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INFLUENCE OF PETROL AND PETROL PRODUCTS ON SOILS PROPERTIES AND THEIR AGRICULTURAL USE

The influence is described of oil and petroleum products on agrochemical, agrophysical and microbiological soils characteristics
***Keywords*: petrol, soil, agricultural lands.**

Preface

Actuality. Modern tempoes of industry development and growth of mankind energetic demands lead to every year petroleum extraction throughout the world, that's why in last decades questions connected with influence petroleum and oil-refining enterprises on ecological situation in different regions especially in Ukrainian Polissya became more actual.

That's why the **goal** of article is to give total assessment of soils destruction under influence of petrol pollution.

The objects of research are soils in the area of influence of main Ukrainians pipe lines.

Methods of research are traditional general scientific – analysis of literature sources, Internet resources, statistical data

Analysis of recent researches. Such researchers as Miroshnichenko, Ilarionov, Haziev studied this question. We generalized their materials and added new data.

Results of researches. That's why a large number of high-fertility chornozems of agricultural use are taken away from use like soils on the territories of oil-refining enterprises and oil pipe-lines. Surface and underground waters are polluted by oil-products and accompanying toxic substances. They transform fertility chernozems into ecologically critical ecosystems. One of recipients of petroleum pollution is soil. Soil pollution is closely connected with negative influence of harmful substances on flora and fauna. Self-purification abilities of soil are also broken as the consequence of petroleum pollution.

No organization has any reliable information about soils conditions and pollution. Still more differences about enterprises and regions doing treatment of foil and oil products

Petrol products bring significant harm to the environment. It's well-known fact, that 2 g of petrol make soil unsuitable for plants and microflora life, 1 liter of petrol deprives oxygen for 40 thousands liters of water, 1 ton of petrol pollutes 12 km^2 of water surface.

They bring considerable changes to soil physical-chemical characteristics. Especially is the aftereffect of soil structure destruction and dispersion of soil parts permeability to water is reduced and also filtration regime is disturbed. In polluted soils there is high correlation between carbon and nitrogene high growth (because of content of carbon in petroleum). It makes worse nitrogene regime and worsens plants roots nutrition.

Soil cover – is a comparatively stable component of geosystem which has practically unlimited property to accumulate, hold and process pollutants. The condition of its component is determined by following basic indicators:

• level of pollution by chemical elements ;
• level of activity of self-purification processes, destructuration of mineral substances;
• ability of natural fertility upkeep and fertility recovery;
• fertility as the basis of recovery of flora and consequently of fauna.

That's why the reclamation of damaged and polluted lands in oil deposits and reached balance in the damaged agrolandscapes is one of the most important tasks. Lands need reclamation and return into agricultural production. With the help of modern agrotechnical phytomeliorative and microbiological technologies there exists real opportunity to return damaged and polluted lands to usual natural conditions in the shortest possible term.

The total area of damaged lands in Ukraine is 144,5 thousands of hectares. During 2010 year 477,9 ha of such lands had been reclamated, in 2011 – 571,1 ha, in 2012 – 683,5 ha (86% of this lands – 589,6 ha are agricultural lands. Financing and organizations of works for lands protection lead from state and regional budjets but is very slow. In 2012 and 2013 years there were no costs provided by state budjet of Ukraine.

The total area of polluted lands were 119 thousands ha during 2012, 2,5 thousands of hectares were conserved; 1,3 thousands of hectares from it – with the help of forestation, 1,2 thousands of hectares – with the help of meadow creation.

In spite of this fact that percentage of petroleum deposits in Ukraine is 40-50 during its working out and exploitation it's necessary to avoid soil pollution and to preserve flora. It can be done with the help of such measures: working out and implementation of efficiency methods of clinker separation from auger sewage waters and its removal to special places;

decrease of volumes of use of flushing solutions with the help of second use of auger sewage waters, enhancement of techniques and technologies of its purification; implementation of new ways of removing auger towers (using phneumatic tools etc. Working out and implementation microbiological of soils purification from petroleum and petroleum products'; speeding up the building of system of gathering and working over of oil gas and gas condensate. The most informative data about ecological safety of oil-products for soil ecosystem are results of determination of soil toxic influence on organisms especially phytotoxic – ability of soil to make depression influence on plants which lead to infringement of physiological processes, worsening quality of plants production.

