JOURNAL OF WATER AND LAND DEVELOPMENT
e-ISSN 2083-4535

Polish Academy of Sciences (PAN), Committee on Agronomic Sciences
Institute of Technology and Life Sciences (ITP)

JOURNAL OF WATER AND LAND DEVELOPMENT
2021, No. 49 (IV–VI): 79–84; https://doi.org/10.24425/jwld.2021.137099

Available (PDF): https://www.itp.edu.pl/JWLD; http://journals.pan.pl/jwld

Received 15.07.2020
Reviewed 04.10.2020
Accepted 17.11.2020

The minimization of impact of oil pollution on soils in the area of railways using glauconite

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For citation: Chayka O., Petrushka I., Ruda M., Paranyak N., Matskiv O. 2021. The minimization of impact of oil pollution on soils in the area of railways using glauconite. Journal of Water and Land Development. No. 49 (IV–VI) p. 79–84. DOI 10.24425/jwld.2021.137099.

Abstract

The analysis of ecological hazards on soil pollution by oil products has been provided in the impact zone of the railway. The results of oil product migration in soils in the area of influence on section Lviv–Khodoriv are given. To study this problem, a method was used to take soil samples according to the standard DSTU ISO 10381-4: 2005. To determine the content of petroleum products used the method MVV No. 081/12-0116-03 Pochvy. Based on the results of the study it was found that contamination with petroleum products in the study area exceeds the norm in the area of influence of the railway at a distance of 5 to –50 m on average 3.5 times. It is proposed to make management decisions to prevent violations of the sanitary protection zone of the railway and the placement of agricultural plots on it. For rehabilitation of contaminated soils, it is advisable to use a natural sorbent – glauconite, which is widespread in the bowels of Ukraine. The adsorption capacity of glauconite relative to diesel fuel has been experimentally established. According to our experiments it is proved the high efficiency of the proposed sorbent, which is 90%. Therefore, in the future it is necessary to periodically monitor the condition of the soil in the area to prevent pollution. This study proves that this practice is necessary.

Key words: *ecological safety, glauconite, oil products, pollution, railway transport, soil contamination*

INTRODUCTION

The results of anthropogenic activity are increasingly influencing the deterioration of the ecological situation on the planet. Contamination of the hydrosphere with nitrogen and phosphorus compounds in municipal drains has led to the rapid development of blue-green algae [SAKALOVA *et al*. 2019], which have become a significant environmental threat to many countries [MALOVANYY *et al*. 2016; NYKYFOROV *et al*. 2016]. The lack of an efficient solid waste management system in several stilcountries (including Ukraine) has caused leachate pollution of groundwater and surface water [MALOVANYY *et al*. 2018; 2019]. Pollution of surface waters and soils with petroleum products has become significant [ZELENKO *et al*. 2019]. Various modes of transport, including railways, remain a powerful polluter of oil products from soils and surface waters in the area of their influence.

Ukraine has one of the most developed railway networks in the Europe. The relief of Ukraine is quite favourable for the construction of railways. Since only 4% of the territory is under mountain massifs, the rest is flat, the southern and central parts of Ukraine are particularly beneficial. Construction of the railway in Ukraine began at the end of the 19th century. In the 1860s, the first railway was built, and the second in 1865, the Odessa–Balta section [GRINCHISHIN 2015].

The state of the environment is affected by rail transport as a large consumer of fuel, forest, and land resources, as well as mineral and construction materials. Although compared to other types of transport (especially road), rail transport causes less environmental damage [HRYHORCHUK 2018].

Like other modes of transport, the railway has been and remains a potential source of danger – accidents and other emergencies. Besides, man-caused danger during the operation of railway transport arises not only as a result of accidents but also in the process of its operation in normal mode. The condition of railway technical facilities in Ukraine has significantly deteriorated in recent years and does not guarantee a fully safe operation. This fact poses a threat directly to people involved in transportation and the environment [SISA *et al*. 2017]. The influence of the mode of operation of railway transport on the condition of the soils adjacent to the track is one of the determining factors of the ecological safety of these territories. While other harmful factors of railway traffic, such as noise or vibration, are to some extent regulated by regulations, oil pollution of the soils adjacent to the railway is almost not covered by state or departmental regulation.

