1. INTRODUCTION

The City of Constanța is the Romanian "gate" to the Black Sea and the World Ocean. With an operating capacity of 85 million tons per year, the Constanta Harbor is the main Romanian harbor and the largest of the Black Sea.

The hinterland of the Constanța Harbor includes a vast region in Romania, Central and Eastern Europe, connected to the harbor for shipping and receiving goods.

In the port, there is a terminal specialized in crude oil and gasoline import and export of refined petroleum and other chemical products derived from petroleum. With over 9782 thousand tons handled in 2002, *S.C. Oil Terminal Constanța S.A*. is the most important operating company for this type of products.

The Constanța Port is connected to the national pipe system. A subsystem of the national imported petroleum pipe network of 1200 km allows for the oil to be transported from Oil Terminal-Constanța to the refineries in the Pitești, Onești and Midia areas. The pipeline between Constanța and Cernavodă is used for delivery towards Danubian countries. A sub-system of the network is used for the transport of refined products between refineries and between storage facilities.

To facilitate the transit of petroleum products from and towards the Constanța Port, Oil Terminal includes several large storage facilities. Oil Terminal North Storage Area, in operation for over 100 years, is situated in the southern part of the City of Constanța (Figure 1.1). Oil Terminal South Storage Area, dating from the early 80's, is situated South of Constanța City, immediately outside the perimeter of the city. These two major storage facilities are connected between them and connected to the port terminal through oil pipelines.

Figure 1.1 *Location of the Oil Terminal Constanța Storage Areas*

Having passed through two major world wars and operating over long periods of environmental negligence of the humanity, it is expected to find a significant amount of petroleum product contamination in the Oil Terminal Constanța perimeters. Currently, when environmental protection is a major component of human activity, Oil Terminal Constanța has placed a significant amount of effort on the environmental assessment of the two storage facilities. Moreover, in 2002, the Ministry of Research and Education, along with the local authorities, decided to extend the investigations on the petroleum product contamination to the vicinity of Oil Terminal Storage Areas. This edition presents the scientific research activities performed for the assessment of the environmental situation in the area of these storage facilities in Constanța, from the source area to the extent of the contamination.

Research Area

The present study presents the results of the geoecological investigations performed between 2001 and 2003 in several parts of the area including the Oil Terminal Storage

Areas. In 2001, at the request of Oil Terminal, the first investigations performed by the authors of this paper took place inside Oil Terminal South Storage Area. Shortly afterwards (2002), with the guiding sponsorship of Oil Terminal Constanța, the investigations were extended over the second area of concern in the southern part of Oil Terminal North-1 Storage Area.

Moreover, the geoecological investigations continued the same year in the framework of a MENER project focused on the hydrocarbon contamination of the environment in the vicinity of the two storage areas. Several areas were selected for investigation. The selection was based on the available data on hydrocarbon contamination inside the Oil Terminal Storage Areas. The location of the high level contamination inside the storage areas, the tendency of migration of the petroleum contamination and the risk associated with the migration process in the vicinity of the storage areas were considered. For this purpose, Oil Terminal S.A. provided archive data on the geoecological state of the storage areas.

In general, the research activity results presented here occurred in the following areas (Figure 1.2):

1. Oil Terminal North-1 Storage Area,
2. the area East of Oil Terminal North-1 Storage Area (Mangalia Avenue area),
3. Oil Terminal South Storage Area,
4. the areas South and East of Oil Terminal South Storage Area and
5. The area located between Oil Terminal North-1 and Oil Terminal South Storage Areas.

The area East of Oil Terminal North-1 Storage Area bounders the most contaminated area of the Oil Terminal North-1 Storage Area. The environmental risk here is very high due to the fact that this residential area is neighboring the most contaminated spot inside the storage area.

Figure 1.2 – *Investigation Perimeters for Assessment of the Contamination in the Zones of Oil Terminal North and Oil Terminal South Storage Areas*

The area East of Oil Terminal South Storage Area is located near the highest level of petroleum products accumulated on the aquifer inside the storage area. In this detailed research area, the contamination with petroleum products is observed on the soil surface where the aquifer comes out along with free product accumulated on its surface.

The area South of Oil Terminal South Storage Area is important because it is located on the main movement direction of the aquifer. The results of the 2001 investigations do not indicate any hydrocarbon contamination outside the southern limit of the storage area. However, a certain amount of incertitude existed here, because the Pleistocene deposits slope towards the South, and the drilling did not go deep enough to reach the interval which may contain the petroleum contamination.

