5.0 ASSESSMENT OF THE HYDROCARBON CONTAMINATION EAST OF THE PERIMETER OF OILTERMINAL SOUTH STORAGE AREA

5.1 STUDY AREA

Dan C. Jipa, Marian Malageanu

This area is located immediately South of Constanța City, between the Oil Terminal South Storage Area and Constanța South Harbor (Figure 5.1).
The eastern vicinity of the Oil Terminal South Storage Area is a zone that was submitted to significant morphologic changes during the construction works for the enlargement of Constanța Harbor. Therefore, it was necessary to obtain a new topographic plan containing enough details needed for our geoecological investigations. The topographic plan (Figure 5.1) was made at the scale 1:4 000, by combining planimetric and altimetric works. The ground morphology was reproduced by elevation isolines 1 m apart.

Figure 5.1 *Geoecological Research Perimeter East of the Oil Terminal South Storage Area*

Figure 5.2 *Location of the Boreholes within the Perimeter East of the Oil Terminal South Storage Area*

This area is crossed by the Constanța – Mangalia railway, which branches out towards Oil Terminal South Storage Area and Constanța South Harbor. There is a paved road parallel to the main railway, from which a dirt road leads to the Harbor.
The main railway is placed on a flat ground surface, like most of the ground at Oil Terminal South Storage Area. Immediately eastward of this flat zone and the Constanța – Mangalia railway, there is a steep slope, continued by a zone with relatively irregular morphology that lowers gently towards the Harbor. There is also a small lake towards the base of the steep slope.
The zone located immediately eastward of Oil Terminal South Storage Area is significant for the springs discharging water with visible petroleum products on the steep slope mentioned above. There is no additional information regarding any investigation of this area. Our study appears to be the first investigation on this matter.
Data from six boreholes (f25 – f30), located East of Oil Terminal South Storage Area, were discussed in the previous chapter and presented in Table 5.1 and Figures 5.3-5.5 below, as they were used for the flow model in the Oil Terminal South Storage Area. This chapter focuses mainly on the petroleum contamination in the eastern vicinity (Figure 5.2).

Table 5.1
Ground Elevations and Water Table Elevations in the Six Boreholes Located East of Oil Terminal South Storage Area

Borehole	Ground elevation (m)	Water table depth (m)	Water table elevation (m)
f25	16.35	4.85	11.50
f26	19.73	4.50	15.23
f27	25.89	2.40	23.49
f28	24.71	2.30	22.41
f29	19.50	dry	-
f30	16.21	1.15	15.06

Figure 5.3 *Lithological Columns of the Study Boreholes within the Perimeter East of the Oil Terminal South Storage Area*
Figure 5.4 *Geological Cross-Sections through the Pleistocene Deposits within the Perimeter East of the Oil Terminal South Storage Area*
Figure 5.5 *Hydrostatic Heads in the Zone East of the Oil Terminal South Storage Area*

5.2 GEOELECTRICAL STUDY EAST OF OIL TERMINAL SOUTH STORAGE AREA

Victor Niculescu, Mihai Mafteiu

The VES geoelectric study was performed along the following cross-sections:
- S4-4' outside the storage area;
- S5-5' along the road limiting the Harbor zone;
- S6-6' in the Harbor zone, lower than the level of the springs discharging contaminated water.

Figure 5.6 *Sketch of the Locations of the Vertical Electric Soundings and the Geoelectric Cross-Sections along the Eastern Border of the Oil Terminal South Storage Area*
Figure 5.7 *Interpretative Geoelectric Cross-Section 4-4' – East of Oil Terminal South; horizontal scale 1:2000, vertical scale 1:200*
Figure 5.8 *Interpretative Geoelectric Cross-Section 5-5' – East of Oil Terminal South; horizontal scale 1:2500, vertical scale 1:200*
Figure 5.9 *Interpretative Geoelectric Cross-Section 6-6' – East of Oil Terminal South; horizontal scale 1:2500, vertical scale 1:200*
Figure 5.10 *Apparent Resistivity Map at 7 m deep – East of Oil Terminal South; scale 1:4000, local coordinates*

The measurement results reveal the three geoelectric regimes listed below, each attributed to a specific type of lithological structure affected by the infiltration of complex petroleum contaminants (miscible and non-miscible), associated to highly polluted infiltration waters. This process led to the change of the natural resistivity of the geological structure, as described herein:

- dry silty clays (macroscopic loess) emphasized in the geolectric cross-section by values over 20 Ohmm (here, the maximum value is 54 Ohmm);
- inside the wet silty clays (macroscopic loess) that constitute the formation where the oil pollutants are located; the 20 Ohmm limit indicates the depth and extension of the zone affected by oil contamination;
- abnormal values under 20 Ohmm (20-10-5 Ohmm) contour, on one hand, the limit between loess and the basal brown/red clay; on the other hand, on the background value of 20 Ohmm, intensively polluted zones are represented by resistivities under 10 Ohmm.

