



# Article Analysis of the Remediation of Coal Tar-Contaminated Groundwater Using Ex Situ Remediation

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Abstract: The article describes the remediation of contaminated groundwater during the ex situ remediation of coal tar contamination following the closure of a coking plant in the Moravian-Silesian Region (Czech Republic). The aim of the article is to point out the advantages of ex situ soil remediation via the excavation of the contaminated geological environment combined with thermal desorption, a method of removing contaminants both from soil and groundwater. Its advantage is the absolute qualitative and quantitative control over the contaminated soil with the possibility of precise segmentation into contaminated and non-contaminated soils. Next, all contaminated groundwater may be pumped off upon the construction of sealing walls to control groundwater flows. To excavate the soil, it is necessary to reduce the contaminated groundwater level inside the sealing walls and thus create conditions for the extraction of contaminated soils using standard machinery. In detail, the article describes the removal of the contaminated groundwater and compares the quality of the pumped and inflowing water before and after the remediation. The locality is characteristic of a high horizontal and vertical grain-size heterogeneity of gravel-sand, which led to a varying filtration coefficient affecting the capacities of pumped groundwater quantity during the remediation. At the start of the remediation process, the contaminant levels exceeded the limits by the Czech Environmental Inspectorate several times. The post-remediation monitoring showed that all the contaminant levels were below the limit. Surprisingly, the overall groundwater contamination amounted to 232.86 t of contaminants as non-aqueous phase liquids, and 6872.9 kg of dissolved contaminants. As much as 12,200 t of contaminants were removed from the soil.

**Keywords:** groundwater decontamination; coal tar-contamination; ex situ remediation; remediation dugout; contaminated soil excavation; alluvial sediments; Moravian–Silesian Region; Czech Republic

# 1. Introduction

The motivation behind the study was an analysis of remediation of groundwater contaminated by coal tar when applying ex situ dugout decontamination. The aim is to indicate the advantages of ex situ remediation of a locality contaminated by coal tar (Figure 1). An application of in situ remediation leads to the formation of a gap between the water-lowering wells in the lower part of the contaminated permeable environment, where water does not flow toward the wells (Figure 1). This gap is characteristic of a cone of depression with an angle dependent on the friction slope, permeability of the rock (soil) environment, filtration coefficient, and distance between the wells. However, when the soil



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). is extracted and the decontamination occurs ex situ, e.g., by means of thermal desorption, as in the case of the locality of interest, this problem is eliminated.

Scientific point of view  $\rightarrow$  ex-situ remediation of groundwater contaminated by coal tar  $\rightarrow$  a case study



Figure 1. Scheme of the research aim of the study.

When dealing with coal tar remediation, it is important to distinguish between *ex situ remediation* [1–4], and *in situ remediation* methods applied directly in the soil massif [5–8]. An important specific condition for the application of the ex situ remediation method of removing coal tar from alluvial sediments is the extraction of all the soil and its ex situ decontamination using thermal desorption. At the same time, it is important to drain the whole remediation dugout and treat the contaminated groundwater in a decontamination station. If in situ remediation was implemented using wells to pump away the contaminated water, an overlap of cones of depression could occur. Groundwater occurring in the overlap of cones of depression at the bottom of the dugout cannot be pumped or treated. This means that using ex situ remediation, when all the soil is extracted and the impermeable bedrock is exposed, no contaminated groundwater remains in the dugout. The thermal desorption mentioned is an ex situ remediation method used for cleaning soil materials. It has the advantage of short site remediation time and, above all, high contaminant removal efficiency. The principle of this method is to heat the contaminants present in the soil. This heating is carried out in a so-called rotary desorber, which is resistant to high temperatures. A distinction is made between direct and indirect thermal desorption, whereby in direct desorption, specific soil grains are heated by burners, and in indirect desorption, the desorber shell is heated, which indirectly transfers heat to the

contaminated soil grains. The heating transfers the contaminants to the gaseous state. After cooling, the contaminants are concentrated in the liquid condensate, which is disposed of as hazardous waste.

The main goal of the study was to focus on *ex situ remediation of groundwater* contaminated by *coal tar*. It was implemented by means of a case study of one of the biggest environmental strains in the Czech Republic (Moravian–Silesian Region, east part of the Czech Republic). This is mainly to highlight the main advantages of using ex situ remediation through this mentioned case study, since ex situ remediation refers to the pumping and subsequent treatment of water away from the site of pollution.

