

The Impacts of Industrial Processing of Oil on Soil Quality

ZOIA APOSTOLESCU¹, OANA ROXANA CHIVU¹, AUGUSTIN SEMENESCU^{2*}, CLAUDIU BABIS¹, CATALIN AMZA¹, GABRIEL IACOBESCU¹, MARIA ALINA GLIGOR³, DAN NITOI¹, GEORGE MIHAIL ADIR¹

¹ University Politehnica of Bucharest, Faculty of Engineering and Management of Technological Systems, 313 Splaiul Independentei, 060021, Bucharest, Romania

² University Politehnica of Bucharest, Faculty of Material Science and Engineering, 313 Splaiul Independentei, 060021, Bucharest, Romania

³ University Lucian Blaga of Sibiu, Faculty of Engineering 10 Victoriei Blvd., 550024, Sibiu, Romania

Soil, the one of the main components of the environment, is constantly subjected to the action of pollutants existing both in air and water from rainfall and also in groundwater. Soil pollution recorded in the current stage varying degrees of contamination in relation to the demands manifested, chemical contamination occupying a preferential place being pronounced across the globe, regardless of zone. In view of the above purposes, the paper aims to highlight the impact of industrial processing of oil activity on soil quality, near a chemical plant in Constanta County.

Keywords: pollutants, groundwater, chemical contamination, soil quality

Soil pollution is mainly caused by:

- precipitation waters contaminated with various substances present in the atmosphere;
- discharge on the ground, the household solid waste and discharge of domestic waste water;
- treating the agricultural land with chemicals;
- downloading on the ground of the solid and soft waste from the industry;
- deposition of atmospheric dust containing toxic substances.

If in terms of damage that pollution causes directly to the crops, they are obvious and can be identified easily by the symptoms presented by plant, the matter of the chemical structure of soil damage turned out to be considerably more complicated in terms of air pollution, often interfere with the usual pollution which it brings itself through agriculture fertilizers, pesticides, waste and even soil type [1-3].

Experimental part

Soil samples were collected monthly in May - September 2011 - 2015 of 5 points namely : NAVODARI, OVIDIU, LUMINA, SACELE and CORBU.

The soils in the investigated area, part of the group of regional and azonal, acid type, under a lithologies dominated by fine texture clays and a location relatively on flat land .

Units of soils present in the monitored area, can be grouped as follows:

- white and brown luvisols with varying degrees of podzolite and pseudogley;
- Solonchak with a pronounced argillaceous feature and a higher percentage of organic matter in the various thicknesses of the soil profile.

The common feature of the most important soil units represent their high clay character. The frequent presence of over 45 % clay in horizons B, has a major negative repercussions on plant development.

Due to this characteristic, soil drainage is very slow, in which case, during rainy periods, reaching water stagnation at the surface or at the argilloaluvial horizon with pseudogley effects [6-8].

In dry periods, due to a low permeability, the soils lose water easily and form cracks which further accentuates the drought and the crops are compromised.

Detailing the mineralogical structure of clays extracted from the existing acid soils in the area of influence, is shown in table 1. Parameters obtained by X-ray diffraction individuals and the exposure of the clay fraction is < 0.001 mm albic luvisol from NAVODARI.

The data obtained highlights the presence of the following minerals:

- quartz: given by the characteristic diffraction peaks at 3.33 Å in the saturated sample with calcium ions;
- kaolinite: indicated by the diffraction peaks at 3.57 Å and 7.19 Å;
- illite: pointed by the 10.08 Å peak for the saturated sample with K and 10.10 Å for the saturated sample with Ca;
- dioctahedral vermiculite: given by the spacing of 11.50 Å for sample saturated with Ca and 14.52 Å for the sample saturated with K;
- interstratified mineral: identified by spacing of 12.65 Å for sample saturated with calcium and 13.05 Å for the sample saturated with K.

The greater range of the degree of expansion shows, that these types of acidic soils, present a non negligible inconvenience in the presence of water, processes related to the contraction and swelling.

Mineralogical structure of the clay extracted from luvisols from the studied area, indicates the presence of the interstratified minerals in amounts below 2%, involved in the phenomenon of absorption of chloride and sulphate anions.

