Article

Extraction of Aged Hydrocarbons from Contaminated Soil Using Plant-Oil-in-Water Emulsions Combined with Oil/Water Separation by Reusable Non-Wovens

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Abstract: A novel technique for the in situ removal of mineral hydrocarbons from aged brownfields is described. The approach uses emulsions of plant oil (5–10%, rapeseed) in water, which were found to extract 50–85% of mineral hydrocarbons in one leaching step from the non-saturated zone. The emulsion was allowed to travel though the ground and was pumped off from the groundwater level. Approximately 15–50% of the plant oil stayed in the soil. By flushing the area with water afterwards, that amount can be reduced to 10–30%, and in some cases to <5%. This process is only suitable for sand, not for clay. It can be a good preparation for subsequent enzymatic cleavage and microbiological degradation, as part of a multi-stage in situ treatment process. Additionally, plant oil that infiltrated into the saturated zone was used to flush mineral hydrocarbons, which could be pumped off from the groundwater level. It was further tested whether the separation of mineral oil/plant oil and water can be performed by oil-absorbing, reusable non-wovens. Residual concentrations of <2% of water in oil, and 0.3–0.7 mg/L of oil in water were found. In this work, lab trials led to field trials, where more than 500 m^3 of water were sent over a pilot installation for oil/water separation using non-wovens. A slightly better separation performance than by oil separators was observed. This process has the potential to be combined with a regular oil separator to allow water purification to a level at which it can be reintroduced into the ground. The technique was tested on a brownfield in Lower Austria, a former refinery site abandoned approx. 80 years ago with a peak hydrocarbon contamination of 40,000 mg/kg of dry soil and free-floating mineral oil on the groundwater level. Since in situ techniques can be more environmentally benign and less costly than traditional remediation approaches, this novel approach holds an interesting potential, which could be proven at a technology readiness level (TRL) of 5.

Keywords: brownfield; mineral oil; remediation; in-situ; fleece; land recycling; cleanup; decontamination

1. Introduction

Human activity has led to widespread soil contamination. Polycyclic aromatic hydrocarbons (PAHs) and mineral or petroleum hydrocarbons (MHs, PHs) can reach the ground through emission from remote sources, or by industrial activity such as petroleum refining, tar production, coke production, or spillage from cleaning and washing operations. Petroleum hydrocarbons are considered amongst the most widespread contaminants in the modern environment [1]. PAH contamination in the soil of industrial regions was measured to be between 7 and over 16,500 mg/kg, and in non-industrial regions (agriculture and forests) between 0.2 and 2 mg/kg [2]. Soil can be classified as "contaminated" above 0.2 mg/kg of PAH. The extent of the problem is huge; in Europe alone, local soil contamination in 2011 was estimated at 2.5 million potentially contaminated sites in the EEA-39

(EEA = European Economic Area). About one third of an estimated total of 342,000 contaminated sites in the EEA-39 have already been identified, and roughly 15% of them have been remediated. Contaminated soil continues to be commonly managed using "traditional" techniques, e.g., excavation and off-site disposal, which accounts for about one third of management practices. In Situ and Ex Situ remediation techniques for contaminated soil are applied more or less equally [3–6]. In Situ techniques are considered advanced remediation approaches with the potential for cost savings.

1.1. Contaminated Land Management

Contaminated land cannot be left unattended, at least not in the long run. The sources of contamination are many [7], including military activity, waste dumping and industrial operations being common routes. Dangers arise for soil, water and air, as well as the people and animals exposed to them, both directly and indirectly, e.g., though food grown on such land. A contaminated site can be "secured" by sealing it off from the environment (i.e., containment of the toxic materials), or be "cleaned up". A complete restoration of the initial, unpolluted state is often not feasible for economic reasons, or otherwise virtually impossible. The costs of contamination cleanup can become immense, due to the often-large volumes of soil and groundwater involved, so decades or even centuries after creation of a known "dirty spot" it quite often is still there, particularly in "remote" areas with low value. There is a pressing need for more cost-effective remediation techniques. "Digging and incinerating" is a costly route, while in situ techniques offer the potential for cost savings, as well as environmental benefits.

