rossenet” was constructed as a separate port outside the small bay. This terminal is located at a considerable distance from the city and serves the “Lukoil” refinery in Bourgas. The terminal “East” comprises the old port that has been exploited since 1893. The old harbor has a clearly defined protected harbor area with an entrance to it. A new breakwater and two piers are built in the small Bourgas bay after the biggest expansion of the Bourgas port, which forms three new internal port basins: aquatory between the terminal 2A and the new breakwater- the basin of terminal 2A, aquatory between the terminal 2A and the West terminal - the basin of terminal RO-RO and aquatory between the West terminal and the private Fish Port- the basin of Container terminal. These basins are only partially protected by the new breakwater, because
the small bay is open to the sea. There is no navigation turn circle water area and the new approach channel runs along the head of the breakwater and the ships reach the berths in the internal basins with complex maneuvers. The boundary of the port aquatory separating it from the waters of the small bay from southwest is marked only with navigational buoys limiting the depth of the approach channel. Since the port basins are open to the waters of the bay the impact of port activities and of adjacent industrial units activities on coastal waters cannot be considered separately and they must be assessed on the basis of a special comprehensive and integrated monitoring in the entire bay.

*The port activities interact with activities of adjacent industrial units in Burgas Bay*

Under these new environmental conditions in the port of Bourgas in case of necessity at any time to identify the source and the cause of a contamination there are no data enabling the estimation the water exchange between the port of Bourgas aquatory and the waters of the Bourgas bay. Hence the task of the port self monitoring is considerably complicated and important as it concerns as well the activities of the local industry and urban problems of the whole Bourgas municipality. Therefore, these urban environmental problems should not be resolved only by the port authorities since apart the port they are of concern of all users and stakeholders of the Bourgas bay and the Bourgas community.

For reasons to find correct and acceptable solution from an economic standpoint, the Pilot monitoring plan of the Bourgas port is divided in two stages - preliminary or investigative monitoring and operative monitoring. Preliminary monitoring aims at providing necessary information for an overall assessment of the changes in the environment, mainly in the water and sediments of the small Bourgas bay, resulting from the widespread anthropogenic activities, and at an attempt to answer the question: who is the main polluter in the Bourgas bay – the city with its industrial activities or the port? The results from the preliminary monitoring will help to develop,
optimize and design the next stage – the operative monitoring program. The present investigative monitoring can also be regarded as a first small step to organizing of a large-scale integrated monitoring of the whole Bourgas bay, which the city authorities will be obliged to take sooner or later. Important item of the study is a preliminary monitoring of the sediments in the bay as well as the water quality. This approach is justified by the fact that the sediments have a memory and keep historical information about pollutions at the place where the monitoring points are located.

Formulation of the research assignment

The monitoring is proposed to be conducted in the internal port basins in two stages - preliminary and full operative one.

### Scheme of the methodological sequence in port monitoring

The preliminary or investigative monitoring in the port of Burgas (first stage) includes the following research tasks:

- Identification of the locations with a high risk of oil pollution in the port waters through numerical modeling and simulations of oil spill drifts in the Bourgas Bay;
- Sediment and water sampling from the bottom and the water of the aquatory of the port and the bay of Bourgas;
- Revealing the most polluted areas in the small Bourgas bay and the port waters through the following studies:
  - analysis of the physico-chemical parameters of the water in situ;
  - testing hydrocarbons in the sediments;
  - testing organic matter in the sediments;
  - bio-testing bacterial phosphatase activity in the sediments;
  - measurement of elements concentration in the marine sediments through X-ray Fluorescent Analysis;
  - laboratory chemical analysis of water;
- General conclusions and recommendations.
The results from investigative monitoring tasks must provide the answer to the question about the location of the most polluted places in the port waters, the degree of contamination of water and sediments in the coastal waters in the Bourgas bay and who is the main polluter in the small Bourgas bay – the port or the town with its local industry.

**Determination of locations with a high risk of oil pollution** *(Numerical modeling and simulations of oil spill in the Bourgas Bay and contamination of the port waters)*

Numerical modeling of the water circulation and currents gives us information about the movement of pollution - oil spills and other liquids dangerous for the environment of the Bourgas bay and the port waters. The results of the numerical simulation help us in the selection of monitoring stations in the harbor and clarify the extent of protection of the harbor after the last port extension during 2000-2008.

