

Hazard of petrochemical pollution of ponds of the "Olexandria" arboretum (Bila Tserkva)

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Received: 05.12.2019 Received in revised form: 14.01.2020 Accepted: 01.04.2020 **Abstract.** Groundwater pollution in the territory of Bila Tserkva aircraft repair plant developed in a latent form for decades, in a similar fashion to the territory of any object of the supply of petroleum products. In the early 90s of the last century, the first signs of this pollution were detected in places of natural drainage of the groundwater flow directed to the

ponds cascade of the Western Hollow. It should be noted that this cascade of ponds located on the border of the arboretum protects the rest of the park by absorbing pollutants that migrate from the plant territory. More than 10 years of research of the contaminated area with the goal of designing remediation measures began and continued after that. This project was not implemented in full because of a lack of funds. Based on a comparative analysis of the results of ecological and hydrogeological studies of the past years and a modern survey of the western part of the arboretum "Olexandria" and the adjacent territory of the former aircraft repair plant, it was established that pollution of the pond "Poterchata" continues to this day. Over the past 12 years, the scheme of pollutants incoming into ponds has changed. At first, the main stream of oil pollutants directed to the upper reaches of the beam was considered as very dangerous. Nowadays, perhaps due to the remediation measures taken, this flow seems to be exhausted. However, there were signs of discharge of a polluted underground stream in the lower reaches of the pond "Poterchata". In the soil samples from wells drilled near the water edge, the oil content is 600-900 mg/kg, and in places of water sampling from ponds, the content of dissolved hydrocarbons varies from 2 to 3 mg/dm³, that is, 60 times higher than the standard for fish farms ponds. It is assumed that LNAPL and contaminated groundwater move towards the cascade of ponds of the Western Hollow not in a continuous stream, but in the form of narrow tongues in places of increased conductivity, which are consistent with the lateral shallow gullies crossing the slope of hollow. It is possible that over time, oil pollution will reach the lower "Rusalka" pond. However, one cannot exclude the assumption of natural attenuation processes, the significance of which increased after the closure of the plant and a decrease in the volume of LNAPL because of its extraction from the subsoil. In order to confirm or refute the assumptions made and decide on the need to protect the ponds of the arboretum it has been planned to equip the observation points in places where we should expect influent of pollutants.

Keywords: Oil pollution. Geological environment, Remediation measures, Groundwater and Surface water, Pollution hazard

Небезпека нафтохімічного забруднення ставків дендропарку«Олександрія» (Біла Церква)

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Анотація. Забруднення підземних вод на території Білоцерківського авіаремонтного заводу, як і будь-якого об'єкту нафтопродуктового забезпечення, розвивалося у прихованому вигляді десятки років. На початку 90х років минулого сторіччя були виявлені перші ознаки цього забруднення в місцях природного дренування грунтового потоку, спрямованого в бік каскаду ставків Західної балки, яка розташована на границі державного дендропарку «Олександрія». Тоді ж розпочалися і продовжувалися більше 10 років дослідження забрудненої території з метою обгрунтування проекту ремедіаційних заходів. Через брак коштів цей проект не було реалізовано в повному обсязі. На основі порівняльного аналізу результатів екологогідрогеологічних досліджень минулих років і сучасного обстеження західній частині дендропарку «Олександрія» та прилеглої до неї території колишнього авіаремонтного заводу встановлено, що нафтопродуктове забруднення найближчого до верхів'я балки ставка «Потерчата» триває до теперішнього часу. За останні 12 років змінилася схема надходження забруднювачів у ставки. Якщо раніше основним і реально небезпечним вважався потік нафтопродуктів, спрямований у верхів'я балки, в наш час, можливо завдяки проведеним ремедіаційним заходам, цей потік видається виснаженим. Натомість виявлено ознаки розвантаження потоку нафтопродуктового забруднювача в нижній частині ставка «Потерчата». У зразках ґрунту з свердловин, пробурених поблизу урізу води, вміст нафтопродукту складає 600900 мг/кг, а в місцях відбору проб води зі ставків вміст розчинених вуглеводнів змінюється від 2 до 3 мг/дм³, тобто в 60 разів перевищує ГДК для рибоводних ставків. Припускається, що нафтопродуктова рідина і забруднені ґрунтові води рухаються в бік каскаду ставків Західної балки не суцільним фронтом, а у вигляді вузьких язиків в місцях підвищеної провідності, які узгоджуються з бічними улоговинами, що пересікають схил балки. Можливо згодом можна очікувати надходження нафтопродуктового забруднення до ставка «Русалка», який розташований нижче за течією від ставка «Потерчата». Однак не можна виключати припущення про процеси природнього послаблення, значимість яких зросла після закриття заводу і зменшення обсягу легкого нафтопродукту в результаті його вилучення з надр. Для того, щоб підтвердити або спростувати висунуті припущення і вирішити питання щодо необхідності захисту дендропарку передбачається облаштувати пункти спостереження в місцях, де слід очікувати надходження забруднювачів у водойми.

