3. ASSESSMENT OF THE PETROLEUM PRODUCT CONTAMINATION EAST OF THE PERIMETER OF OIL TERMINAL NORTH-1 STORAGE AREA

In order to extend the geoecological research in the vicinity of the Oil Terminal North-1 Storage Area, the perimeter chosen was immediately East of the facility. The choice of the perimeter was determined mostly by the available information from the investigation on the hydrocarbon contamination within the storage areas. Thus, the location and degree of contamination of various zones, the development tendency of the contamination processes, as well as the resulting risk for the zones adjacent to the storage area were taken into consideration.

In the case of the Oil Terminal North-1 area, the zone located in the eastern vicinity was chosen taking into account the location of the most important center of contamination by hydrocarbons.

Figure 3.1 *Location of the Geoecological Study Perimeter East of the Oil Terminal North-1 Storage Area*.

The studied area East of Oil Terminal North-1 Storage Area is located in the southern part of Constanţa City, in the Abator area (Figure 3.1). The geoecological research work took place in the area between by the storage area to the West, 1 Mai Boulevard to the East, Caraiman Street to the South and Tunetului Street to the North.

3.1 LITHOFACIAL SEQUENCE, GEOLOGICAL STRUCTURE AND HYDROSTATIC LEVEL IN THE AREA EAST OF OIL TERMINAL NORTH-1 STORAGE AREA

Dan C. Jipa, Gicu Opreanu

Borehole Network

In the study area East of the storage area, the geological and hydrogeological data available are only from Quaternary deposits. These data were collected in two investigation campaigns.

The first campaign was conducted by Oil Terminal S.A. through Prolif S.A. Constanţa, from the end of 2001 to the beginning of 2002. The locations of the 13 boreholes are presented in Figure 3.2. S.C. Oil Terminal allowed access to all their borehole data.

The second campaign was conducted in the framework of the research program of the Priority Project MENER, and those results are presented here. During this campaign, ISPIF drilled 7 boreholes, placed in the same area covered by the 13 boreholes from the previous campaign (Figure 3.2). Overlapping the two studies was necessary because the ISPIF boreholes had specific geological objectives.

Figure 3.2 *Location of the Boreholes Placed around Mangaliei High Street, East of the Oil Terminal North-1 Storage Area*

The Lithology of the Sedimentation Columns

The lithological columns from the ISPIF boreholes (Figure 3.3) revealed the general sequence:

- the upper level of soil/fill material,
- the loess level consisting of silt,
- the level dominated by paleosoil, represented by thick silty clays, and
- base clay level.

Figure 3.3 *Lithological Columns of the Boreholes Located East of the Oil Terminal North-1 Storage Area*

Geological Cross-sections

The geological cross-sections performed in the area East of Oil Terminal North-1 (Figure 3.4) reveals the smooth lowering towards the East of the main Pleistocene lithological horizons. There is a clear concordance between the geological structure of the Quaternary deposits and the morphology of the actual relief.

Figure 3.4 *Geological Cross-Sections East of Oil Terminal North-1 Storage Area*

Hydrogeological Data from the Area East of Oil Terminal North-1 Storage Area

The measurements for the groundwater level were collected using an electrical bifilar marked cable, with a two electrode capsule and a DC power source of 6 V. All locations of the boreholes were raised topographically, and based on the altitude, the groundwater head was determined.

The groundwater head data inside the storage area were collected in three investigation campaigns (June 2002, September 2002 and May 2003) as presented in Table 3.1. For the area East of the storage area, the data were collected on: May 14, 2003, September 10, 2003, and October 31, 2003.

The data analysis indicates that the seasonal variations are low, usually lower than 1 m.

Table 3.1
Hydrostatic Heads measured in Boreholes from the Eastern Vicinity of Oil Terminal North-1 Storage Area

Measurements made on May 14, 2003			
Borehole no.	Depth of water table (m)	Water table elevation (m)	Thickness of the oil layer (m)
F1E	3.40	30.78	
F2E	1.95	24.76	
F3E	2.45	24.91	
F4E	1.00	30.15	
F5E	5.22	24.61	
F6E	1.95	27.92	0.1

Measurements made on September 10, 2003			
Borehole no.	Depth of water table (m)	Water table elevation (m)	Thickness of the oil layer (m)
F1E	3.44	30.74	
F2E	2.75	23.96	
F3E	1.83	25.53	
F4E	3.31	27.84	
F5E	6.54	23.29	
F6E	2.17	27.70	0.3

Measurements made on October 31, 2003			
Borehole no.	Depth of water table (m)	Water table elevation (m)	Thickness of the oil layer (m)
F1E	2.99	31.19	
F2E	2.18	24.53	
F3E	1.67	25.69	
F4E	2.77	28.38	
F5E	6.03	23.80	
F6E	2.04	27.83	0.2

Compared to the perimeter of Oil Terminal North-1 Storage Area, where the hydrostatic levels in the northwestern part of the storage area are over 40 m, in the area East of the storage area, most of the groundwater heads are below 25 m (Table 15).