Brownfields are defined as areas that have been affected by a former industrial use and accordingly contain soil contamination. Apart from industrial sites, former military sites, abandoned railways, landfills, etc., are included in the definition. They are described as unused and derelict [8].

Chemical leaching and solvent extraction are ex situ chemical processes for separating contaminants from excavated soils, sludges or sediments [9]. Chemical leaching typically utilizes inorganic liquids, such as acids, for separating and recovering metals or salts from soils and sludges, whereas solvent extraction makes use of non-aqueous solvents to separate organic contaminants from soils and sludges. Leaching or extraction may be combined in a soil-washing process to reduce the volume of contaminated soils for disposal [10].

Remediation measures involving plants, fungi, bacteria, and soil amendments are also subsumed as so-called Gentle Remediation Options (GROs) [11], e.g., phycoremediation [12] or phytoremediation [13].

For examples of successful brownfield redevelopments, see [14]. An overview of techniques is given in [15].

1.2. Aged Hydrocarbons

Spilled hydrocarbons start degrading aerobically, and the more easily degradable compounds, such as aliphatic hydrocarbons, break down over time, whereas the fraction of more stable molecules such as aromatics, increases. Former industrial, polluted sites (known as "brownfields") can continuously pollute the surrounding environment [16] from seeping reservoirs, and natural degradation is slow. There are different techniques that can be applied to deal with such hydrocarbon contaminations. Excavating and incinerating the soil ex situ in a treatment plant is a common, but costly, approach, particularly when the affected soil volume is large. Classic soil remediation methods include "*excavation, solidification, vitrification, electrokinetic, soil washing, flushing and oxidoreduction*" and "*have shown to be effective in small areas but they need special equipments, are labor intensive, energy-cost and highly-expensive*" [17]. There exist several in situ techniques for hydrocarbons based on oxidation [18]. In general, a problem with aged hydrocarbons is their high viscosity, which makes dispersants ineffective [19].

Phytoremediation, the use of plants and their associated microbiota to remove, contain, or render harmless environmental contaminations, has been shown to be effective for hydrocarbon-contaminated soils [13,17].

Biological methods for in situ hydrocarbon degradation are bioremediation [20–22] biostimulation [23] and bioaugmentation [24]. "*Bioremediation is based on the capacity of microorganisms to degrade organic pollutant compounds, such as hydrocarbons*" [25]. Bioaugmentation "*is defined as the addition of pre-grown microbial cultures to perform a specific remediation task in a given environment*" [26]. Biostimulation consists of the activation of native soil microorganisms through the addition of nutrients. Moisture and nutrient availability are among the most critical factors limiting oil biodegradation [26]. One established technique for the remediation of hydrocarbon-contaminated soil is landfarming. It is an on-site technique. "*Landfarming involves the degradation of soil hydrocarbons through the activation of natural microorganisms by the incorporation of inorganic fertilizers, water and periodic tilling to mix and aerate the soil. The presence of larger number of appropriate microorganisms and the synergistic effect of fungi and bacteria is a key to successful bioremediation*" [27].

Another possibility is advanced oxidation, e.g., with the oxidants hydrogen peroxide, Fenton reagents, potassium permanganate, and sodium persulfate [28].

For an overview of hydrocarbon-remediation techniques, see [29].

1.3. Combined (In Situ) Processes

In the pertinent literature, several combinations of remediation techniques have been described, e.g., by Ivshin et al. [30].

M.E. Mancera-Lopez et al. [25] studied a combined system of biostimulation–bioaugmentation with filamentous fungi [25].

