THE INTERACTIONS OF EXOGENOUS HYDROPHOBIC LIQUIDS WITH ORGANIC AND MINERAL SOIL SUBSTANCES *

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Abstract
The main task of investigations was to study the mechanisms of interactions of exogenous liquid hydrocarbons (HC) with organic and mineral soil components and their transport and distribution in soils. The experiments were carried out on modelling of HC transfer in clayey leached chernozem with homogenous structure - moistened up to the field capacity and air-dried. With use of headspace chromatography analysis method the thermodynamics and kinetics of HC sorption was studied on different components of soil-plant systems and also natural mineral absorbents influence on barrier functions of leached chernozem in relation to HC. The received results allowed us to outline the role of main processes of HC transfer (filtration, sorption, biodegradation, evaporation, diffusion) and their determining factors. It was demonstrated that exogenous HC significantly impair water-physical soil properties and reduce the function of leached chernozem as sorption barrier against contaminants. They also strongly influence the realization of gaseous functions by soil, in particular upon the increase of concentration that is threshold by toxicity for the microorganisms in soil.

Introduction
Technogeneous hydrocarbons (HC) flows are formed in the presence of extraction, transportation and conversion of the combustible raw materials, especially oil and gas. They play a significant role in anthropogeneous changes of natural matter rotation and cause an intense contamination of the nature environment, soils and groundwater in particular. Among all of soil contaminants, even the most toxic ones, oil is the most widespread and has the greatest number of the sources of contamination. The localized HC flows upon the floods of oil and petroleum products affect the landscape in an especially bad way. HC become degraded very slowly when reaching the soil surface and then the aerated soil environment. They are sorbing in separate soil horizons and also can vertically migrate in the soil profile with the water flow, and further into groundwater **[8-10]**.
The remediation of soils is quite a difficult task **[13]**. The search of the fast and economical way of remediation is especially difficult because of the complexity of the processes of transport and distribution of HC in soils **[11]**.

I. Hydrocarbon sorption on organic and mineral matter
Hydrocarbons (HC) sorption is one of the key processes impacting HC movement in soil-plant systems **[6,11,12,14-16]**. The failure to take sorption into account can result in a significant underestimation of the amount of a contaminant at a site as well as the time required for it to move from one point to another.
The aim of this section was the comparative estimation of character and magnitude of sorption interactions of HC with organic and mineral sorbents and the revelation of mechanisms of HC vapor sorption. **The following basic tasks** were solved: to determine the main soil sorption parameters for different classes of HC; to estimate the type of HC sorption on soil and the effect of sorbent humidity on HC sorption and to compare the values and parameters of HC sorption on different organic and mineral sorbents.

Methodology:
HC were: n-heptane, n-octane, n-nonane, n-decane, decaline ([4,4,0]-bicyclodecane) and p-xylene (representatives of typical components of oil products). Sorbents: Soils (leached chernozem, soddy podzolic and gray forest soils), natural zeolite containing material (ZCM), bentonite clay, limestone, soil humic acids extracted from leached chernozem, leaves and roots of maize. On the basis on headspace gas chromatographic analysis method vapour sorption isotherms were obtained and represented as a dependency of the sorbate uptake (V_S) on its thermodynamic activity (P/P_0) **[4]**. The approximation of isotherms was made with the help of BET equation.

Results
a) Sorption of hydrocarbons on dry whole leached chernozem.
The sorption isotherms of n-heptane, n-octane, n-nonane, n-decane, p-xylene and decaline had a similar type. On **Fig.1** isotherms of HC of different classes are compared. They were not described by BET equation in all activities range **[6]**. This may have to do with the heterogeneity of sorption

centres of leached chernozem as soil is a complex porous multi-component media and accords with idea about soil as a 'double' sorbent possessing both mineral and organic parts.