Considering the strong hydraulic gradient resulted from the low distances between isolines, it may be assumed that the groundwater head is raised due to water loss from the water pipes or sewage lines. In the area of Boreholes F2E, F3E, F4E and F6E, the basements of some buildings are flooded for several years, indicating a possible artificial influence on the groundwater level or the flooding of the duct channels.

In F4E, the water head is higher than the altitude of some nearby alleys. Near this borehole, there the floods from the subsurface are more obvious. Taking in consideration the fact that, whenever any quantity of water is extracted from this borehole, the recharge is almost instantaneous, it may be safely assumed that it

communicates with a discharge channel or a damaged duct area. The artificial supply of the aquifer is also suggested by the existence of some flooded areas on the seaside slope adjacent to the perimeter. The water is discharged towards the seaside slope, replacing the old springs, through the various channels intersecting the slope (ducts, ditches, etc.). In the end, the water reaches the storm water discharge system of the Harbor. Moreover, this water has an intense chlorine and detergent odor.

Piezometric Map - The initial piezometric map in Figure 3.5 indicates the flow direction. In the Mangaliei Street area, East of Oil Terminal North-1, the isolines indicate a flow direction towards Northeast.

Figure 3.5 *Piezometric Map of the Unconfined Aquifer in the Oil Terminal North-1 Storage Area and Eastward (zone of the Mangaliei road) – May 2003*

3.2 HYDROCARBON CONTAMINATION IN SOIL, SEDIMENTS AND GROUNDWATER IN THE AERA EAST OF OIL TERMINAL NORTH-1 STORAGE AREA

Gicu Opreanu, Rodica Popescu, Consuela Milu, Ecaterina Grosu

Free Petroleum Product on the Groundwater East of Oil Terminal North-1 Storage Area

Gicu Opreanu

The investigations performed in boreholes East of Oil Terminal North revealed that there was no free petroleum identified on the groundwater in this area except in Borehole 6E (Table 3.1) where a petroleum film was identified (0.1 – 0.3 cm).

Table 3.2
Analysis Performed by Oil Terminal Constanta on Water Samples from Boreholes East of Oil Terminal North-1Storage Area

Borehole	Date of analysis	S.E.T. mg./l	Petroleum product mg/l	Detergents mg/l
Samples from the Eastern Vicinity				
F1E	28.05. 2003	4		
F2E		2		
F3E		2		
F4E		2		
F5E		4	2,5	
F6E		5	3,1	

Analysis: S.E.T. organic cold solvent extraction S.R.7587- Precision (12+-2)%, Petroleum Product S.R.7877/2 - Precision 15%, Detergents HACH 8028

The virtual lack of free petroleum product in this area is due to a general reduction in the amount of free petroleum, which is due to an active pumping out activity performed by S.C. Oil Terminal, which began in 2002.

Dissolved Hydrocarbon in Groundwater East of Oil Terminal North-1 Storage Area

Rodica Popescu, Consuela Milu, Ecaterina Grosu

In order to collect the groundwater samples, the same equipment was used as for the measurement and collection of free product samples. However, in those boreholes where there was no free product, a metallic support device with glass bottles was used.

Figure 3.12 *Contamination by Oil Products in Boreholes Located East of Oil Terminal North-1 Storage Area*

These results are similar to the results on the free petroleum distribution, meaning that the plume extended up to the residential area East of Oil Terminal North-1 Storage Area (Figure 3.12). The chemical specific analysis of the groundwater samples in Boreholes 5E and 6E from the residential area, which was performed by ECOIND (Table 3.3), revealed extremely high quantities of petroleum product, especially in 6E.