Petrol pollution creates mew ecological situation and leads the deep change of all links of natural biocenosis and its full transformation. General peculiarity of all kinds of soils polluted by oil – is change of the species variety and limitation of pedobionts (soil mezzo-, microfloura and microfauna).

Types of reactions in reply to different types of pedobionts are mixed:

- there is place mass death of soil mezofauna: three days later after that majority of soil animals fully disappeared or it quantity becomes not more 1% from priviour. For even light fractions of petrol are toxic.
-complex of soil microorganisms after short-term inhibition reads to the petrol pollution by rising up their gross quantity and increase of their activity. At first turn grow up very much quantity of hydrocarbon oxidizing bacteria. Developing such called "special" groups which take part on different staged of hydrocarbon utilization.
- maximum of microorganisms quantity response to horizons of fermentation and decrease in soils profile. The main "explosion" of microbiological activity began at the second stage of natural degradation of petrol.
- In the process of petrol destruction of soils the general quantity of microorganisms approach to background indices but the general quantity of petrol-oxidizing bacteria for a long time higher than for similar groups of non-polluted soils (in Polyssia – 10-20 years).
- Changing ecological situation lead to depriving of plants organisms of photosynthetic activity. First of all it influences to development of soils the algae: from their depriving and changing by other groups to absolutely perishing of all algafloura. Especially significantly is inhibit development of algae for the crude oil and mineral water.
- Also change photosynthetic functions of high plants, especially cereals. For example, in Polyssia conditions under high dozes of pollution (more than 20 l/m^2) even a year later plants cannot develop as usual

Soil phytotoxicity, level of inhibition of plants growth and development directly depend on intensity and term of pollution. It can be explained like oil toxicity either acquired hydrophobic soil ability. Especially under high pollution (96 h/kg) soil with plants purification for 61,7%, without plants – 69,7%. In the same period under lower pollution (48 h/kg) plants become physiologically active, they adapt, switch on inner protection mechanisms, oppositing to this stress and actively take part in destroying oil products in soil.

The activity of majority of soil enzyme are increases in polluted soils (N.M. Ismailov, Y.I. Pikovsky, 1985). At any level of pollution hydrol are inhibited hydrolases, proteases, nitrotreduktases, degidrogenases of soils, are decrease its ureasis and catalasis activity. Soil breathing also reacts into petrol pollution. In the first period when microflora deprived by significantly quantity of hydrocarbons, breath intensity decreases and with growing up of microorganisms quantity breathing intensity increases. [5, 6].

So the level of the development of plant cover in the determinated territory testify to the level of soil pollution (escape mechanic plants destroy).

The Daughter enterprise “PricarpatZahidTrans” of South-Western joint stock of company of transport of petroleum products expluatate magistral pipeline for transportation of petroleum products for oil-refining enterprises in Ukraine and abroad. Objects of this enterprise are situated in the territory of 7 regions – Zhytomir, Khmelnitsk, Rivne, Volyn, Lviv, Ternopil and Transcarpathions (total length of oil pipe-line is 1218,4 km). The product line is secured on the place threw 1 km distance and on the place of turning in determination and signal signs (columns). Area for which limitation in using lands plots in the protected zones of MPPPL is spreading is 23 681 thousand of hectares. Product line 273-530 mm in diameter which is situated on Zhytomir, Rivne, Khmelnitsky, Ternopil, Lviv, Transcarpathion regions of daughter enterprise “Pricarpatzahidtrans” (table 1).

The reason of frequent emergencies on pipe-lines is unauthorized interpol of outlier persons in consequence of pipe-line depressurized on the hundreds of kilometers of track with the flowout of oil-products and it put on the soil’s surface. As a result – spots with tens of square kilometers size are created.

It was established that the main influence into kinetics of absorption of diesel fuel by soils makes by content of small sand and physical clay. Researched soils can be ranged in following way: “turf clay sandy > brown forest > turf deep clay >usual black soil > grey forest. Exist the opinion that weak pollution can be removed in the process of self-purification during first 2-3 years, middle pollution during 4-5 years. Beginning of serious

ecological losses is soil's pollution in concentration which are higher then 13 g/kg, because begin migration of petrol products to subterranean waters, ecological balance significantly disturbed in soil biocenosis.