Ключові слова: нафтопродуктове забруднення, геологічне середовище, ремедіаційні заходи, ґрунтові і поверхневі води

Introduction. Arboretum "Olexandria" (Bila Tserkva city) is known not only in Ukraine, but also beyond its borders as one of the oldest objects of the nature reserve fund of Ukraine, it has undoubted scientific, aesthetic and historical value. Since 1946, the arboretum has been subordinated to the National Academy of Sciences of Ukraine (NAS). The main objective of the management of the arboretum is the implementation of scientific research aimed at preserving the plant gene pool in the forest-steppe conditions of Ukraine and the restoration and reconstruction of historical park landscapes [Galkin & Kalashnikova, 2013]. However, in the broader list, in addition to the tasks usual for landscape parks, there should also be protection of that part of the environment, which, due to its increased sensitivity to the influence of technological factors and the dynamism of the processes that occur in it, requires attention not only on the protected area, but also beyond its boundaries. This is not about pollution of the atmosphere and surface water, which nowadays is the subject of constant attention, but about the underground hydrosphere, or rather its upper part, which is most sensitive to the polluting effect of technogenesis. This article discusses the peculiarities of formation of ecological and hydrogeological situation in the western part of the arboretum under the influence of technogenesis from the adjacent territory of the residential and industrial borough "Hayok".

Research purpose. The research aims at determining the current level of oil pollution of the western part of the arboretum and evaluation of the dynamics of the hazard of this process in the future. Realization of this goal is necessary for planning of remediation activities. Previously we consider two possible situations. If stabilization or intensification of the hazard of contamination is detected, active protective measures should be initiated. Hazard reduction justifies the introduction of a controlled natural attenuation strategy (EPA, 1999; NRC, 2000).

Study of the territory. Arboretum "Olexandria" is located on the outskirts of the city of Bila Tserkva. From the northeast side, industrial enterprises of the Bila Tserkva city have a negative impact on it. At least, such a conclusion can be drawn from the results

of hydrogeological studies 2001 presented in (Kulik, 2003). For several decades, a large airbase operated to the west of the arboretum, and with it an aircraft repair plant, designed to serve this airbase. (Fig. 1).

Nowadays, the air base does not exist anymore, and in 2000 the Municipal Enterprise "Belotserkivsky Cargo Aviation Complex" (BCAC) was established on the basis of the factory and the military airfield. At the BCAC industrial site, the buildings of two workshops, access roads and railways, fuel storage, etc. were kept in working order. It is not possible to determine whether active sources of petroleum product contamination of the geological environment are available in this territory now. However, it can be argued that high content of petroleum hydrocarbons in the soil in groundwater that have been formed in recent years are still preserved. This is already a feature of the petroleum pollution centers of the geological environment this pollutant is able to migrate in a concealed way for several decades towards the natural or economic objects, which may require protection later (CL, 2014; Cohen & Mercer, 1990; Mironenko & Rumynin, 1999; Thomas & Middleton, 2003).