Pseudo character of the most soil units appear as a natural consequence of very slow drainage [4-5].

Another common feature of the majority of the soil units is the *podzolite* (high acidity and the appearance of mobile substances toxic to plants, such as aluminum, iron and manganese and others).

The appearance of some morphological differences (horizon A₂ astructure enriched in silica without structure and impoverished a lot in humus and nutrients; B₁ horizon with accentuated clay character and rocky structure) that worsen further physical properties and productivity of soils,

* email: augustin.semenescu@upb.ro

Table 1
 DETAILING THE MINERALOGICAL STRUCTURE OF CLAYS EXTRACTED FROM EXISTING ACID SOILS IN THE AREA OF INFLUENCE

Cation absorbing	Reticulated parameters, KX								Degree of swelling
	3	3	3	4	4	4	4	5	
K	3.34	3.57	3.70	4.24	4.65	4.80	4.98	-	-
Ca	3.33	3.57	3.69	4.25	4.44	-	4.98	5.50	-
Ca -	3.33	3.57	3.70	4.25	-	-	4.98	5.40	-
EG	Reticulated parameters, KX								
5	6	7	7	8	10	11	12	14	-
-	6.30	7.19	7.95	-	10.08	-	12.60	14.52	5.85
-	-	7.19	-	-	10.10	11.50	12.65	14.79	-
5,55	-	7.04	-	8.70	10.38	-	-	14.37	1.85

which are added and chemical characters that have become unfavorable as a result of the podzolit phenomenon, make further complicate the issues raised by these soils in the study of the environment and pollution [9-12].

Refer to these soils is mentioned and other features, such as: groundwater relatively large depth; reaction (pH) generally acid - consistent with the genetic evolution; the variable content of humus depending on the genetic processes and uses; the depth of the horizon surface; variation of the basic micro-elements (N, P, K) necessary for plant nutrition (according to the genesis and lithology) and reducing the alkalinity due to genetic processes influenced of natural conditions.

Azonal soils, although occupy small areas presents many more variations, such as cartographic distribution and especially as stratifications. Including ground units due the collusion, delineated in types of alluvial and colluvial soils, they differ from the soil zonal units by age and lithology.

The most important characteristics of azonal soils are: textural variation, most often mottled, appearance of some of layers, unfavorable for plant growth, differentiation from water inducing variable gleyzation over time, the acid reaction up to alkaline, very high content in humus and and generally appreciable differences in terms of the content of nutrients.

On the other hand, soil, one of the main components of the environment, is constantly subjected to the action of pollutants existing in both air and water from rainfall and in groundwater.

In the following are presented data on the dynamic evolution of the chemical composition of soil in different cultures, with different degrees of resistance to the

phenomenon of pollution, structured on specific elements of acidity, fertility and pollution elements.

It should be emphasized that the soils in the area of influence of the plant, falls mostly in the class of acid, with a natural low fertility and buffering variable capacity for pollutants, which requires increased attention to them, to avoid the phenomena of pollution. This study, with qualitative and quantitative assessments of macro indicators and agrochemical synthetic test which directly intervene in plant nutrition, compared with phytotoxicity limits over a large area situated on a possible egret around the plant, has emerged as an necessity objective.

The soil samples were collected from the arable layer of the soil at the same crops and vegetation phases as samples of plants, from lots of private producers and the sole of the research units in the area, where they applied all the technological sequences specific crop plants considered. [13-15]

Analytical data are presented in tables 3-7, including in the table 2 the interpretation limits of the values obtained for these types of soils.

