2. PETROLEUM PRODUCT CONTAMINATION INSIDE THE PERIMETER OF OIL TERMINAL NORTH-1 STORAGE AREA

The Oil Terminal North Storage Area for petroleum products belonging to S.C. Oil Terminal Constanța has been in operation for over 100 years. During this time, the City of Constanța expanded such that this storage area is currently inside the city (Figure 2.1). This storage area is located in the southwestern part of the city, between the I.C. Bratianu, Aurel Vlaicu and 1 Mai boulevards. Gates 4 and 5 of the Port of Constanța are located immediately East of 1 Mai Boulevard.

Figure 2.1 *Location of the Oil Terminal North-1 Storage Area within the City of Constanța*

The geological works for the investigation of the subsurface hydrocarbon contamination process were carried on only inside Oil Terminal North-1 Storage Area, which is the southern part of the entire Oil Terminal North Storage Area.

The geoecological investigations presented here were carried on by the Institute for Marine Geology and Geoecology – GEOECOMAR in Bucharest, and by University of Bucharest – Faculty of Geology and Geophysics. These works were initiated by S.C. Oil Terminal Constanța.

The drilling works, which were the main research method for the geoecological state, were performed by S.C. Prolif Constanța, under a work contract with S.C. Oil Terminal.

2.1 PREVIOUS STUDIES ON THE ECOLOGICAL STATE OF OIL TERMINAL NORTH STORAGE AREA

Dan C. Jipa, Gicu Opreanu

In order to evaluate the petroleum product contamination inside the perimeter of Oil Terminal North-1 Storage Area, in 1992, S.C. Oil Terminal ordered the execution of a large number of investigations (presented in Table 2.1).

The petroleum contamination in the storage area was first investigated by GERA S.R.L. At the request of S.C. Oil Terminal, they performed the "Radiestesy Study on the Oil Terminal Storage Area-1 and Surroundings".

This study had the main objective of identifying the losses of petroleum products in the storage area and surroundings (Carmeco S.A., Cartier Abator, and Gate 2).

Using radiestesy methods, the company identified a few subsurface flow directions for the petroleum contamination, some contaminated areas and sources of contamination. This way, in the Medeea reservoir park, several subsurface petroleum flow directions were identified. Another area of heavy contamination was identified in the eastern part of the storage area between Tank 761 and Unirea Park (Caraivan, 1992).

To verify the results of the radiestesy study, 7 geotechnical boreholes were installed (3”-diameter, 4-8 m depth) on the contamination flow trajectories.

In 1994, GERA S.R.L. performed the study called “Biogeophysical Study to Identify the Petroleum Contamination Source of Subsurface Contamination in the Fortuna S.A. Soft Drinks Area – Constanța”. The study involved a detailed radiestesy investigation in order to identify the source of contamination.

In this study, the depth of contamination was approximated to be around 6-7 m near Tank 13 and around 5-6 m in the Carmeco S.A. area.

The first hydrogeological study in the area was “Hydrogeology Study – Storage Area-1, Medeea Oil Terminal”, which was performed by Prolif Constanța. The main objectives of the study were:

- To establish the depth to the aquifer and groundwater flow direction in the Storage Area-1 Medeea area and the southern neighboring area (VINVICO S.A. and the soft drinks facility).
- To recommend methods to lower the groundwater level.

To accomplish this, 40 boreholes were drilled (3”-diameter, 5-6.5 m depth) in the southern part of the storage area (inside Oil Terminal) and inside some facilities located South of the storage area on Caraiman Street (Vinvico S.A., soft drinks factory, dry cleaner, Heliofarm S.A.). During the drilling operations, several soil samples were collected, and then the groundwater level was measured.

The boreholes intercepted the following formations:

- on the surface, a horizon of brown clayey silt (with local yellowish intercalations), 0.5-1.5 m thick.
- a horizon of yellow clayey/loess silt of variable thickness, of high porosity, with local brown-brownish red clayey silt intercalation, and
- a horizon of clayey silt of various thickness and irregular intercalations.

Groundwater is mostly present in the clayey silts, which are above the silty clay horizon. From the piezometric map, the resulting groundwater flow direction is from West and Northwest to the East.

The study identified two contaminated areas:
- The largest surface contaminated by leaks from containers includes Tanks 11 to 14 and continues towards the Southeast up to the entrance into the soft drinks facility.
- The southwestern area (East of BIOFARM near the barrier), smaller in size, has contaminated soils from the underground duct system.

During the same year (1995), PROLIF drilled 10 boreholes (F1-F10), 400 mm diameter and 10 m depth, meant to be used for pumping in order to lower the groundwater level (contract 1/1995 - Interception Boreholes to Lower the Groundwater Level in the Storage Area-1 Medeea Oil Terminal). The boreholes are placed on the southern and eastern limits of Tank 13, and they are not part of a hydrogeological study.

Table 2.1

Investigation Works on the Hydrocarbon Contamination by S.C. Oil Terminal in the Oil Terminal North Storage Area between 1992 and 2000

(previous to the study performed by Geoecomar and the Faculty of Geology and Geophysics)

Title	Year	Performed by	Number and type of boreholes	Conclusions
Radiestesy Study on the Oil Terminal Storage Area-1 and Surroundings	1992	GERA S.R.L.	7 investigation boreholes, 3” diameter, 4-8 m depth	Evaluation of the contamination scale and source identification, Identification of the contamination movement directions, Remediation proposals.
Biogeophysical Study to Identify the Petroleum Contamination Source of Subsurface Contamination in the Fortuna S.A. Soft Drinks Area – Constanța	1994	GERA S.R.L.	2 investigation boreholes, 3” diameter, 6.6-7.5 m depth	Evaluation of the contamination scale and source identification, Identification of the contamination movement directions, Remediation proposals.
Hydrogeology Study – Storage Area-1, Medeea Oil Terminal		PROLIF	40 boreholes, 3” diameter, 5-6.5 m depth	Identification of: groundwater level, groundwater flow direction, Delineation of soil contamination, Remediation proposals.

Interception Boreholes to Lower the Groundwater Level in the Storage Area-1 Medeea Oil Terminal	1995	PROLIF	10 boreholes, 400 mm casing diameter, 10 m depth	No study
Monitoring Boreholes – Storage Area-1 Medeea	1995	PROLIF	6 boreholes, 8” casing diameter, 6 m depth	No study
Investigation Boreholes in the Northern Storage Area	2001	PROLIF	20 boreholes, 3” diameter, 3.5-7.5 m depth	Contamination extent around Caraiman Street.

In 1995, PROLIF drilled 6 additional boreholes (F1-F6) of $8^{5/8}$"-diameter, for monitoring purposes. The boreholes are 6 m deep and are located on the eastern side of the storage area. The lithology columns were described along with visual observations on the contamination of the deposits, but no complete hydrogeology study was performed.

In the lithology column, the following horizons were identified:

- horizon of vegetal soil, brown clayey silt or broken rock of maximum 0.6 m thickness,
- horizon of brown clayey silt,
- horizon consisting of yellow loess/clayey silt (gray from contamination) containing carbonates,
- clayey horizon consisting of clayey silt or red silty clay (horizon reached by only part of the boreholes).

The deposits are almost all visibly contaminated with petroleum products. The groundwater head measured during the drilling was between 0.7 m deep in Borehole F6 located near Caraiman Street, and 4.7 m deep in Borehole F1 located North of Gate 2, at the surface impoundment.

The last hydrogeological study performed by PROLIF ("Investigation Boreholes in the North Storage Area") in 2001 aimed at establishing the extent of the petroleum contamination in the Caraiman Street area. To perform the study, 20 boreholes (3"-diameter, 3.5-7.5 m depth) were installed. The boreholes were located in the southern part inside the Oil Terminal North Storage Area, and South of Caraiman Street. It was observed during the study that the loess got thinner from East to West as the clay level increased, such that in the eastern extremity of the area studied the clay was found at a depth of 1.7 m.