In recent decades, due to the rapid development of transport, in particular rail, there has been a significant increase in the concentration of various pollutants in the soil, among which emit heavy metals and petroleum products. A special place among the pollutants of the soil cover belongs to petroleum products. This term refers to different types of mixtures of saturated hydrocarbons with a certain range of boiling points (fractions), which are obtained by distillation of oil and are usually used as fuels and lubricants [CHAYKA *et al*. 2016].

Petroleum products – environmentally hazardous substances that get into the components of the environment (soil, water), significantly affect all life processes that take place in them. Once in the soil, petroleum products reduce respiratory activity and microbial self-cleaning processes, change the relationship between certain groups of natural microorganisms and the direction of metabolism, inhibit the processes of nitrogen fixation, nitrification, destruction of cellulose, cause accumulation of microflora degradation and with agricultural products enter the human body [BABADJANOVA *et al*. 2012].

Contamination by petroleum products leads to a profound change over in all components of natural biocenoses or even their complete transformation. A common characteristic of all oil-contaminated soils is the change in the number and limitation of species diversity of pedobionts (soil meso- and microfauna, and microflora) [PROTSKO 2010].

The purpose of the study is to analyze the content of petroleum products in soils, namely areas that can be used for agricultural purposes, which are negatively affected by rail transport. We considered two types of soil pollution in the area of influence of the railway: scattered pollution, which occurs as a result of constant pollution from locomotives, and pollution due to emergencies during the spillage of fuel and lubricants. The first type of pollution was studied by analyzing the content of petroleum products in soil sampling sites from the area adjacent to the tracks on the section of the railway connection Lviv–Khodoriv The subject of the study was the assessment of the content of petroleum products and their migration in soils. Regarding the second type of contaminants, recently adsorption methods using natural dispersed sorbents are widely used. Therefore, the second type of pollution was investigated by establishing the adsorption capacity of the sorbent (glauconite) relative to petroleum products used as fuel in locomotives (diesel fuel). In the future, it was envisaged to use this sorbent for the regeneration of accidentally contaminated soils in the area of influence of the railway.

MATERIALS AND METHODS

OBJECT OF RESERCHES

The territory through which the railway track, which is a part of the Lviv–Khodoriv section in Lviv, passes was selected for the study. The track length is 1 km. This plot belongs to the private sector, in which land is used for agricultural purposes. This section carries out large numbers of freight and passenger traffic that uses both electric traction and with the use of locomotives on internal combustion engines of the railway. We assume that emissions from fuel combustion in these engines, as well as contamination with lubricants from parts of rolling stock mechanisms, are the main sources of oil products entering the soils adjacent to the track. There are no other potential sources of soil pollution by hydrocarbons.

The current soil cover of the city of Lviv is a mosaic--structural formation in which natural, natural-anthropogenic and anthropogenic components complement or replace each other. Lviv soils are classified into three main types: chernozem, eluvial, and peat-swamp. Chernozem-type soils are dominant on the forest base. However, they are not as saturated in humic substances as in the steppes. For a long time, forests that degraded them grew on those soils. Most Lviv soils are characterized by the absence of genetic horizons and the presence of differences in colour and thickness of the layers of artificial origin and increased density. Soils are contaminated with construction debris, emissions from industrial facilities and vehicles, as well as various toxic xenobiotics. Up to 30–40% of the area of residential built-up territories consists of sealed soils (screen soils), in areas of new buildings – soil-like bodies – replant soils [SLYCHKO *et al*. 2017].

Degradation of ecological functions of natural soils and slow formation of integral functional features of anthropogenic soils is noticeable in the city conditions. Anthropogenic soils, which take an important place in the structure of the soil cover of the modern city, can perform most of the ecological functions. Some of the functions of the soil, due to the specifics of the environment, are lost or partially performed, while the quality of other functions is crucial for the existence of the urban ecosystem [CHAYKA *et al*. 2019].