NAVODARI

- the soil was harvested in the field of agricultural research extension of the resort, which applied all pedoameliorative technological sequences, specific crops and soils acidic (table 3);

- argillic soil type is type luvisc albic, whose key feature is the presence of aluminum in quantities exceeding the phytotoxicity;

- by fining aluminum ions are demoted in stable chemical compounds, insoluble in water, the type *gibbsite* and *variscit*;

Table 2
 THE INTERPRETATION LIMITS OF THE CHEMICAL COMPOSITION OF SOIL IN THE INFLUENCED AREA OF THE S.C. XXX FROM CONSTANTA COUNTY

The degree of assurance	Elements of acidity					Elements of pollution				Moisture %
	pH	Ah	S _B	T	V	Al ³⁺	N-NO ₃	SO ₄	Cl ⁻	
	H ₂ O	me/100g soil			%	ppm				
Low	>6.8	>1.5	<7.0	<12.0	<50	>10	<15	<50	<50	<12
Medium	6.0-6.8	1.6-2.5	7.0-10.0	12.0-16.0	50-70	10-15	16-20	50-100	50-100	12-15
Normal	5.7-6.0	2.6-3.5	10.0-15.0	16.0-24.0	70-75	15-20	21-25	101-120	101-120	-
high	5.5-5.7	3.6	15.0-25.0	24.0-32.0	75-93	25-30	26-30	121-150	121-150	-
very high	<5.5	6.0	>25	>32	>93	30-50	31-35	151-200	151-200	-
Phytotoxicity Limit	<5.0	>10	<7.0	>25	<70	>50	>40	>200	>200	-

Table 3
THE RANGES FOR
CHEMICAL
COMPOSITION OF THE
SOIL CULTIVATED IN
THE AREA OF
INFLUENCE OF
S.C. XXX IN MAY -
SEPTEMBER 2011 - 2015
PLACE HARVEST:
NAVODARI

Date of harvest	Elements of acidity					Elements of pollution				Moisture %
	pH H ₂ O	Ah	S _B	T	V %	Al ³⁺	N-NO ₃	SO ₄	Cl	
		me/100g soil								
May	5.05-5.98	2.8-6.3	8.6-13.4	11.9-18.5	67.0-82.4	1.2-56.9	0.4-21.0	18.8-68.5	42.6-78.5	7.9-25.4
June	5.13-5.99	3.1-5.45	8.6-13.8	14.1-18.0	61.3-80.9	3.5-35.9	0.5-49.8	16.8-64.8	62.5-80.9	8.9-23.8
July	5.34-5.94	3.8-5.0	11.8-13.3	15.9-16.3	72.9-80.5	3.7-23.8	3.1-16.3	19.3-63.2	62.0-95.5	8.8-24.5
August	5.27-5.99	3.7-4.9	12.3-15.2	16.6-19.2	71.5-79.4	1.2-19.5	0.4-12.1	32.0-68.2	30.7-65.5	8.2-21.5
September	5.26-5.95	1.7-4.9	12.1-15.6	13.8-19.6	71.9-87.4	3.7-20.0	1.6-13.2	17.0-66.1	32.4-70.1	9.2-23.7
Phytotoxicity Limit	<5.0	>10	<7.0	>25	<70	>50	>40	>200	>200	-

- in conditions of severe drought, the aluminum ions go again, in the soil solution increasing its concentration, situation in which the plants are subjected to synergistically type combined stress with major negative effects on crop level;

- the soil ensured optimal plant nutrition;
- those two forms of acidity, actual and potential, have been recorded areas of greater variation, in this station exceeding the optimum pH variation for plants;
- fertility items were located in a normal range of variation for the period investigated, plant-specific basis;
- the culture of maize, the potassium content increased to fall, being the result of at least two processes synergistic: one for removal of this element to maturity of the plant and one of the concentration in soil solution through a reduction in the absorption by plants participating in this, the dynamic balance, absorption complex tendency;

- elements of soil pollution during growth and development of plants and not only those specific to the plant, had a greater range of variation, but at levels that do not exceed phytotoxicity;

- the fairly large ranges for the tested items, are a consequence of the weather, otherwise known aspect of literature.