The study evaluates the behavior of different types of soil when they become contaminated with petroleum products, but it does not offer clear information on the extent of the contamination. Also, it does not refer to the groundwater flow direction or pollutant transport directions.

When the boreholes were drilled, the groundwater level was at a depth between 2.5 m (at the intersection of C. Brătescu Street and A. Ivireanu Alley) and 7.3 m (at the southwestern corner of the storage area). Figure 2.2 shows the locations of boreholes drilled for the various studies mentioned above.

Figure 2.2 *Location of the Study Boreholes Drilled between 1995 and 2001 within Oil Terminal North-1 Storage Area*

2.2 LITHO-FACIAL SEQUENCE, THE GEOLOGICAL STRUCTURE AND THE GROUNDWATER HEAD INSIDE OIL TERMINAL NORTH-1 STORAGE AREA

Dan C. Jipa, Gicu Opreanu

Observation Borehole Network

To investigate the petroleum product contamination level, between 1995 and 2001, numerous boreholes were drilled inside Oil Terminal North-1 Storage Area. Year 1995 was one of intense environmental investigations using borehole data inside the storage area. A total of 56 boreholes were drilled under S.C. Oil Terminal contracts (Table 8; Figure 24), as follows:

- 40 boreholes, 3”-diameter, uncased,
- 6 boreholes, 8”-diameter, cased,
- 10 boreholes, 400 mm, cased.

In addition to these boreholes, 20 more 3”-diameter uncased boreholes were drilled in 2001. However, only 10 of those boreholes were available for sampling and data collection.

From all the boreholes installed between 1995 and 2001, inside Oil Terminal North-1 Storage Area, in 2001, only 6 boreholes were properly maintained in order to be used for the investigation of the aquifer (6 additional boreholes were eventually repaired). Moreover, in accordance with the objectives of these studies, all boreholes were concentrated in the southern part of the storage area (Figure 2.2.)

To investigate the entire area inside the storage area, a new borehole network was designed and installed between 2001 and 2003 (Figure 2.3). PROLIF Constanța installed 24 boreholes, with a 400 mm diameter and 6.2 to 20 m deep (usually between 8 and 12 m). In addition to those, 4 boreholes (400 mm-diameter), were installed outside the storage area (to the Southeast).

Figure 2.3 *Location of the 400 mm-Diameter Boreholes for Geoecological Research, Installed in 2001 – 2002 inside the Perimeter of the Oil Terminal North-1 Storage Area*

Lithology Columns

The lithology columns obtained from the boreholes installed inside the Oil Terminal North Storage Area were 8 to 20 m long.

Dominant Lithology Sequence

Overall, inside a lithology column from the Oil Terminal North perimeter, the following lithology levels were identified (Figure 2.4):

- *The current surface soil and fill deposits* in the upper part of the columns varied in thickness from less than 1 m (in Boreholes: F4, F13, F16, Fc1 and Fc7) to over 2 m (in Boreholes: F11, F15, F17, F18, Fc8 and Fc10). The fill deposits (human intervention) are most abundant in F10, F11 and Fc8.

- *The loess layer* was of smaller grain size, with a thickness between 3 m (Borehole F3) and approximately 8.5 m (Boreholes F4, F6, F7, F9, F16 and F22).
- *The clayey silt layer (paleosoil)* consisted of clayey silt deposits (silty) of brown, gray, greenish or reddish color. The drillings penetrated from less than 1 m (Borehole F7) to 10.5 m (Borehole F22) the clayey silt layer.
- *The greenish clay layer* (Upper Sarmatian?) was identified in only two boreholes at very different depths (17.6 m to 20 m in F4 and 11.1 m to 12 m F21).

Figure 2.4 *Lithological Columns of the Boreholes (2001 – 2002) inside the Perimeter of the Oil Terminal North-1 Storage Area*

However, the borehole drillings did not meet the red clay layer, even though they reached a depth of 20 m, possibly a Sarmatian level. This was due to the local facies variation. The absence of this key level caused some difficulties in the evaluation of the contamination process.

Particular lithology column
In some particular cases, the drillings evidenced some lithology sequences, which were not in accordance with the sequence presented as representative. The main difference is the presence of a second loess level separated from the main loess level by a silty clay intercalation. This was observed in the columns of F4 and F16 (Figure 7), where the sedimentary sequence included an additional loess layer up to 4 m in thickness.

In the sedimentary columns obtained during drilling activities, the four main generalized lithology levels were searched for. In most cases, only the upper levels were identified because most boreholes did not reach the lower limit of the silty clay.

The East-West cross-sections (Figure 2.5) clearly indicate that the lithological units shape the actual relief in the area under investigation. Therefore, overall, the geological structure is characterized by a dominant slope to the East.

On the North-South direction (Figure 2.5), the relief has local variations, which shows the corresponding modification of the structure of Quaternary deposits.

Figure 2.5 *Geological Cross-sections through the Pleistocene Deposits inside Oil Terminal North-1 Storage Area*

During the drafting of the investigation plan for the Oil Terminal North area, in order to evaluate the environmental state resulted from the petroleum contamination, it was stressed that structure maps should be performed for the upper part of the Lower Pleistocene red clay level. This type of map was also useful in the investigations carried out in the Oil Terminal South area.

Because at Oil Terminal North the red clay facies was not identified, the only structure level well defined was the base of the loess horizon. Consequently, it was decided that the structure map would be executed for this level.

Figure 2.6 *Structure Map at the Bottom of the Loess Deposits (A) and Variation Map of the Loess Thickness (B) in the Oil Terminal North-1 Storage Area*
(The numbers represent values of the bottom elevation (m) in figure A.)

The structure map of *the bottom of the loess deposits* (Figure 2.6) indicates the morphology of this layer. Following the structural character of the geological cross-sections, the base plane of the loess level clearly slopes towards East.

A different morphological character, over the eastern slope, is the higher and rounded relief positioned WSW-ENE, which is present in the central area of Oil Terminal North-1 Storage Area. North and South of this area, two large depression areas are observed.

The thickness map of the loess level- the horizontal variation of the loess thickness is presented in Figure 2.6. Overall, the thickness of this lithological level (most significantly contaminated) varies between 6 and 14 m. The thickness of the loess varies significantly across the studied area. The largest thickness (up to 14 m) is in the northeastern corner of the Oil Terminal North area. The minimum thickness (under 7 m) may be in the southwestern area. However, this possible conclusion is based on data from only two boreholes.

Hydrostatic Heads of the Aquifer

Two sets of hydrostatic head measurement data were collected during the 2002 investigation. These two measurement campaigns were 45 days apart. The data are presented in Table 2.2.

The measurements were performed on the 28 boreholes (400 mm-diameter) installed in 2001-2002. The highest values for the hydrostatic level were registered in the northwestern part of the storage area, in the New Ramp area and at the western limit of the Old Ramp, an area where the topographic elevation was also the highest (47-50 m with respect to the Black Sea level of 1975). During the investigation, on this area, there was typical lacustrine vegetation, which is indicative of the fact that the aquifer level is seasonally at very low depth.

The Old Ramp was built on an excavated area, and its lowest part is very close to the highest potentiometric level (observed in spring time). The report called "Geotechnical Studies for the Refurbishing of the Old Ramp-North Storage Area- 2002" by A. Spiridonică, mentions the fact that in f3 and f4 (3"-diameter uncased boreholes from 2001) the aquifer level was at a depth of 0.30 m (from the soil surface). These data cannot be verified (the boreholes were closed). However, there is a theoretical possibility for this area to get flooded during storm events.

The lowest values for the hydrostatic head were registered in the northeastern extremity of the storage area, an area where the aquifer was at a depth of 11.5 m from the soil surface, so the general aquifer flow direction is from West to East. Figure 2.7 shows the piezometric map of the unconfined aquifer, based on the groundwater heads measured in September, 2005.