The combination of biochar with bioaugmentation suggested synergies in bioremediation [31]. In another work, three different strategies were deployed: bioaugmentation (BA), biostimulation (BS) and biostimulation–bioaugmentation (BS–BA). The trials showed the highest reduction rates of hydrocarbons in soil of 92–93% by BS–BA (down from 30, 703 to 860 and 1020 mg/kg, respectively) [1].

In [2], chemical oxidation and biodegradation were combined for the remediation of polycyclic-aromatic-hydrocarbon (PAH)-contaminated soil, with a focus on the persulfate oxidation and anoxic biodegradation of PAHs in subsurface soil. Promising results were obtained. However, it was found that the strong oxidant, at high application rates on the order of 3% (weight), had a negative influence on the soil bacteria.

Another combined in situ approach was studied by Liu et al. [32].

1.4. Soil Flushing and Soil Washing for the Extraction of Hydrocarbons

A potentially interesting approach for in situ mineral hydrocarbon removal is their extraction. The soil can be washed (flushed) with a suitable agent, or an adsorbent can be applied.

Several authors apply the term "soil flushing" to the in situ application, whereas "soil washing" describes the use of a solvent in an on-site process [33].

In [34], polyurethane microparticles were used to capture PAHs from the ground. The enrichment factor was found to be 70. PAH concentrations in biodegradable polyurethane particles were 70 times higher than those in soil [34].

Soja et al. [35] infiltrated 40 L of rapeseed oil in contaminated soil. Within 19 days, 17% of that plant oil could be captured, and it contained 5.4 g of PAH (EPA 16) [35].

Among the advantages of soil flushing over pump-and-treat methods are predominantly lower costs and reduced exposure to health hazards for workers. However, a major disadvantage is the risk that contaminants become mobilized and the contaminant plume spreads beyond the recovery zone [10].

In order to avoid said plume migration, groundwater flow must be controlled, e.g., through barriers and pumping off. Soil flushing is also only suitable for permeable soils

such as sand or gravel. For the flushing solution, a non-toxic, biodegradable solvent is recommended [10]. Table 1 provides an overview.

Table 1. Types of flushing agents for soil. Source: [10].

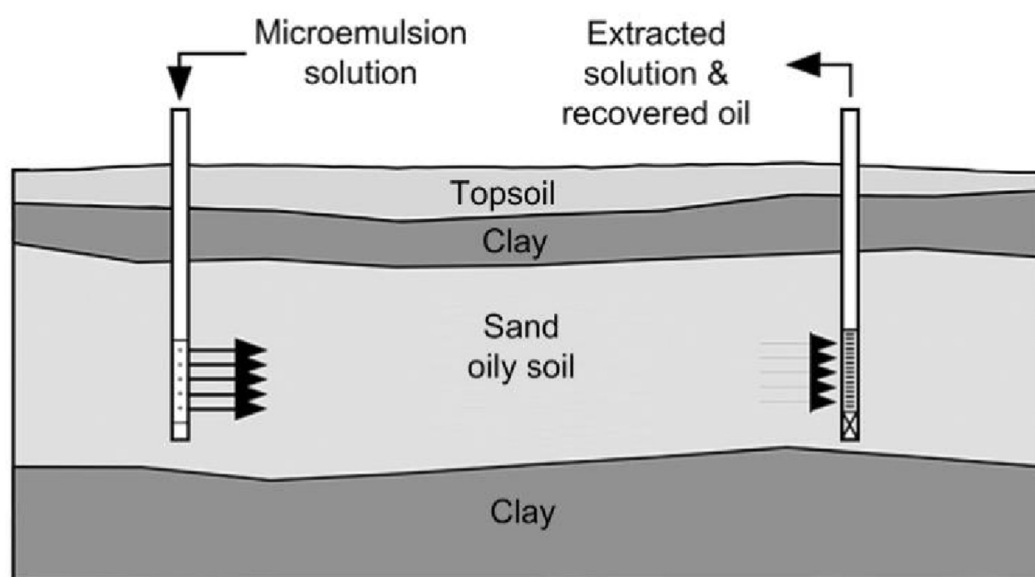| Flushing Agent	Contaminants Targeted
clean water	High-solubility organics; soluble inorganic salts
surfactants	Low-solubility organics; petroleum products
water/surfactants	Medium-solubility organics
cosolvents	Hydrophobic contaminants
acids	Basic organic contaminants, metals
bases	Phenols, metals
reductants/oxidants	Metals