On **Fig.1** are also presented sorption isotherm parameters determined on BET equation: sorption constant (C) and sorbat monolayer volume (V_m). The specific soil sorbent surface (S) calculated from V_m of nonane formed 11 m^2/g. This value was compared with S values received by us for low-porous limestone (1 m^2/g) and high-porous ZCM (44 m^2/g). The comparison showed a presence of a significantly large soil surface available for the interaction with HC.

V_m for aromatic p-xylene in the P/P_0 range 0,1-0,5 was 30-40% higher than that of saturated HC. The S value for leached chernozem determined from V_m for p-xylene was almost 2 times higher than that from V_m of non-aromatic HC. Probably it points at non-coplanar location of aromatic molecule flat relatively to the sorbent surface upon the formation of HC monolayer (if sorption occurs on the interface between phases) or this shows more greater sorption capacity of soil organic phase (if HC sorption passes in a volume of soil organic matter).
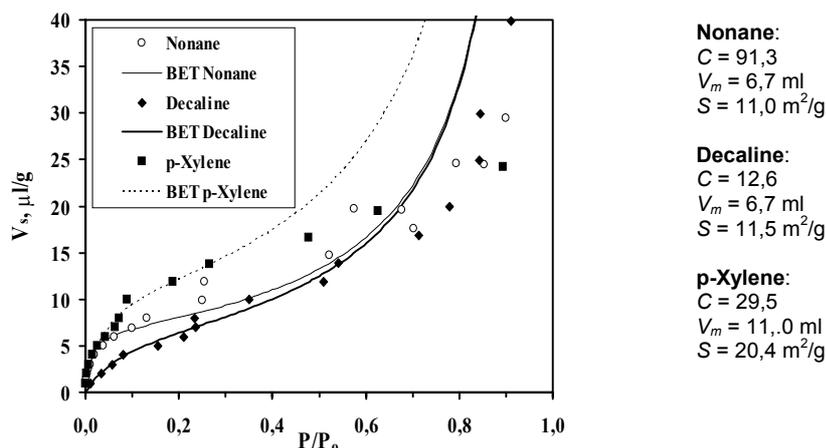

Graph legend:
○ Nonane
— BET Nonane
◆ Decaline
— BET Decaline
■ p-Xylene
···· BET p-Xylene

Y-axis: V_s, μl/g
X-axis: P/P_0

Nonane:
C = 91,3
V_m = 6,7 ml
S = 11,0 m^2/g

Decaline:
C = 12,6
V_m = 6,7 ml
S = 11,5 m^2/g

p-Xylene:
C = 29,5
V_m = 11,.0 ml
S = 20,4 m^2/g

Fig.1. Isotherms and parameters of n-nonane, decaline and p-xylene sorption on dry leached chernozem.
C - Sorption constant, V_m - Sorbat monolayer volume, S - Specific sorbent surface.

b) Fractal dimension of soil surface.

For the evaluation of structure of soil sorption surface and sorption type, we have determined the fractal dimension of leached chernozem surface (D). The received value (D=5,4) significantly exceeded D-values for sorbents with 'rigid' structure (not changing during sorption interaction). This abnormally high fractality value suggests that molecules of organic sorbent during the interaction with sorbent distribute ('dissolve') in the organic phase of leached chernozem.

It is possible that the same reason has caused sharp increase of sorption affinity of studied HC when P/P_0 were lower than 0,05, **Fig.1.** This type of isotherms was distorted only in the case of decaline – probably due to the bicyclical structure of its molecules that troubles diffusion of decaline into the sorbent volume. The illustration of sorbat 'dissolving' in soil organic matter can be fractality data for sorbents that do not have organic matter. According to the literary, the values of fractality for sorbents with highly developed surfaces but without organic matter do not exceed 3 (silica gel has D=2,94, highly porous kaolinite soil has D =2,92).

So we have established that leached chernozem has a highly developed and heterogenous sorption surface exhibiting low selectivity upon the interaction with HC.

c) Effect of humidity on hydrocarbon sorption on leached chernozem and zeolite containing material.