The case study had the following specific conditions (Figure 1). The first specific condition was contamination by coal tar. Contamination by any chemical brings along specific limiting conditions that affect the type of remediation and many other aspects. The same applies to coal tar contamination [9-11]. In the locality of interest, the environmental strain was caused by the long operation of a coking plant, lack of technological discipline, industrial accidents, and changing technologies in time that had their drawbacks. The second specific condition is the geological conditions in the locality. There are alluvial sediments of partially permeable fine-grained soils of an average 4 m thickness and coal tar-contaminated permeable gravel sand of an average 4 m thickness. The geological structure of the wider area of interest was also described [12–14]. The third specific condition is the hydrogeological conditions with an unconfined groundwater body in the depth of approximately 4 m. The unconfined groundwater body is predominantly bound onto permeable gravel-sand. The *fourth specific condition* is the applied *ex situ remediation method*, which means that all the soil was remediated outside its original location. The main decontamination method was a low-temperature thermal desorption based on the principle of heating the contaminated materials over the temperature (560° in this case) at which the pollutants volatilize. The fifth specific condition is the technology of ex situ remediation executed using a remediation dugout. As much as 1.5 million tons of contaminated soils were extracted all the way to the impermeable clayey Miocene bedrock. After the decontamination, the soil was returned to the dugout, while the original grain-size composition was preserved. The sixth specific condition was the occurrence of the different contaminants that predominantly corresponded to coal tar contamination. The Czech Environmental Inspectorate determined the limits for the concerned contaminants as follows: benzo(a)pyrene 12.5  $\mu$ g/L, benzene 250  $\mu$ g/L, naphthalene 6300  $\mu$ g/L, phenol 25,000  $\mu$ g/L (25 mg/L), and non-polar extractable substances 50,000 μg/L (50 mg/L) [15].

## 2. Methods

#### 2.1. Study Area

The industrial complex, where the environmental strain was located, was established in connection with the start of the black coal mine in 1842. From 1858 there was a coking plant, a power plant, an iron and steel production facility, and a heavy machinery industry. The complex was closed down in 1990. The combination of all of the industrial activities, predominantly due to the operation of the coking plant, led to one of the largest environmental strains in the Czech Republic. Figure 2a is an aerial photo of the locality of interest in 1955, when the coking plant was in full operation. It also gives the lines of foundations that were dug out during the remediation process. The spread of the contamination by coal tar is shown in Figure 2b. The next photo shows the area where the remediation dugout was refilled with decontaminated soil (Figure 2c) and Figure 2d is a photo of a newly built shopping center.



**Figure 2.** Locality of interest: (**a**) Aerial photo of 1955 marking the lines of foundations which were dug out during the remediation process, (**b**) spread of the contamination by coal tar, (**c**) remediation dugout refilled with decontaminated soil, (**d**) current photo of a newly built shopping center.

#### 2.2. Groundwater Remediation

The aim of the article was to point out the advantages of ex situ remediation achieved by the excavation of the contaminated geological environment combined with thermal desorption. It is a method of removing contaminants both from soil and groundwater. Its advantage is the absolute qualitative and quantitative control over the contaminated soil with the possibility of precise segmentation into contaminated and non-contaminated soils. Next, all contaminated groundwater may be pumped off having constructed sealing walls to control the groundwater flows. To excavate the soil, it was necessary to reduce the contaminated groundwater level inside the sealing walls and thus create conditions for the extraction of contaminated soils using standard machinery. When in situ remediation and water-lowering wells are applied, the overlap of cones of depression forms at the level of the aquifer. This means that contaminated residues remain at the bottom as they do not flow toward the wells.

The section does not aim to describe all the technological details of the remediation process, but only those related to groundwater remediation. At the start, *cutoff walls and* 

*diaphragm walls were installed* into the impermeable Miocene clay bedrock (Figure 3a). Their purpose is the geotechnical and hydraulic insulation of the contaminated space. This made it possible to gradually lower the groundwater level and thus create conditions for the subsequent extraction of the contaminated soil and refill when remediated. Next, *groundwater was pumped off* from the dugout in combination with gutters (Figure 3b). The water-lowering wells were gradually shortened and reconnected. When drained, the different branches or their parts were replaced with pumping from the gutters at the bottom of the dugout (Figure 3c). Water pumping was terminated after the contaminants were extracted and the lower soil layer refilled. Monitoring wells were gradually constructed in parts refilled with the decontaminated soil.