1.1 STRATEGY FOR THE INVESTIGATION OF THE HYDROCARBON CONTAMINATION IN THE AREA OF SOME PETROLEUM PRODUCT STORAGE FACILITIES IN CONSTANȚA

Dan C. Jipa

In general, the strategy developed by the authors of this study to investigate the contamination process in the study area aimed at collecting data and drawing conclusions for a realistic evaluation of the environmental state and of ways to improve it (Table 1.1).

In the different areas studied, the first step implied a preliminary investigation, the main objective being the evaluation of the available data from past investigations. Additionally, new data was collected in order to use it to develop a chart of the research strategy and prepare for the next step.

The next step involved a detailed study of the contaminated areas, for a documented evaluation of the environmental state in regards to the hydrocarbons present in the soil and groundwater.

During the investigation of the oil contamination in the soil and groundwater inside Oil Terminal Storage Areas, the aim was to figure out the contamination process involving the main geological and hydrogeological factors.

- the lithology and the geological structure of the impacted soil, and
- the dynamics of the groundwater (aquifer flow directions and flowrates).

During the fist part of the investigation, it was observed that in the area studied, besides the well known control factors, the migration process of the petroleum contamination is strongly influenced by another geological factor:

- the Quaternary paleo-relief (the geometry of the upper surface of the red clay layer)

The main tendencies of the hydrocarbon contamination process are better evaluated using data from larger areas. That is why it was attempted to get significant data from points distributed throughout the entire area of the storage facilities.

The research work performed was meant to build the scientific support for the drafting and implementation of measures meant to stop the sources of the hydrocarbon contamination and to remediate the area.

Objectives of the Geoecological Investigation – The research work performed at the petroleum storage areas involved geoecological assessment methods due to the fact that the contaminants were mostly present in the subsurface soil and groundwater.

The initial objective of the assessment was the investigation of the aquifer. The research included the evaluation of the extent of the free product contamination accumulated on the water table as well as the dissolved phase of petroleum products.

During the field work, it was noted that the surface soil was also strongly contaminated, so the assessment plan was amended to include the surface soil assessment among the main objectives. Consequently, throughout the assessment, the scientists considered most important the proper understanding of the migration process of the contamination.
The investigation of the migration process was based on primary data from:

- Core sample evaluation,
- Surface soil evaluation,
- Borehole sample evaluation and
- Analytical results.

Table 1.1

Strategy for the Investigation of the Hydrocarbon Contamination in the Area of Some Petroleum Storage Facilities in Constanța

Phase 1: Preliminary Assessment

- Objective: Evaluation of the available data in order to develop a strategy for geoecological research in each area of study
- Stages of development of the preliminary investigation:
  - Study of the archive data needed for the geoecological assessment
  - Reconnaissance activities to document the possible infiltrations of hydrocarbons on the soil surface
  - Informative geoelectrical studies
  - Drafting of the methodology used in the geoecological study

Phase 2: Detailed Research

- Objective: Assessment of the level of petroleum product contamination in soil and groundwater in each area of study
- Stages of development of the site investigation:

1. Detailed study boreholes
2. Electrometry measurements (elaborate network)
3. Sedimentological, hydrogeological and geochemical interpretation of the data collected in Stages 1 and 2.

   Main objectives:
   - lithological composition and geological structure of the contaminated soil
   - level of contamination in soil
   - level of contamination in groundwater
   - aquifer flow regime
4. Evaluation of the main aspects of the hydrocarbon contamination process, monitoring of the petroleum product contamination during the investigation, assessment of the risk associated with the petroleum product contamination of the environment, and proposed measures for remediation of the contaminated areas.

Phase 3: Extended Research

- Objective: An integrated conceptual model for the migration of the contaminants inside the Oil Terminal facility areas
- Stages of development of the site investigation

1. Borehole investigations (large network)
2. Electrometry measurements (elaborate network)
3. Sedimentological, hydrogeological, geochemical interpretation of the data collected

The core and borehole data were compared to and accompanied by electrometric data obtained using a high performance, nondestructive and inexpensive method of investigation.

The sedimentological, hydrogeological and geochemical data obtained were evaluated separately and integrated in order to draw conclusions on the main aspects of the migration process.

Table 1.2 presents the geoecological objectives and the main investigation methods used.