Table 3.3
Analysis of Groundwater Samples from Boreholes Located East of Oil Terminal North-1 Storage Area by ECOIND – Bucharest

Nr.	Constituents	units	Borehole		Analysis Method
			F5E	F6E	
1	BTEX total	mg/l	<0.0001	0.24	SR ISO 11423/2-2000
	Benzene	mg/l	<0.0001	0.099	
	Toluene	mg/l	<0.0001	0.141	
	Ethyl benzene	mg/l	<0.0001	<0.0001	
	Xylene	mg/l	<0.0001	<0.0001	
2	total petroleum product	mg/l	5.72	292.57	EN ISO 9377/2-2000
		%	25	45	
	C10-C14	%	40	35	
	C14-C20	%	25	15	
	C20-C26	%	10	5	
	C26-C34	%	<5	<5	
	C34-C40				

Chromatography and luminescence methods were then used to evaluate the level of contamination in boreholes. Samples from Boreholes F1E, F2E, F3E, F4E, F5E, and F6E were analyzed. From these, only F6E had a film of petroleum identified. The luminescence in F6E was also the highest (Table 3.4).

Table 3.4

Luminescence of Groundwater Samples from Boreholes Located East of Oil Terminal North-1 Storage Area

Borehole	**Luminescence Intensity**
F1E	X
F2E	X
F3E	X
F4E	XX
F5E	X
F6E	XXXX
Legend: X - very weak; XX – weak; XXXX- very strong	

The luminescence of the other samples had various intensities. However all of them, including F6E, were on the same color line – blue, corresponding to light hydrocarbons. While in F5E there was a relatively low content of petroleum, the content in F6E is very substantial (159.97 mg/L).

Tabel 3.5

F5E-F6E Chromatography Results

Constituents	unit	Simbol probă. Valori determinate		Data colectării probelor	Metoda de analiză
		F5E	F6E		
TPH	mg/l	< 0,05	159.97	March 2003	EN ISO 9377/2 - 2000
C 10-C 14					
C 14-C 20	%	< 5	50		
C 20-C 26	%	< 5	45]		
C 26-C 34	%	< 5	5		
C 34-C 40	%	< 5	< 5		
	%	< 5	< 5		
		F5E	F6E		
TPH	mg/l	< 0,05	143,00	October 2003	
C 9-C 14	%	< 5	50		
C 14-C 20	%	< 5	33		
C 20-C 25	%	< 5	16		

From the point of view of the types of hydrocarbons found, these are mostly C10-C20. The heavy hydrocarbons are at low and insignificant levels shown also in the blue instead of brown coloring of the luminescence. However, the 6 boreholes were sampled at various times in March 2003 and October 2003. The samples collected in March 2003 were analyzed using the chromatography method to determine the total content of hydrocarbons. Only F5E and F6E were also analyzed using this method in October 2003. The solvent used for the analysis was methylene chlorine (CH_2Cl_2) and the apparatus used was a Perkin-Elmer Autosystem XL chromatograph. The chromatogram for F1E revealed a low level of contamination with C1-C16 hydrocarbons (0.069 mg/L).

The F2E chromatogram indicated an even lower level of contamination (0.0065 mg/l). This was expected considering its location, close to F6E, which is the most contaminated (Table 3.5).

Figure 3.6 *F1E Chromatogram*
Figure 3.7 *F2E Chromatogram*
Figure 3.8 *F3E Chromatogram*
Figure 3.9 *F4E Chromatogram*
Figure 3.10 *F5E Chromatogram*
Figure 3.11 *F6E Chromatogram*

Table 3.6

F1E, F2E, F3E, F4E Chromatography Results

Borehole	RETENTION TIME	mg/l
F1E	3.877	0.0478
	8.558	0.0044
	9.147	0.0042
	13.130	0.0093
F2E	3.821	0.0065
F3E	3.829	0.0047
F4E	3.832	0.0042

The low levels are also observed in F3E and F4E, which are similar. These chromatograms performed on water extract showed the following levels of contamination: 0.0047 mg/L in F3E and 0.0042 mg/L in F4E.

The F6E sample is complex due to the fact that circa 25 different compounds were identified (nC9-nC25 hydrocarbons). These are aromatic hydrocarbons, confirmed also by the luminescence results. The hydrocarbons had a large distribution area, which is indicative of crude oil.

In conclusion the GC method on water indentified contamination levels between 0.0047 in F3E and 159.23 in F6E.