FIELD METHODS

For analysis, 13 soil sampling sites were taken in Lviv near the railway track at the following addresses: H. Chuprynky St., Gordienko St., Botkin St., Sarnenska St., Smetany St., Rudnytsky St. Railway District, direction Lviv–Khodoriv (Fig. 1). This path of the study was chosen because the site is sloping downwards, as a result, the migration of petroleum products is possible in this direction.

Soil sampling sites were taken in the warm season following the requirements of DSTU ISO 10381-4: 2005.

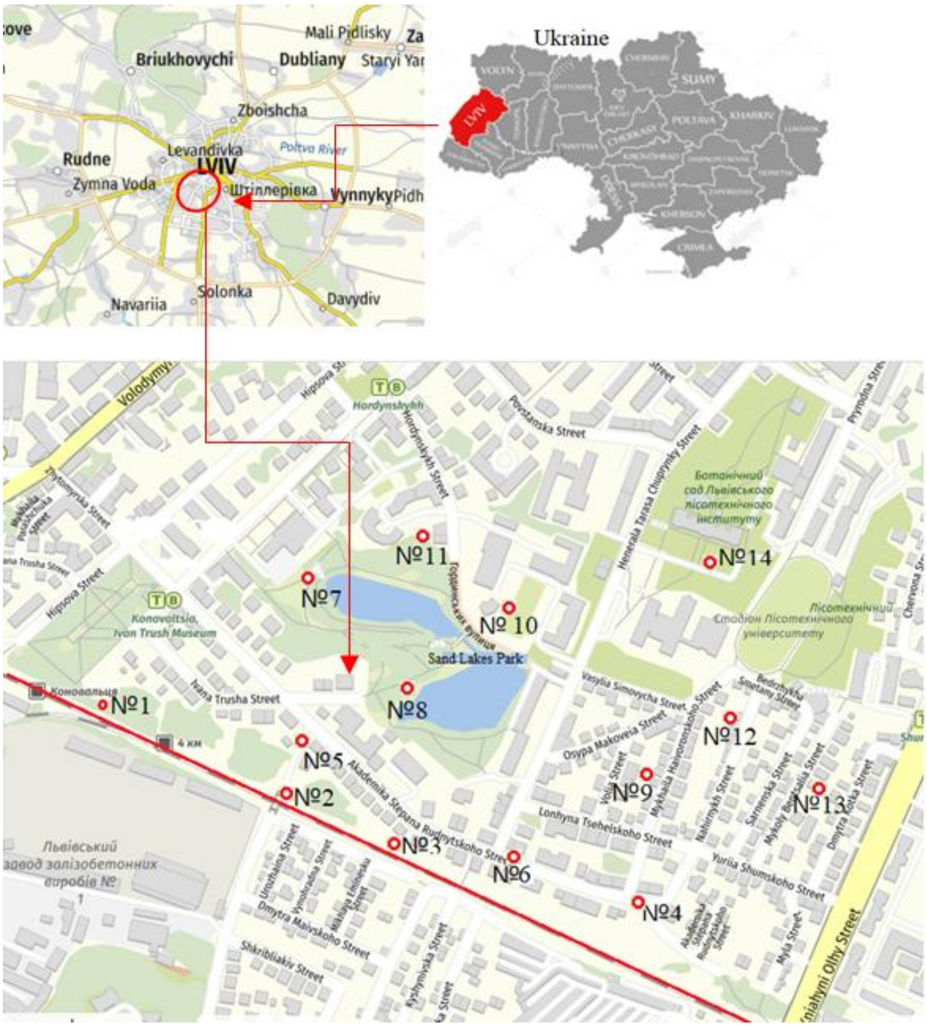

Fig. 1. Map of Lviv streets with the indicated points of soil sampling;
source: own elaboration based on DSTU ISO 10381-4: 2005.