Table 1.2

Geoecological, Hydrogeological, Geochemical Objectives Used in the Assessment of the Hydrocarbon Contamination Level in Soil and Groundwater

Main objective	Results expected	Investigation stages
Evaluation of the contaminants in soil	Geological characteristics of the contaminated sedimentary intervals	Lithostratigraphy
		Analysis of the physical properties of the soil
		Geological structure evaluation
		Contamination level data
		Determination of the horizontal and vertical extent of the contamination
Evaluation of the contaminants in water	Information on the free product and dissolved phases of the aquifer contamination	Hydrostatic level data
		Hydrodynamic numerical modeling (Groundwater flow regime)
		Tri-dimensional delineation of the free product accumulated on the water table
		Groundwater contamination distribution data

1.2 METHODS AND TECHNIQUES USED FOR THE GEOECOLOGICAL ASSESSMENT OF THE HYDROCARBON CONTAMINATION IN THE OIL TERMINAL AREA, CONSTANȚA

Dan C. Jipa, Rodica Popescu, Consuela Milu, Irina Dinu, Victor Niculescu, Mihai Mafteiu, Gicu Opreanu, Anca Donici

Lithological Description of the Drilled Sedimentary Column

Because most part of the studied area is mostly occupied by buildings or paved, the only practical way to investigate it was drilling boreholes. The investigators used 3" and $8^{5/8}$" diameter manual drills. In the North-1 and South Storage Areas, they also drilled 400mm boreholes.

The borehole casing had the screen under the water table, and outside the casing, a gravel filter pack was placed (grain size of 3-7 mm). A clay cap was placed on top of the filter pack, and above it, a concrete barrier (dimensions: 0.5 m/ 0.5 m/ 0.5 m).

Samples of turbid water were collected during the drilling and used for the grain size analysis. For the $8^{5/8}$" and wider boreholes, every 2 meters additional undisturbed soil samples were collected in steel containers, to determine the physical characteristics of the soil (humidity, density, porosity, etc.).

The macroscopic lithological description of the Quaternary formations was also performed during the drilling, which was further used in determining the physical characteristics, in other analysis and to develop the lithological columns.

In the field, the observations on the level contamination were at first made visually, then using filter paper.

The lithological description was performed in the following terms:

- texture (thick clay, clay, silty clay, clayey silt, silt),
- consistency (fluid, semi-fluid, soft, semi-consistent, viscous consistent, consistent),
- humidity (dry, damp, wet, saturated) and
- porosity (macro pores, micro pores, low porosity).

Confidence of Lithological Core Data Correlation

The correlation of the lithological core data form the Oil Terminal Storage Areas perimeters implies serious difficulties and uncertainties.

The main difficulty in data analysis and integration comes from the fact that, looking at the regional variation between the Danube and the marine littoral, the loess in the Constanța-Agigea area is significantly finer than the characteristic grain size of this lithological category. Consequently, the loess deposits drilled in the perimeter studied are clayey silt, close to the paleosoils, which are silty clays. In general, the grain size is low, and this implies the following difficulties:

- The analytical data is more uncertain, because the grain size analysis has a higher degree of uncertainty when applied to fine deposits.
- In the case of this studied perimeter, the uncertainty is even higher due to the physical modifications undergone by the loess and paleosoil sample during the procedure of elimination of the organic and calcareous material, a mandatory procedure in grain size analysis.
- Because grain size domain is very limited and analytically sensitive, the change of the analytical method and of the specific procedures could produce more difficulties in data correlation, if the available data to be compared come from different sampling events between 1995 and 2003.
- Another factor of grain size uncertainty comes from the fact that the visual observation of the lithology during the drilling operations is highly subjective and various, especially when the samples are disturbed during collection, and when core sampling is discontinuous.

Qualitative Description of the Hydrocarbon Infiltration in Subsurface Soil

Along with the macroscopic lithological description of the samples collected during the drilling, visual observations were made on the petroleum product contamination in the soil along with filter paper tests. To evaluate the contamination level, the following criteria were used:

- Color – determined by the petroleum product contamination (the gray, blackish, black spotted and greenish colors in the lithological description are caused by contamination),
- Odor – (weak, moderate, intense and very intense odors), arbitrary criterion.

The presence of hydrocarbons in soil is observable due to the color change of the affected deposits. This way, the infiltrated crude oil produces the gray-blackish or black coloring, usually in layers visible in all types of soil, while the volatiles (benzene, toluene, etc.) produce a light-gray greenish color, more visible in silt and yellow clay.

Besides the color, petroleum products in soil produce an oily-shiny aspect on the deposits evidenced by the filter paper tests.

The identification of the hydrocarbons by odor is extremely relative (especially for volatiles), and it is highly dependent on timing and the wind factor.

A special attention was given to the evaluation of the thickness of the petroleum product layer accumulated on the aquifer. A special device (bailer) was build to measure it. The bailer was a transparent tube with a bottom valve, so water and petroleum are captured from the borehole. When the bailer is raised, the valve closes retaining the water and petroleum products inside the tube. The thickness of the petroleum layer in the tube is then measured. The precision of the measurement is 0.5 mm.