When collecting information about the history of the formation of the pollution zone in the study area, we were convinced of the absence of full and overall accounting for production losses of fuel. The article by the former director of the "Olexandria" arboretum, included in the collection of articles (Kolyshni ..., 2003), states that the volume of lost NAPLs is approximately 500-600 tons. The source of this information is uknown; therefore it is very difficult to assess its reliability. Based on the experience of researching similar objects located in various regions of Ukraine, we assume that here a significantly larger amount of oil products was lost and penetrated into the subsurface for 30-40 years, as a result of systematic leaks and, possibly, accidental spills. The geological environment, which has a significant assimilative capacity, absorbed the pollutant and delayed its spread for some time. As presented in numerous articles that describe the behavior of lost hydrocarbons (CL, 2014; Cohen & Mercer, 1990; Ognyanik et al., 2006), a long stage of formation in the subsoil of the mobile layer of a light non-aqueous phase liquid



Fig. 1. Site overview

1 - boundary of the territory of the arboretum; 2 – contour line; 3 – geological environment polluted by oil products (information of the Pravoberezhna Geological Expedition 1990); 4 – fuel storage; 5 – cascade of artificial ponds; 6 – mobile layer of LNAPL (information of Institute of Geological Sciences of NAS 2007); 7 – aircraft repair workshop – probable source of ground water pollution.

(hereinafter LNAPL or lens^{1*} of LNAPL) and a plume of dissolved hydrocarbons elongated in the direction of groundwater flow begins. Only in the early 90s of the last century, when the pollution front reached the place of natural drainage of groundwater in the upper reaches of the Western Hollow, does LNAPL spill on the earth surface and the film of oil products becomes visible on the water of the "Poterchata" pond. Thus, the pollution process finished the state of latent development. In the next ten years, various organizations performed large-scale geo-ecological studies in the arboretum and adjacent areas.

Due to the lack of information about unregulated fuel losses at the regime facility that was the aircraft repair plant, it can be only assumed that during 30-40 years, as a result of systematic and possibly accidental leaks (discharges), a considerable amount of NAPL came into the soil.

Obviously, for some time, a geologic environment with significant assimilative capacity absorbed the pollutant and delayed its spread. And then, as usual, there is a long stage of formation in the soil thickness of the mobile layer of light petroleum liquid (hereinafter NAPL or lenses *) and the advance plume of dissolved hydrocarbons elongated in the direction of the groundwater flow. Only in the early 1990s, the pollution front reached the point of natural unloading of groundwater, that leakage to the surface of the NAPL was found in the upper reaches of the Western Beam, and an oil film appeared in the water. Thus, the contamination process has emerged from the stage of latent development. Given the undeniably negative impact of oil pollution on freshwater ecosystems (Nikanorov & Stradomskaya, 2008; Green & Trett, 1989), large geo-ecological studies have been carried out in the territory of the arboretum and adjacent areas by different organizations and programs.

The most complete information on hydrogeological conditions and pollution of the geological environment is contained in the materials of the Pravoberezhna geological and hydrogeological expedition (Kulik, 2003). As the results of these detail geochemical investigations, probable sources of pollution, contouring the area of maximum contamination of soil, ground and surface waters with mainly hexavalent chromium compounds and petroleum products. In 1990, mobile LNAPLs were found only in the upper reaches of the Western Hollow and near the fuel storage in the northwestern part of the plant territory (see the Fig. 1). In the rest of the plant, where there should be sources and a pathway of pollutants migration in the geological environment, the presence of NAPL is detected only with the help of organoleptic analysis, that is, by the specific smell and color

^{1 *} A lens is an outdated definition for a mobile LNAPL layer that can be used as a simplified expression

of moraine loam detected by exploratory wells^{2*}. According to the Pravoberezhna geological and hydrogeological expedition data (Kulik, 2003), the contour of the LNAPL-lens in the upper reaches of the hollow has not changed for 10 years since the beginning of the study, except that the thickness of the LDL layer in the observation wells decreased by 3040 cm. The width of the oil product flow at the site of its drainage on the slope of the hollow reached 35 m. The content of hydrocarbons dissolved in water at the place of drainage of the LNAPL fluid reached 5.6 mg/dm³.