Hydrocarbon Contamination in Soil/Sediments in the Perimeter East of Oil Terminal North-1 Storage Area
Gicu Opreanu

The strongly contaminated intervals were identified using the visual and odor intensity criteria (Table 3.7). Based on the intensity and apparent age of contamination, several intervals of contamination were identified (Figure 29).

Table 3.7
Hydrocarbon Content of Quaternary Soil/Sediments East of Oil Terminal North-1 Storage Area

Analysis according to STAS 7107/1-76	**Depth**	**F1E**	**F3E**	**F5E**	**F6E**	**7E**	**F8E**	**F9E**	**F10E**	**F11E**
Saturated hydrocarbon (%)	**1m**	-	3.01	0.45	1.62	1.10	-	-	1.81	2.25
	2m	1.91	2.49	0.56	2.91	1.18	4.88	-	-	-
	3m	-	2.79	0.83	2.02	1.93	-	-	3.37	2.54
	4m	0.58	2.50	0.88	2.17	1.51	3.39	4.19	-	-
	5m	-	1.65	0.98	1.52	1.23	-	-	-	1.96
	6m	0.67	-	0.96	2.31	2.04	1.85	2.18	-	-
	7m	-	-	1.27	2.51	2.23	-	2.61	2.31	2.44
	8m	-	-	1.83	0.36	1.11	1.89	-	-	-
	9m	-	-	0.98	0.62	-	-	-	-	-
	10m	-	-	1.51	1.31	-	-	-	-	-
	11m	-	-	0.82	1.41	-	-	-	-	-
	12m	-	-	2.31	-	-	-	-	-	-
	13m	-	-	0.55	-	-	-	-	-	-

Preliminary Description of Drilling Events- The following are data on the drilling activities, which are relevant.

Borehole F6E was drilled through surface soil and loess contaminated throughout the extent of the borehole. The odor seems very intense and the contamination seems new. The sediments from Borehole F5E were almost all visibly contaminated, the contaminations does not seem very new. The drill reached a hard surface at the depth of 1.75 m, which could be a petroleum pipeline. When asked, the locals indicated that these are old petroleum pipelines, no longer in use.

Borehole F2E contained a lower amount of contamination of the soil. At the groundwater level there was no color modification of the sediments. However, the hydrocarbon odor was present. It was unclear whether the odor was coming from the soil or from the groundwater. Boreholes F1E, F3E and F4E are not obviously contaminated by the visual or odor intensity criteria.

3.3 GEOELECTRICAL STUDY IN THE AREA EAST OF OIL TERMINAL NORTH-1

Victor Niculescu, Mihai Mafteiu

In order to evaluate the contamination extent in the area East of Oil Terminal North-1 Storage Area, 25 geoelectrical measurements were taken in a network with a total area of 100 m/100 m. The area studied was between Caraiman Street to the South, the eastern fence of the storage area to the West, Tunetului Street to the North and 1 Mai Boulevard to the East.

The Geoelectrical study extended to the depth of 14 m, to evidence the level of the bedrock (clayey-silty) and the possible contamination plumes, which were indicated by minimum resistivity or a resistivity value of about 10 Ohmm. The measurements were taken on East-West profiles (S1, S2, S3 and S4) and North-South profiles (S5, S6, S7 and S8). Two geoelectrical maps were made for the level of the sewer line (-2.0 m and - 4.0 m) to identify the extent of contamination.

Figure 3.13 *Geoelectrical Cross-Section S3-3' from the Eastern Oil Terminal North Gate to 1 Mai Boulevard; horizontal scale 1:1000, vertical scale 1:200*
Figure 3.14 *Geoelectrical Cross-Section S6-6' along Mangaliei Street (East of Oil Terminal North storage area); horizontal scale 1:1000, vertical scale 1:200*
Figure 3.15 *Geoelectrical Cross-Section S8-8' along Mangaliei Street (East of Oil Terminal North storage area); horizontal scale 1:1000, vertical scale 1:200*
Figure 3.16 *Geoelectrical Interpretative Apparent Resistivity Map at 2 m depth (East of Oil Terminal North storage area); scale 1:2500*
Figure 3.17 *Geoelectrical Interpretative Apparent Resistivity Map at 4 m depth (East of Oil Terminal North storage area); scale 1:2500*

Interpretation of the Geoelectrical Cross-sections and Maps
The measurement results revealed three geoelectrical regimes attributed to a particular type of lithological structure affected by petroleum pollutants in pore water. This contamination led to a change in the natural electrical resistivity of the geological structure, as follows:

- The dry silty clays (macroscopical loess) have a resistivity (in the geoelectrical cross-section) of over 20 Ohmm (here maximum 100 Ohmm);
- For the wet silty clays (macroscopical loess), which is contaminated with petroleum products in this case, the 20 Ohmm limit indicates the depth and the extent of the contamination.
- The values below 20 Ohmm (20-10-5-1 Ohmm) delineate the limit of the loess on one hand and the intense contamination inside the loess indicated by values below 10 Ohmm.