Figure 3. Principle of ex situ remediation in the context of groundwater conditions.

The groundwater was decontaminated (Figure 3d) using a decontamination station with a constant flow of 10-15 L/s. The treatment combined 4 subsequent methods, namely gravitational separation, aeration, filtration, and activated carbon adsorption. The first applied method was gravitational separation, during which substances of different densities than water and of a supersaturated solution concentration were separated as nonaqueous phase liquids. Among others, this method separated the following contaminants: benzo(a)pyrene, benzene, and non-polar extractable substances. At the same time, mechanical impurities and partially iron hydroxides were separated via sedimentation. The second was aeration, which caused the oxidation of bivalent iron ions and their conversion into ferric hydroxides. A displacement of volatile contaminant components also occurred, which passed from water into the air to be cleaned via the sorption filters and activated carbon. The third method was filtration with the use of two parallel sand pressure filters to remove the remaining mechanical impurities and iron hydroxides. The fourth water treatment method was activated carbon adsorption (6 sorption filters) to remove the remaining concentrations of contaminants (non-volatile matter in non-polar extractable substances, benzene, benzo(a)pyrene, and phenols). The water cleaned to the required limits was discharged as wastewater into the Ostravice River.

Water needed to be pumped away before the *remediation dugout* and earthwork could be executed (Figure 3e). This means that each soil level to be extracted had to be dewatered. Moreover, the bottom of the dugout was drained by extra gutters. The

excavated soil was predominantly transported for thermal desorption. Thermal desorption was applied to decontaminate 92.5% of the soil and 0.1% of the soil was decontaminated using biodegradation. The remaining percentages of the soil were transported to 3 types of disposal sites, namely a waste disposal site (5.1%), a combined site for hazardous waste and a single-type waste disposal site (2.0%), and a combined waste disposal site (0.3%).

*The remediation dugout was refilled* (Figure 3f) with the decontaminated soil in slanted beds of 0.5 m thickness so that the soil could be compacted using a vibrating roller. The soil was refilled to respect the original grain-size structure of the soil environment. This means that the bottom of the dugout, consisting of gray-blue Miocene clay, was filled with gravel and complemented with rock material of analogous grain-size (particularly spoil). This layer was followed by two layers of fine-grained soils, each 2 m thick. The beds had an inclination of 3.33° so that rainwater could run off naturally. The ground morphology was almost analogous to the original, including the fact that the new anthropogenic geological environment had to have analogous hydrogeological conditions with an unconfined groundwater body.

In the next phase, the *cutoff walls were removed* (Figure 3g). This phase was important to gradually create hydrogeological conditions analogous to those before remediation. The diaphragm walls remained to protect the nearby buildings. Having removed the cutoff walls, the *natural groundwater flow could be restored* in the refilled dugout and the groundwater level could be adjusted in line with the existing unconfined groundwater body (Figure 3h). This took 2 years based on the heterogeneity of the alluvial sediments and in line with the distribution of filtration coefficient in the existing soils.

Having terminated the remediation earthwork, post-remediation monitoring was implemented at the site of the dugout to observe the *quality of groundwater and its depth* (Figure 3i). For this purpose, 12 monitoring wells were drilled evenly across the dugout. Samples were regularly drawn at the aquifer level. The aim of the monitoring was the verification of the groundwater quality and quantity, and whether the contaminant levels were below the limits set by the Czech Environmental Inspectorate.

Photodocumentation of the site of interest during remediation is shown in Figure 4.



**Figure 4.** Photodocumentation of the locality of interest in the course of remediation (**a**) decontamination station, (**b**) inflow into the stripping unit via gravity separators, (**c**) detail of a gutter to trap contaminated groundwater that cannot be pumped by water-lowering wells (a view from the west), (**d**) panorama of the locality taken from the east.

The contaminants (benzo(a)pyrene, benzene, naphthalene, non-polar extractable substances, phenol) were determined in certified laboratories according to the applicable Czech standards and according to the limits set by the Czech Environmental Inspectorate, with the values of input (before remediation), output (after remediation) and their difference (what was removed by remediation).