LABORATORY METHODS

The mass fraction of petroleum products in the soil was determined by gravimetric method (MVV No. 081/12-0116-03 Pochvy). This method is based on the extraction of organic matter from a portion of the soil with chloroform, removal of chloroform, dissolution of the residue in hexane, separation of polar compounds on a column of alumina, removal of hexane and gravimetric measurement of the mass of the residue. The mass fraction of petroleum products was determined based on the results of gravimetry by the calculation method. The accuracy of this method is characterized by the limits of the total tolerance of ±5–15%, and as the value of the error is smaller, the greater the mass fraction of petroleum products in the soil. The order of the study is also determined by the approximate value of the content of petroleum products: the amount of soil required and the volume of chloroform for extraction decreases.

The native soil sample was weighed, spread on filter paper, and dried for several hours until air-dry. A portion of dried soil weighing 30 g was placed in a conical flask, moistened with a volatile solvent (chloroform) to a wet state. Extraction with chloroform (ether) was performed several times (to obtain an unstained extract, but not less than three times) using portions of 5 to 15 cm^3. The extracts were filtered into a beaker through "a white tape" filter. Filtration was performed in an empty beaker weighing on analytical balances with a capacity of 100 cm^3, previously brought to constant weight. From the combined filtrate, the solvent was blown out with a fan. The beakers with the residue after sample preparation and with the residue after preparation of the blank sample were kept for 30 min at room temperature to bring to constant weight. The repeated weighing was performed every 10 minutes. If the difference between the results of two consecutive weighings did not exceed 0.0008 g, the weighing was stopped. The obtained results were recalculated per 1 kg of dry soil taking into account its humidity, determined from individual soil sampling sites according to the classical method [KARABYN *et al*. 2019].

The possibility of using natural sorbents – glauconites, which are widespread in the bowels of Ukraine, was studied for the regeneration of accidentally contaminated soils.

Glauconite (from the Greek (Glaukos) – blue-green) – a mineral of the class of silicates (groups of hydromica), $(K, Na, Ca)(Fe^{3+}, Al, Fe^{2+}, Mg)_2[Al_xSi_{4-x}O_{10}](OH)\cdot nH_2O$ where $x \leq 1$, n = 1–2.

The content of components varies widely: SiO_2 44–56%; Al_2O_3 3–22%; Fe_2O_3 0–27%; FeO 0–8%; MgO

0–10%; K_2O up to 10%; H_2O 4–10% [PAVLYSHYN *et al*. 2013].

Impurities of Li and B are also known. High-magnesium glauconite is called celadonite, high-alumina glauconite is called scolite. Crystallizes in the monoclinic syngony and have a ball structure. Distributed in the form of fine-crystalline, sometimes soil-like aggregates. Colouring green of various shades, hardness 2–3, density 2200–2900 $kg\cdot m^{-3}$. It has high cation exchange properties (up to 50 mg-eq. per 100 g). Formed during the diagenesis of sediments, as well as in soils and weathering crusts. Characteristic of all geological systems since the Precambrian. It is one of the main minerals used to determine the age of sedimentary rocks [PAVLYSHYN *et al*. 2008].

The mineral sorbent glauconite of the Adamiv group of deposits of the Khmelnytskyi region (Ukraine) is natural sand containing 50–70% of the mineral glauconite. Glauconite micro concretions have an effective specific surface area, high cation exchange, and monolayer capacity.

To determine the adsorption capacity of glauconite to diesel fuel, 10 glasses were taken, in which 100 g of glauconite were placed in each and a certain amount of diesel fuel and the contents of the glass were well mixed with a glass rod. Glasses with mixtures were left for 6 days. Then in each beaker was added 200 cm^3 of water, stirred and allowed the mixture to settle. Diesel fuel, which was not adsorbed, was washed away by water and formed a fatty layer on its surface. This water was decanted and analysed.

RESULTS AND DISCUSSION

Data from studies of the content of petroleum products in soil sampling sites selected and analysed according to the methods described above are presented in Figure 2.