Analysis of the Hydrocarbon Contaminated Groundwater

In order to establish the level of groundwater contamination in the area, analyses were performed on some of the samples collected from the area.

During the first phase of the study, the contamination level was estimated using the ultraviolet light method. This method can perform a qualitative evaluation (whether or not hydrocarbons are present). The light intensity on the samples being analyzed is compared to the light through an uncontaminated water sample used as standard. For this evaluation, light intensity is given a certain number of stars, the number of stars being directly proportional to the level of hydrocarbon contamination.

Physical and Chemical Analyses

The following types of analyses have been carried out during the investigations of the degree of contamination by hydrocarbons: gas-chromatography (after SR EN ISO 6468), cold solvent extraction (after STAS 7107/1-76), ultraviolet luminescence of the chloroform extract (paper chromatography - after Bordenave, 1993), and ultraviolet luminescence of the chloroform drops of solid samples (Bordenave, 1993).

Gas Chromatography (GC) Method

The water samples were analyzed by this method. The samples were previously chemically treated with chloroform (solvent) to extract the organic components; the solution was further diluted with chloroform and injected in the GC.

Luminescence Method

Due to the capability of bitumens to present UV luminescence, their identification was possible in both water and soil samples. Being a qualitative method, this technique was used only to establish the presence or absence of bitumens in samples. For the *soil analysis*, the sample was crushed in fine pieces and solvent was added to it and kept for a fixed period of time. A chromatographic paper was added to the resulting solution, and on the paper the different bitumen fractions travelled differently on the paper. Finally, using UV light, the luminescence of the spots was observed. For the water analysis the UV light was passed through the sample placed in a dark room. A standard was used to compare the analysis results.

Cold Solvent Extraction Method

The soil samples were first dried to remove the water, and then petroleum ether was used as a solvent to extract the hydrocarbons. The sample was weighed before and after the extraction to evaluate the amount of (non volatile) hydrocarbons in the initial sample. These samples did not contain volatiles, as they were lost before the arrival at the laboratory.

Grain Size Analysis

In order to determine the soil particle dimensions, the method used combined sieving and pipeting. The method was chosen because it is suitable for clay or clayey soils. Also, the pipeting method produces less disturbance of the suspension during sedimentation, compared to the hydrometer.

Because the samples had a high content of organic matter (in average more than 5%), the samples had to be oxidized with hydrogen peroxide, and then heated to 50-60 ºC to eliminate the excess peroxide.

To have consistency in the method for obtaining lithological data and be able to compare the results to past investigation results from Oil Terminal North-1 and Oil Terminal South, the technical grain size scale used was STAS 1913/5-85, which gave the following results: sand grain size of 2.0 – 0.05 mm (-1 to 4.30 phi), silt grain size of 0.05-0.005 mm (4.30-7.65 phi) and clay grain size lower than 0.00 mm (7.65 phi).

Hydrostatic Level Determination

To measure the hydrostatic level, a device (groundwater probe) was built from a standardized electrical cable, containing a two-electrode capsule, a measuring device and 6V continuous current. All components are connected in series, and the circuit closes when the electrodes touch the water surface.

The hydrostatic level measuring method had centimeter-magnitude accuracy, and did not account for the petroleum product accumulated on the aquifer.

In the case of the $8^{5/8"}$ boreholes, the thickness of the petroleum on the aquifer was measured simultaneously to the hydrostatic level, using the device described in Chapter 3.5.

Numerical Modeling

A model involves a simplified representation of reality. This representation must match as much as possible the simulated processes. The numerical model includes a series of equations to describe the phenomena under study.

Hydrogeological models are based on the porous medium flow law, which includes parameters such as hydraulic conductivity, storage coefficient and infiltration coefficients. Modeling consists in solving the differential equation using values for these parameters and terms describing the external stress and imposed conditions. The flow model solution is the hydrostatic head or hydrostatic pressure. The solution can be reached by analytical or numerical methods. The analytical methods are mathematically precise, but they imply assumptions such as homogenous geological conditions and uniform stress, which are not realistic. The more realistic approach is numerical modeling, which is able to consider complex geological structures and variable stress.

Among the numerical modeling methods, the finite differences method and finite element method are mentioned.

The flow model used in this study was the tri-dimensional finite difference method using the MODFLOW program. The main principles of the method are described below.