The zones of minimum resistivity, between 10 and 20 Ohmm, and located at 8 - 9 m deep (upper part of the aquifer) represent the geoelectric effect of the macroscopic loess impregnated by petroleum products. The width and the position of this strip is controlled by the fluctuations of the water table. The zone denoted as "mipp" (meaning "intense petroleum products smell") is comprised between the 20 Ohmm isoline, at the upper part, and the 10 Ohmm isoline, at the lower part (Figures 5.7-5.9).
The distance of the eastern profile 4-4' with respect to the eastern fence of the storage area is 100 m. As it was presumed that the width of the contaminant plume is higher than 100 m, the distance between VES was chosen 50 to100 m.
The investigation depth is 14 m, enough to catch the water table and to reach the red clay.
For the interpretation of the geoelectric information, data provided by the study boreholes were correlated to the VES data provided by the four available geoelectric cross-sections (1-1' in the zone of the loading ramp of the Oil Terminal South Storage Area, presented in the previous chapter), 4-4', 5-5' and 6-6' East of the storage area.
First of all, the geoelectrical research emphasized the eastward continuity of the pollutant plume. The intensively polluted zone is located on the geoelectric cross-section 4-4' on the VES os64 and os66, corresponding to the direction on which the springs discharging petroleum products on the seaside slope appear at the VES os178-179 and os182-183. Therefore, we can say that the flow direction, mainly northeastward, carries away the petroleum products, along this direction, towards the seaside slope.
On the geoelectric cross-section 5-5', the prevailing discharge zone is located 8 m lower than the main road, under the military unit.
The geoelectric map (Figure 5.10) at 7 m deep was made in order to provide information concerning the main discharge direction of the polluted unconfined aquifer from the Oil Terminal South Storage Area.

5.3 HYDROCARBON CONTAMINATION EAST OF OIL TERMINAL SOUTH STORAGE AREA

Dan C. Jipa, Gicu Opreanu, Rodica Popescu, Viorel Gheorghe Ungureanu

Location of the Hydrocarbon Infiltrations Visible at the Surface

The perimeter located East of the Oil Terminal South Storage Area is well known for the occurrence of visible hydrocarbon infiltrations. This process was observed in a zone located on the morphological slope, denoted as "seaside slope" (Figure 5.11).

The area with springs discharging contaminated water is around 250 m long and 50 m wide. These springs have low flow rates and the floating hydrocarbon layer is maximum 1 mm thick. Water discharged by these springs supplies some small lakes.

Figure 5.11 *Zones Visibly Contaminated by Hydrocarbons East of the Oil Terminal South Storage Area*

There are many points where contaminated water emerges. Many of these small springs are drained by hand-made systems, in order to recover the petroleum products.

Other visibly, but less intensively contaminated zones were located in the following places:

- at the railway passage over the oil pipeline (Figure 5.11);
- in the small lake formed at the base of the steep morphological slope (Figure 5.11), where the water is obviously contaminated with hydrocarbons.

Hydrocarbon Contamination of the Soil and Sediments

The intervals of soil/sediment contaminated by hydrocarbons in the sedimentary columns of the study boreholes (situation from 2001) were contoured based on visual and olfactory observations. Thus, several categories of intervals were identified, for the intensity of the petroleum product odor (Figure 5.12). The main conclusions on contamination of the sedimentary columns in this zone are:

- contamination of sediments occurs only in the northward boreholes (f25, f26 and f27);
- three visibly contaminated intervals were delimited in Borehole f27, one interval in Borehole f26 and two intervals in Borehole f25; according to the intensity of the petroleum product odor, differing contamination degrees were noted;
- the presence of oil at the bottom of all the three boreholes from the northern alignment, but also for the Borehole f28 from the southern alignment.