The minimum resistivity zone between 10 and 20 Ohmm, located at a depth of 6-8 m (upper part of the aquifer) indicates the geoelectrical effect of the macroscopical loess contaminated with petroleum products. The width and the location of this zone are controlled by the hydrostatic level variation.

Interpretation of Geoelectrical Cross-sections

On the **3-3' cross-section** (Figure 3.13) extending from the eastern gate of the storage area towards 1 Mai Boulevard (VES o17, VES o18, VES o7, VES o8 and VES o9), the geoelectrical gradient is correlated to the points of contamination identified in the boreholes. The 20 Ohmm limit is very close to the soil surface at circa 0.7 m deep, so the intense contamination is estimated to start at minimum 2 m deep. This way, the geoelectrical measurement VES o7 is in agreement with the level of contamination found in Borehole f5B at depths between -2 m and -4 m. From VES o8 to VES o9, where the hydrostatic level is approaching the soil surface, there is another area of contamination caused by the leaks from the sewage pipes.

Cross-section 6-6' (VES o27, VES o24, VES o6, VES o7, VES o15 and VES o16) (Figure 3.14), placed on the western side of Mangaliei Street from the PECO gas station to the Tunetului Street near the new Borehole 5E, shows apparent resistivity values under the 20 Ohmm limit down to 5-6 Ohmm in the deeper part. The contamination here may also occur due to the leakage in sewage lines (one found near Block A), and Borehole 1E West of the gas station has a slight petroleum odor at a depth of -2 m. To the northern edge of the cross-section at VES o16, there is an intensely contaminated zone at depths of -7 m to -14 m, in correlation with the data obtained from Boreholes F5E and f10b.

On the **8-8' cross-section** (VES o3, VES o4, VES o9, VES o10 and VES o11) (Figure 3.15), extending from the western side of 1 Mai Boulevard from the Lighthouse Park to the kindergarten near Industrial High School Nr 1, the hot spots are at the level of the sewage line. The observation is confirmed in VES o9 (resistivity level of 3-6 Ohmm) and Borehole 2E. The resistivity measurements and their correlation with the relief suggest that the contamination plume is moving towards the East.

Interpretation of Geoelectrical Maps

From the interpretation of the resistivity values on the map for a depth of -2 m to -4 m (Figures 3.16 and 3.17), the same direction towards the East for the contamination plume movement is observed. The existence of a slight petroleum odor in Borehole 1E West of the gas station indicates a probable movement of contamination towards the North also. Moreover, this direction in agreement with the topography is probably related to the main sewage line. The local population also complained about the fact that contaminated water has infiltrated into the basement of their buildings.

3.4 HYDROCARBON CONTAMINATION EAST OF OIL TERMINAL NORTH-1 STORAGE AREA - SUMMARY AND DATA INTERPRETATION

Dan C. Jipa, Marius Albu, Corneliu Dinu, Alina Pavel

Soil Contamination in the East of the Oil Terminal North-1 Storage Area

Various levels of contamination were found in the area East of Oil Terminal North-1 Storage Area. The hydrocarbon levels found in the westernmost boreholes were higher than inside the storage area. Towards East and North the contamination decreased down to the detection limit. The thickness of the contamination was the highest in the eastern part of the storage area (Figure 2.17). In Borehole F17 the thickness of the contamination was over 10 m. In the area East of the storage area, the westernmost boreholes (F5E and F6E) showed the extension of Zone A; the thickness of the contaminated interval was over 12 m. Other boreholes, more to the Southeast, had thinner intervals of contaminated soil (4.7 m in F3E and 0.9 m in F2E). The non-detect samples collected in several boreholes (F1E, f3b and f4b to the South; f2b, f7b, f8b and f4c to the Southeast, and f11b to the North) were used to delineate most of the soil contamination. Later, Borehole F11E was drilled North of Frigului Street to complete the delineation.
The results of the information collected were summarized and presented on a map of the horizontal extent of contamination (Figure 3.18).