The Tri-dimensional Flow Equation

The tri-dimensional hydrodynamic flow of the groundwater of constant density in porous environment is described by the following differential equation.

$$\frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z}\right) - W = S_s \frac{\partial h}{\partial t}$$

The terms of the above equation have the following meanings:
K_x, K_y, K_z - values of the hydraulic conductivity along the main axes of coordinates x, y, z, which are chosen parallel to the main anisotropy axes [Lt^{-1}];
h – piezometric head [L];
W - volumetric flux on the unit volume of porous medium, representing flow extracted or injected in the aquifer [t^{-1}];
S_s – specific storage coefficient of the porous medium [L^{-1}];
t - time [t].
S_s, K_x, K_y, K_z are usually functions of space while W may be function of space and time.

The equation above, under the imposed conditions for the aquifer limits (flux or head conditions) and the initial head conditions, represents the mathematical representation of an aquifer system:

For continuous flow, this equation becomes:

$$\frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z}\right) = W$$

The modeled domain is divided in cells, and the above equation will be solved for each of these cells. The outcome is a system of equations where the unknowns are the head values in each cell. Numerical modeling offers the support to solve this system and to obtain head values, which in turn are compared to the values measured in the field.

Boundary Conditions

An aquifer is limited in space. At these boundaries, the exchange of water with the external domain is determined by the boundary conditions.

These conditions are of three types:

- Dirichlet specified head boundaries:

h = h

This is typical for the contact between an aquifer and a river, the specified boundary condition here being the exit water head. Also, this condition is specified when a limited portion of the aquifer is modeled. In this case, the boundary head is determined by interpolation or extrapolation based on a piezometric map.

- Neumann boundary conditions of specified flux:

$$\frac{\partial h}{\partial n} = \frac{\partial h}{\partial x} 1_x + \frac{\partial h}{\partial y} 1_y = \varnothing ,$$

where : n = the external normal to the considered boundary
1_x, 1_y = the projections of this normal on the axes
$\varnothing$ = prescribed flux on the boundary

When the specified flux is zero, the boundary is impervious. The equipotential lines are perpendicular to this boundary, and the flow lines are parallel to them. A boundary is considered impermeable when it is a flow line (not crossed by any flow) or when it separates two zones with the ratio of hydraulic conductivities between them of minimum 10^5.

- Fourier or mixed conditions:

$$h + \lambda \frac{\partial h}{\partial n} \text{ , specified.}$$

This condition allows for the specification of a relationship between hydraulic head and flowrate. It is true in the case of a drainage trough a semi-permeable layer from a surface water body or a shallower aquifer, which is not represented. The Fourier condition may also apply in the case of drainage from drilled columns.

Model Calibration

This operation involves the adjustment of values and spatial distribution of the parameters from the flow equation. Usually, the hydraulic conductivity is the calibration parameter, and its values are introduced into the model and modified until the difference between the simulated hydrostatic heads and the measured hydrostatic heads is small enough to have an acceptable representation of the aquifer.

At the same time, the model calibration must aim for acceptable values for the specific parameters; their order of magnitude must correspond to the type of rock in the aquifer.

Porosity and Natural Humidity

Porosity values were calculated using the specific gravity method using the following formula:

$n = \gamma_s - \gamma_a / \gamma_s \cdot 100$ where:
ṇ = porosity
γ_s = specific weight of the solid phase $kg/m^3 * m/s^2 = kg/m^2s^2$
γ_a= dry volumetric weight.

Based on the porosity values, the pore index can be calculated as:

$$e = n/(1 - n),$$

where:
e = pore index
n = porosity

In order to determine the volumetric weight, fixed volumes of sample were collected from the corer. The samples where dried, weighted and the volumetric weight was determined using the formula:

$$\gamma_a = m_s / v ,$$

where:
m_s= mass of the dry sample
v = volume of the sample

The specific weight of the solid phase was determined by weighing the dried and crushed sample.

The natural humidity was determined at the same time as the volumetric weight, using the formula:

$W = (m_{um} - m_s) / m_s \cdot 100$,
where:
m_{um} = the mass of the wet sample

The humidity values found are between 9% and 33%. In general, the values calculated in the laboratory are a few percentages lower than the real values, due to water evaporation during sampling, storage, transportation and core processing. The soil humidity has a constant tendency to increase in deeper layers; a sharp increase is observed in the soil beneath the first aquifer.

The porosity values are also related to depth, generally lower in deeper layers, and to the lithology of the formations. The clayey silt and yellow clay are more porous than the brownish-red clay.

Continuous Current Electrical Investigation Method (Vertical Electrical Sounding – VES)

The apparent resistivity is the main physical parameter to characterize, from an electrical point of view, rocks or other objects in the subsurface, and the Vertical Electrical Sounding (VES) method is based on it. In this case, where the base rock is loess with pores containing water (more or less mineralized), ionic conductivity occurs with a resistivity between 10 and 20 Ohmm, which is specific to water containing dissolved petroleum products. The base rock is macroscopic loess with an apparent resistivity of 30-60 Ohmm. The geoelectrical contrast is used in determining the areas containing polluted water. Resistivity depends more on ion concentration and less on the chemical composition of the dissolved compounds.