### 3. Results

#### Changes in the Hydrogeological Conditions during Remediation

Changes in the hydrogeological conditions will be explained using 4 model maps of groundwater-table contours and 4 diagrammatic sections that document the principal hydrogeological changes during the remediation process. The gradual extraction and refilling of soil is explained in two time frames (Figure 5a,b), where parts of the contaminated locality (left-north) are extracted gradually all the way to the permeable gravel and later refilled with decontaminated soil. A gap is formed to separate the contaminated section of the locality (right-south) all the way to the impermeable Miocene bedrock, where water is drained by means of two gutters. The course of groundwater level may be observed in the section as it lowers towards the gutters. This procedure was applied in the direction north–south. Thus, the last section to be decontaminated was in the south. The two diagrammatic sections represent the whole process behind the remediation dugout, while the bottom geometry changes when progressing from the north to the south.



**Figure 5.** Two time diagrammatic sections of the gradual extraction and refilling documenting the work sequence in the dugout (**a**) earlier in time, (**b**) later in time.

The following section describes the basic changes in the hydrogeological conditions that occurred during the remediation works. The *first situation* represents the time (Figures 6a or 7a) when the soil in the locality was extracted and refilled with the decontaminated soil (92.5%, or 11,290 t) using thermal desorption. It is still possible to see

the hydraulically closed system of the locality due to the cutoff and diaphragm walls. As for hydrogeology, the groundwater level inside the closed system is influenced only by precipitation; no water flows in from the surroundings. Outside the closed system, there is an unconfined groundwater body characteristic of water flow from SW to NE.



**Figure 6.** Map of groundwater-table contours in the area of interest: (**a**) start of flooding, (**b**) situation after the partial removal of cutoff walls in the west, (**c**) situation after 2 years–groundwater leveled off before the 106-meter-long underground piling wall was opened in the east, (**d**) steady state.



**Figure 7.** Diagrammatic sections of the area of interest: (**a**) section A-A' of the start of flooding, (**b**) section B-B' having partially removed the cutoff walls in the west, (**c**) section C-C'-situation 2 years later when the groundwater leveled off and before the 106-meter-long underground piling wall was opened in the east, (**d**) section D-D'-steady state.

*The second situation* represents the time Figure 6b or Figure 7b, when the closed system was partially opened as the cutoff walls were removed in the west. This was done to hydrogeologically accommodate and restore the remediated locality, i.e., to re-flood it with groundwater and restore the natural groundwater flows in the form of an unconfined groundwater body. The cutoff wall was kept in the east, where remediation still continued in the heap of the Žofie's foundry using in situ water pumping and treatment, including vapor. The course of the groundwater-table contours is characteristic of gradual flooding of the remediated locality and leveling-off the groundwater level in the dugout after the soil refill.

*The third situation* represents the time (Figures 6c or 7c) characteristic of the locality approximately 2 years after the removal of the cutoff walls in the west (106-meter-long underground piling wall), when the groundwater level had leveled off with the surround-ings. The steeper hydraulic gradient in the west and east (Figure 6c) is given by higher soil permeability of the original conditions when compared to the newly refilled and compacted remediated soil of a lower hydraulic gradient.

*The fourth situation* represents the time (Figures 6d or 7d) upon the opening of the cutoff walls in the east, 3 years after the soil refill (one year later than the previous situation). The groundwater level inside and outside the walls documents the fact that the *original groundwater flows were fully restored*. The residues of the diaphragm walls in the north

and south do not pose a problem in terms of hydraulics as they constitute a minor obstacle with respect to the low hydraulic gradient in the area of interest.

The initial exploratory survey estimated the contamination to 958 kg, broken into non-polar extractable substances with 30.5% (292 kg), naphthalene with 29.4% (282 kg), benzene with 22.8% (218 kg), and phenols with 17.3% (166 kg).

### 4. Discussion

#### Evaluation of Groundwater Contamination

The groundwater in the locality was contaminated by coal tar, both in its dissolved form and as non-aqueous phase liquids. It had the character of "wash oil". The spread of coal tar contamination depends on the geological structure and its permeability. It means that in the environment of alluvial sediments, the spread of contamination is influenced by the specific conditions of alluvial sediments [16,17].

Coal tar as dense, non-aqueous phase liquids (DNAPL) was identified in the amount of 232.96 t (as a mixture of organic compounds). It was only analyzed for characteristics vital for its disposal, such as sulfur content, viscosity, and high heat value. In the dissolved form, the contaminants were identified, and their values were observed in the course of the remediation work and compared with the limits set by the Czech Environmental Inspectorate.