Oil spills in the bay of Bourgas can be caused by the tankers that deliver the product to the Oil terminal of the Bourgas port which supplies LUKOIL refinery with raw oil. For numerical modeling it has been used the Marine forecasting system of National Institute of Meteorology and Hydrology - Bulgarian Academy of Sciences (NIMH-BAS). The operation system is fully automatic and uses state-of-art numerical models. It runs twice daily (based on 00 and 12 UTC). The system is driven by 3 hours average values of surface winds from the numerical weather prediction models *ARPEGE* and *ALADIN*.

The study of trajectories (oil drift) consisted of simulations of a large number of scenarios of combination of incident type, current field and local winds in the Bourgas bay. The oil spill model MOTHY calculates the spreading and diffusion and slick drift of an oil particle at the water surface due to the winds, waves and currents.

The main research tasks of the study are:

a. Identification of oil pollution accidents in the Bourgas bay and the port waters during the last 10 years;

b. Determination of the most probable information supplied to the model including specification of the oil type, the duration of the release and the probable location of the spill sources;

c. Calculation of the trajectories of oil droplets taking into account the physical and chemical properties of the product, and under different environmental conditions in the port and near shore waters;

d. Determination of the potentially affected areas of the port waters and visualization of the results.

The study of oil spill drift consisted in simulations of 240 different oil spills scenarios that combined the accident types, the current fields and local winds in the Bourgas bay. The oil spill model MOTHY calculates the movement of an oil particle at the water surface as the addition of its spreading and diffusion and slick drift due to the wind currents and permanent currents. Scenarios covered spills of Bunker fuel (Fuel oil No. 6) oil type. Oil density is accepted as 930 kg/m³; the duration of the release is 4 hours, the durations of the spill simulations up to 168 hours (7 days). The simulations are made for 4 seasons for the study area – Bourgas bay.

The numerical simulations were carried out for the area of the Bourgas bay and port waters for 20 locations imitating potential and real oil accidents along the main (existing) traffic route (corridor) to the port of Bourgas (terminal “East”, terminal 2A, terminal “West”) and near to the Oil terminal “Rosenetz”. The range of the
hypothetical scenarios includes various wind and current conditions. The starting points for the simulations were chosen along the main transport route (fairway) to the terminals of the port of Bourgas.

Input data for MOTHY model are bathymetry, monthly mean climatic fields of the sea currents in the Bourgas bay calculated by an non-stationary 3D numerical model, wind and mean sea level pressure fields.

*The simulations yielded the following area oiling results:*

As one might expect, environmental resource locations closest to the spill sites had the greatest risk of contact.

In case of oil pollution simulation with sources in small Bourgas bay the simulation output shows that the internal basins between the new breakwater, terminal 2A, terminal “West” and fish port are affected by significant oil pollution in various meteorological conditions. The basin of the terminal “East” (the old harbor of Bourgas) is not affected by oil pollution. A pollution of this terminal occurs only in a case of accidents inside the harbor.

In case of an accident in the area of roadsteads or in the area of the approach channel (external port waters) the simulations also show that there is a risk for oil pollution mainly for the internal basin between the new breakwater and the terminal 2A.

In case of an accident east of the roadsteads (east of the oil terminal Rosenetz) the probability for pollution of the terminals in the Bourgas port is much lower and is negligible. Because the main route of the tanker ships is east of Rosenetz (where there is some chance of a big oil accident) *the terminals in Bourgas are well protected against such accidents.*

*The zones that are at risk of oil pollution or other floating pollutants:*

- in red - area with significant risk will be affected in any conditions; in yellow - area with average risk depending on predominant conditions (winds and currents); in green-area-with not negligible risk during the specific meteorological conditions; other areas of the port - without risk.

About the Oil terminal Rosenetz: in cases of accidents east of its roadstead the probability for pollution of the terminal is low, due to the circulation in the Burgas Bay, which lead to a pollution south of the Bourgas bay. In case of an oil accident in the roadstead of the Oil terminal there is some risk in case of NE wind, but its breakwater protect at least the north part of the terminal. In case of an accidents with oil pollution west of Rosenetz or nearby the terminal itself the risk is significantly higher due to
the circulation regime and in such case the simulations show that the whole terminal will be heavily polluted or at least its southern part will. Because the climatic currents in different seasons are with very similar regime these conclusions are valid for all seasons.