The Vertical Electrical Sounding Method uses a quadruple-pole symmetrical device AMNB, with the emission line AB of a maximum length of 100 m, is fed with continuous current of maximum 20 mA and 150 V, and through the reception line MN the electrical potential difference produced by the injected current is measured.

The apparatus used is a high resolution TERRAMETER SAS 300 C Ohmm meter, produced by ABEM-Sweden. There were 18 VES measurements at an investigation depth of 14.5 m and 40 m distance between the stations.

The automatically processed data is presented in the form of a geological diagram based on the resistivity diagram, where the geoelectrical values are indicated, and elements from the geological, hydrogeological and geotechnical interpretation. The interpretation of this geoelectrical diagram leads to a geological cross-section indicating the zones of different contamination content.

The following information results from 2D (3D can also be accomplished based on the network of profile data) processed profile data:

- hydrostatic head,
- stratigraphical limits,
- structure elements,
- local and regional homogeneity absence,
- vertical delineation of contamination, etc.

Method Advantages

The technological and cost elements, which constitute the advantages of this geoelectrical investigation method, are:

- the rapidity of data collection with reliable equipment,
- automatic data processing and integrated interpretation with borehole data and geological mapping data,
- coverage of a large investigation area in a short period of time, and
- very low cost when compared to other traditional geophysical, hydrogeological, or geochemical methods.

1.3 A SHORT HISTORY OF THE INVESTIGATIONS ON THE HYDROCARBON CONTAMINATION IN THE AREA FROM SOME PETROLEUM PRODUCT STORAGE FACILITIES

Dan C. Jipa

At the S.C. Oil Terminal S.A. initiative, the assessment of the petroleum contaminated areas began in 1992 (see Table 1.3).

In the beginning, Prolif S.A.- Constanța performed drillings and hydrogeological studies inside the Oil Terminal South and Oil Terminal North-1 (Spiridonică, 1995-2000). These investigations focused on the lithology and hydrogeology of the investigated areas, collecting at the same time the first set of information on the hydrocarbon contamination in soil.

GERA S.R.L. also performed radiestesy investigations in the Oil Terminal North-1 Area (Caraivan, 1992-1994). The objective was to identify the path of the subsurface transport of petroleum products, the contaminated areas and the sources of contamination.

Between 2001 and 2002, the National Institute of Marine Geology and Geoecology and the Faculty of Geology and Geophysics at the University of Bucharest (Jipa et al., 2001a, 2001b, and 2002) performed systematic investigations, which evidenced the general characteristics of the hydrocarbon contamination in the soil and groundwater at the Oil Terminal South and Oil Terminal North-1 storage facilities. These studies aimed at identifying the hydrocarbon contamination process and the control factors. Monitoring and remediation proposals for the areas in the vicinity of the Oil Terminal Storage Areas were also presented.

In the second half of 2002, the Ministry of Education and Research adopted the Research and Development National Plan, which included the priority project “Assessment of the Level of Petroleum Product Contamination in Soil, Agriculture Products and Groundwater in the Constanța County, Especially in the Vicinity of the Midia Năvodari Plant, Oil Terminal Storage facilities and Petrotrans Pipeline (Priority Project 6, EVCONPET). The investigation activities in the vicinity of the Oil Terminal-Constanța Storage Areas were performed by the National Institute of Marine Geology and Geoecology and the Faculty of Geology and Geophysics at the University of Bucharest in collaboration with the National Institute for Industrial Ecology and the Institute for Study and Design of Public Works (Jipa et al, 2002, 2003a, 2003b). These investigations aimed at getting the scientific support for the design and implementation of measures to stop the contamination and remediate the contaminated areas.

Table1. 3

Investigation Activities on the Hydrocarbon Contamination in the Oil Terminal North-1 and Oil Terminal South Storage Facilities between 1992 and 2003