DNAPL was predominantly drawn from the wells. When the level of DNAPL could not be pumped directly, it was pumped along with water and separated using gravitational separation in the decontamination station. DNAPL, possibly with tar-in-water emulsion, and remaining contaminated water were pumped into containers to settle for several days into contaminants and water. Having been separated into two phases, the contaminated water was pumped into gravitational separation and continued via the whole water treatment process. The settled DNAPL was separated in gravity separators and passed on for disposal as waste. Coal tar as light, non-aqueous phase liquid (LNAPL), the amount of which was negligible (below 1%), was separated in the gravity separators and passed on for disposal as waste. Separate records for LNAPL quantities were not made.

As for the contaminants in the *dissolved form*, the quantities of the pumped contaminants were calculated from the average monthly concentrations of the different contaminants on the premises and the monthly inflow into the decontamination station. The monthly inflow does not include the water from "clean" gutters.

The contamination spread is shown in Figure 8, where Figure 8b shows the contamination in the unsaturated zone (alluvial fine-grained soils). Figure 8c shows the contamination spread in the saturated zone (alluvial gravel sand) with groundwater level. Figure 8d describes the spread of contamination in the saturated zone without the groundwater level. Coal tar has a specific chemical composition, which was a subject of a number of studies [18–21].

Out of all the contaminants in the groundwater in the dugout (dissolved form) *benzene* (250  $\mu$ g/L) exceeded the limit most. The maximum value of 43,100  $\mu$ g/L, it exceeded the limit 172 times. On average, it exceeded the limit (3847.46  $\mu$ g/L) 15.4 times (Figures 9 and 10). However, it is important that after remediation and the first year of monitoring, the contaminant concentration dropped below the limit by over 99% (1.67  $\mu$ g/L), which was confirmed in the subsequent years of monitoring. In the second year of monitoring, the benzene contamination was 0.5% (1.20  $\mu$ g/L) and decreased to 0.4% (1.03  $\mu$ g/L) in the third year (Figure 10). The overall mass of the contaminant was 134 kg, which corresponds to 1.9% of the overall mass of all contaminants. The estimation before the groundwater remediation project started to set the quantity of the pumped contaminant to 218 kg (22.8% of the total estimated amount of all contaminants). It is clear that there was less benzene from the start of the remediation works by 84 kg (Figure 11).



**Figure 8.** Layer of liquid coal tar in the different lithological layers: (**a**) diagrammatic representation of the geological structure in the area of interest, (**b**) coal tar layer in the unsaturated zone (alluvial fine-grained soils), (**c**) coal tar layer in the saturated zone (alluvial gravel sand) with groundwater level, (**d**) coal tar layer in the saturated zone (no groundwater).



Figure 9. Cont.



**Figure 9.** Quantities of different contaminants in the dissolved form before (maximum value, average value) and after remediation (3 years of monitoring) in the groundwater with marked limits of the Czech Environmental Inspectorate: (**a**) logarithmic axis range, (**b**) normal axis range.

The second worst situation as for contamination was in *benzo(a)pyrene*, where the maximum contamination (852.8  $\mu$ g/L) exceeded the limit (12.5  $\mu$ g/L) 68.2 times, while the average value of 16.33  $\mu$ g/L exceeded the limit only 1.3 times (Figures 9 and 10). Having remediated the locality, the contaminant amounted to only 0.56% (0.07  $\mu$ g/L) of the limit in the first year of monitoring (Figure 10). The trend continued to fall during the following 2 years of monitoring (in the second year it was 0.5% (0.06  $\mu$ g/L) and in the third year 0.2% (0.03  $\mu$ g/L) below the limit). The amount of benzo(a)pyrene was the lowest, i.e., 3.35 kg (0.05% of all the contaminants in the dissolved form). The amount of benzo(a)pyrene was not estimated before the remediation project.