Red placemarks - possible monitoring locations in areas of the port with significant risk for oil pollution

The most important results are the predicted paths of oil slicks under the prevailing conditions whether beaching is likely to occur. The modeling outputs present a range of useful information on potential oil movement and behavior. It should be remembered that these results are based on probabilities and that the exact areas oiled and travel times and locations cannot be predicted with complete accuracy. Modeling can be a very useful response tool but should be used in conjunction with all other available information.

Sampling performance from the bottom and the water (in situ) in the port and the bay of Bourgas (selection of experimental equipment and methodology)
Experimental equipment suitable for taking water and sediment samples in the aquatory of Bourgas bay and the area of the port complex should be done in the short terms envisaged in the monitoring program. This selection should meet three basic requirements:
- The specific requirements of the sample representativeness;
- Sufficient reliability of the sample taking and sample quality according to the requirements;
- Possibility for delivery of the necessary equipment according to the monitoring schedule.

The most reliable equipment, in accordance with the up-stated, was chosen:
- for point water samples – the probe Jukovski type;
- for sediment samples – the sample taker Petersen type.

The supplied equipment was subjected to testing in real conditions. The tests passed successfully and the devices showed good functionality and full fitness for the upcoming operations.
The monitoring region is part of the Bourgas Bay, where the whole port complex is situated. The selection of this region has followed the instructions in the Pilot monitoring plan of the Bourgas port and is adequate to the tasks of the project. Twenty three monitoring points or stations are chosen as two of them (p.22 and p.23) are reference points.

The sampling for the preliminary monitoring was done on 26 April 2011. The work was done aboard of a service cutter. The cutter was equipped with a GPS navigation system and was being positioned at the coordinates of each monitoring point. Sampling performance of each point includes two water samples (one from the bottom layers and one from 1 meter depth) and one sediment sample.
Sampling performance of water

Each sample is analyzed in situ for temperature, barometric pressure, dissolved oxygen (DO), conductivity, ORP, pH, resistivity, specific conductance, salinity, using the following equipment - Professional Plus Multiparameter handheld (with Quadro cable) and ProODO. Then each sample is transferred into a plastic bottle and stored in a refrigerator box for laboratory analyses.

In situ analyses of water samples

Sampling performance of sediments
Part of each sediment sample was sealed in a sterilized bottle for the next coming biological analyses. The other part was for physicochemical analyses. The protocols from sampling performance are given in Appendix 1 and Appendix 2.

The selection of all required equipment is based on detailed analysis of the work’s requirements. The choice is also complied with possible the delivery time. The sampling performance is realized according to the schedule by experienced professionals. The representativeness of the samples is adequate for execution of the preliminary monitoring.

**Analysis of physicochemical parameters of water in situ**

The current in situ analysis aims at defining the risk areas and critical points of contamination in the port of Bourgas aquatory. The status of the coastal waters in the harbor will be estimated on the basis of the physic-chemical analysis of samples. The parameters and their threshold limit values, which coastal waters must meet, are defined by Regulation No 8/2001.

According to the Pilot Monitoring Plan of Port Bourgas physicochemical measurements of water samples are carried out in 23 points of Bourgas Bay and port waters. The measurements were done with the devices of YSI Inc. – The Professional Plus Multi parameter handheld (with Quadro cable) and ProODO.

The YSI Professional Plus handheld multi parameter meter provides extreme flexibility for the measurement of a variety of combinations for dissolved oxygen, conductivity, specific conductance, salinity, resistivity, total dissolved solids (TDS), pH, ORP, pH/ORP combination, ammonium (ammonia), nitrate, chloride and temperature.

The calibration was done with YSI’s solutions that are NIST traceable. Confidence solution was used to check accuracy of the measurements.