Table 1

List of main oil products pipelines state enterprise "Pricarpatzahidtrans" which are situated on the Ukrainian Polyssia [4]

Object name	Place of dislocation
Main oil-product pipe-line "Section 42" diameter 530 mm	Zhytomir, Rivne, Khmelnisk regions
Main oil-product pipe-line "Line 12"Section 42" (2 branches) 273 mm in diameter	Zhytomir region
Main oil-product pipe-line "Line 18 "Section 23" 530 mm diameter	Volyn region
Main oil-product pipe-line "Sections 1, 16, 13 "Line 43" 530 mm diameter, "Section B, Line 43 325 mm diameter	Rivne, Ternopil, Lviv, Transcarpathions regions
Main oil-product pipe-line "Sections 15 "Line 43" 325 mm diameter	Lviv region

In accordance with specialists' data absolutely majority (89-96%) of emergency oil spill call strong and irrevocable damage of natural biocenosis. On the tracks of pipe-lines width of zone of damage varies from 40 m to 400 m for one magistral line.

In the process of studying the species variety of plants which are in the direct neighbourhood to these lands it was determined that under present conditions there is no technogenic impact upon the vegetation cover because the turf stratum of the territory is compact, without gaps, in the collected natural material there are plants specific for this locality, there was observed no violation in their growth. That is, the state of the ecological safety of soil cover corresponds to the normative one in these conditions.

Most numerous in the collected material are species the characteristics of which is given below:

- Grassy perennial plant (Silenevulgaris), of 35-80 height, flowers are heterogeneous;
- Annual plant (Kochiascoparia (L.) Schrad) of 30-50 cm height;
- Biennial plant (Erigeroncanadensis) of 10-100 cm height. Spread on open sandy places;
- Perennial plant (Elytrigiaelongata (Host) Nevski) of 75-150 cm height, forms large compacted turfs. Occurs on sandy soils;
- Perennial plant (Leymusarenarius), of 60-120 cm height. Occurs on

sandy soils;

- Perennial plant (Bromopsisinermis), of 80-150 cm height. Occurs on slopes, on sandy soils, among weeds;
- Perennial plant (Festucavalesiaca), of 35-50 cm height, sometimes up to 70 cm. Occurs on fertile soils and on slopes;
- Perennial compacted turfy plant, up to 20-25 cm height. Grows on compacted soils, on dry meadows;
- Grassy plant (Medicagosativa L.) with well developed stem, of 60-100 cm height;
- Perennial grassy plant (Salvianutans) of 50-70 cm height;
- Perennial grassy plant (Plantagomajor L.) of 60 cm height. Grows on meadows, along openings, on cultivated areas and as a weed on seed plots, a tree of Robiniapseudoacacia 15-25 m.

In case of soil pollution the most dangerous are petroleum products and seldom wastes of drilling which enter soil, make it sour (as a result of high concentration of water ions) and contribute to the intensive oxygen substitution. This stipulates irreversible changes of agrochemical soil properties and decreases its agronomic value [1].

The contents of petroleum products in soils is regulated by temporarily admissible concentration (TAC) (table 2).

Table 2

Indices of soils pollution level by petroleum products phenols, mg/kg [1]

Pollution level	Petroleum and petroleum products	Phenols
First (admissible)	<ТАСн	<ТАСph
Second (low)	1000 – 2000	-
Third (average)	2000 – 3000	1 – 5
Fourth (high)	3000 – 5000	5 - 10
Fifth (very high)	>5000	>10

ТАСн = 4000 мг/кг, ТАСph = 1,28 мг/кг

According to the order of Ministry of natural environment protection of Ukraine №149 of 4.04.2007 petroleum and petroleum products are referred to the 1st group of danger.

In view of the fact that a part of the territory of agro-industrial complex of Ukrainian Polissya is in oil extraction district today it is perspective to produce the agro-ecological evaluation of soils. At the present-day stage the sphere of the analytical control over polluted objects of environment may be referred to sufficiently secured in the methodical plan of analytical

chemistry chapter.

Gravimetrical method. Extractions of PP from the sample by low-polar solvents (chloroform, hexane, pentane); purification of extract from polar substances by its passing through a column with sorbent (aluminium oxide of 11 degree containing 3% H_2O), silica gel, florosil (base silicate of magnesium), removal of extractant by its evaporation and weighing remnants to obtain the sum of "petroleum products".