The highest concentrations of contaminants in the dissolved form were recorded in *non-polar extractable substances*, when the average value amounted to 6500 µg/L. Their limit is 50,000 µg/L (Figure 9), which means that the average value was 87% below the limit (Figure 10). However, in its maximum value, the contamination was 65,000 µg/L, which exceeded the limit 1.3 times (Figure 10). Upon the termination of the remediation, the contamination dropped by 99% (Figure 10), while in the first year of monitoring the contamination was 41 µg/L (0.08% of the limit), in the second year it was 44 µg/L (0.09% of the limit) and in the third year, it was 22 µg/L (0.04% of the limit). As for the absolute amount of the contaminant in the dissolved form, there were 5944.9 kg of non-polar extractable substances in the dugout, which corresponds to 86.5% of the total amount of contaminants in the dissolved form. The estimation before remediation was 292 kg, which was 30.5% of the total quantity of the contaminants. The difference between the estimation and reality was 5653 kg, which is a difference of 2035.9% (Figure 11).

As for the concentration of *naphthalene*, its maximum value was  $68,220 \ \mu g/L$  (11 times the limit). However, its average value (5034.69  $\mu g/L$ ) was 20% below the limit (6300  $\mu g/L$ ) of the Czech Environmental Inspectorate (Figures 9 and 10). The subsequent monitoring identified a reduction in the contamination by 99% (Figure 10). In the first year of monitoring, the contamination level was 0.09% (5.69  $\mu g/L$ ) of the limit, the second year

0.02% (1.25 µg/L), and the third year 0.01% (0.87 µg/L) (Figure 9). From the start of the remediation work, 705 kg of naphthalene in the dissolved form (10.3% of all contaminants) was removed. The initial investigation estimated the amount of naphthalene to 282 kg (29.4% of the total estimated quantity of contaminants). This means that the estimate was exceeded by 423 kg (Figure 11).

On average, the concentrations of *phenol* (Figure 10), the last of the observed contaminants, were 88% below the limit (25,000  $\mu$ g/L) with 3100  $\mu$ g/L, while the maximum value was 76,540  $\mu$ g/L (3.1 times the limit) (Figures 9 and 10). After the remediation works, the phenol contamination dropped to 39  $\mu$ g/L (0.2% of the limit) in the first year of monitoring, 49  $\mu$ g/L (0.2% of the limit) in the second year, and 36  $\mu$ g/L (0.1% of the limit) in the third year (Figure 9). In total, 86.05 kg of phenol (1.25% of the total quantity of contaminants) were removed despite the estimate of 166 kg. The real quantity of phenol was lower by 79.95 kg (Figure 11).



**Figure 10.** Quantities of different contaminants in the dissolved form before and after remediation (3 years of monitoring) in the groundwater: (**a**) proportion of the minimum value and limit of the different contaminants; percentage of the minimum value out of the contaminant limit (%), (**b**) proportion of limit and concentration of the different contaminants in the first year of monitoring; percentage of the limit and concentration of the contaminants from the first year of monitoring (%), (**c**) proportion of the maximum value and limit of the different contaminants; percentage of the maximum value out of the contaminant limit (%), (**d**) proportion of the limit and concentration of the different contaminants; percentage of the different contaminants in the second year of monitoring; percentage of the limit and concentration of the average value out of the average value and limit of the different contaminants; percentage of the average value out of the contaminant limit (%), (**e**) proportion of the average value and limit of the different contaminants; percentage of the average value out of the contaminant limit, (**f**) proportion of the limit and concentration of the different contaminants in the third year of monitoring; percentage of the limit and the contaminant concentration in the third year of monitoring (%).



Figure 11. Quantities of different contaminants in the dissolved form (total mass in kg).

#### 5. Conclusions

The case study showed an extensive contamination of groundwater, when the extracted and refilled soil quantity of 771,816 m<sup>3</sup> (1,505,042 million tons of soil) included 92,371 m<sup>3</sup> of contaminated groundwater. From the groundwater, we removed 251.5 m<sup>3</sup> (1.08 coefficient for non-aqueous phase liquids—232.9 t) of contaminants as non-aqueous phase liquids and 6872.9 kg of contaminants in the dissolved form. The non-polar extractable substances participated with 86.5% (5944.9 kg), benzene with 1.9% (133.6 kg), benzo(a)pyrene with 0.05% (3.4 kg), naphthalene with 10.3% (705 kg), and phenol with 1.3% (86.1 kg).

The initial exploratory survey estimated the contamination to be 958 kg. The real contamination was higher by 717.07%, where the biggest difference (2035.9%, or 5952.9 kg) was in non-polar extractable substances. In naphthalene, the difference was smaller, but still 250% (423 kg). On the other hand, the real contamination lower than the estimate was in benzene by 61.29% (-84.4 kg) and by 51.8% (-80 kg) in phenol. This was caused by a rather high heterogeneity of the alluvial gravel sand and fine-grained soils combined in the locality of interest.