The following conclusions could be made on the basis of the information gained after the analysis and interpretation of the available data (*the protocol of measurements and results is given in Appendix 3*):

**Salinity** - The measured salinity at the coastal area is within the norm.

**DO** - This parameter measures the dissolved oxygen that can be utilized by the aquatic life for breathing. When the water is nutrient rich, the microorganisms tend to increase and consume dissolved oxygen, resulting in a low level of the latter. When the level of dissolved oxygen is too low, it can result in the ruination of the aquatic life. The permissible concentration of DO is 6.2 mg/dm³ according to Regulation No 8/2001. The obtained results show that the quantity of dissolved oxygen is typical for the season. The last measurements show some rising of the concentration, because of underground rivers and some waste waters discharge. Additional measurements were done using optical luminescent technology ProODO.

**pH** – the seawater is naturally alkaline. The normal pH range for seawater is 7.2-8.7. According to the quoted above regulation the allowed limits of pH concentration is between 6.5 and 9.0 mg/dm3.

**Conductivity** of the sea water depends strongly on its temperature, somewhat less strongly on the salinity, and very little on the pressure. There is two results for each point - conductivity and specific conductance (corrected conductivity with measured temperature). The results are typical for the local conditions.

**ORP** is usually measured to determine the oxidizing or reducing potential of a water sample. It indicates possible contamination. ORP can be valuable if the user knows which component of the sample is mainly responsible for the observed value. For
example, excess chlorine will result in a large positive ORP value while the presence of hydrogen sulfide will result in a large negative one.

**Sediment testing in the port and the small Bourgas bay**

*Testing Hydrocarbons in sediments:* According to scientific literature, the anthropogenic activities in Burgas bay caused petroleum pollution of the environment and accumulation of resistant to biodegradation high molecule hydrocarbons on sea bottom. This test reveals the level of petroleum pollution and will help in the interpretation of bioassay data. Hydrocarbons in sediments are determined gravimetrically by threefold extraction of 5 grams of sediment sample with 15 ml chloroform for 30 minutes each. The extracts are collected and evaporated with vacuum evaporator at 160 rpm and 40°C. The weight of the residue was calculated as milligrams of total hydrocarbons per gram dry sediment.

Based on some published works, total hydrocarbons content in sediments more than 0.5 mg/g is indicative for a polluted, while sediments containing less than 0.01 mg/g of total hydrocarbons may be considered as unpolluted. In accordance with this rule, sediments from stations 19, 22, 4, 7, 23, 10 and 12 can be considered as unpolluted; sediments from stations 8 and 9 – as low polluted and the others – as heavily polluted. Totally, basins “Terminal Container” and “Terminal Oil” are most impacted of oil pollution.

![Bar chart showing total hydrocarbons (mg/g) in sediments from different sampling stations](chart.png)

*The level of total hydrocarbons in the Burgas bay sediments is high - up to 8.97 mg/g dry wt sediment*

It is very important to note that hydrocarbons extracted from the bottom sediments may be originated from petrogenic and/or biogenic sources and the gravimetric analysis is low precise in differentiating them. The share of hydrocarbons in total organic matter of Bourgas bay sediments varied in the range 0 - 8%, except station 2 where it increases up to 11%, *Appendix IV.*
The levels of hydrocarbons in the sediments of harbor basins and outside of the port

**Testing organic matter in sediments:** Organic matter accumulation on sea bottom is an indicator both of the organic matter pollution and the rate of nutrient turnover. The level of organic matter accumulation and its nature impact also on bacterial activity, in particular phosphatase activity. The data received from the test are used for calculation of bacterial phosphatase activity per milligram organic matter accumulated in the sea bottom sediments. The organic matter in sediments was determined by Turin’s method based on its oxidation by dipotassium dichromate.

In most of the sampling stations, the bottom of the Bourgas bay is muddy (except stations 19 and 21 where it is sandy) rich with organic matter. The concentration of bottom organic matter varies from 28 mg/g (station 20) to 372 mg/g dry wt sediment (station 13) and the most abundant of organic matter are the sediments of basin at Container terminal or terminal “West”.

**Organic matter concentrations in the different sampling stations**
The high organic matter concentration in the sediments of Container terminal is another indicator of the Vaya lake adverse effect on water and sediment quality in the basin.