Fluorimetric method. It is little different from luminescent chromographic one based on the extraction of petroleum products by hexane, purification if necessary of extract with the subsequent measurement of the intensity of its fluorescence emerging as a result of optical excitation. With the help of fluorimetric method are determined not only petroleum products but also other organic compounds of different origin. Most spread in light fractions of petroleum products among policyclic aromatic hydrocarbons (PAH).

Ultra-violet-spectral-photometric method. To determine PP is used rather seldom which is connected with non-structuralness of spectres of absorption of PP.

Method of infra-red – spectroscopy IR). To monitor petroleum hydrocarbons it is the most spread method of IK_spectrometry which permits to determine the sum of aliphatic hydrocarbons and PAH.

The respective methods of the analysis are based on extracting PP from the sample by organic solvent (CC14 or chladone 113), on purifying the extract from polar compounds by the method of column chromatography and CH_3-, CH_2-groups of aliphatic and alicyclic hydrocarbons and also CH connections of aromatic substances.

Method of gas chromatography GC. It belongs to the most efficient methods of discovering not only petroleum products but also sources of their entry into environment. The essence of the method lies in dividing petroleum hydrocarbons in non-polar phase under the regime of temperature programming. The analytical signal is the summary area of peaks on chromatogram beginning with the peak on alkane hydrocarbon ($C_{10}H_{22}$) and finishing with peak on n-tetracontan ($C_{40}H_{82}$).

Gas chromatography with mass-spectral detector permits not only to find the general content of PP but also to identify and determine quantitatively individual petroleum hydrocarbons which gives the possibility to find really the source of pollution (determination of PP type) and also to take measures to remove negative consequences.

Method of channel thin-stratum chromatography. It is used to find PP under field conditions. The essence of the method is in extracting PP by carbon tetrachloride. The portion of the extract is put into lower dilated part

of “channel” separated on a plate which is processed by chloroform in closed chamber, dried in the air and subjected under the action of iodine steams. Within “channel” hydrocarbons are found in the form of rectangular brown spot the area of which is assessed visually [3].

Biological monitoring of petroleum polluted soil. With the help of monitoring are revealed critical situations and factors acting in the environment and also critical (most sensitive) elements of biosphere.

To evaluate the ecological danger of polluting natural environment by petroleum products it is necessary to characterise such indices: 1) the content of petroleum products in several components (such data are obtained in standard regime after carrying out monitoring observations); 2) the rate of their chemical and biological destruction (on the basis of carrying out the complex of long-term and labour consuming experiments by volume under field and laboratory conditions); 3) the level of petroleum products toxicity concerning live organisms.

As a result of non-mono-factorial character of petroleum and petroleum products action the toxic activity of soil is difficult to forecast because several components interacting between themselves and soil environment are able to be activated or inactivated by various exterior factors. Norms of ecological regulation are comprehensive and take into consideration the petroleum action upon soil biota and physical chemical soil properties. Bio-testing, bio-indication and eco-toxicology, along with methods of analytical chemistry, give the possibility to get as a whole the complete picture of the degradation of soils polluted by petroleum products. The principle of bio-indication is built on the fact that that each organism concerning the acting factor possesses unique physiological reaction scope.

At the same time each particular group of organisms is influenced by other numerous factors which are not always possible to consider. Therefore, the comprehensive evaluation of the eco-toxicity of soils polluted by petroleum is advisable to carry out on the basis of bio-tests of various trophic levels, in particular: of soil exo-ferments, of soil micro-flora and fauna, of plant indicators, of plants-remediants, etc.

In selecting test-organisms it is essential to use bio-tests most sensitive to the action of pollutants. The second important requirement concerning test-organism lies in the fact that the action of toxicant upon it must obligatorily cause the reverse reaction of the organism.

Vegetative test-systems are rather reliable and convenient in determining the degree of the toxicity of certain pollutants, besides they give the possibility to assess the summary effect of the action of different types of pollutants, including the evaluation of the degree of the degradation of soil eco-systems which undergo the anthropogenic influence

of various plans. The most informative data concerning ecological danger of petroleum products for soil eco-system is the establishment of the phyto-toxicity - the ability of soil to exert oppressive influence on plants which leads to the violation of physiological processes, to the worsening of the quality of vegetative produce.