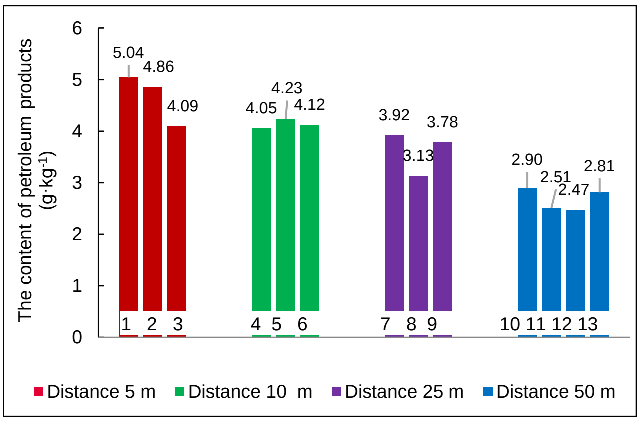

Fig. 2. Dependence of oil content on the sampling distance; 1–13 sampling points; source: own study

In Ukraine, the maximum concentration limit for oil and its products in soils is not defined by regulations; there is only information on approximate permissible concentrations (APC). In particular, in HSTU 41-00 032 626-00-007-97 defined maximum permissible concentration for soil 4 $g\cdot kg^{-1}$. Obviously, this figure is slightly overestimated because the Clark hydrocarbon content in soils in European countries ranges from 0.02 to 0.5 $g\cdot kg^{-1}$. For North American conditions, McGill set the upper safe level of soil oil at 1 $g\cdot kg^{-1}$. Background areas of sod-medium-podzolic loamy soils of Belorussian Polissya contain on average 0.005 $g\cdot kg^{-1}$ per dry weight of hexane bitumoids for the chernozem zone of Ukraine.

To determine the degree of soil contamination with petroleum products, a sample was taken from the control area, which is outside the impact of human activities that is the protected area No. 14 as shown in Figure 1. According to the results of laboratory studies, it was determined that petroleum products in the soils of the control area are contained in the amount of 1.18 $g\cdot kg^{-1}$. The content of petroleum products depending on the distance from the track is distributed in the soil in different ways, this phenomenon can be explained by the uneven terrain, the number of greenery, soil density, the presence of surface water and other factors.

According to the results of laboratory results, which are presented in Table 1, it is determined that petroleum products in soils, in the area of influence of the railway, at a distance of 5–50 m are in significant excess, and on average, the excess is 3.5 times. The diagram shows the dependence of the content of petroleum products on the sampling distance as shown in Figure 2.

Thus, analysing the study, we conclude that the study area has a geochemical anomaly because the statistical parameters of the distribution of the chemical element are likely to differ from the geochemical background. The high degree of soil contamination is not only the process of changing and restructuring the ratio of microorganisms, which is very different from uncontaminated but also an alteration of some chemical and physical properties of the soil.

The State Sanitary Rules for Planning and Development of Settlements state that residential buildings should be separated from railway lines by a sanitary protection zone 100 m high from the axis of the extreme railway track, provided that the normative noise levels in adjacent facilities and on the construction site are ensured. With the placement of the railway in the lowlands and the implementation of special noise protection measures, the size of the sanitary protection zone is determined taking into account the provision of standard noise levels in residential areas, but not less than 50 m. At least 50% of the sanitary protection zone should be landscaped. The same document specifies that the distance from the boundaries of garden plots to the axis of the extreme railway track must be at least 50 m with the obligatory use of noise-protective landscaping with a width of 25–30 m or other noise protection measures. In practice, we often see something else – ignoring all regulations and prohibitions, new buildings are placed close to the railway tracks, plowing and planting areas of protective soil strips, in return cutting down forest protective strips, etc.

In the most European countries, if the content of oil in the soil exceeds 10 $g\cdot kg^{-1}$, they begin a detailed study of the causes of pollution, and when it reaches values of the order of 20 $g\cdot kg^{-1}$, the area is declared an ecological disaster zone [KACHALA 2017].

The implementation of measures to reduce the negative impact of railway transport on the environment, with the establishment of effective environmental activities in other modes of transport can significantly improve the environmental situation in Ukraine. Means related to the improvement of the environmental situation are directly related to the modernization of railway transport and, especially, important here is the transition of railway transport to environmentally-friendly electric traction.