![Bar chart showing organic matter concentrations in sediments of harbor basins and Bourgas bay](image)

Organic matter concentrations in sediments of harbor basins and Bourgas bay

The accumulation of high concentrations of organic matter on the sea bottom, especially on that of “Terminal Container” is a result of the low self-purification capacity of the Bourgas Bay.

**Testing bacterial phosphatase activity in sediments:**
Phosphatase activity of sediment bacterial communities is chosen as a biomonitor taking into account the importance of organic matter degradation and the cleavage of the orthophosphate group from organic phosphate compounds. Phosphorus is the growth limiting factor for phototrophic organisms in the sea and its supply depends largely on the regeneration of the phosphate from organic matter accumulated on the sea bottom. The regeneration process is carried out by exoenzymes called phosphatases.

This test indicates whether sediment bacterial communities in the different points of sampling are intoxicated and what the levels of intoxication are. In phosphatase assay, the phosphate group of p-Nitrophenylphosphate (p-NPP) is hydrolytically cleaved by sediment bacteria and the products of the cleavage are orthophosphate and p-Nitrophenol (p-NP). The color compound can be spectrophotometrically measured quantitatively. The routine assessment of sediment phosphatase activity follows a standard format, measuring only alkaline phosphatase concerning the values of environmental pH. In 15 ml centrifuge tube 1g sediment, 4 ml of 1M Tris-hydrochloride buffer (pH 9.0) and 1 ml 0.2M p-NPP (Sigma) are added. Samples are immediately mixed for 2-3 s in a Vortex mixer and incubated in dark at 22°C for 2 hours. The reaction is stopped and color is developed at the end of the incubation by adding 1 ml 0.5M CaCl₂ and 4 ml 0.5M NaOH to the sample. The sample gets centrifuged at 3 000 rpm for 10 min to pellet the sediment and supernatants are measured spectrophotometrically (CECIL 3021) at 420 nm. Absorbance readings are converted to μg of p-NP per gram dry sediment/milligram dry dead organic matter per hour by comparison to a p-NP standard curve. Spectrophotometric blank sample gets
prepared replacing the p-NPP from the reaction mixture with 1ml 0.2M Tris buffer (pH 9.0). All samples are analyzed in triplicate and average values were calculated, Appendix IV.

Bacterial phosphatase activities (μg/mg sediment organic matter/h) in the basins of the Bourgas port are relatively stable and equal to that of the referent stations (outside of the port waters – stations 21 and 22) on average, except that of the terminal 2A and the Container terminal where the rate of reduction is around 40%. The stability in bacterial phosphatase activities across the sea bottom is a result of the persistence and the long lasting history of pollution, as well as the capacity of bacterial communities to adapt to the new created environment changing their structure and composition. The sediment bacterial communities from basins of the Container terminal and the terminal 2A could not overcome the anthropogenic stress resulting in inhibited phosphatase activities and therefore reduced share in nutrients’ cycling.

Average bacterial phosphatase activity (μg/mg sediment organic matter) in the Bourgas bay basins.

The basin of the Container terminal is highly eutrophic and unfavorable for bacterial growth while the values of the environmental factors measured in the basin of the terminal 2A are much better. The low bacterial phosphatase activity in the terminal 2A basin may be a result of the toxicity of Zn whose concentration is the highest among the basin’s sediments measured or with grater probability - the impact of unstudied factor/factors (environmental and/or anthropogenic) in the survey.

Bacterial phosphatase activity (μg/mg sediment organic matter) varies among the sampling stations in the basins and the lowest values are recorded at the following stations: terminal “East” – station 3; terminal 2A - station 6; terminal Ro-RO – all the stations are relatively equal; Container terminal - station 13; the Oil terminal is represented only by station 2; Private ports – station 18; The approach channel is represented only by station 20. This variability is consequence of the sea bottom
heterogeneity manifested in the different rates of accumulation of organic matter and pollutants, as well as the different types of bottom substrata.

Bacterial phosphatase activity (μg/mg organic matter/h) in the sediments of sampling stations

The ecological state of the sediment bacterial communities (express by bacterial phosphatase activity) is in the range from “Moderate” at basins of the Container terminal and the terminal 2A to “Good” at the basins of the terminals “East”, “Ro-Ro” and “Oil”.