For soils diverse humidity is typical. It is known that in humid soils HC sorption occurs competitively with water. An especially large amount of HC goes into soils during spring melting of snow when soil humidity reaches a state of 'field capacity'.

For evaluation of the competitive sorption effect we have received sorption capacity values for leached chernozem with different humidity for nonane, decaline and p-xylene. The evident decrease of nonane sorption was found already with the 1% soil moisture content. Further (5% of moisture) sorption continued to lower steadily, and with 33% ('field capacity') it reached the limit value that was the same as nonane sorption from water. In the latter case sorption of all HC turned out to be small and practically the same.

For comparison of humidity effect on soil and mineral sorbent sorption capacity the sorption of nonane on ZCM has been studied. The 1% moisture content did not influence HC sorption: isotherms on dry and on moistured ZCM were completely the same. This pointed at the presence in ZCM structure of micro pores, totally inaccessible to HC. On the other hand, probably in the structure of the internal porous space of leached chernozem there are no sufficient limitations that would make HC sorption difficult.

d) Sorption of hydrocarbons on humic acids.

Each of soil humic substances fractions has been shown to play a significant role in the fate of hydrophobic organic contaminants in ecosystems. We have thought it would be most expedient not to

imitate the soil organic matter **[16]** but to extract its components and to study sorption using them. We have prepared humic acids, the main humus component in leached chernozem.

The sorption of nonane on oven-dry humic acids turned out to be significantly lower (almost 8 times) than on the soil. But it must be noted that naturally humic acids change their spatial configuration upon the extraction from soil. Hence it is possible that native humic acids hold a higher sorption activity towards HC than that of humic acids extracted in an individual state. With such a suggestion agree the results of studies **[7]** demonstrating that non-hydrolysed residue humin is the main sorbent for HC in soil. So our investigations will be continued.

e) Sorption of hydrocarbons on plant materials.

We have been compared sorption isotherms of nonane on maize roots and leaves with nonane isotherms on leached chernozem and humic acids extracted from it (all sorbents oven-dry). At P/P_0 =0,4 sorption value for humic acids was 1,8, for leaves 2,8 and for roots 2 times greater. In comparison with plants, sorption value of nonane on soil was even 4-6 times greater. The differences between maize roots and leaves may be caused by HC sorption on plant proteins.

f) The influence of soil granulometry and soil organic matter contents on hydrocarbon sorption.

In **Table 1** the main thermodynamic parameters of nonane sorption on different oven-dry natural organic and mineral sorbents are summarized.

Table 1. Thermodynamic parameters of n-nonane sorption on different oven-dry natural sorbents (V_m - sorbat monolayer volume, V_S – sorption capacity, S - specific sorbent surface)

Sorbent	V_m, mkl/g	V_S, mkl/g (P/P$_0$=0,4)	RSD*	S, m^2/g
Soddy podzolic soil	0,89	1,31	1,04	1,4
Light-gray forest soil 1	5,63	9,25	0,57	9,2
Light-gray forest soil 2	4,64	7,52	0,25	7,6
Leached chernozem	8,20	13,2	0,74	13,4
Humic acids	1,28	1,78	0,14	2,1
Bentonite clay	26,5	43,0	6,20	42,4
Limestone	0,60	1,10	1,08	1,1
Zeolite-containing material	107	165	22,1	175
Leaves of maize (Zea mays L.)	2,82	2,82	0,15	4,6
Roots of maize (Zea mays L.)	2,09	3,25	1,29	3,4

* RSD - residual standard deviation by approximation of V_S using BET equation.