The impact of petroleum pollution upon plant organisms occurs in two ways: directly (as a result of the penetration of oil components via root system or leaves breathing and their inclusion into metabolism) and indirectly (via the change of physical-chemical soil composition and the violation of its biotic properties).

The direct impact of petroleum on vegetation cover is in the fact that the plant growth is slowing, functions of photosynthesis and breathing are violated, various morphological violations are discovered, rot system, leaves, stems and reproductive organs suffer greatly.

To diagnose and assess the toxicity of petroleum pollutes soils are usually taken into consideration such indices as plant height, number, length and width of leaves, the length of petioles, quantity and length of shoots, quantity of flowers, sizes of blossoming parts, the quantity of fruits and seeds in a fruit, the total mass of a plant and the mass of its parts, etc. Physiological biological and cytogenetic parameters of vegetation test-systems are suitable for the quantitative evaluation of the action of factors under conditions of technogenic pollution. Bio-indication of petroleum polluted soils in agro-ecosystems is done on the basis of reactions of agricultural crops with different sensitivity to a given factor.

On the basis of literary data and results of our own researches it is possible to draw a conclusion that studied test-reactions of phyto-remediants (table 3) are sensitive to petroleum action, therefore it is expedient to use them as test-systems in phyto indication of oil polluted territories and plants to restore oil polluted soils.

The operative information on the phytotoxicity of polluted soil it is possible to obtain using as test-objects seeds and plant sprouts. Test-functions used in biotesting are rather manifold: dynamics of seed germination, percentage of germination, length of main and lateral roots, length of a sprout, etc. On their basis is determined the phyto effect of a soil. To compare the toxicity by growth test of phyto indicator the scale is developed of levels of soils toxicity (table 4).

In biotesting the main parameter for assessing pollution is not the concentration of a pollutant but a reaction on live organism response. The advantage of toxicity biotesting for polluted environment is the consideration of the influence of antagonistic and synergetic interactions of pollutants, the evaluation of the summary biological activity of the impact

of physico-chemical factors on biota [2].

Table 3

Vegetation test-systems under conditions of soil pollution by petroleum [2, 3]

Test systems	Morphological and biometric parameters
1	2
Seed V.faba	Seeds germinating capacity under influence of oil and oil products concentration
Whole plant C.hirta and V.faba	plants biomass; plants survival ability in field and laboratory conditions
Vegetative organs of plants	roots' lengths C.hirta; height of plants shoots C.hirta and V.faba
Leaves of plants C.hirta and V.faba	length and width of leaf blade; number of stomata per unit of leaf surface content of photosynthetic pigments; presence of chlorosis, necrosis etc. character of pubescence of leaf blade C.hirta

Table 4

Scale of levels of soils toxicity [3]

Level of depression of growth processes (photosynthetic effect), % (0-20)	Toxity level
0- 20	Absence or weak toxity level
20,1 - 40	Middle level
40,1 – 60	Higher then middle level
60,1 – 80	High level
80,1 - 100	Maximal level

Conclusion.

Thus the pollution by oil products –is an ecological disaster. Oil when it appeared in soil violates process of life activity. It deprives microbe self purification, changes trend of metabolism. Petrol products in natural conditions decompose during many years and bring big harm to nature. Processes of natural regeneration of the agrocenosis on polluted territories take place very slowly .To provide safe operation of pipe-lines it's necessary to work out system of isolation measures .

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ВПЛИВ НАФТИ ТА НАФТОПРОДУКТІВ НА ВЛАСТИВОСТІ ҐРУНТІВ ТА ЇХ СІЛЬСЬКОГОСПОДАРСЬКЕ ВИКОРИСТАННЯ

Описаний вплив нафти та нафтопродуктів на агрохімічні, агрофізичні та мікробіологічні характеристики ґрунтів
***Ключові слова*: нафта, ґрунт, сільськогосподарські землі.**

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ВЛИЯНИЕ НЕФТИ И НЕФТЕПРОДУКТОВ НА СВОЙСТВА ПОЧВ И ИХ СЕЛЬСКОХОЗЯЙСТВЕННОЕ ИСПОЛЬЗОВАНИЕ

Описано влияние нефти и нефтепродуктов на агрохимические, агрофизические и микробиологические характеристики почв
***Ключевые слова*: нефть, грунт, сельскохозяйственные земли.**