Organic contaminants such as NAPLs (non-aqueous phase liquids) can be flushed with surfactants or co-solvents [36]. The use of microemulsions allows the extraction of NAPLs in a single, low-viscosity phase [36].

One should try to recycle the flushing fluids as much as possible. The extraction of the contaminants from the flushing solution can be performed via air stripping, liquid/liquid extraction, precipitation, filtration, or distillation [36].

In 2007, the ASCE (American Society of Civil Engineers) stated: "The costs of soil flushing are estimated to be between $75 and $300 per cubic yard of contamination plume. This estimate includes injection and recovery well and pump installation, operating and maintenance labor, sampling well installation, utilities, flushing solution preparation system installation, chemicals, flushing solution treatment, system installation, site supervision, site quality assurance and health and safety support, sampling and analysis for process control, and off-site disposal of sludge residual from flushing solution treatment. The estimate does not include project design and management, regulatory fees, site characterization, treatability, site pretreatment and contingencies."

With 1 cubic yard being 0.764 m^3 and 1 USD in 2007 corresponding to 1.34 USD in 2022 (1.18 €), it leaves the estimated costs at 116–463 €/m^3.

The flushing agent is obviously the main cost driver, which means recycling can yield strong cost reduction. Additionally, the type of flushing agent has a strong impact on costs. A soil-flushing setup is shown in Figure 1 below.

Figure 1. Soil flushing. The first application was enhanced oil recovery. Reprinted with permission from [37].

The technique shown in Figure 1 is based on the surfactant-polymer flooding process [37], where the aim was to mobilize hydrocarbons in an enhanced oil-recovery process. It is also applicable to brownfield remediation.

In soil washing, a common approach to reduce treatment costs is to separate the fine material from the relatively contaminant-free coarse materials in the excavated soil [10].

Flushing agents include detergents, plant oils, or plant-oil-in-water emulsions. Biodiesel has been suggested as solvent [38]. Alcohols and other solvents are an option too, always bearing in mind the biodegradability, toxicity and mobilization of pollutants.

1.5. The Petroleum Refinery Droesing

In this project, field trials were carried out in an actual brownfield, the former petroleum refinery Droesing [39]. According to the Austrian federal environmental agency, the petroleum refinery operated from 1899 to 1937. Among others, kerosene, light, medium and heavy gasoline and petroleum were produced. Acidic, highly viscous mineral-oil hydrocarbons were not processed further and ended up as waste in an acid tar pit, which held 2000 m^3 by the end of the production period. Today, mineral-oil contamination is found on a large part of the former operations' premises. The extent of the underground areas heavily contaminated with mineral oil can be estimated between approx. 55,000 m^2 and approx. 100,000 m^3, of which around 30,000 m^3 are in the groundwater fluctuation area. The spread of the pollutants in the groundwater is currently low. No significant emissions of pollutants into the groundwater outflow are expected in the near future. The heavily contaminated area poses a significant threat to the environment [39]. Equipment from the site, and the concession, were transferred to the refinery Schwechat/Lower Austria [40], which is still in operation today as Austria's single petrochemical refinery.