Activity	Year	Author	Observations
Radiestesy Investigation of the Oil Terminal Storage Area-1 and Surroundings	1992	GERA S.R.L. Constanța	Ordered by S.C. Oil Terminal
Biogeophysical Investigation for the Identification of the Petroleum Product Subsurface Contamination Source in the S.A. Soft Drink Fortuna Plant – Constanța Area	1994	GERA S.R.L. Constanța	Ordered by S.C. Oil Terminal
Hydrogeological Study. Light Petroleum Product Unloading Ramp	1994	PROLIF S.A., Constanța	Ordered by S.C. Oil Terminal
Geotechnical and Hydrogeological Study in the Storage Area IV South	1994	PROLIF S.A., Constanța	Ordered by S.C. Oil Terminal
Hydrogeological Study – Storage Area I Medeea Oil Terminal	1995	PROLIF S.A., Constanța	Ordered by S.C. Oil Terminal
Interception Boreholes for Lowering the Water Table in Storage Area I Medeea Oil Terminal	1995	PROLIF S.A., Constanța	Ordered by S.C. Oil Terminal
Observation Boreholes - Storage Area I Medeea Oil Terminal	1995	PROLIF S.A., Constanța	Ordered by S.C. Oil Terminal
Investigation Boreholes in the Storage Area North	2001	PROLIF S.A., Constanța	Ordered by S.C. Oil Terminal
Sedimentological and Hydrogeological Study inside Oil Terminal South Storage Area to Determine the Ecological State due to the Subsurface Infiltration of Petroleum Products	2001	GEOECOMAR and Faculty of Geology and Geophysics - Bucharest	Ordered by S.C. Oil Terminal

Project for Installing a Monitoring System for Groundwater Quality inside the Oil Terminal South Storage Area	2001	GEOECOMAR and Faculty of Geology and Geophysics - Bucharest	Ordered by S.C. Oil Terminal
Analysis of the Available Data and Geoelectrical Investigation of the Perimeter of Oil Terminal North-1 Storage Area, to Be Used in the Geoecological Assessment of the Site	2001	GEOECOMAR and Faculty of Geology and Geophysics - Bucharest	Ordered by S.C. Oil Terminal
Study on the Ecological State of Oil Terminal North-1 Storage Area due to the Subsurface Infiltration of Petroleum Products	2002	GEOECOMAR and Faculty of Geology and Geophysics - Bucharest	Ordered by S.C. Oil Terminal
Assessment of the Petroleum Product Contamination in Soil, Agricultural Products and Groundwater in Constanța County, Especially in the Vicinity of the Midia-Năvodari Production Facility, Oil Terminal Storage Facilities and Petrotrans Pipeline (Priority Project 6, Evconpet; MENER Program)	2002-2003	GEOECOMAR and Faculty of Geology and Geophysics – Bucharest, ECOIND, Bucharest ISPIF, Bucharest	

1.4 GENERAL GEOLOGICAL AND HYDROGEOLOGICAL DATA FROM THE OIL TERMINAL CONSTANȚA AREA.

Corneliu Dinu, Dan C. Jipa

General Geological Setting

Pre-Proterozoic crystalline schists and Upper Proterozoic green schists constitute the geological foundation of South Dobrogea. The Upper Silurian and Triassic deposits were found in samples from deep drillings.

One of the most important geological characteristics of South Dobrogea is the accumulation of calcareous deposits inside the Jurassic-Barremian sedimentation cycle. The Jurassic deposits belong to the Malm (Bathonian-Kimmeridgian), while the Cretaceous deposits are of Valanginian-Barremian age. The epicontinental Upper Jurassic-Lower Cretaceous calcareous sedimentation covers an extended area.

On the South Dobrogea territory, after the Jurassic-Barremian cycle, between Middle Cretaceous and Neogene, platform conditions are established with repeated emergences. Overall, the epicontinental and platform type Cretaceous represents the most important geological sedimentary constituent of South Dobrogea.

Due to the Ypresian-Lutetian transgression initiated in the Varna Basin in the South Dobrogea zone, nummulitic lime deposits are placed on top of the Cretaceous deposits, supporting the Neogene limestones.

The South Dobrogea Neogene deposits are basically Tortonian limestones, which extend transgressively over different Cretaceous and Eocene deposits. The second Neocene sequence, the Middle Sarmatian, consists mainly of lumachelic and oolitic limestones of increasing thickness towards the South. In the Romanian Black Sea coast area, the calcareous Upper Sarmatian lays unconfomably over the undeveloped Middle Sarmatian. In Quaternary, loess assumed to be of Aeolian origin covers the entire Dobrogea area, lying directly on Sarmatian limestones, like an almost continuous cover. The loess deposits, or loess-like deposits, consist of fine sand, silty and clayey, with calcareous concretions and clayey intercalations considered fossil deposits. The detailed lithology of South Dobrogea is presented in the lithostratigraphical column on the Constanța Page of the Geological Map (scale 1:200 000) of Romania.

The Pleistocene Lithology Sequence

South Dobrogea is known as an area typical for the development of Quaternary (Pleistocene) deposits, consisting of loess and paleosoil.