Table 2.2

Hydrostatic Heads Measured in Boreholes inside Oil Terminal North Storage Area

Borehole no.	Date of measurement of the water table elevation		
	June 20, 2002	September 5, 2002	May 20, 2003
F1	31.87	31.69	32.10
F2	33.85	33.59	34.09
F3	36.72	36.42	36.82
F4	dry	21.95	22.35
F5	38.10	37.88	38.31
F6	41.68	41.42	42.19
F7	40.32	40.01	40.71
F8	40.24	39.96	40.69
F9	43.97	43.75	45.01
F10	27.44	27.83	27.99
F11	36.11	36.00	36.24
F12	29.81	30.76	30.46
F13	44.45	44.10	44.21
F14	45.52	42.54	43.13
F15	26.63	26.29	26.85
F16	21.77	21.27	22.19
F17	26.11	26.86	26.32
F18	28.61	28.94	29.69
F19	30.69	30.57	31.18
F20	30.45	30.55	30.89
F21		38.08	37.64
F22		25.52	25.90
F23		42.06	43.10
F24		45.23	45.88
FC1	38.9	38.70	39.28
FC7		37.42	
FC8		37.82	34.96
FC10		34.84	
FC 10		41.97	

In the marine coastal area in front of the storage area, a few low flowrate springs were identified, some of which were captured while the rest were free and drained into concrete ditches. There were not enough hydrogeological boreholes in the area between the beach and the storage area to determine whether or not the aquifer is discharging at the base of the seaside slope. No petroleum film was observed in the spring water. However, the spring water had a chlorine and detergent odor, which could probably mean that the sewage system may be leaking.

2.3 FLOW MODEL OF THE UNCONFINED AQUIFER IN THE ZONE OF OIL TERMINAL NORTH-1 STORAGE AREA

Irina Dinu

The unconfined aquifer, located in Pleistocene loess, in the zone of Oil Terminal North-1 Storage Area, was modeled using Visual Modflow, which is based on the 3D finite difference method.

The piezometric map of the unconfined aquifer in zone of the storage area is shown in Figure 2.7. It indicates that the aquifer is supplied from the West and the Southwest and discharges to the East and the Northeast. Unlike the zone of Oil Terminal South Storage Area, in this case, the distribution of piezometric heads does not indicate an additional inflow by effective infiltration due to local loss from water pipelines. The piezometric heads vary between 45.23 m in the western part (F24) of the storage area and 21.27 m in the northeastern part (F16).

The domain was discretized in a grid with 38 rows and 42 columns, with the horizontal dimensions 25 m x 25 m and the height usually equal, to the aquifer thickness intercepted by the study boreholes.

As most of the boreholes did not reach the bottom of the unconfined aquifer, that is the impervious clay underlying the Pleistocene loess, it wasn't possible to have an accurate representation of this aquifer. Therefore, in the zones with higher elevation, located in the western part of the represented domain, the aquifer thickness had to be increased, so that the final bottom elevation was set lower than the base of the boreholes. This image was considered closer to reality.

The boundary conditions of the model are constant-heads, prescribed by interpolation between the measured piezometric heads, in the Boreholes F4, F6, F9, F10, F13 – F16, F24, Fc1, Fc7, Fc8 and Fc10. All these are located close to the boundaries of the represented domain.

Recharge due to effective infiltration from precipitation was also introduced in the model, with an estimated average value of 50 mm/year. Unlike the zone of Oil Terminal South Storage Area, the piezometric heads don't seem to indicate an additional inflow due to losses from water pipelines.

The model was calibrated on the piezometric heads measured in the boreholes located inside the represented domain, respectively F1 – F3, F5, F7, F8, F11, F12, and F17 – F23.

Calibration of the model was achieved by the trial-and-error method, by adjusting the values of hydraulic conductivity of the aquifer. The model was considered well calibrated when, in all the observation points corresponding to the boreholes located inside the storage area, the differences between calculated and measured piezometric heads became less than or equal to 0.6 m.
The piezometric map of the aquifer obtained after the calibration of the model, is shown in Figure 2.8 .

Figure 2.7 *Piezometric Map of the Unconfined Aquifer in the Oil Terminal North-1 Storage Area Based on the Measured Heads in September 2002*

Figure 2.8 *Piezometric Map of the Unconfined Aquifer in the Oil Terminal North-1 Storage Area Resulted After the Calibration of the Model*

The values of hydraulic conductivity of the aquifer, resulted from the calibration of the model are between 0.01 m/day locally, in the zones of the Boreholes F12 and F21, as well as in the southern part of the represented domain, and 5 m/day in the eastern part, in the zones of the Boreholes F5, F18 and F20. On the largest part of the represented domain, the hydraulic conductivity is 1 m/day (Figure 2.9).
The flow model also provided the map with the groundwater flow directions (Figure 2.10) and the map with pathlines in the aquifer (Figure 2.11). Both maps show that the aquifer is supplied from the West, and the main flow directions are eastward and northeastward.
The calculated water balance of the unconfined aquifer in the zone of Oil Terminal North resulted after the calibration of the model is presented in Table 2.3.
The water balance shows that the aquifer is supplied by effective infiltration and through the western boundary, while the main discharge zones are the eastern and northern boundaries. This is also shown on the maps with the flow directions and pathlines (Figures 2.10 and 2.11).

Figure 2.9 *Distribution of the Hydraulic Conductivities (m/day) in the Oil Terminal North-1 Storage Area Resulted After the Calibration of the Model*

Figure 2.10 *Groundwater Flow Directions in the Oil Terminal North-1 Storage Area Resulted After the Calibration of the Model*

Figure 2.11 *Pathlines in the Unconfined Aquifer in the Oil Terminal North-1 Storage Area Resulted After the Calibration of the Model*

Table 2.3
Calculated Water Balance of the Unconfined Aquifer in the Zone of the Oil Terminal North-1 Storage Area

Recharge/discharge	Inflow (m^3/day)	Outflow (m^3/day)
Effective infiltration	74.24	
Western boundary	142.20	
Southern boundary		- 5.21
Eastern boundary		- 77.11
Northern boundary		- 134.12
TOTAL	216.44	- 216.44

The groundwater flow direction could partially provide an explanation for the high thickness of the oil layer accumulated on the water table, in Boreholes F10, F12, and F18 – F21. All these boreholes are located to the East, along the main groundwater flow direction. Local sources of contamination, probably damaged pipelines, are also supposed to be close to these boreholes.
The geometry of the unconfined aquifer in the zone of Oil Terminal North-1 Storage Area could have been represented more accurately if the existing boreholes had reached its bottom.
Nevertheless, we appreciate that, taking into account the available data, the model emphasizes the general flow tendencies of the aquifer in this area and synthesizes the present-day information.

2.4 GEOELECTRICAL STUDIES AT OIL TERMINAL NORTH STORAGE AREA IN CONSTANȚA

Victor Niculescu, Mihai Mafteiu

In 2001, in the perimeter of Oil Terminal North-1 Storage Area, electrometer measurements were performed on profiles located on the western and eastern limits of Medeea Storage Area (S1-1' and S2-2'), on a profile parallel to the New Ramp (S3-3'), on a profile located on the Constanța –Mangalia railroad line (S4-4') and on a profile on Caraiman Street (S5-5').

The measurements evidenced the following three geoelectrical regimes attributed to a particular type of lithological structure affected by infiltrations of petroleum pollutants (miscible and stable). The infiltrations contributed to the change in natural electrical resistivity of the geological structure, as follows:

- dry silty clays (macroscopic loess) usually register a geoelectrical resistivity of over 20 Ohmm (a maximum of 100 Ohmm);
- wet silty clays (macroscopic loess), which is the medium where the petroleum pollutants are found, the 20 Ohmm line indicates the vertical extent and direction of the petroleum polluted waters;

- the abnormal values, which are under 20 Ohmm (20, 10, 5, and 1 Ohmm), indicate on one hand the limit between the loess and red clay, and on the other hand, under 10 Ohmm, areas of intense contamination.