The obtained values of sorption capacities (V_S at P/P_0=0,4) for monoaromatic p-xylele on soddy podzolic, light- and dark-gray forest soils and leached chernozem we have putted together with ones presented in literature for toluene and benzene sorption on soils with different granulomethry and soil organic matter contents **[5,12,14]**.
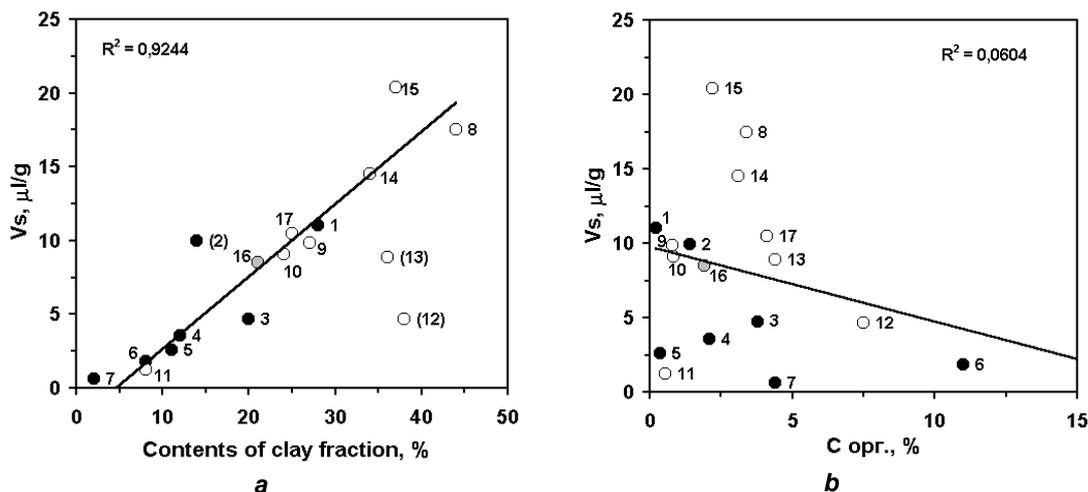

Fig.2. The dependence of sorption capacity of different soils to alkyl benzenes on clay fraction (*a*) и organic carbon (*b*) contents in soil.
Hydrocarbons: ● Toluene, ○ p-Xylele, ● Benzene.
Soils: 1–Marcus hook **[14]**; 2–Adelphia **[14]**; 3–Quakertown **[14]**; 4–Pequest **[14]**; 5–Plainfield **[14]**; 6–Great Meadows **[14]**; 7–Cohansey **[14]**; 8–Leached chernozem; 9–Light-gray forest soil 1; 10–Light-gray forest soil 2; 11–Soddy podzolic soil; 12–Dark-gray forest soil, layer 3-10 cm; 13–Dark-gray forest soil, layer 10-20 cm; 14–Dark-gray forest soil, layer 20-30 cm; 15–Woodborn **[5]**; 16–Webster **[12]**.

On **Fig.2a** all these data are correlated with soil clay particles contents (<0,002 mm accordingly to ISSA). The good correlation testifies the crucial contribution of highly dispersed clay soil fraction in

the sorption processes. This result is justified by high values of nonane sorption capacity of mineral sorbents in comparison with organic ones.

The conclusion of the main contribution of mineral sorption processes in the common HC sorption on soils attests also the absence of correlation between sorption capacities and soil organic carbon contents (**Fig.2b**) and also low values of parameters for nonane sorption on humic acids extracted from chernozem, **Table 1.**

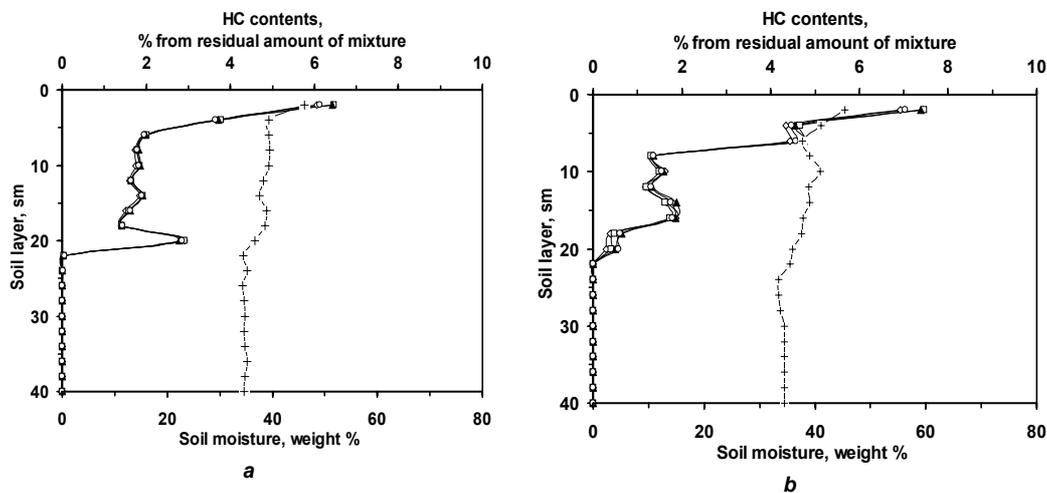## II. Transport and distribution of hydrocarbons in soil