Figure 3.18 *Extent of the Hydrocarbon Contamination of the Soil/Sediments in the zone East of the Oil Terminal North-1 Storage Area, Constanța*
(sketch based on borehole data; the boundaries of the contamination zones are approximate, established by interpolation)

The results were summarized as follows:

- The intense contamination of the soil inside the Oil Terminal North-1 Storage Area extended into the residential area East of the storage area;
- The contamination in the soil did not reach 1 Mai Boulevard, being mostly delineated by the Mangaliei Street line;
- Additional boreholes and geoelectrical studies are necessary to assess the area between Frigului Street, Mangaliei Street and 1 Mai Boulevard.

Free Petroleum Product Contamination of the Groundwater

The accumulation of light hydrocarbons on the aquifer was identified. The measurements performed in boreholes (May 2003) indicated that in the residential area East of Oil Terminal North-1 Storage Area there was no significant amount of free petroleum. A very thin layer was observed in Borehole F6E only (Table 3.1). Immediately West of Borehole F6E, inside the Oil Terminal North-1 Storage Area, the presence on free product was identified in a study performed by Oil Terminal S.A. (Jipa et al., 2002). Even if the free product amount was reduced drastically by active pumping out; the measurement performed in May 2003 revealed the continuous presence of a free product layer with a thickness up to 13 cm (Table 3.1).

Figure 3.19 *Oil Product Accumulation on Top of the Water Table in the Eastern Part of the Oil Terminal North-1 Storage Area and Eastward, May 2003*

As presented in Figure 3.19, the data may be summarized as follows:

- A free petroleum product layer was identified on the groundwater in the eastern part of the Oil Terminal North-1 Storage Area;
- This accumulation is very limited in space and has minimum values East of the storage area;
- There is and active source of petroleum contamination and active pumping controls the further spread of the contamination.

Dissolved Hydrocarbon Contamination of the Groundwater East of Oil Terminal North-1 Storage Area

The presence of petroleum products in groundwater (Tables 3.5 and 3.6) was identified immediately outside the storage area to the East. In Borehole F6E the level of contamination was very high.

Advancement and Control of the Hydrocarbon Contamination Plume in the Area East of Oil Terminal North-1

The petroleum contamination in the residential area East of Oil Terminal North-1 and the advancement direction of the plume were determined based on the available borehole data and geoelectrical data. The movement direction of the hydrocarbon contamination was determined to be towards the East (or the East-Southeast).

The data obtained during the drilling activities indicated that there were some human factors contributing to the advancement towards the East of the contamination. Specifically, leaks in the sewage lines and other pipelines (some of them in use, other no longer used) contributed to the advancement of the contamination outside the perimeter of the storage area towards the East.

The soil contamination extended vertically generally due to the variation in water head, due to the fact that they float on top of the aquifer. However, the 13 m thick contamination intervals found may be indicative of some other deeper sources (buried old pipes possibly). These other potential sources not identified during the study are crucial in the remediation effort.

3.5 GEOECOLOGICAL MONITORING OF THE HYDROGEOLOGICAL SITUATION AND ASSESSMENT OF THE GROUNDWATER CONTAMINATION EAST OF OIL TERMINAL NORTH-1 STORAGE AREA

Dan C. Jipa, Gicu Opreanu

The 6 boreholes drilled in the area East of Oil Terminal North -1 were used for the hydrogeological and contamination monitoring. Figure 3.21 shows the detailed picture of the variation in time of the water head.

An important environmental factor monitored during the study East of Oil Terminal North-1 was the potentiometric level of the groundwater. The water head measurement results are presented in Table 3.1. Three potentiometric maps were done to compare the situation between the three measurement events, also presented in Figure 3.22. The uniformity (between the three events) of the potentiometric lines observed in the maps showed that the groundwater flow direction had been the same, from the Southwest to the Northeast. The variation of the water head in each borehole was also recorded (Figure 3.21).

During the measurement of the hydrostatic level, the presence of free petroleum product was also monitored. The thickness of the free product layer was measured separately using a special bailer consisting of a transparent Plexiglas tube with a bottom valve to retain the water and the layer of petroleum. The relationship between the groundwater flow direction and the apparent tendency of spreading of the hydrocarbon contamination East of the Oil Terminal North-1 Storage Area is presented in Figure 3.20.