The areas of minimal resistivity between 1 and 20 Ohmm, placed at depths of 6-8 m (upper part of the aquifer), are the geoelectrical effect of the contaminated macroscopic loess. The width and position of this area is controlled by the variation of the groundwater level. The heavily polluted area is between the 20 Ohmm (upper vertical limit) and 1 Ohmm (lower vertical limit).

Figure 2.12 *Geoelectrical Interpretative Cross-Section S1-1' inside West Medeea (Oil Terminal North)*
(horizontal scale 1:2000, vertical scale 1:200)
Figure 2.13 *Geoelectrical Interpretative Cross-Section S2-2' inside East Medeea (Oil Terminal North)*
(horizontal scale 1:2000, vertical scale 1:200)

For the cross-sections 1-1' (VES 48, 5362, 74-81) (Figure 2.12) and 2-2' (Figure 2.13) (VES 45, 66-73, 65, 85), a series of 4-10 Ohmm resistivity anomalies are observed. The values are associated with petroleum contamination in the loess of a thickness of 8 m. The borehole data presented in parallel to the geoelectrical cross-sections confirm the existence of the wet loess with a strong petroleum odor (F301). The profiles are crossed by fire-water pipes. These pipes unfortunately have leaks, such that water infiltrates the loess and creates an anthropogenic aquifer containing petroleum contamination. The infiltrated petroleum products come from leaks in the petroleum pipe system or from the corroded tanks.

On the 3-3' cross-section (Figure 2.14) from Gate 3 to Gate 2 (VES 75, 82-95), where some repair work was performed on the underground pipes and where leaks from the fire extinguisher network, there are very low values for resistivity (1-2 Ohmm), which characterize the anthropogenic aquifer mentioned above. The 20 Ohmm resistivity limit is very close to the soil surface at circa 0.7 m depth, indicating an intense contamination source at the pipes buried at 2 m depth.

Figure 2.14 *Geoelectrical Interpretative Cross-Section S3-3' between Gates 2 and 3 (Oil Terminal North Storage Area)*
(horizontal scale 1:2000, vertical scale 1:200)

Figure 2.15 *Geoelectrical Interpretative Cross-Section S4-4' between Caraiman Street and Unirea Storage Area (Oil Terminal North Storage Area)*
(horizontal scale 1:2000, vertical scale 1:200)

Figure 2.16 *Geoelectrical interpretative cross-section S5-5' between Caraiman Street and the Gas Station (Oil Terminal North Storage Area)*
(horizontal scale 1:2000, vertical scale 1:200)

On the cross-sections 4-4’ (VES 6-26, 33) (Figure 2.15) and 5-5’ (VES 27-48, 50-52) (Figure 2.16) placed on the side of the railroad and on Caraiman Street, respectively, the apparent resistivity values that are below the set limit of 200 Ohmm reach values as low as 2-6 Ohmm. The leaks in sewage pipe network can possibly affect these results.

On the 4-4’ cross-section, the hot spots are close to the railroad near Romgaz (VES 24-26) at gate 2 and on 3-3’ cross-section (VES 12). A cluster of hot water pipes creating a channel under the railroad also exists in this area. Therefore, a way for the petroleum contamination to cross over is present.

To the right of VES 38 on the 5-5’ cross-section, it is estimated that a petroleum layer is present on the aquifer up to the end of the geological cross-section at PECO (VES 27). This phenomenon is certainly very old, a result historic leaks of petroleum products. In the VES 50 area where the cluster of oil pipes connects to Oil Terminal South and the Port, the geoelectrical values indicate the existence of a more recent contamination, closer to the surface like in 3-3’ cross-section.

From the processing and interpretation of geoelectrical data collected by November 1, 2001, several polluted areas were identified.

2.5 DATA ON THE CONTAMINATION WITH HYDROCARBONS IN SOIL, SEDIMENTS AND GROUNDWATER INSIDE OIL TERMINAL NORTH-1 STORAGE AREA PERIMETER

Gicu Opreanu, Rodica Popescu, Consuela Milu

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

Reconnaissance Trip to Identify the Possible Hydrocarbon Infiltrations Observable on the Soil Surface

Oil Terminal North-1 Storage Area is placed on Quaternary loess formations, which have a high porosity. Therefore, the accidental leaks of petroleum products infiltrate rapidly all the way to groundwater without leaving visible marks on the ground. Also, rain water washes down the products in area where infiltration is slower and covers the marks with soil eroded from the neighboring banks.

The land inside the storage area, which is not covered by concrete, is covered by vegetation such as grass or bushes (*Rosa canina, Prunus spinosa, Rubur caesius,* etc.) adapted to the petroleum product contamination. The vegetation is poorer or absent in areas with frequent leaks of petroleum (the ramp areas, and surface impoundment area). In areas where the vegetation is absent, the stains indicating contamination are visible on the soil; the soil is blackish brown instead of brownish gray.

The infiltration of petroleum products almost all over the inside of the perimeter is easier to identify in excavated areas, where the modification in the color of the soil or liquid phase petroleum can be observed. The infiltration is also proved by the presence of free petroleum product in most of the boreholes installed. The petroleum layer had a thickness of up to 90 centimeters.

The areas most affected by the contamination, by visual observation, are the ramp areas and the eastern area (the separator, the surface impoundment area, the pumps). In the eastern part, near Gate 2, in Borehole F2, the thickness of the petroleum layer was 90 cm in October 2001.

The area South of Tank 13, where previous studies identified a flow channel for the groundwater with free product, is well covered by vegetation. However, on this channel Borehole F1 was installed, where the measured thickness of the free product layer was 21 cm in October 2001.

Porosity and Natural Humidity Values

The determination of porosity and natural humidity values may be performed only on undisturbed samples. These samples were collected from only three boreholes (F6, F14 and F15).

The humidity values are between 14% and 23% (Table 2.4). Most values are between 18% and 21%. The almost constant value for humidity is due to the same lithology of the soil and the fact that the majority of samples are from underneath the water table. The specific weight, wet volumetric weight and dry volumetric weight of the soil samples in Table 2.4 are expressed as values relative to the specific weight of water.

In general, the values obtained in the laboratory are with a few percentages lower than the real values due to the water loss through evaporation during collection, transport and processing.

The porosity values are lower with depth, and depend on the lithology of the formations. Therefore, the surface soil samples had porosity values of 42-44%, while the sub-surface soil samples (10-12 m deep) had porosity values of 36-39%. The clayey silts and the yellow clays are more porous than the brownish-reddish clays.

The porosity values at a depth of 2-6 m are significantly lower than usual due to the artificial compaction of the soil in time for the building of some facilities on-site.

Chemical Analysis on the Soil Samples

For the Oil Terminal North-1 perimeter, 163 samples were analyzed for different depths in 16 boreholes.

The analysis method used was solvent extraction. The samples were initially dried to remove the water content. On the dry samples the extraction was performed using petroleum ether, a solvent for petroleum hydrocarbons. The weight removed from the sample indicates the amount of hydrocarbon initially in the sample.