The intensity of the UV luminescence of the sediment samples collected during the drilling of the boreholes indicated high hydrocarbon content in f27 and low hydrocarbon content in f30:

Table 5.2
Intensity of the UV Luminescence for the Water Samples Collected from Boreholes f27/2 and f30/2

Borehole	UV luminescence
f27/2	****
f30/2	*

Hydrocarbon Level in the Contaminated Springs

Samples from the springs were also analyzed by means of the UV luminescence, in order to determine the level of hydrocarbon contamination. The quantitative relationship between water and hydrocarbon was determined on samples collected during a standard time interval.

The water samples from the springs contaminated by petroleum products were analyzed from two points of view:

- intensity of luminescence of the water samples collected from the springs (Table 5.3)
- the quantitative relationship between water and hydrocarbons for each of the springs (Tables 5.4 and 5.5)

Table 5.3
Intensity of the UV Luminescence for the Water Samples Collected from the Springs

Sample #	Spring #	UV luminescence
1	I	–
2	II	*
3	III	*
4	IV	*
5	V	*
* degree of luminescence intensity		
– no luminescence		

Table 5.4
Parameters of the Water Samples Collected from the Springs

Sample #	Spring #	Water		Hydrocarbons	
		volume (ml)	sampling time	volume (ml)	sampling time
1	I	530	9"	47	2'
2	II	525	11.5"	495	52"
3	III	480	37"	190	2'
4	IV	410	59"	210	2'
5	V	505	19"	475	83"

Table 5.5
Quantitative Relationship Water – Hydrocarbons for the Samples Collected from the Springs

Sample #	Spring #	Rate		Ratio water rate/ hydrocarbon rate (A)
		Water (ml/s)	Hydrocarbons (ml/s)	
1	I	58.80	0.39	150.77
2	II	45.65	9.51	4.86
3	III	12.97	1.58	8.2
4	IV	6.94	1.75	3.96
5	V	26.57	5.72	4.64

Analysis of the results for the samples collected from the springs indicates that in the place where the water rate is very high, the petroleum products rate becomes relatively low; therefore the degree of water contamination becomes insignificant. This happens in the case of the spring I, for which the water sample doesn't show luminescence and therefore, it is not contaminated, comparing to the samples from the other springs with obviously lower rate (the A ratio is significantly lower for the springs II, III, IV and V (Table 5.5).

5.4 BOUNDARIES AND TENDENCIES OF CONTAMINATION EAST AND SOUTH OF THE OIL TERMINAL SOUTH STORAGE AREA

Dan C. Jipa, Victor Niculescu, Mihai Mafteiu

Data on the Petroleum Product Contamination East of Oil Terminal South Storage Area

Integrating the data concerning the contamination of soil, sediments and groundwater in the eastern part of Oil Terminal South Storage Area and in its eastward vicinity, the following image is contoured, corresponding to the situation in 2003 (Figure 5.13):

- contamination of the soil and Pleistocene sediments, occurring in almost the whole zone of Oil Terminal South Storage Area, is significantly restricted in its eastward vicinity (it becomes more narrow on the North – South direction, but extends eastward);
- the free hydrocarbon accumulated on the water table occurs on a zone extending eastward until the junction with the steep morphological slope, where it occurs at the ground surface;
- the geoelectric study shows that there is a prevailing drainage zone of the hydrocarbons, located at 8 m deep with respect to the North – South main road, under the military unit.
- there is no information concerning the contamination of the unconfined aquifer by dissolved hydrocarbons East of Oil Terminal South Storage Area, but it makes sense for us to assume that this one extends to the East, towards the sea.

Figure 5.13 *Sketch of the Integrated State of Contamination in the Eastern Part of Oil Terminal South Storage Area, 2003*

Possibility of Hydrocarbon Contamination in the Southern Vicinity of Oil Terminal South Storage Area

Data concerning the presence of the free product layer on top of the water table inside the perimeter of Oil Terminal South Storage Area (Figure 4.15) may suggest that the area of the contaminated sediments does not extend southward. At the same time, the area of high dissolved hydrocarbon concentrations in the southern vicinity is significantly smaller compared to the eastern one.
Moreover, these data show that, in the western part of Oil Terminal South Storage Area, the ecological situation is not alarming as nowadays there are only accidental and reduced infiltrations of petroleum products in that area.
On the other hand, the flow model in the Oil Terminal South zone clearly emphasized that, in the western part of the storage area, there is a high risk of potential contamination, as there is an inflow from the West.
Another reason of concern in the Oil Terminal South zone is that the water table decreases southward, while the thickness of the sedimentary sequence appears to increase on the same direction, due to the influence of the major slope of the pre-Quaternary relief. These variations could hide the extent of contamination, as the southward extension of the contaminated zone could have occurred at deeper, out of the reach of the study boreholes.