In 2007, the Institute of Geological Sciences of the National Academy of Sciences of Ukraine, on the request of the State Governance for Environmental Protection in the Kiev region, carried out pre-designed works that were integrated into the ecological and geological studies of contaminated sites adjacent to the territory of the arboretum. Private firms "Ingeokom" (development of a working draft), "EcoHydroGeo" (drilling works) and "Zemelna kompaniya" (commissioning) were involved in these works. As a result of research work in the central part of the study area, a layer of free LNAPL was discovered and contoured (hereafter "the southern lens"). This lens extended almost 600 m from the aircraft repair workshop to the western boundary of the arboretum (Fig. 1). The lens area was almost 65 000 m². The maximum thickness of the LNAPL layer, determined by measuring the levels of water and LNAPL in the well, reached 1.5 m. It seems that, moving to the right side of the hollow, the lens was divided into two branches directed to the lateral shallow gullies crossing the slope of the hollow, which are quite clearly defined in the relief. Thus, in 2007 the LNAPL lens was located at a distance only 120-150 m far from the pond. Therefore, the threat of contamination of the "Poterchata" pond from this side already seemed quite probable at that time. However, due to the existing restrictions on hazardous work in the townships, the remote site of location of north lens near the headwaters of the Western Hollow was chosen as the site of recovery measures. After that, the potential hazard of the southern lens was forgotten.

Thus, the project was approved, but, its authors did not participate in the implementation of the remediation actions, and the IGS the NAS of Ukraine does not have information about these actions and their impact on the environment. Usually, "entrepreneurs" at their own expense and at their discretion, extract lost petroleum products from the bowels. In the absence of proper control and additional financing, they are not interested in environmental monitoring. Exactly so, with few exceptions, Ukraine is fighting ground-water oil pollution (Ognyanik, 2017).

Assessment of the condition of environmental hazard. 12 years have passed since the last inspection of the western part of the arboretum. Until 2007, there was an opinion that the influx of LNAPL and dissolved hydrocarbons into the water bodies of the Western Hollow occurs only in the upper reaches of the "Poterchata" pond. At the beginning of the 90s the maximum inflow of LNAPL was approximately up to 500 liters per a day. As for the aforementioned southern lens, which moved across the western slope of the hollow and was 120-150 m far from the pond, its discharge into the reservoir was considered only deferred in time. However, to calculate this time due to poor knowledge of the geological and hydrogeological conditions of the slope of the hollow was almost impossible. The lack of reliable baseline data makes it necessary to think up with different versions of the development of the pollution process. So, if the level of groundwater on the slope of the hollow is contained in weakly permeable moraine loams, the front of the lens can move at a speed of several meters per a year. And this means delaying critical pollution of the pond for several decades. An alternative version assumes the transformation of moraine loams in places of lateral depressions, where local replacement of fine material with coarse sand can occur. It is in these places a significant acceleration of the flow of groundwater and, of course, migration of the pollutant can be expected. Presenting the main material. In May 2019, the Institute of Geological Sciences of the NAS of Ukraine, under the agreement on scientific cooperation with the State Dendrological Park of the NAS of Ukraine "Olexandria", resumed monitoring of the contaminated area (Bricks, 2008).

We will divide all planned studies into three parts in order of execution. First, it is necessary to determine the legal capacity of the monitoring network used in the past. As expected, many of observed long-drilled wells have partially worn out for twelve years without any supervision. Private entrepreneurs still use some of them to produce petroleum liquid products. At the time of the examination, the LNAPL thickness at the measurement points had the smallest values at which the use of simple and therefore the most common hydraulic remediation methods were not effective. However, the measurement results are also evidence that the clusters of mobile LNAPL in the territory adjacent to the arboretum is preserved. This means that there is still a danger of their migration to ponds.

^{2 *} Our version of the distribution of LNAPL in the subsoil of this territory is presented in [Bricks, 2008]

Then, before proceeding with an active search for signs of modern pond oil pollution, it is advisable to conduct a visual inspection of the surface of the slope of the hollow and the water surface near the coast. In general, the right coast of the "Poterchata" pond forms an almost smooth line. However, there is an exception three small coves, which are the estuarine part of the lateral shallow gullies, which cross the surface of the slope (Fig. 2).

It is appropriate to think about the origin of these shallow gullies. The first thing that comes to mind is the effect of the erosive action of surface (rain) flows. There is almost no doubt about the definition of the first shallow gully located in the upper reaches of the Western Hollow. This, of course, is the effect of a peak erosion, which usually leads to the advancement of the upper reaches of the hollow to the watershed. However, it is rather difficult to explain the origin of other lateral shallow gullies only by the effect of slope erosion. The formation of gullies, leads to the excessive cultivation of the land; however, no one has been using this territory for a long time. In addition, dense vegetation completely protects the slope from erosion. Therefore, let us recall the possible connection between the relief forms and the geological structure of the study area.