Out of all the contaminants in the locality of interest, the limit  $(250 \ \mu g/L)$  of allowed benzene contamination set by the Czech Environmental Inspectorate exceeded 15 times on average, and 172 times in the maximum values. The other average values of the observed contaminants exceeded the limits less than twice, but in the case of the maximum values the situation was more negative. For example, benzo(a)pyrene (12.5  $\mu$ g/L) exceeded the limit 68 times, naphthalene (6300  $\mu$ g/L) 11 times, and phenols (25,000  $\mu$ g/L) 3 times.

Upon an evaluation of the results of coal tar contaminated groundwater remediation applying ex situ remediation using thermal desorption, a decontamination station, and a dugout, we indicated that the remediation was successful and efficient. The subsequent monitoring showed a 99% improvement as opposed to the set limits. The aim of the article was to point out the advantages of ex situ remediation achieved by the excavation of the contaminated geological environment combined with thermal desorption. It is a method of removing contaminants both from soil and groundwater. Its advantage is the absolute qualitative and quantitative control over the contaminated soil with the possibility of precise segmentation into contaminated and non-contaminated soils.

Despite a number of in situ remediation methods, the only complex remediation in this case is the ex situ remediation of contaminated soil and groundwater and their ex situ decontamination, refilling, and recreation of the original hydrogeological conditions. Although the ex situ remediation is effective, it is more expensive. It is suitable in case of complicated contaminations due to a higher flexibility in the use of ex situ decontamination methods and better control over the remediation efficiency. The method may be utilized only where earthworks (dugout) may be implemented in the site to be remediated. This means the site must be void of any buildings or structures. This method demands a relative technological discipline because the structure of the original soil massif is changed. It is important that the newly created geological and hydrogeological conditions are as close to the original as possible. This is achieved by placing layers of analogous grain-size. The soil must be gradually compacted to create almost analogous aquifers. This way, the natural groundwater flows are restored in line

with the surrounding geological structure and hydrogeological conditions. The scientific use of the study is related to the application of the reported information and application of similar remediation methods (ex situ remediation of coal tar) in analogous geological conditions of alluvial sediments.