Table 2.4
Physical Characteristics of the Soil Samples from Oil Terminal North-1

Borehole/ depth (m)	Humidity W (%)	Specific weight	Wet volumetric weight	Dry volumetric weight	Porosity n (%)	Pore index e
F6/2	14.67	2.69	1.78	1.55	42.55	0.74
F6/4	18.88	2.70	1.91	1.61	40.44	0.68
F6/6	19.21	2.71	1.85	1.57	42.56	0.74
F6/8	21.05	2.70	2.02	1.63	40.95	0.69
F6/10	18.95	2.72	1.97	1.69	37.90	0.61
F6/12	19.95	2.71	1.99	1.64	39.73	0.66
F14/2	19.97	2.69	1.95	1.62	40.35	0.68
F14/4	20.63	2.70	1.98	1.65	39.73	0.66
F14/6	19.33	2.70	1.86	1.59	41.12	0.70
F14/8	18.83	2.72	1.92	1.61	41.59	0.71
F14/10	20.71	2.71	2.01	1.62	39.01	0.64
F15/2	21.15	2.70	1.80	1.49	44.81	0.81
F15/4	20.50	2.70	2.05	1.70	37.03	0.59
F15/6	21.55	2.71	1.94	1.59	40.95	0.69
F15/8	22.78	2.71	1.97	1.60	40.71	0.69
F15/10	19.65	2.72	1.98	1.64	37.81	0.61
F15/12	21.38	2.71	2.12	1.72	35.91	0.56

The results (Tables 2.5a, 2.5b and 2.6) show that the differing lithology within the Pleistocene loess deposits doesn't appear to influence the location of hydrocarbons. For example, within the clayey silt horizon, the hydrocarbon content varies between 0.073% and 1.073% in Borehole F1, and between 0.0708% and 0.2849% in Borehole F9. Another example, this time for silty clay, is Borehole F3 where the hydrocarbon contents at various depths, vary between 0.0468 – 0.05574%.
However, it is obvious that, the hydrocarbon contents of the samples from higher depths are lower. Data show that, for most of the boreholes, contamination of the sediments is higher between 6 and 8 m depth, except for Boreholes F9 and F16. This statement is also confirmed by the visual observations on the core of each borehole. The presence of hydrocarbons in the soil and/or sediment samples is visible by the coloration they produce in the horizons they infiltrated. Thus, the raw petroleum products (crude oil and fuel oil) produce a brown-blackish or black coloration, most of the times, with stripes,

visible in all types of sediments. Meanwhile, more volatile products (gasolene, toluene, etc.) produce a light grey – greenish coloration, more visible at the silt and yellow clay horizons.

The analysis results are presented in Tables 2.5a and 2.5b. The results indicate no particular lithological preference for the hydrocarbons. For the same type of lithology (clayey silt, for example) the hydrocarbon content varies between 0.073% and 1.073% in Borehole F1, and in Borehole F9 between 0.0708 and 0.2849. Examples of this type are for other lithological compositions. In Borehole F3 (silty clay) at different depths there are levels of hydrocarbon between 0.0468 and 0.05574%.

It is obvious that usually there are lower levels in samples collected deeper. We may say that in most boreholes the soil is most contaminated at depths of 6-8 m (except in Boreholes F9 and F16).

Besides coloration, the petroleum products present in soil create a greasy aspect, more clearly emphasized through testing of the soil and clay samples by filter paper.
Identification of the presence of hydrocarbons by the smell is relative (especially for the volatile hydrocarbons), as it depends of the time difference between the moments of contamination and observation. The volatile petroleum products can evaporate few days after contamination.
Using the criteria exposed above, intervals contaminated by petroleum products were delimited in the borehole columns (Table 2.6).

Hydrocarbon Contaminated Intervals in Pleistocene Sediments
The presence of hydrocarbons in soil samples collected during the installation of boreholes is visible due to the color alteration of the affected soil. Therefore, the crude petroleum products produce a blackish coloration in soil, most of the time black stripes are visible in all types of sediments. However, the more volatile products (gasoline, etc.) produce a light gray to green color, more visible in silts and yellow clays.

Aside from the color, the petroleum products in soil are oily, and their presence was determined also by the use of filter paper for testing.

The identification of hydrocarbons by odor intensity is relative (especially for volatiles). However, the intense odor areas were documented.

Using the above mentioned criteria, the contaminated intervals were identified in the drilled columns. These contamination results are presented in Figures 2.17 and 2.18 and 2.19.

Figure 2.17 *Thickness and depth of the oil products contamination of soil/sediments (depth to the upper limit of the contaminated sedimentary intervals)*

Figure 2.18 *Location of the Hydrocarbon Contaminated Intervals on Geological Cross-Sections (Oil Terminal North-1)*

Figure 2.19 *Thickness distribution (m) of the hydrocarbon contaminated soil/sediment intervals in the zone of the Oil Terminal North-1 storage area (2002); 0.5 m between thickness isolines*

Figure 2.20 *Distribution of the Zones Highly Polluted by Dissolved Hydrocarbons (Relative Content According to the UV Luminescence Degree) in the Oil Terminal North-1 Storage Area and Relationship to the Main Groundwater Flow Directions*

Figure 2.21 *Accumulation of Oil Products on top of the Water Table on Two Different Measurement Dates - Oil Terminal North-1 Storage Area*

Table 2.5a

Hydrocarbon Content (%) of the Soil and Sediment Samples- Boreholes in the Oil Terminal North Storage Area

Location of the sample in the borehole column	Hydrocarbon content (%)							
	Borehole F1	Borehole F2	Borehole F3	Borehole F4	Borehole F5	Borehole F6	Borehole F7	Borehole F8
1 m	0.7322					0.3537		
2 m	0.0731	2.7027	0.1558	0.0582		0.3638		0.5494
3 m		0.0083	0.1585	0.0711				0.4619
4 m	0.3157	3.7689	0.0468	0.4463		0.369		0.067
5 m	0.5218	0.4635	0.2912	0.1745	0.7923	0.0815	0.1867	
6 m		2.3104	0.5574	3.7321	0.0312	0.0119	0.1886	0.2747
7 m	1.0737	0.1445	0.1718	0.1239	0.0608	0.6725	0.1121	0.0663
8 m	0.1197			0.9952	0.91	0.1187		0.8728
9 m								0.1481
10 m								0.126
11 m						0.0195		0.5685
11.4 m						0.1824		
12 m								0.6
13 m								

Location of the sample in the borehole column	Borehole F9	Borehole F10	Borehole F11	Borehole F12	Borehole F13	Borehole F14	Borehole F15	Borehole F16
1 m	0.0708			0.1982			0.0963	1.9649
2 m	1.2725		1.2346	0.12			0.0397	0.1406
3 m	0.1124	0.1068	0.2345	0.1261	0.177		4.8283	0.2195
4 m	1.788		0.9839	0.0649	0.0097	0.4247	0.0932	
5 m	0.2849	0.2329	0.9709	0.0194		0.0297	0.0698	0.0181
6 m	0.1368	0.1348	0.1592	0.0887	0.142	0.0974		25.697
7 m	0.0885	0.0677	1.0289	5.7788		0.304	0.4828	0.115
8 m	0.1114	0.75	0.7552	0.7465	0.7883	0.0796		0.5371
9 m	0.2222	0.0587	0.0761	0.4287		0.1658	1.6136	0.2029
10 m	0.1346		1.3892			0.0285	0.0353	0.0843
11 m	0.1358						5.5689	
11.4 m								
12 m				0.1038			1.8716	
13 m								1.1224

Table 2.5b

Hydrocarbon Content (%) of the Soil and Sediment Samples- Boreholes in the Oil Terminal North Storage Area

SAMPLE NO.	BOREHOLE / DEPTH (m)	HYDROCARBON CONTENT (%) AT LARGER DEPTHS
1.	F4/13	0.1085
2.	F4/14	0.1108
3.	F4/15	0.133
4.	F4/16	0.3021
5.	F4/17	0.0601
6.	F4/19	0.0265
7.	F4/20	0.1784
8.	F6/12	0.2733
9.	F6/13	0.2806
10.	F6/14	0.1884
11.	F6/15	0.1621
12.	F6/16	0.0165
13.	F6/17	0.1546
14.	F6/18	0.113
15.	F6/20	0.0437
16.	F22/13	0.1739
17.	F22/14	0.0289
18.	F22/15	0.0522
19.	F22/16	0.084
20.	F22/17	0.193
21.	F22/18	0.0085
22.	F22/19	0.1118
23.	F22/20	0.0167

Remark:

The hydrocarbon content is expressed in percentage and cannot be transformed in mg/mg sample now, because the mass of the sample was not always the same. It varied between 1.5 and 2 g.