The typical loess is characterized by:

- the predominance of very fine sandy particles, sometimes silty, and the significant presence of clay (30% or more),

- homogenous aspect, indicated by the absence of internal stratigraphy,
- increased porosity (45-60%),
- yellow and reddish color, and
- variable content, but mainly carbonates.

The loess in the Oil Terminal area is not typical for this lithological category. It has a smaller grain size.

The observations performed on outcrops in South Georgia indicate the existence of several layers of loess (usually 5 layers) in Pleistocene deposits. The thickness of these layers decreases from the Danube towards the sea, as the grain size decreases.

The study of the Dobrogea Pleistocene was the object of detailed pedological studies, the most detailed ones by Ana Conea (1970), Rădan et al. (1984; 1990) and Ghenea, Rădan (1993), who investigated the Pleistocene deposits from the paleomagnetic point of view.
Figure 1.3 presents the lithology columns from outcrops around the city of Constanța in the Agigea area, from Ana Conea's (1970) work on the Dobrogea Quaternary. This figure indicates that the Dobrogea Pleistocene sequences are correlated with the paleosoil groups, by determining the paleosoil type and the group order. The layer-by-layer correlation of the loess strata and the group-by-group correlation of the paleosoil level can be accomplished only by investigation of the entire Pleistocene sequence.

Figure 1.3 *Succession of the Pleistocene Deposits in the Constanța – Agigea Zone, Provided by Investigations on Outcrops (modified after Conea, 1970)*

The vertical continuity of the loess deposits is interrupted by the intercalation of fossil soil deposits. These soils are of two types (Conea, 1970):

- steppe paleosoils
- forest paleosoils

Among the forest paleosoils, the red clays have a special characteristic; their thickness could reach several meters. On the Carasu Valley (presently the Poarta Alba-Navodari Canal), East of the Nazarcea town, Ghenea and Rădan (1993) mention the existence of a red clay baseline horizon (considered of Early Pleistocene age) 7-8 m thick. The authors stress that this horizon was also observed in other parts of Dobrogea, below the Pleistocene loess and paleosoils.

The Simplified Pleistocene Lithological Sequence Based on Borehole Data

By contrast with the consistency of the outcrop data, the lithological sequences based on borehole data are influenced by the inconsistency of the data resulted from the columns. Therefore, it was necessary to establish a simplified model for the South Dobrogea Pleistocene sequence in order to assist the data processing. This model is based on the observation, agreed by Spiridonică (1995a, 1995b), that in the upper part of the majority of the columns, the silty clay rocks dominate. In this context, the simplified model of the Pleistocene sequence contains the following (Figure 1.4):

Figure 1.4 *Standard, Simplified Lithology Sequence of the Pleistocene Deposits, Emphasized by Boreholes in the Oil Terminal Constanța Area*
(same legend as in Figure 1.3)

Loess horizon - The upper part of the lithological sequence consists mostly of clayey silt sediments, which are included in the loess category. Between the layers of loess, clay sediments are intercalated, along with paleosoil, which probably belong to the GS1 and GS2 (Conea, 1970).

Paleosoil horizon **-** The middle part of the lithological sequence is mostly represented by silty clay grain-size rocks, corresponding to paleosoil. Thin layers of loess are intercalated between the clayey silt layers. In several cases, the total thickness of the horizon of paleosoils varies between 5 and 10 m, of which 1-2 m up to 3.5 m is usually loess. The paleosoil horizon seems to correspond to the soil groups GS3, GS4 and GS5 (Figure 1.4).

Red clay horizon – The lower part of the Pleistocene sequence consists mostly of red clays. In the red clay horizon, some relatively thicker loess (pedolite) intercalations show up. The red clay horizon was noticed in many points in South Dobrogea (Ovidiu, North-Constanța, Neptun – Conea, 1970; Nazarcea- Ghenea, Rădan, 1993; etc.). In the lithology profile from Agigea, the red clayey lower part (about 4 m thick) is attributed to soil groups GS6 and GS7.

For the investigations considered here, the simplified Pleistocene sequence is the *standard model* of the sequences obtained from borehole data.

General Hydrogeological Conditions

Two major aquifers are identified in South Dobrogea (Țenu et al., 1997):

- the lower aquifer, in the Jurassic-Barremian limestones
- the upper aquifer, in the Sarmatian limestones

These two aquifers are of financial importance due to their large area and groundwater flow.

From a chemical point of view, the water quality is extremely good, with few pollutant elements with levels under the quality standards. The upper aquifer-Sarmatian- is more contaminated compared to the lower one; the nitrates and nitrites are over the allowable levels.

Besides the above-mentioned main aquifers, there is also another aquifer in the Pleistocene deposits. The financial value of this aquifer is lower, and the contamination levels are over those observed in the Sarmatian aquifer.