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# References

- 1. Höckenreiner, M.; Neugebauer, H.; Elango, L. Ex situ bioremediation method for the treatment of groundwater contaminated with PAHs. *Int. J. Environ. Sci. Technol.* 2015, 12, 285–296. [CrossRef]
- Kuppusamy, S.; Palanisami, T.; Megharaj, M.; Venkateswarlu, K.; Naidu, R. Ex-situ remediation technologies for environmental pollutants: A critical perspective. In *Reviews of Environmental Contamination and Toxicology*; Springer: Cham, Switzerland, 2016; Volume 236, pp. 117–192.
- Vidonish, J.E.; Zygourakis, K.; Masiello, C.A.; Sabadell, G.; Alvarez, P.J. Thermal treatment of hydrocarbon-impacted soils: A review of technology innovation for sustainable remediation. *Engineering* 2016, 2, 426–437. [CrossRef]
- Xinhong, G.A.N.; Ying, T.E.N.G.; Wenjie, R.E.N.; Jun, M.A.; Christie, P.; Yongming, L.U.O. Optimization of ex-situ washing removal of polycyclic aromatic hydrocarbons from a contaminated soil using nano-sulfonated graphene. *Pedosphere* 2017, 27, 527–536.
- Cassidy, D.P.; Srivastava, V.J.; Dombrowski, F.J.; Lingle, J.W. Combining in situ chemical oxidation, stabilization, and anaerobic bioremediation in a single application to reduce contaminant mass and leachability in soil. *J. Hazard. Mater.* 2015, 297, 347–355. [CrossRef] [PubMed]
- Scholes, G.C.; Gerhard, J.I.; Grant, G.P.; Major, D.W.; Vidumsky, J.E.; Switzer, C.; Torero, J.L. Smoldering remediation of coal-tar-contaminated soil: Pilot field tests of STAR. *Environ. Sci. Technol.* 2015, 49, 14334–14342. [CrossRef] [PubMed]
- Rostmark, S.C.; Colombo, M.; Knutsson, S.; Öberg, G. Removal and Re-use of Tar-contaminated Sediment by Freeze-dredging at a Coking Plant Luleå, Sweden. Water Environ. Res. 2016, 88, 847–851. [CrossRef] [PubMed]
- 8. Meegoda, J.N.; Janitha, H. Briefing: In situ decontamination of sediments using ozone nanobubbles and ultrasound. *J. Environ. Eng. Sci.* **2017**, 12. [CrossRef]
- 9. Ehrlich, G.G.; Goerlitz, D.F.; Godsy, E.M.; Hult, M. Degradation of phenolic contaminants in ground water by anaerobic bacteria: St. Louis Park, Minnesota. *Groundwater* **1982**, *20*, 703–710. [CrossRef]
- 10. Pereira, W.E.; Rostad, C.E.; Garbarino, J.R.; Hult, M.F. Groundwater contamination by organic bases derived from coal-tar wastes. *Environ. Toxicol. Chem.* **1983**, *2*, 283–294.
- 11. Rostad, C.E.; Pereira, W.E.; Hult, M.F. Partitioning studies of coal-tar constituents in a two-phase contaminated ground-water system. *Chemosphere* **1985**, *14*, 1023–1036. [CrossRef]
- Kempa, T.; Marschalko, M.; Yilmaz, I.; Lacková, E.; Kubečka, K.; Stalmachová, B.; Bouchal, T.; Bednárik, M.; Drusa, M.; Bendová, M. In-situ remediation of the contaminated soils in Ostrava city (Czech Republic) by steam curing/vapor. *Eng. Geol.* 2013, 154, 42–55. [CrossRef]
- Lamich, D.; Marschalko, M.; Yilmaz, I.; Bednářová, P.; Niemiec, D.; Durd'ák, J.; Kubečka, K.; Duda, R. Utilization of engineering geology in geo-tourism: Few case studies of subsidence influence on historical churches in Ostrava-Karvina District (Czech Republic). *Environ. Earth Sci.* 2016, 75, 128. [CrossRef]

- 14. Marschalko, M.; Zástěrová, P.; Yilmaz, I.; Jelínek, P.; Růžička, J.; Růžičková, K.; Duda, R. A case study assessing thermal activity at a significant geotourism locality of Ema coal tailing dumps in the mining landscape of Ostrava, Czech Republic. *Q. J. Eng. Geol. Hydrogeol.* **2017**, *50*, 53–59. [CrossRef]
- 15. Czech Environmental Inspectorate, Limits [Online]. Ministry of the Environment. 2021. Available online: https://www.cizp.cz/ en (accessed on 16 June 2022).
- DeBruyn, J.M.; Chewning, C.S.; Sayler, G.S. Comparative quantitative prevalence of Mycobacteria and functionally abundant nidA, nahAc, and nagAc dioxygenase genes in coal tar contaminated sediments. *Environ. Sci. Technol.* 2007, 41, 5426–5432. [CrossRef] [PubMed]
- Vulava, V.M.; Vaughn, D.S.; McKay, L.D.; Driese, S.G.; Cooper, L.W.; Menn, F.M.; Levine, N.S.; Sayler, G.S. Flood-induced transport of PAHs from streambed coal tar deposits. *Sci. Total Environ.* 2017, 575, 247–257. [CrossRef] [PubMed]
- Burchill, P.; Herod, A.A.; Pritchard, E. Investigation of nitrogen compounds in coal tar products. 2. Basic fractions. *Fuel* 1983, 62, 20–29. [CrossRef]
- 19. Wise, S.A.; Benner, B.A.; Byrd, G.D.; Chesler, S.N.; Rebbert, R.E.; Schantz, M.M. Determination of polycyclic aromatic hydrocarbons in a coal tar standard reference material. *Anal. Chem.* **1988**, *60*, 887–894. [CrossRef]
- Wang, P.; Jin, L.; Liu, J.; Zhu, S.; Hu, H. Analysis of coal tar derived from pyrolysis at different atmospheres. *Fuel* 2013, 104, 14–21. [CrossRef]
- Jiao, T.; Li, C.; Zhuang, X.; Cao, S.; Chen, H.; Zhang, S. The new liquid–liquid extraction method for separation of phenolic compounds from coal tar. *Chem. Eng. J.* 2015, 266, 148–155. [CrossRef]