Table 2.6

Extractable Substances with Organic Solvents (%) in the Soil Samples from Boreholes F4, F6 and F22

Borehole no./ Borehole depth (m)	**Extractable substances with organic solvents (%)**							
	13 m	**14 m**	**15 m**	**16 m**	**17 m**	**18 m**	**19 m**	**20 m**
F4	0.1085	0.1108	0.133	0.3021	0.0601		0.0265	0.1784
F6	0.2806	0.1884	0.1621	0.0165	0.1546	0.113		0.0437
F22	0.1739	0.0289	0.0522	0.084	0.193	0.0085	0.1118	0.0167

Petroleum Product Accumulated on the Aquifer inside Oil Terminal North-1 Storage Area

Gicu Opreanu

In order to evaluate the extent of the petroleum contamination, the thickness of the free petroleum product layer accumulated on the aquifer was measured. A device consisting of a transparent tube was used, as described in Chapter 1.2.

The values of the thickness of the petroleum layer are presented in Table 11. These data were collected at the same time as the water table level data in June 2002, September 2002 and May 2003.

The decrease in the thickness of the petroleum product layer (Table 11) is due to the pumping works carried out by S.C. Oil Terminal in the some of the boreholes from the Oil Terminal North-1 Storage Area. Moreover, some of the local sources of contamination (from the pipeline network as well as other installations) were identified and fixed.

Figure 2.20 shows the distribution of the thickness of the free hydrocarbon layer at two moments: June 2002 and September 2002.

Table 2.7

Thickness of the Free Product Layer Accumulated on the Water Table in the Oil Terminal North-1 Area

Borehole no.	Thickness of the free product layer (cm) June 20, 2002	Thickness of the free product layer (cm) September 5, 2002	Thickness of the free product layer (cm) May 20, 2003
F1	film	film	film
F2	0.70	0.20	0.80
F3	film	film	film
F4	-	film	film
F5	0.05	film	film
F6	6.00	5.50	1
F7	film	-	film
F8	film	film	film
F9	film	film	-
F10	49.00	1.20	2.00
F11	film – residues at the ground surface	film – residues at the ground surface	film
F12	15.00	4.00	film
F13	film		film
F14	film	-	-
F15	film	film	-
F16	film	film	-
F17	film	film	-
F18	55.00	32.00	2.50
F19	7.00	6.00	8.00
F20	16.00	26.00	13.00
F21	-	20.50	0.70
F22	-	film	-
F23	-	52.00	10.00

Note: The term *film* is used when the presence of the free product is not clearly determined (it might be absent).

Petroleum Products Dissolved in Groundwater

Rodica Popescu, Consuela Milu

Samples were used from a total of 20 boreholes in order to determine the relative concentration of dissolved hydrocarbons. The data are presented in Table 13. The method used was that of the dissolving in a dilute alkaline solution (NaOH – 0.1N) and extraction in organic solvents (chloroform).

The luminescence of the ultraviolet beam of the chloroform layer was used to determine the relative quantity of hydrocarbon in the water sample. In order to reduce the amount of uncertainty in the ultraviolet beam luminescence intensity method, a blank sample (distilled water) was also analyzed and compared to the F-1 through F20 samples.

The results clearly indicate that the contamination is higher in F2, F10, F12, F18, F19 and F20 (Tables 2.8 and 2.9)

Also, in F10, F12, F18 and F20, the liquid samples are only free petroleum product (F10 and F18) or water and free product (F12 and F20), with the higher luminescence. Samples from the northeastern (F15, F16, F17), southeastern (F3, F5, F7, F8, Fc1) and western (F9) zones show relatively low contents of dissolved hydrocarbons.
F14 is the least polluted, while F6 and F11 are moderately polluted.

The area distribution of the luminescence is presented in Figure 2.20. Please note that it is difficult to successfully correlate these data due to the fact that a large area was not sampled, so the extrapolation would not be relevant in this case.

The map drawn based on the degree of luminescence of the samples shows maximum pollution with dissolved hydrocarbons in the eastern zone of the investigated perimeter, at the limit between the Oil Terminal North-1 and North-2 Storage Areas. Moderate contamination was also determined in the northern and southwestern zones of the Oil Terminal North-1. Besides, minimum values were also determined, in the southern and northeastern zones of the Oil Terminal North-1.
The method of luminescence was also used to get more detailed data on the samples showing petroleum films.

Table 2.8
Results of the UV Luminescence Analyses

Borehole	**Degree of contamination**	**Visual observations**
F1	Low luminescence - X	
F2	*Very high luminescence - XXXX*	
F3	Medium luminescence - XX	
F5	Medium luminescence - XX	
F6	High luminescence - XXX	
F7	Medium luminescence - XX	
F8	Medium luminescence - XX	
F9	Medium luminescence -XX	
F10	*Very high luminescence - XXXX*	*Petroleum product;* Yellow luminescence, heavier hydrocarbons
F11	High luminescence - XXX	
F12	*Very high luminescence - XXXX*	*Water + petroleum product;* Yellow luminescence, heavier hydrocarbons
F13	Medium luminescence - XX	
F14	Low luminescence - X	
F15	Medium luminescence - XX	
F16	Medium luminescence - XX	
F17	Medium luminescence -XX	
F18	*Very high luminescence - XXXX*	*Petroleum product;* Yellow luminescence, heavier hydrocarbons
F19	*Very high luminescence - XXXX*	
F20	*Very high luminescence - XXXX*	*Water + petroleum product;* Yellow luminescence, heavier hydrocarbons

Table 2.9

Analyses Carried out by Oil Terminal Constanța on Water Samples Collected from Boreholes from the Oil Terminal North-1 Storage Area

Borehole	Date of the analysis	S.E.T. (mg./l)	Petroleum product (mg/l)	Detergents (mg/l)
F1	07.05. 2003	170		0.082
F3	26.05. 2003	129		0.058
F12	09.05. 2003	140		0.074
F12	13.05. 2003	140		0.074
F12	21.05. 2003	160		0.076
F12	26.05. 2003	58	24,3	0.085
F17	25.04. 2003	195		0.100
F18	22.05. 2003	148		0.061
F18	26.05. 2003	83	22,6	0.094
F19	26.05. 2003	72	72	0.069
F20	20.05. 2003	110		0.065

Analyses:
S.E.T. Substances extractable by organic solvents Precision of the method (12 +/-2)%, Petroleum product S.R.7877/2, Pr. met. 5%, Detergent HACH 8028 Pr. met. +- 0,0035

By gas-chromatography analysis on groundwater samples, intervals contaminated by petroleum products were delimited, as well as the dissolved hydrocarbon concentrations (Table 2.10).

Table 2.10

Analyses of the Groundwater Samples Using the Gas-Chromatography Method Oil Terminal North-1 Storage Area

Borehole no.	Sampling depth (m)	Quantity of petroleum products (mg/l)
F1	2.98	0.3157
F2	2.16	2.7027
F3	2.54	0.5574
F4	9.60	0.9952
F5	3.80	0.369
F6	6.72	0.6725
F7	5.37	0.1867
F8	5.34	0.2747
F9	5.97	0.2849
F10	3.36	1.2329
F11	2.73	0.2046
F12	3.36	0.7610
F13	2.73	0.1770
F14	1.80	0.4247
F15	6.30	0.6136
F20	12.06	6.9076

The analyses by gas-chromatography made on groundwater samples showed that the whole area is impregnated by petroleum products. The results provided by the chromatograms presented herein are in agreement to the results obtained from the UV luminescence analyses.
Two chromatograms (F7 and F19) were selected in order to show the difference between a sample lightly contaminated and another one, strongly contaminated by petroleum products.

Figure 2.22 *F7-chromatogram*

The F7-chromatogram (Figure 2.22) identified 4 chemical compounds, specific for hydrocarbons. The peak area indicates low concentrations (traces) of petroleum products. Thus, the peak with the retention time 2.7 minutes (C9) presents a concentration of 0.0162%, the peak no.2 (C11) presents a cover area of 0.0071% and the peak no.3 (C12) presents a concentration of 0.0045%. The last peak (C13) indicates a concentration of 0.0146%. According to these data, the sample shows a low degree of contamination

Figure 2.23 *F19-F20 chromatograms*

The F19 sample (Figure 2.23) is extremely complex from the chemical point of view. 33 various compounds were identified. Each compound showed relatively high hydrocarbon concentration: nC10 - 3.9325%, nC12 - 4.2633%, nC14 - 2.7380%, pristane - 1.0504% etc. This sample is representative for a high degree of contamination. Besides the peak area, which provides information concerning the amount of hydrocarbons in the sample (about 35% from the category C9-C33), the type of contaminant in the sample was also determined. This one is crude oil. The chromatograms confirm the fact that the eastern area, were Boreholes F19 and F20 are located, is the one with the most advanced contamination.