OVIDIU

- the impact of the plant on the soil activity was studied in lots of individuals;
- the chemical structure of tillage soil was studied in dynamic on different sole, with varying degrees of application the culture technologies (table 4);
- in the first 3 months of the monitoring period, has studied wheat crop, sola being mediocre to medium provided with nutrients while soil acidity, well above

Table 4
THE RANGES FOR
CHEMICAL
COMPOSITION OF THE
SOIL CULTIVATED IN
THE AREA OF
INFLUENCE OF S.C.
XXX IN MAY -
SEPTEMBER 2011 - 2015
PLACE HARVEST:
OVIDIU - LAND OF
PRIVATE PRODUCERS

Date of harvest	Elements of acidity					Elements of pollution				Moisture %
	pH H ₂ O	Ah	S _B	T	V %	Al ³⁺	N-NO ₃	SO ₄	Cl	
		me/100g soil								
May	5.18-6.13	4.1-8.6	7.1-13.2	14.0-18.5	45.5-73.5	0.2-88.4	1.9-18.7	25.8-60.5	42.4-82.8	9.0-23.5
June	4.93-6.01	2.5-5.3	7.2-15.6	12.2-19.2	59.1-80.6	0.2-57.6	0.4-64.4	25.0-68.5	43.2-78.5	10.8-21.5
July	5.02-6.02	2.1-6.1	6.3-13.8	12.4-19.2	50.6-80.0	1.0-61.5	2.1-29.2	24.7-58.6	47.2-73.4	7.75-23.5
August	5.07-5.98	3.2-6.9	6.4-20.1	12.2-22.6	52.2-92.8	2.6-42.5	0.3-35.3	25.0-58.4	31.9-85.2	7.9-26.1
September	5.07-5.98	2.1-6.9	6.5-15.9	12.2-19.4	48.7-83.0	7.8-41.5	0.3-22.4	22.5-58.9	48.5-85.2	12.0-21.7
Phytotoxicity Limit	<5.0	>10	<7.0	>25	<70	>50	>40	>200	>200	-

Date of harvest	Elements of acidity					Elements of pollution				Moisture %
	pH H ₂ O	Ah	S _B	T	V %	Al ³⁺	N-NO ₃	SO ₄	Cl	
		me/100g sol								
May	5.36-5.86	3.1-4.2	8.1-13.8	12.5-21.5	64.6-82.8	3.0-16.2	0.4-95.1	34.0-80.5	44.7-120.7	10.9-19.6
June	5.20-5.97	1.3-4.2	6.4-19.8	10.6-29.3	60.5-95.6	3.9-18.5	2.1-86.1	42.8-72.1	46.9-81.1	5.3-19.7
July	5.15-5.92	3.0-4.5	5.6-19.5	9.3-23.9	60.6-82.2	2.5-34.5	0.4-119.7	27.0-68.5	49.6-82.6	7.2-19.6
August	5.22-5.95	3.0-4.7	6.2-19.5	10.0-24.1	62.0-82.4	5.1-37.1	0.5-65.1	27.0-67.4	21.3-85.2	7.9-18.6
September	5.33-6.10	2.9-5.0	6.3-19.6	10.3-23.8	60.5-83.2	2.3-29.6	0.8-29.8	41.9-71.7	53.2-106.5	9.2-20.6
Phytotoxicity Limit	<5.0	>10	<7.0	>25	<70	>50	>40	>200	>200	-

Table 5
THE RANGES FOR
CHEMICAL
COMPOSITION OF
THE SOIL
CULTIVATED IN THE
AREA OF
INFLUENCE OF S.C.
XXX IN MAY -
SEPTEMBER 2011 -
2015 PLACE
HARVEST: LUMINA -
LAND OF PRIVATE

Date of harvest	Elements of acidity					Elements of pollution				Moisture %
	pH H ₂ O	Ah	S _B	T	V %	Al ³⁺	N-NO ₃	SO ₄	Cl ⁻	
		me/100g soil								
May	5.37-6.06	0.3-2.7	14.7-30.3	16.7-31.4	88.3-97.9	0.2-7.9	0.5-6.3	1.0-73.0	32.0-284.0	10.5-21.5
June	5.43-6.03	0.2-5.3	10.0-27.7	14.6-24.5	69.2-97.2	0.2-12.8	2.0-11.5	6.3-75.0	15.3-149.2	8.9-18.1
July	5.6-6.81	0.5-3.5	14.2-27.2	16.2-29.5	87.1-97.1	0-20.1	0.5-10.2	9.0-49.7	11.2-138.0	8.7-21.0
August	5.74-6.79	1.2-3.5	14.8-27.1	16.8-30.0	88.1-95.5	0-18.3	0.4-12.6	12.7-56.8	15.4-104.5	7.9-28.8
September	5.81-6.81	0.7-3.3	14.8-29.0	17.0-29.8	86.2-97.1	0-9.0	0.8-4.3	11.2-70.5	24.1-104.5	9.9-20.4
Phytotoxicity Limit	<5.0	>10	<7.0	>25	<70	>50	>40	>200	>200	-