The eutrophication and pollution of the Bourgas bay started with the beginning of the industrialization of the region (1965-1970) and continued till the 1990 when a new environmental legislation limited the rate of anthropogenic impact of human activities on the Bay. Great changes occurred in the marine communities during this long lasting period, and the sensitive species reduced their number or completely vanished while the resistant once flourished and proliferated. These changes make marine communities more flexible and well adapted to the new environment created as a result of the human activities.

**X-ray Fluorescent Analysis of sediments:** Energy dispersive X-ray fluorescent method is one of the most popular methods for determination of element concentrations in environmental samples, especially marine sediments. This is because of the simultaneously determination of many elements (32), relatively simple sample preparation procedure and information from large amount of the sample. Detection limits for the different elements are between 1 and 10 μg/g, depending on the matrix and Z of the element. Relative uncertainty between 1 and 10% are typical for a trace element analysis. The EDXRF laboratory of the Institute for Nuclear Research Nuclear Energy (BG) is equipped with all necessary spectrometric systems: 1)Si(Li) detector with 25 μ Be window and 170 eV energy resolution at 5.9 keV Mn-Ka line (PGT); 2) the second system is equipped especially for light element analysis with Si pin diode detector, Peltie cooling, with 7μ Be window and 140 eV (KETEK); 3) the third system is equipped with Si pin diode detector, Peltie cooling, with 7μ Be window and 170 eV (KETEK) energy resolution at 5.9 keV Mn-Ka line.

Specialized software (X-Ray Fit) is developed in the laboratory for data processing (spectra and concentration equations) Energy Dispersive X-Ray – Fluorescent Analysis.
(EDXRFA), developed for 32-bits Windows based platforms. The software is used for spectrum accumulation, spectrum processing, qualitative and quantitative analyses. Calibration for sediments, based on International standards Marine sediment GM8 (IAEA) is performed.

**Measured Spectra**

*Comparison between the element concentrations in different sampling points; IAEA are threshold limit values*
The obtained results show that no significant deviation was found, except high concentrations of Cu, Zn and Pb in samples 5, 11 and 14. The seventh point in the graphic shows the results for sample marine sediment from the Proficiency Test (IAEA). No amount of Hg was detected, because of relatively higher detection limit for Hg – about 5 mg/kg. The protocol from the measurements and analysis are given in Appendix 5.

Natural background levels of heavy metals exist in the majority of sediments due to the mineral weathering and the natural soil erosion. Man’s activities, by pollution, accelerate the accumulation and increase the background level of heavy metals to level that has already detrimental effects on the environment. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of the essential metals, however, can be detrimental to the organism. Non-essential heavy metals of particular concern to organisms are cadmium, chromium, mercury, lead, arsenic, and antimony. The Bourgas bay sediments are much more loaded with heavy metals than the sea water and the most abundant of them are copper (Cu), zinc (Zn), manganese (MN), strontium (Sr) and lead (Pb). The concentrations of Cu in the sediments of the Bourgas bay basins exceed from 7 to 26 times that of control station (32 ppm) as the most polluted is station 11 located in the Ro-Ro terminal. Some of the metals recorded in the sea sediments are radioactive (Sr, Rb, Ba, La, Ce, Y, Pb) and their adverse effects on benthic organisms could be expected to be both chemical and radiological. Most of the radionuclides, except Sr, are in low and relatively equal concentrations across the sea bottom indicating their background origin and therefore non to negligible adverse effects on benthic organisms.

**Laboratory chemical analysis of the water samples** from 6 monitoring stations (sample 2 – Oil terminal; sample 5- terminal East /old harbor/;sample 8 – terminal 2A;sample 11 – terminal Ro-Ro; sample 14 - Container terminal and sample 22 - point of reference) were carried out in the laboratory of NIMH. The Permanganate oxidation, ammonium, nitrite ions, nitrate and phosphate ions are analyzed immediately after shipment with Spectrophotometer DR/2010 HACH.

The electrothermal atomic absorption spectrometry (ETAAS) measurements of heavy metals are carried out using a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer. A continuous flow (CF) vapor generation accessory (VGA-77, Varian) connected to an atomic absorption spectrometer (SpectrAA 55B, Varian) are employed.
for HG-AAS measurements of As and Hg. The protocol from measurements and comical analysis are given in Appendix 6.