5.5 CONCLUSIONS CONCERNING THE HYDROCARBON CONTAMINATION EAST OF OIL TERMINAL SOUTH STORAGE AREA

Dan C. Jipa, Victor Niculescu. Mihai Mafteiu, Rodica Popescu, Consuela Milu, Gicu Opreanu

The geoecological investigations carried out East of Oil Terminal South Storage Area emphasized the eastward extension of the hydrocarbon contamination by in the soil, sediments and groundwater already identified inside the perimeter of the storage area.

In the eastern vicinity of the Oil Terminal South Storage Area, hydrocarbon contamination is a major environmental concern. Unlike other research perimeters in the Oil Terminal zone, in this area East of the Oil Terminal South Storage Area, contamination is visible on the ground surface, as the free product accumulated on top of the water table is discharged on the seaside slope. The study did not extend enough eastward to assess the influence of hydrocarbon contamination on the marine zone (Figure 5.13).

5.6 ENVIRONMENTAL RISK ASSESSMENT – HYDROCARBON CONTAMINATION - OIL TERMINAL SOUTH STORAGE AREA

Cristina Angheluta

General Risk Assessment Considerations - Oil Terminal South Vicinity Area
The following were the general considerations used in the risk assessment process:

- groundwater and subsurface soil hydrocarbon contamination, the plume is not delineated,
- contamination is moving eastwards (numerical modeling has been performed),
- free product is present on the water table inside the deposit and outside the deposit,
- contaminated groundwater and free product come to the surface eastwards of the deposit, the Black Sea is 500 to 800 m east and downhill of the surface contamination, and
- no water or sediment data is available from the Black Sea.

Human Health Risk Assessment - Oil Terminal South Storage Area
Cristina Angheluta

1. *Hazard Identification*

For people exposed to petroleum hydrocarbons, the long-term exposure to TPH (total petroleum hydrocarbons) and BTEX (benzene, toluene, ethylbenzene and xylenes, substances known to be toxic) were considered.

2. *Dose-response Evaluation*

The quantitative relationship between the chemical and the health hazard has been presented earlier, in chapter 3.7.

3. *Exposure Evaluation- Oil Terminal South*

The following were assumed in the exposure evaluation:

- no exposure via water : groundwater/surface water is not used as drinking water, not a residential area,
- no significant exposure via soil : there are no residents; access is limited (fence) to the surface contamination, people have no access to subsurface contaminated soil, and
- no significant exposure via air: no residents.

4. *Risk Characterization - Oil Terminal South*
Because there is no significant human exposure to the contamination, there is no significant human health risk in the present.

Ecological Risk Assessment - Oil Terminal South Storage Area
Cristina Angheluta

1. *Problem Formulation*

The objective is to estimate the adverse ecological impacts. The area immediately east of the storage area is an industrial area with no significant ecological value. The closest area of ecological value is the Black Sea littoral.

The “contaminants of potential ecological concern” are the PAH - polynuclear aromatic hydrocarbons, persistent, ecotoxic and bioaccumulative (Holder,1999). They affect an entire food chain (benthic organisms, fish, aquatic birds). The marine

sediments are considered here the probable contamination source for the marine environment.

2. *Analysis*

Based on our data, the subsurface soil and the groundwater are contaminated with petroleum hydrocarbons. The contamination is moving South-East and East. Hydrocarbons (free product) are also found in surface soil, surface water springs. Underground and surface contamination is moving towards the Black Sea. There are no data from the sea sediments, fish tissue, or the marine aquifer. Additional sampling and analysis is needed, to evaluate the actual exposure.

3.*Risk Characterization - Oil Terminal South*

The following are considered exposed marine ecological resources to hydrocarbon contamination: benthic invertebrates, fish and aquatic or amphibian birds. According to the Black Sea Red Book (1999), 11 benthic invertebrates and 36 fish species are threatened species. Aquatic and amphibian birds are also exposed to PAH through the food chain. The reference levels are 3.4 ppm PAH in sediments, for benthic organisms and fish (Holder, 1999). Below this value the risk is not significant. A dose below 0.3mgPAH/kg/day for birds has no significant risk associated with it (Holder, 1999). However, delineation East of Oil Terminal South and PAH analysis are needed for a proper ecological risk characterization.