As for the regeneration of accidentally contaminated soils in the area of influence of the railway, it is worth using the experience of regeneration of such soils in case of emergency spills of petroleum products [BABADZHANOVA *et al.* 2015]. When choosing a sorbent should pay attention to all its essential characteristics. Consider the sorption properties of the most effective sorbents in the process of purification from petroleum products. The main requirement for materials that sorb petroleum products is the presence in the material of a highly developed porous structure with a hydrophobic surface, as well as the possibility of petroleum products desorption, utilization or regeneration of the sorbent. According to research by MATVEEVA *et al.* [2012], it has been proven that the most effective sorbents for cleaning the soil petroleum products pollution are: glauconite, zeolite and bentonite. The main criteria that indicate their effectiveness are the sorption capacity of sorbents and their fraction. For comparison, the sorption capacity of the sorbent with a fraction from 0.3 to 3.0 mm for the petroleum product is:

– glauconite – 2.9 kg per 1 kg of sorbent;
– zeolite – 0.9 kg per 1 kg of sorbent;
– bentonite – 0.14 kg per 1 kg of sorbent.

Therefore, after analysing the results of previous studies, we concluded that the most effective sorbent for cleaning soils from petroleum products is glauconite, which is widespread in the bowels of Ukraine. The application of glauconite sorbent should be used to neutralize the contamination of the upper layers (to a depth of 0.4–0.6 m) of the aeration zone. Substantially, this method means mixing the sorbent and the contaminant within the affected soil.

Before the work on the initiation of the sorbent is a visual inspection of the site, in order to pre assess its nature and shape. Visual assessment includes the collection of information about the nature of the microrelief, the directions of surface runoff, the direction of groundwater movement. Determination of the parameters of the pollution and its intensity is carried out based on a set of engineering, lithological and geochemical studies. The calculation of sorbent application rates relies on the analysis of geological and geochemical information and is based on its sorption capacity.

Therefore, we performed studies of the adsorption capacity of glauconite relative to diesel fuel according to the method described above. The research results are shown in Figure 3.

As may be noted from Figure 2, 90% of the adsorption efficiency of diesel fuel on glauconite occurs when the ratio of glauconite to diesel fuel is 15 kg·dm^{-3}, which allows us to recommend this ratio for use in soil cleaning technologies from oil spills.

Additional studies have also been performed to determine the binding stability of adsorbed petroleum products to glauconite. For this purpose, two–three stages of

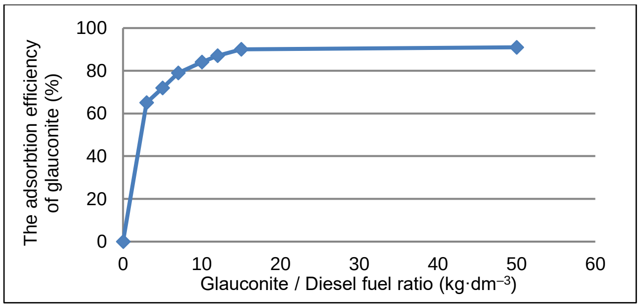

Fig. 3. The dependence of absorption efficiency of glauconite to the correlation of glauconite vs. diesel fuel; source: own study

desorption of diesel fuel from glauconite, which was previously subject to the adsorption cycle, were studied. Studies have shown that only traces of diesel fuel have been found in the desorbed water, suggesting that diesel fuel is satisfactorily bound by glauconite during desorption. The obtained value of the adsorption capacity of glauconite relative to diesel fuel serves as the source of information for calculating the required amount of glauconite for application to the site of accidentally polluted soil for its rehabilitation.

CONCLUSIONS

According to studies on the content of petroleum products in the study area, it was found that the actual figures exceed the norm in the area of influence of the railway at a distance of 5–50 m on average 3.5 times. We proposed to clean the oil-contaminated area with a natural sorbent – glauconite, the efficiency of which reaches 15 kg·dm^{-3} for this pollution. As a result, we received 90% purification of the contaminated area, which proves the high efficiency of the proposed sorbent. Therefore, in the future it is necessary to periodically monitor the condition of the soil in the area to prevent pollution. This study proves that this practice is necessary.

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