Additional data were provided by gas-chromatography during the investigations in 2003. Table 2.11 presents these results.

Table 2.11
Analyses of the groundwater samples using the gas-chromatography method
Oil Terminal North-1 Storage Area (additional data from 2003)

Borehole no.	**Sampling depth (m)**	**Quantity of petroleum products (mg/l and %)**
F1	2.98	<0.05 mg/L - 0,00005%
F2	2.16	<0.05 mg/L - 0,00005%
F3	2.54	<0,05 mg/L - 0,00005%
F4	9.60	<0.05 mg/L - 0,00005%
F5	3.80	<0.05 mg/L - 0,00005%
F6	6.72	<0.05 mg/L - 0,00005%
F7	5.37	<0.05 mg/L - 0,00005%

Borehole no.	Sampling depth (m)	Quantity of petroleum products (mg/l and %)
F8	5.34	0.2747 mg/L – 0,00027%
F9	5.97	0.2849 mg/L – 0,00028%
F10	3.36	<5 mg/L – 0,005%
F11	2.73	<5 mg/L – 0,005%
F12	3.36	24.3 mg/L – 0,024%
F13	2.73	<0.05 mg/L - 0,00005%
F14	1.80	<0.05 mg/L - 0,00005%
F15	6.30	<0.05 mg/L - 0,00005%
F19	11.30	27.04 mg/L – 0,027% degradable GASOLINE
F20	12.06	28.24 mg/L – 0,028% degradable GASOLINE

Gas-chromatography analyses on groundwater samples showed that the zone Oil Terminal North-1 Storage Area is entirely impregnated with petroleum products. At the same time, these results are in agreement with the other geoecological investigations. The contamination of the unconfined aquifer is presented in Figure 2.24.

Figure 2.24 *Classification of the Contaminated Zones of the Unconfined Aquifer in the Oil Terminal North-1 Storage Area*

2.6 HYDROCARBON CONTAMINATION INSIDE OIL TERMINAL NORTH-1 STORAGE AREA – SUMMARY AND DATA INTERPRETATION

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Soil Contamination in the Oil Terminal North-1 Area

Based on the 27 contaminated sedimentary intervals, the following may be stated (Figure 2.25):
- in 6 cases the contamination starts from the soil surface;
- the contamination begins at 1-2 m depth in most cases;
- rarely the contamination starts deeper than 2 m.

The contaminated soils versus the geological structure are presented in Figure 2.25. It is obvious that in most cases the highest level of contamination is in the loess level. the exceptions from this general observation are the following:

- the contamination affects the surface soil and the fill material;
- the contaminated intervals are sometimes in the upper part of the silty clay layer;
- the contamination extent in the silty clay is significant (3-4 m) in the case of F8, F17, F18, and Fc1.

For the loess level, the following may be stated:

- very often the loess level is completely contaminated, or in most part contaminated;
- the exceptions (where only a fraction is contaminated) are F4, F7 and F16.

Figure 2.25 *Lithological Columns and Contaminated Intervals Emphasized by Boreholes in the Oil Terminal North-1 Storage Area, in 1995*

Figure 2.26 *Hydrocarbon Contamination of the Soil/Sediments - Comparison between the Boreholes Made in 1995 and 2001-2002*

Figure 2.27 *Oil Terminal North-1 Storage Area - Comparison between the Thickness of Contaminated Soil/Sediments in 2002 and 1995*

Distribution of the Variation in Thickness of Contaminated Intervals
In order to delimitate the areas of most intense contamination in soil, a map of the horizontal distribution of the thickness of the contamination was obtained. When using this map, one should consider the fact that there were an insufficient number of boreholes to collect data from, so large parts of the storage area were not properly investigated.

The map of the contaminated interval thickness inside Oil Terminal North-1 Storage Area shows that the most contaminated area is in the eastern part of the studied area, at the southern limit of the Oil Terminal North-2 Storage Area perimeter. This area is marked on the map in Figure 2.17 as Zone A (where the thickness of the contamination is up to 10 m).

Other strongly contaminated areas are also at the western limit of the Oil Terminal North-2 Storage Area, in the central and eastern part of the North-1 Storage Area, and in the exterior of the Oil Terminal North area. Compared to Zone A, these 4 areas are insufficiently investigated considering the low number of boreholes installed there; the contamination extent in those areas is approximated.

Dissolved Hydrocarbon Contamination in Groundwater in the Oil Terminal North-1 Area

After the first groundwater investigation campaign inside Oil Terminal North-1 Storage Area, the water samples were analyzed for their hydrocarbon content. The method of luminescence of the ultraviolet beam was used, so the values obtained are relative. Based on the available data (insufficient in terms of horizontal distribution), the minimum, moderate and strongly contaminated areas were contaminated.

The area located at the eastern limit of the North-1 Storage Area (Figure 2.24) includes the highest content of dissolved hydrocarbon in groundwater.

On a lower scale in terms of contamination level, there are two areas in the center and the Southwest of the storage area with moderate quantities of hydrocarbons dissolved in groundwater. The data from these areas are from a single borehole; the contamination extent is unknown.

The southeastern and northeastern limits of the North-1 Storage Area are the least contaminated in terms of dissolved hydrocarbons in groundwater.

Delineation of the Free Petroleum Product Accumulation on the Aquifer in the Oil Terminal North-1 Area

The thickness of layer of free petroleum product on the aquifer was measured in two periods: June and September 2002. Comparing the results obtained (Figure 2.21), the measurements for the two periods are very similar. Some additional contamination signs are present in the second set of measurements.

From the thickness measurements, the following image for the accumulated free product is obtained for Oil Terminal North-1 Storage Area (Figure 2.21):

- Zone A of advanced contamination is not moving, even though the maximum thickness of the petroleum layer has significant variations (from 55 to 2.5 cm in Borehole F18); this zone is indicated by all the investigations that have been carried out: the thickness of contaminated sediments that reaches even 10 m (Figure 2.27); the thickness of the free hydrocarbon layer as well as the amount of dissolved hydrocarbons (Figure 2.20)
- Zone B-1, of moderate contamination, appears around Borehole F21 (installed after June 2002) in the second round of measurements;
- Zone B-2, of moderate contamination, is confirmed in all measurements taken;
- Zone B-3 characterized by a very thick petroleum layer is confirmed in the second round of measurements; however this was considered as a zone of moderate contamination because it is indicated only by the thickness of the free product layer (Figure 2.21).

The minimum amount of free product is found at two locations (Figure 2.21):

- Zone C-1, observed only in the June 2002 measuring round, has minimal levels of accumulated petroleum (the layer thickness is less than 5 mm) corresponding to the same area where dissolved hydrocarbons were identified.
- Zone C-4 is characterized by reduced accumulation of petroleum product (between 0.7 and 2 cm).

Zones C-2 and C-3 do not have free petroleum product accumulated on the aquifer.

The majority of measurements performed in the second round (September 2002) indicate the reduction in time of the thickness of the accumulated layer, except in F20. This modification reflects the result of the pumping activities to extract the petroleum and contaminated water from the aquifer, performed by S.C. Oil Terminal in 38 boreholes.

Discussion on the Hydrocarbon Contamination Areas
in Oil Terminal North-1 Storage Area

The inventory of the contaminated areas inside the Oil Terminal North Storage Areas must be looked at like an evaluation of the current level of information based on the data obtained from this study. Table 2.12 includes a list of the presently known contamination according to the criteria described in the previous chapters.