The highest water nutrient loading is the basin of Container terminal. Physico-chemical characteristics of port waters are shown in Table

<table>
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<th>STANDARDS/ Validated Methods (VM)</th>
<th>Reg. № 8/ 2001</th>
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<th>Sample 5</th>
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<td>0,80</td>
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<td>0,00</td>
</tr>
<tr>
<td>9</td>
<td>((\text{NO}_2^-)) , mg/l</td>
<td>BDS EN 26777</td>
<td>-</td>
<td>0,026</td>
<td>0,000</td>
<td>0,020</td>
<td>0,020</td>
<td>0,038</td>
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<td>10</td>
<td>((\text{NO}_2 - N)) ,mg/l</td>
<td>BDS EN 26777</td>
<td>0,03mg/l</td>
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<td>11</td>
<td>((\text{NaNO}_2)) , mg/l</td>
<td>BDS EN 26777</td>
<td>-</td>
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<td>0,030</td>
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<td>12</td>
<td>((\text{NO}_3^-)) ,mg/l</td>
<td>BDS ISO 7890-3</td>
<td>-</td>
<td>5,80</td>
<td>2,40</td>
<td>2,40</td>
<td>2,40</td>
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</tr>
<tr>
<td>13</td>
<td>((\text{NO}_3 - N)) ,mg/l</td>
<td>BDS ISO 7890-3</td>
<td>1,5mg/l</td>
<td>1,40</td>
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<td>0,60</td>
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<td>0,60</td>
</tr>
<tr>
<td>14</td>
<td>((\text{PO}_4^{3-})) ,mg/l</td>
<td>BDS EN ISO 6878-1</td>
<td>-</td>
<td>0,06</td>
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<td>15</td>
<td>((\text{P}_2\text{O}_5)) ,mg/l</td>
<td>BDS EN ISO 6878-1</td>
<td>-</td>
<td>0,04</td>
<td>0,02</td>
<td>0,02</td>
<td>0,02</td>
<td>0,16</td>
<td>0,002</td>
</tr>
<tr>
<td>16</td>
<td>((\text{P})) ,mg/l</td>
<td>BDS EN ISO 6878-1</td>
<td>0,1mg/l</td>
<td>0,02</td>
<td>&lt;0,001</td>
<td>0,02</td>
<td>&lt;0,001</td>
<td>0,08</td>
<td>&lt;0,001</td>
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</table>

The basin of Container Terminal (sample 14) is affected by the wastewater treatment plant discharge into the port basin through a connecting channel. The basin bottom substratum is a grey-black mud smelling of hydrogen sulfide (H\(_2\)S) which is the end product of anaerobic biodegradation of detritus and indicator of anoxic conditions in the mud. The high concentrations of NH\(_3\)-N, as well as the high values of inorganic phosphorus (PO\(_4^{3-}\), P\(_2\text{O}_5\), P) are indicative for the eutrophic character of the port waters. The levels of heavy metals in harbor waters are under the threshold concentrations according to Bulgarian Regulation N0. 8/2001.
General conclusions and recommendations about the execution of the Pilot Monitoring Plan

After the Bourgas port expansion the newly built terminals “West” and “2A” enter the sea and together with the new breakwater form three semi open to the sea internal basins, where the berths are situated. That way the waters of the small Bourgas bay, in which the town wastewater treatment plant and waste water from industrial zones discharge, and the port aquatory waters are in permanent interaction due to the coastal circulation currents. These new circumstances made necessary application of an investigative approach to the organization and implementation of the port self monitoring system. According to the Pilot monitoring plan one of the primary tasks is the determination of the most polluted zones in the port aquatory, including the ones potentially endangered by oil and other hazardous liquids spills from ships in the Bourgas port. In parallel with the assessment of the port water and sediments pollution it is important to identify the dominant pollution source – the growing city with its industry or the port with its activities.

On the basis of the results of the performed exploration monitoring of the water and sediments in 23 points in the small Bourgas bay, including 5 internal port basins, the following conclusions and recommendation could be made:

1. A single monitoring point or station would be sufficient enough for monitoring the water of each port basin, as the difference in the water quality characteristics in various points across every separate basin is in a range which does not matter in general. This is due to the dynamic circulation, water exchange and currents, as well as to the relatively small area of the port basins. This conclusion gives freedom of the permanent water monitoring stations position selection. The monitoring point can be located nearby the quay wall or positioned on a floating buoy.