Fig.3. Contents of hydrocarbons (HC) and water in profile of leached chernozem (layer 0-40 cm) after HC imbibition into the soil moistened up to the 'field capacity' during (*a*) 6 days and (*b*) 40 days – **Primary hydrocarbon contamination**.

◇ n-Nonane, □ Decaline, ▲ 1-Methylnaphthalene, ○ n-Tetradecane, ✦ Water
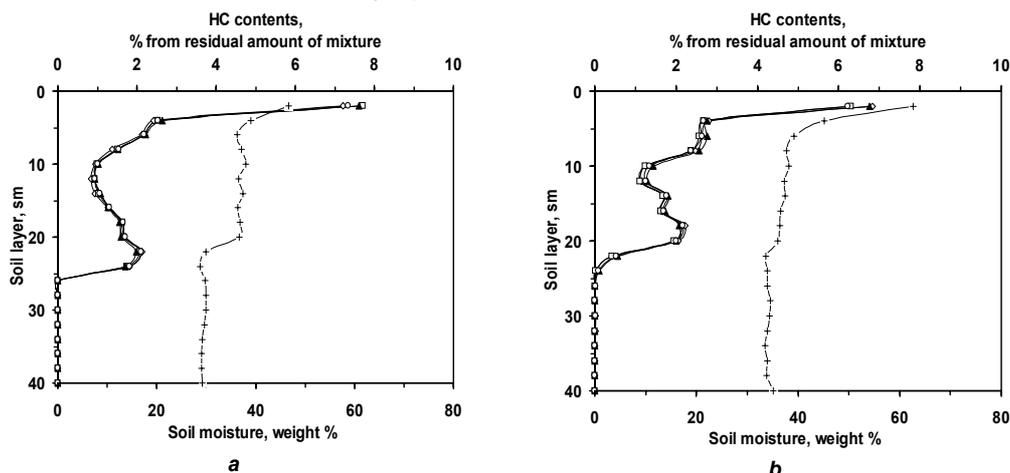

Fig.4. Contents of hydrocarbons (HC) and water in profile of leached chernozem (layer 0-40 cm) after 7 months of distilled water drainage in soil with HC-contamination originally moistened up to the 'field capacity' during (*a*) 6 days and (*b*) 40 days – **Secondary hydrocarbon contamination**.

◇ n-Nonane, □ Decaline, ▲ 1-Methylnaphtalene, ○ n-Tetradecane, ✦ Water

The character of hydrocarbon (HC) filtration in various agro- and geochemical landscapes depends on many factors **[1-3]** and in the first place on the soil moisture. It creates the capillary barrier on the way of HC movement and has a significant influence on the soil structure.

The aim of this section was the intensification of the ability of soil as a sorption barrier against HC spreading into the soil and further into the groundwater. **The following basic tasks** were solved: to study the soil structure dynamics during moistening (vacuum-capillary method) and to investigate the HC filtration in leached chernozem (soil columns, 0-40 cm layer) with homogeneous structure, high clay content, wetted up to 'field capacity'. **The model mixture of HC** was: nonane, tetradecane, decaline and 1-methylnaphtalene (composition of main petroleum products used as fuels and solvents), 1:1:1:1 w/w.