Based on the level of contamination, there are three categories of contamination centers:

1) Category A, which includes Zone A with the highest level of contamination;
2) Category B, which includes severely contaminated areas that are insufficiently known, Zone B-1 and Zone B-3, and moderately contaminated areas, Zone C-2, confirmed in all investigated media, and
3) Category C for the lower level of contamination.

The geoecological investigations performed inside the Oil Terminal North perimeter generated information on the hydrocarbon contamination centers. These data come from different subsurface media (petroleum product in soil, in groundwater or accumulated on the aquifer) and from different investigation events. Contamination centers such as Zones A, B-1, B-2, C-1 and C-4 were confirmed in all subsurface media. Other centers such as Zone B-3 are not confirmed in all available data.

Table 2.12

Contamination Centers in the Oil Terminal North Storage Area – Listing and Characterization

Name of the Contamination Center	Location (see Figures 18, 20 and 22)	Affected Media	Relative Intensity of the Contamination	Relative Level of Knowledge
Zone A	Eastern extremity of the perimeter	Soil/sediments, dissolved in groundwater, accumulated on the water table	Advanced contamination (large horizontal extent and thickness up to 55 cm)	Best known area, data from 5 boreholes
Zone B-1	Northern part of the North-1 Storage Area	Soil/sediments, dissolved in groundwater, accumulated on the water table	Advanced contamination (thickness up to 20.5 cm)	Insufficiently investigated (1 borehole)
Zone B-2	Southwestern part of the North-1 Storage Area	Soil/sediments, dissolved in groundwater, accumulated on the water table	Moderate contamination	Insufficiently investigated (1 borehole)
Zone B-3	Western part of the North-2 Storage Area	Soil/sediments, dissolved in groundwater, accumulated on the water table	Advanced contamination (free product thickness up to 52 cm)	Insufficiently investigated (1 borehole)
Zone C-1	Southern part of the North-1 Storage Area	Soil/sediments, dissolved in groundwater, accumulated on the water table	Low level contamination (free product thickness up to 0.5 cm)	Data from 3-6 boreholes
Zone C-2	Western extremity of the North-1 Storage Area	Soil/sediments, dissolved in groundwater	Low level contamination	Insufficiently investigated (2 boreholes)
Zone C-3	Northeastern part of the North-2 Storage Area	Soil/sediments, dissolved in groundwater	Low level contamination	Data from 3 boreholes
Zone C-4	Eastern part of the North-1 Storage Area	Soil/sediments, dissolved in groundwater, accumulated on the water table	Low level contamination	Insufficiently investigated (2 boreholes)

Attempted Comparison between 1995 Data and 2002 Data inside the Oil Terminal North-1 Perimeter

The change in the environmental state between 1995 and 2002 was limited to an evaluation based on the soil contamination data available. No groundwater investigation was performed in 1995. Moreover, the comparison is based only on visual/odor observation data from lithological columns.

Soil Contamination in 1995 versus 2002
The lithological column information for the total of 56 boreholes drilled in 1995 was documented. The information includes the visual identification of the contaminated intervals. From the examination of the lithological columns obtained in 1995 (Figure 2.26), the following are observed:

- 49 boreholes out of 56 are contaminated with hydrocarbons;
- 7 boreholes were drilled in uncontaminated areas;
- 12 drillings were performed at a depth of 5 m;
- 30 drillings were performed at a depth of 6 m;
- 7 drillings were performed at a depth of 7 m;
- 10 drillings were performed at a depth of 10 m.

Because this was part of the preliminary assessment of the site, the 1995 drillings were relatively shallow; therefore only 4 boreholes reached the deep limit of the contaminated interval. The other 52 boreholes the vertical extent of the contamination remained unknown, so very few boreholes from 1995 can be compared to those from 2002 (or from 2001).

In Figure 2.26, the columns of some 1995 and 2002 boreholes (located close to each other) are presented. Examining the two series of columns, the following may be stated:

- In 5 cases (Figure 21 B, D, E, G), the contamination begins evidently deeper in 1995; the contamination is shallower by 2-3 m in 2001-2002.
- For the A, F, and C (in part) cases, the upper limit of the contaminated interval is deeper in 2001-2002 than in 1995.

The thickness of the contaminated interval was identified in only 4 boreholes in 1995, the hydrogeological Boreholes f10 and f16 and the observation Boreholes F4 and F6. These values were compared to the 2002 values presented on Figure 2.27. The comparison data are included in Table 2.13. From the evaluation of the data, it is obvious that the thickness of the contaminated interval increased significantly from 1995 to 2002.

Table 2.13

Comparison Data for the Thickness of the Hydrocarbon Contaminated Soil/Sediment Interval

Borehole/Location	Contaminated interval thickness in 1995	Contaminated interval thickness in 2002 (approximated from Figure 29)
f10	1.5 m	Approximately 6.5 m
f16	0.8 m	Approximately 5 m
F4	3.5 m	Approximately 6 m
F6	2.6 m	Approximately 7 m

2.7 CONCLUSIONS ON THE PETROLEUM PRODUCT CONTAMINATION LEVEL INSIDE THE PERIMETER OF OIL TERMINAL NORTH-1 STORAGE AREA

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The investigations described in the previous chapters are the first ever research results on the hydrocarbon contamination in the soil and groundwater inside the Oil Terminal North-1 perimeter.

The geoecological research study was based on data from 24 boreholes (f1-F24) inside the storage area perimeter and 4 boreholes (FC1, FC7, FC8, FC10), located inside some facilities South of Caraiman Street. The boreholes were installed by Prolif-Constanța under contract with Oil Terminal.

Based mainly on visual observations, the hydrocarbon contamination was vertically delineated in the sedimentation columns. These observations were performed by Prolif-Constanța during the lithological mapping, and further on in the laboratory by GeoEcoMar.

Most of the contaminated soil intervals have a thickness of 4 to 9 m. In most cases, the contamination starts at a depth of 1-2 m. The contamination is mostly in the loess. In order to determine the most contaminated areas, a map of the contamination thickness distribution was obtained.

A total of 163 soil samples were analyzed in the laboratory. The results of the laboratory analysis indicate that in most boreholes, the highest level of contamination occurs at 6-8 m depth.

By comparison with the data from 1995, in 2002 the contamination is closer to surface by 2-3 m, and the thickness of the contaminated interval increased significantly from 1995 to 2002.

In order to determine the quantity of petroleum product accumulated on the aquifer, two sets of measurements were performed on June and September 2002. Comparing the results, the centers of contaminations had the approximate same location for both periods. However new free product contamination was identified in some boreholes in the second sampling event. In terms of dissolved hydrocarbon levels, the two sets of data were integrated, and the horizontal extent of the contamination in groundwater was determined inside Oil Terminal North Storage Area.
In some cases, however, a significant reduction in the thickness on the free product layer between the two sampling events was observed. This fact is attributed to the remediation work performed by Oil Terminal inside the perimeter of the North-1 Storage Area (recovery of hydrocarbons by pumping and equipment maintenance work).

Based on the preliminary hydrodynamic model, the piezometric map, the groundwater flow direction map and the pathline map were obtained for the aquifer in the Oil Terminal North area. These maps show that the aquifer is supplied from the West, and the main flow directions are towards the East and Northeast. The groundwater head distribution does not indicate any significant water influx from leakage in the water pipe system.

The geo-ecological investigations performed inside the Oil Terminal North perimeter revealed eight centers of contamination.

Based on the level of contamination, there are three categories of contamination centers:

1) Category A, which includes Zone A with the highest level of contamination;
2) Category B, which includes severely contaminated areas that are insufficiently known, Zone B-1 and Zone B-3, and moderately contaminated areas, Zone C-2, confirmed in all investigated media, and
3) Category C for the lower level of contamination.

Except for the contamination sources inside the perimeter of the storage area, there is also the possibility that some contamination centers (such as B-2 and C-2) have a different source of pollutants located outside the storage area perimeter. In this category we could include the contamination centers in the eastern extremity of the Oil Terminal Storage Area.