The results of this investigation are shown in Table 3.1. In most of the boreholes, the presence of free product was not identified. Only in Borehole 6E a film of petroleum was observed in May 2003, in September 2003 and in October 2003.

Figure 3.20 *Relationship between the Groundwater Flow Direction and the Apparent Tendency of Spreading of the Hydrocarbon Contamination East of the Oil Terminal North-1 Storage Area*

Figure 3.21 *Time-Variation of the Hydrostatic Head in the Unconfined Aquifer, East of the Oil Terminal North-1 Storage Area*

Figure 3.22 *Piezometric Maps Resulted from Monitoring of the Hydrostatic Heads in the Unconfined Aquifer East of the Oil Terminal North-1 Storage Area*

3.6 CONCLUSIONS ON THE HYDROCARBON CONTAMINATION ASSESSMENT IN THE AREA EAST OF OIL TERMINAL NORTH-1 STORAGE AREA

Dan C. Jipa, V. Niculescu, M. Mafteiu, Rodica Popescu, Consuela Milu

The studies carried out East of Oil Terminal North-1, Constanţa revealed the following state of the hydrocarbon contamination:

- The soil and the sediments were contaminated with petroleum products; the contaminated interval reached more than 12 m immediately East of Oil Terminal North-1;
- The presence of free product on the aquifer was observed only in one borehole East of the Oil Terminal North-1; the reduction in the amount of free product and its very limited presence in the residential area East of the storage area was due to the intense pumping out regime started in 2002 by Oil Terminal S.A.

- The chemical analysis revealed the presence of dissolved petroleum product in the water samples collected immediately East of Oil Terminal North-1;
- The geoelectrical investigation results revealed a flow direction towards the East of the contamination plume; present or past sewage line leaks appeared to contribute significantly to the advancement of the contamination.

3.7 ENVIRONMENTAL RISK ASSESSMENT – HYDROCARBON CONTAMINATION OIL TERMINAL NORTH 1 STORAGE AREA

Cristina Angheluta

The process of *risk assessment* of the contamination of the environment with hazardous substances is divided in two main categories:

Human Health Risk Assessment is the study of the potential impact on human health caused by the exposure to hazardous substances in the environment, and

Ecological Risk Assessment is the evaluation of the chance that one or more contaminants in the environment may cause an adverse ecological impact.

The United States of America is the first country to develop standard guidelines and procedures for environmental risk assessment. These are available for the general public via internet (US-EPA web pages, etc.), along with a considerable amount of research data. Several countries (Canada, Australia, Great Britain, Thailand, etc.) have adopted the US-EPA methodologies. This evaluation was also based on US-EPA guidelines and available data.

The objective was to evaluate the risk associated with the contamination of the environment with petroleum hydrocarbons in the vicinity of Oil Terminal North - 1 Storage Area in Constanta, Romania.

General Risk Assessment Considerations - Oil Terminal North-1 Vicinity Area
The following were the general considerations used in the risk assessment process:
- groundwater and subsurface soil hydrocarbon contamination,
- residential area.
- contamination moving eastwards (numerical modeling has been performed) and
- free product present on the water table inside the storage area.

Human Health Risk Assessment - Oil Terminal North-1 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*

A quantitative relationship between the chemical and the health hazard
TPH is the term used to describe a mixture of hundreds of chemicals from petroleum.
-little is known about the toxicity of TPH, many factors are involved.
-IARC (International Agency for Research on Cancer) has identified at least one compound in TPH, benzene, to be a known carcinogen. Other compounds are classified as probable carcinogens. Headaches, blood disorders, immunity system disorders, and lung, skin, liver and kidney diseases are also related to high levels of TPH exposure.

The TPH exposure limit via air is 500 ppm (www.atsdr.cdc.gov/toxfaq.html). Also, the exposure limit via groundwater is1.1mg/L for diesel and 7.3mg/L for gasoline, and the exposure limits via soil are grouped as follows: residential/agricultural and recreational areas - 100mg/kg and commercial and industrial areas - 1000mg/kg (http://www.epa.gov/region4/waste/ots/healtbul.htm).

Also, inhalation of large doses of benzene cause dizziness, increased heart beat, headaches, confusion, fainting, and even death. Drinking water contaminated with benzene may cause vomiting, stomach irritation, dizziness, convulsions, low birth weight, increased heart beat and even death. Benzene is a known carcinogen, long term exposure to benzene causes lukemia (www.atsdr.cdc.gov/toxfaq.html).