Precambrian crystalline rock with a weathering crust and a complex of Quaternary deposits participate in geological structure of the site. The structure of the crystalline massif in the considered area is poorly known. However, it is known that fractureblock structure is characteristic of crystalline massifs, and therefore, the possible relationship between deep fractures and the formation of a ravine-hollow network should not be rejected. Greenish-gray clay with fragments of crystalline rocks represents the weathering crust. Near the ponds, it lies at a depth of 1012 m and, therefore, can hardly affect the process of groundwater pollution.

We also ignore loess-like loams that make up the aeration zone over almost the entire territory adjacent to the arboretum. They can be the object of research



Fig. 2. Scheme of location of the lateral shallow gullies 1 – the Earth's surface contour line; 2 – thalweg of shallow gullies.

at the locations of surface sources of pollution, that is, on the territory of the plant, but in the area of the hollow, these loams are absent.

The most interesting in the context of the topic are deposits of the Dnipro glacial complex (Fig. 3).

Dnipro glacial complex, including supra-moraine sandy loam and sands that make the aeration zone; moraine deposits, represented by heavy loam; submoraine sandy loam and diverse sands. It is in these moraine and sub-moraine sediments on the site of the western slope of the hollow that mobile LNAPL and groundwater with dissolved hydrocarbons has been moving to the pond. Moraine or glacial sediment is mainly heavy loam and clay with fragments of crystalline rocks and has low permeability and very high heterogeneity. Heavy loam or clay without even being completely saturated, but only moistened become impermeable for LNAPL. However, in addition to the clay, it contains quite a variety of granular material, which forms not only isolated lenses but also elongate interlayers. These interlayers are formed, of course, not randomly, but genetically determined, that is, as

a result of the transfer of coarse-grained material by water flows during the melting of the glacier. Thus, it is quite likely that in the strata of low permeable sediments separate zones of preferential (selective) migration of pollutants are present. The credibility of this assumption is confirmed in publications devoted to the description of LNAPL behavior in fluvioglacial deposits, e.g. (CL: AIRE, 2014).

Fig. 3 reflects a generalized geological and hydrogeological section (profile), crossing the Western Hollow, that is, along the main direction of groundwater flow and the estimated migration of pollutants. The right part of the figure shows two variants of the geological structure of the hollow slope and the corresponding variants of the relief line. The first option is typical for a normal slope of the hollow. The second option corresponds to a lateral shallow depression that intersects the slope of the hollow. In both cases, groundwater levels also vary significantly. The level line, designated as GWL1 in the figure, corresponds to filtration in the low permeable moraine loam. This line is gently sloping and only near the surface of the **b**





Fig. 3. Conceptual scheme of the geological structure of the western part of the "Olexandria" Arboretum

1 - root layer; 2 - loess-like sandy loam; 3 - supra-moraine sandy loam and sands; 4 - moraine deposits, represented by heavy loam, containing layers of sand and fragments of crystalline rocks; 5 - sub-moraine sandy loam and diverse sands sub-moraine sandy loams and sands and water-glacial multigrain sands; 6 - sand interlayers in moraine sediments; 7 - layer of mobile LNAPLs (lens); 8 - groundwater level - GWL: GWL1 - within the slope of the hollow, GWL2 - along the side shallow gully; Transverse slope line: SL₁ - prevalent slope line of the hollow; SL₂ - slope line along the side shallow gully.

slope, it abruptly drops to the water level in the pond, and sometimes the line crosses the earth surface where a spring forms. The level line (GWL2) corresponds to the filtration on the site elongate along the side shallow gully, that is, where, by our assumption, there should be many sandy interlayers in the moraine.

A useful conclusion could be made from the above considerations. The location of side shallow gullies as an indirect sign should be used to search for areas of high conductivity in moraine sediments. It can be assumed that the position of these secondary elements of the relief indicates the presence in of the pathways of selective migration of pollutants in the subsoil. Precisely that way we chose among the four possible migration routes of pollutants. The first way, directed to the upper reaches of the Western Hollow, ern" LNAPL lens to the "Rusalka" pond, seems the least likely, but worth verification.