2. The hypoxia (except stations in the old harbor or the terminal “East”), the low values of ORP even negative in some stations, the concentrations of NH3-N exceeding the threshold, as well as the high values of inorganic phosphorus forms (PO4³⁻, P2O5, P) are indicative for the eutrophic character of port waters.

3. The most nutrient loaded basin in the harbor aquatory is the Container terminal basin where the water and sediment quality is under the impact of the wastewater treatment plant discharge into the port basin through a connecting channel, the private Fish port and other industrial units along the coast.

4. The levels of heavy metals in harbor waters are under the threshold concentrations according to Bulgarian Regulation 8/2001.

5. The port water circulation modeling shows that pollution with oil and oil products of the port of Bourgas is possible when the pollution sources are in the small Bourgas bay. Oil spills eastward of the Oil terminal cannot reach the port aquatory in the small Bourgas bay.

6. Values of water quality indicators that exceed the thresholds are detected mostly at places with discharges of urban wastewater from treatment plants and industrial facilities to the harbour area. This shows that the port activities cannot be regarded as a major polluter of the port and the coastal waters. Irrespective of the pollution origin, it is essential a permanent water quality monitoring in the all basins of the port to be carried out. Automatic monitoring stations already exist in two of the harbor basins - terminal “East” and the Oil terminal, and they can be upgraded for water monitoring of the parameters.
included in the Pilot monitoring plan. Similar stations should be set for the remaining three port basins, without interfering cargo handling.

7. The analyses of the sediments taken from various points of the bay show different level of pollution with different pollutants. The level of the total content of hydrocarbons in most of the sediment samples is higher than 0.5 mg/g, and can be categorized as high. The most polluted areas are those of Oil terminal and Container terminal. The concentration of organic pollution is the highest in the sediment samples from the Container terminal.

8. The sediments of the port basins are polluted with heavy metals. The metals with the highest concentrations are Cu and Zn, exceeding on average 10 and 5 times respectively those of the control station. The most polluted with Cu and Zn sediments are that of the terminal “East” and the Ro-Ro terminal.

9. Phosphatase activity of the sediment bacterial communities (calculated per milligram of dead organic matter) are relatively stable across the Bourgas port basins. It is calculated referring to the dead organic matter which is of primary importance for the surviving and high activity of heterotrophic bacteria. The adverse effects of anthropogenic stress on sediment bacterial communities are recorded only in basin of the Container terminal (high levels of nutrients load) and terminal “2A” where phosphatase activity is inhibited by 40%. The anaerobic conditions in the Container terminal sediments inhibit the activity of the aerobic bacterial communities including their capacity to decompose the organic matter and cleavage the orthophosphate group from the organic phosphate compounds.

10. The analyses of the sediments taken in various points of the bay also show different level of pollution with substances of low toxicity. This makes possible the biological species to adapt and to develop resistance capacity to the environment.

11. The most relevant stations for sediment monitoring concerning the state of marine ecosystem are as it follows: terminal “East” – station 5; terminal “2A” – station 8; terminal “Ro-Ro” – every station is relevant according to the homogeneity of the environment; Container terminal – station 14 (regardless the lowest phosphatase activity recorded in the station 13 it not relevant because of the high impact of Vaya lake).

12. The obtained results show that no specific contamination in port waters was found. It should be pointed out that contaminations of other sea ports in the world are similar. The port aquatory is a subject to intensive human impact because of the close proximity of Bourgas town and its industrial zones along the beach. The human activities lead to a significant pollution of the coastal waters by different types of contaminants, mainly petroleum hydrocarbons, organic pollutants and heavy metals.

Appendix 1 Coastal sea water monitoring sampling
Appendix 2 Coastal sea sediment monitoring sampling
Appendix 3 Data from in situ water measurements
Appendix 4 Data from bio-test and chemical analysis of sediments
Appendix 5 Data from X-Ray Fluorescent Analysis of sediments
Appendix 6 Data from Laboratory physicochemical analysis of water