According to IRIS (Integrated Risk Information System), for benzene the following reference data is used in risk calculations: oral dose RfD = 0,004 mg/kg/day and air RfC = 0.03mg/cubic m (1ppm=3200µg/cubic m).

The cancer risk (inhalation of benzene) is:

1 in 10 000 for 13.0-45.0µg/cubic m,
1 in 100 000 for 1.3-4.5µg/cubic m and
1 in 1000 000 for 0.13-0.45µg/cubic m (www.epa.gov/iris/).

The standard values to be used in risk calculations are: 20 cubic m/day inhaled air, 70kg average human weight, 2L/day drinking water intake.

Toluene affects the nervous system; low to medium levels of toluene may cause tiredness, confusion, dizziness and weakness. Long-term exposure may cause kidney disorders, mental disorders, birth defects, even death (www.atsdr.cdc.gov/toxfaq.html).

According to IRIS, the chronic exposure acceptable limits are: oral RfD = 0.2mg/kg/day and air RfC = 0.4mg/cubic m (www.epa.gov/iris/).

Ethylbenzene also causes dizziness, throat and eye irritation, chest pain. Inhaling ethylbenzene affects the nervous system, kidney, liver (www.atsdr.cdc.gov/toxfaq.html). The chronic oral exposure is RfD = 0.1mg/kg/day, and the reference concentration in air is RfC= 1.0mg/cubic m (www.epa.gov/iris/).

Xylenes also affect the brain and cause dizziness and headaches, affect muscle coordination and equilibrium. Short term exposure to xylenes causes skin, eye, nose and throat irritation, lung disorders, memory loss, stomach, liver and kidney disorders; high levels may cause death. The subchronic oral exposure is RfD=0.2mg/kg/day, and the reference concentration in air is RfC=0.1mg/cubic m (www.epa.gov/iris/).

3. *Exposure Evaluation- Oil Terminal North-1*

The following were assumed in the exposure evaluation:

- no exposure via water : groundwater is not used as drinking water.
- no significant exposure via soil: highly volatile substances, and no evidence of surface soil contamination. Subsurface soil is contaminated, but there is no access to it.
- significant exposure via air.

The residents have complained that in some buildings there is a strong hydrocarbon smell. However, there is no air monitoring data. The depth to the contaminated groundwater is 1-5m in the area east of the deposit. The basements could get flooded, and the contaminants released in to the air of the building

Henry's Law was used to estimate the concentration (exposure) of the contaminants in the air.

$H = C_{air}/C_{water}$ (equilibrium conditions, room temperature and 1atm were assumed)

One set of component specific groundwater values were available from the most significant well in the area (F6 - monitoring well).

The air exposure values were calculated based on known H values for benzene, toluene, ethylbenzene and xylene:

$E_{benzene} = H \times C_{water} = 0.0226 mg/L$
$E_{toluene} = H \times C_{water} = 0.0384 mg/L$
$E_{ethylbenzene} = H \times C_{water} =$ non-detect
$E_{xylene} = H \times C_{water} =$ non-detect

The exposure to TPH was also estimated using H values for different fractions.

$E_{TPH} = 6.14$ mg/L or 5030ppm (standard air density)

4. *Risk Characterization - Oil Terminal North-1*

The Hazard Index (HI) was calculated for air exposure only.

HI=E/AL

TPH air exposure: $HI_{TPH}=5030/500=10$

Benzene air exposure: $HI_{benzene}=0.0226/0.00003=753$

> Extrapolating the linear relationship between dose and risk, exposure via air to benzene is associated with an estimated cancer risk of 1 in 10 (www.epa.gov/iris/). This value is associated with the worst case scenario, lifetime exposure of residents to the vapors released from the groundwater (current level of contamination) in the basements of the buildings affected.

Toluene air exposure: $HI_{toluene}=0.0384/0.0004=96$

The HI indicates how many times the acceptable level is exceeded. However, more sampling and analysis data is needed including air monitoring, east of Oil Terminal North-1 Storage Area for periodical reassessment of the health risk.

Ecological Risk Assessment - Oil Terminal North-1 Storage Area
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Based on our data, the subsurface soil and the groundwater are contaminated with petroleum hydrocarbons. Hydrocarbons are usually not found in surface soil; they evaporate rapidly. There are no surface waters in this area. The area of our study is an urban residential area. Urban residential (and industrial) areas do not have a significant ecological value (Holder, 1999). We may assume that there is no present ecological risk.