The scheme of the study area (Fig. 5) shows all the described trajectories of expected migration of the oil pollution.

The diagram shows the soil and water sampling points. The content of petroleum products in water and soil samples was determined in a certified "Laboratory of Petrochemical Studies of the Geological Environment" of the IGN of the NAS of Ukraine using the "Mikran" analyzer by UV spectrophotometry of hexane extract.

In soil samples from other wells drilled in the upper reaches of the Western Hollow (W. 7, 8) and on the way to the "Rusalka" pond (W. 6), we found no signs of oil pollution.



Fig. 4. The film of oil products on the water surface of the "Poterchata" pond*. *The location of the photo point is shown in the Fig. 5.

has been known since the research of twenty years ago (Kulik, 2003). Once here was a LNAPL seeping in the form of a weak stream. Presently, due to the LNAPL recovery at the top of the stream, there is no free flow, but latent contamination is possible. The second way is defined on the basis of the considerable size (width and depth) of the shallow gully, which, by our assumption, may indicate a significant influence on its formation of the geological and hydro-geological factor. The third option is the shortest way for a possible migration of an oil product pollutant from the "southern" LNAPL lens to the aforementioned small cove on the west bank of "Poterchata" pond, where, a film of oil product was found on the surface of the water (Fig. 4).

The fourth option, which points to the possibility of migration of an oil contaminant from the "southAt the sampling points (see Fig. 5), the content of dissolved hydrocarbons fluctuates from 2.0 to 3.2 mg/dm³, which is a clear indication of a significant exceedance of the maximum permissible concentrations of NAPLs for fish ponds^{3*}.

Conclusions. Based on the results of the studies, it can be stated that the process of oil product pollution of the Western Hollow ponds continues to the present day. In past years, the main pathway for migration of the pollutant went from the territory of the former aircraft repair plant to the upper reaches of the hollow. Modern data indicates the depletion of this stream. On the other hand, signs of drainage of the NAPL-pollutant flow were found in the estuary part of one of the lateral shallow gully crossing the surface of

^{3 *} Maximum permissible concentrations of NAPLs for fish ponds 0,05 mg/dm³

the western slope of the hollow ("Poterchata" pond). This gives a reason to build a new conceptual model of contamination site considered. The main idea of this model is that the migration of pollutants from the groundwater recharge zone, where pollution sources are located, to the place of their drainage in the Western Hollow through moraine deposits occurs in zones of increased conductivity formed by interlayers of fluvioglacial sand. According to our assumption, an external sign of such zones location may be lateral basins on the slope of the Western beam. In order to confirm these assumptions, it is necessary to perform monitoring at the sites of the expected selective migration of the pollutant at least for one year.

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Fig. 5. Survey scheme of the western part of the Alexandria arboretum (May August 2019).

1 – wells of the monitoring network that existed before 2007; 2 – test wells drilled in May 2019; 3 – water sampling points (near the shore and at a distance of 3 m); 4 – the first $(2^{nd}, 3^{rd} \text{ and } 4^{th})$ version of a possible migration way for an oil product; 5 – points of photography on May 3, 2019 (see the Fig. 4); 6 – Earth's surface contour lines.

Sampling date	Place of soil and water* sampling	Sample of soil	Hydrocarbons content in soil samples mg/kg
03.05.2019	W.1: 35-40 m from the pond/ depth 2-3 m	Water-saturated light loam	< 0.01
	W.2: 5 m from the pond/ depth 0.4 m	Water-saturated light loam	621
	W.2: 5 m from the pond/ depth 0.9 m	Water-saturated light loam	640
30.07.2019	W.3: 20 m from the pond/ depth 0.8 m	Water-saturated sandy loam	819
	W.4: 2m from the pond/ depth 0.8 m	Water-saturated sandy loam	918
	W.5: 5m from the pond/ depth 0.5-0.7 m	Water-saturated light loam	39.0
	W.6: 35 m from the pond/ depth 2.2 m	Water-saturated light loam or clay sand	26.7

Table. Results of determination of oil product content in water and soil samples

* Note: see the soil sampling locations in the Fig. 5.

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