Methodology: *Experiments in soil columns:* The soil was saturated to 'field capacity' with the distilled water (height of pile - 5 cm) during 6 (variant *a*) and 40 (variant *b*) days. Then the mixture of HC was placed on the soil surface (2 cm) and after its imbibition (the primary soil contamination) the saturation with water was continued during 2-36 months (the secondary contamination). *Analysis of HC content in soil profile:* After the completion of every experiment the soil from the columns was

taken out by layers with step 2 cm. Soil samples were extracted by CCl_4. The analysis of HC contents in extracts was carried out using the gas-liquid chromatograph Biochrom-1.

Results

a) Dynamics of soil structure during moistening to 'field capacity'.
During the experiment on the accumulation dynamics of water infiltrate from leached chernozem the speed of water infiltration decreased but irregularly. Graphs have shown two bends of the curve, which characterize its uneven decreasement: on 6-th and 40-th days of moistening. During the first 6 days the speed of water filtration decreased sharply, further till 40 days - gradually and after 40 days it was practically constant up to 60 days of experiment. Therefore the stabilization of soil structure (connected with the complement of soil particles swelling and sedimentation) was detected: after 6 days non-complete and after 40 days complete.

In a vacuum-capillary installation with leached chernozem layers of 0-20 and 20-40 cm during the period of moistening the soil pores size distribution gradually changed. In both soil layers the volume fraction of smallest pores (<3 μm) increased and of all other (bigger) groups of soil pores - decreased. In the upper soil layer these changes were observed in a great degree after first 6 days. In the lower layer the same changes but slower relaxation of soil structure were observed.

During the moistening, the porous space structures for pounded and monoliths soil samples chummed in (the structure of leached chernozem changed from distorted to that corresponding to the natural soil). So we have determined time intervals necessary for the recovery of soil structure after the moistening of air-dry pounded samples in columns.

b) The study of HC filtration and distribution in leached chernozem.
The primary soil contamination. The amount of HC soaking into chernozem prior moistened over 6 and 40 days, was limited. In columns after 6 days moistening the speeds and volumes of HC soaked were significantly higher: this fact is in accordance with different structure of soil porous space under different times of moistening. On **Fig.3** the final distribution of the residual HC and water in soil is shown (HC amount is stated in normalized mode). In both variants the HC front shifted up to 22 cm and two maximums of HC amount in soil profile were noted: in variant with prior moistening over 6 days the second one shifted further and had a higher value.

The secondary soil contamination. On **Fig.4** the distribution of HC and water in soil profile after the secondary soil contamination (7 months of model mixture filtration in leached chernozem with 'field capacity') is shown. As a result of water ablution upon secondary contamination in both variants (6 and 40 days of moistening) the front and the lower maximum of HC were slightly shifted inland into the soil (2-3 cm). During HC migration in root-inhabited layer (0-40 cm), there were no significant changes in HC ratio in mixture (1:1:1:1 w/w).

Conclusions

The values of hydrocarbon sorption on soil depend on their chemical nature. On leached chernozem aliphatic hydrocarbons are sorbed weaker than aromatic ones. Hydrocarbon sorption occurs not only on outside and inside soil surfaces but also as the 'dissolving' of hydrocarbons into the volume of soil organic matter phase. The increase of sorbent humidity sharply inhibits hydrocarbon sorption. In the absence of water the main contribution in the hydrocarbon sorption on soils is their interaction with mineral soil components. The sorption activity of soil-plant sorbents (including different soil types) essentially differs. The highest activities possess minerals - Zeolite containing material and bentonite clay. Essentially less active are absolutely organic sorbents, the range of sorption activity for them is: roots > leaves > humic acids. The layer of leached chernozem 0-40 cm with homogeneous structure (not distorted with fractures and channels) moistened to the 'field capacity' practically completely prevents hydrocarbon entrance from root-inhabited horizons into the lower layers.

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