Table 6
THE RANGES FOR CHEMICAL COMPOSITION OF THE SOIL CULTIVATED IN THE AREA OF INFLUENCE OF S.C. XXX IN MAY - SEPTEMBER 2011 - 2015
PLACE HARVEST: SACELE - LAND OF PRIVATE PRODUCERS

phytotoxicity was not bound by the amendment or application of manure stable;

- elements of acidity recorded a relatively high amplitude of variation, exceeding the current limit phytotoxicity in June;

- fertility elements have reached quite low levels

LUMINA

Soil samples were taken in dynamic, from different sole of private producers planted with various plants (table 5);

- soil planted with wheat is acid, luvic type with a relatively high present acidity, located in a range of variation under 5.5 pH units, but with low aluminum content, far below the phytotoxicity;

- In June and July, soil acidity recorded very high values, the upper limit of the amplitude exceeding the phytotoxicity, while, the fall in soil fertility is mediocre;

- the wheat is more resistant to soil acidity than maize, which is actually quite sensitive to aluminum content exceeding 20 ppm;

- in corn sola, the acidity was located at lower levels than on wheat, under the conditions in which the fertility was much better than that of the wheat;

- the elements of pollution in those two studied sole, were located fairly low levels, well below the phytotoxicity.

SACELE

- soil samples were collected from a particular manufacturer sola being cultivated for many years with lucerne;

- the soil is a luvic brown type with a reduced acidity and an aluminum content less than 10ppm, as can be seen from the data presented in table 6;

- base saturation level has a rather narrow range of variation;

- ensuring phosphorus level is medium to almost normal in recent years as a result of fertilization base on the last time;

- mineral nitrogen is very low, culture suffering because of this;

- potassium ion concentration is optimal for growing lucerne, knowing that this plant requires high concentrations of nitrogen and potassium;

- the presence of a nutrient imbalance in the soil fairly low levels has however negative influences on plants and hence at the level of harvested green mass production;

- polluting elements have been recorded quite low different ranges, well below phytotoxicity.

CORBU

- soil samples were collected with a grape- sola -living-table;

- grape -vines benefited from optimum nutrition, both in terms of quantity and nutritional balances, carried at all phases of vegetation pursued, the ranges being narrower;

- polluting elements recorded values much below the phytotoxicity;

- the main cause of rising the content of pollutants in soil, must be sought not only in the exceptional climatic conditions this year, but also in treatments and agro-technical measures applied, which induced a synergistic effect of amplification;

- climatic conditions with extreme areas of variation, induced substantial changes in the chemical structure of soil, with the installation of imbalances nutritious enough accentuated, with poisoning do not normally occur, with direct implications on the level of crops, be it the green beans or ground.

Date of harvest	Elements of acidity					Elements of pollution				Moisture %
	pH H ₂ O	Ah	S _B	T	V %	Al ³⁺	N-NO ₃	SO ₄	Cl ⁻	
		me/100g soil								
May	5.95-6.45	0.1-1.7	15.3-29.2	16.9-30.0	90.3-97.2	0-2.1	1.4-15.8	30.5-93.0	40.2-213.0	9.3-20.9
June	5.65-6.20	0.8-1.3	17.1-28.0	18.3-29.3	93.3-97.3	0-2.6	1.9-7.3	12.5-87.0	13.5-70.6	6.0-19.8
July	5.85-6.20	0.6-2.1	16.3-28.4	18.2-24.5	89.6-97.6	0-6.5	1.6-41.6	17.5-185.5	17.8-68.1	8.6-21.6
August	5.86-6.20	0.7-2.9	15.3-27.1	16.8-28.8	90.1-93.6	0-3.9	0.4-9.2	17.8-79.4	31.8-75.2	7.8-26.7
September	5.97-6.22	0.5-2.6	15.3-33.1	16.3-33.5	91.1-96.0	0-2.2	0.2-3.9	15.2-69.9	21.4-69.4	9.7-19.6
Phytotoxicity Limit	<5.0	>10	<7.0	>25	<70	>50	>40	>200	>200	-

Table 7
THE RANGES FOR CHEMICAL COMPOSITION OF THE SOIL CULTIVATED AREA OF INFLUENCE S.C. XXX IN MAY - SEPTEMBER 2011 - 2015
PLACE HARVEST: CORBU

In another paper was studied the impact of industrial processing of oil on fountain water [16].

Conclusions

Simple analysis of those 5 tables of data show the presence of several subtypes of soils, from the luvic albic at the brown luvic, with the content of aluminum exceeding the phytotoxicity for plants in general, to the alluvial type neutral by the agrochemical point of view, without aluminum ions and a pH more than 0.6 units.

Regarding the quantitative changes chemical structure of soil, shown in the tables above, highlights the following general aspects:

- very patchy areas of variation for chemical structure of soil, largely dependent by pedoameliorative measures applied;

- the chemical structure of soil is influenced by the drought;

- to provide optimal nutrition, the ranges of acidity elements are narrower in July, while not imposing specific pedoameliorative main measures, these variations reach maximum values;

- nutrition of soil, expressed by the degree of base saturation is low to average, less influenced by weather conditions, it can be supported by a diverse array of plants;

- synthetic indicators of acidity, expressed by the degree of base saturation and cation exchange capacity, pursuing a very uneven change in time and space;

- the monitored fertility elements, recorded broad areas of variation, depending not only on nutrient tested, but also the extent pedoameliorative applied.

Summarizing the data presented above, result that the chemical structure of soil has not changed because of the activity in the industrial processing of oil, changes made

as a consequence of other cases where not applying pedoameliorative measures are a priority.

From the data presented is clear that the soil in the area of influence of the oil processing industrial activity by SC XXXX, was not polluted with specific chemicals.

References

1. ANGHELESCU, C., STANESCU, I., Economie politica, Editia a II-a, Ed. Oscar Print, 2008
2. AXINTE STELA, Curs de ecologie, Univ. Tehnica, Iasi, 1994.
3. BARBAULT R., Ecologie generale, Ed. Dunond, Paris, 2000.
4. BARDE J. PH., Economie Et Politique De L'environement, P.U.F., Paris, 1992.
5. BARNEA M., PAPADOPOUL C., Poluarea si protectia mediului, Ed. Stiintifica si Enciclopedica, Bucuresti, 1975.
6. BALOIU L.M., ANGELESCU A.I., Protectia mediului ambiant, Ed. Ase, Bucuresti, 1995.
7. BERCA M., Strategii pentru protectia mediului si gestiunea resurselor, Ed. Grand, Bucuresti, 1998.
8. BONNEFOUS E., Omul sau natura, Ed. Politica, Bucuresti, 1976.
9. DADUIANU VASILESCU IOLANDA, Protectia mediului inconjurator, Cide, Bucuresti, 1994.
10. DADUIANU VASILESCU IOLANDA, Mediul si economia, Edp, Bucuresti, 1997.
11. DĂACU V., Eliminarea prin absorbtie a poluantilor organici din sursele de apa, Ipb, Bucuresti, 1995
12. KEMPF H., L'economie A Lepreuve De L'ecologie, Collection Enjeux, Hatier Paris, Aout, 1991.
13. KEOLEIAN G.A., Life - Cycle Design Guidance Manual, Epa, 1993.
14. KERRIDGE A.E., Risk Management: A Project Manager's View, Hydrocarbon Processing, 1994.
15. KRIVIH I.D., Necesitati ecologice, În Stali, Nr. 6, P. 81, Rusia, 1992.
16. CHIVU, O.R., SEMENESCU, A., BABIS, C., AMZA, C., IACOBESCU, G., PASARE, M., PETRESCU, V., APOSTOLESCU, Z., Rev. Chim. (Bucharest), **67**, no. 12, 2016, p. 2577

Manuscript received: 19.09.2016