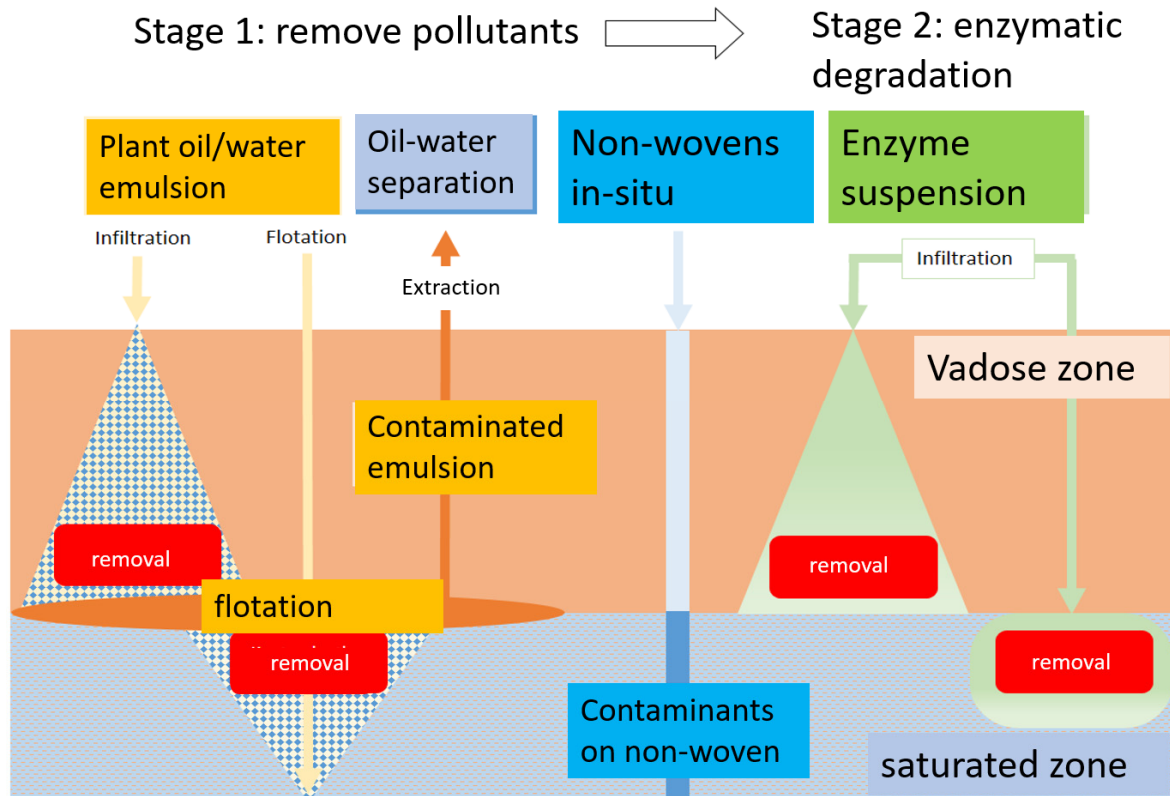Figure 2 shows three pictures from the site.

Figure 2. The brownfield "N77" in Droesing, Lower Austria. **Left**: the acid tar lagoon. **Middle**: oil that was pumped from the groundwater. **Right**: acid tar bubble seeping to the surface.

The area is currently not used. It is located approx. 1 h by train from Vienna, and previous attempts at remediation have failed economically.

The groundwater level, at the time of the field trials from February 2021–July 2021, was approx. at 8.0 to 8.5 m in depth. The oil consists of mostly clay in the non-saturated zone and mostly sand/gravel in the saturated zone. The top layer of 0.5 to 1 m in depth is not natural ground, but instead mostly building rubble and other waste mixed with local soil. The vegetation is mostly thick shrubs of acacia and willow.

2. Experimental

In this project, a multi-stage "cascaded" approach was developed to treat aged hydrocarbons in contaminated soil. The concept is shown in Figure 3.

Figure 3. The project "Cleanup-Cascade" has two steps. See text for details.

The project is based on the idea of sequential pollutant extraction from the soil. The first stage is "pollutant removal", as described in this paper. To this end, plant-oil-in-water emulsions are introduced both into the saturated and unsaturated zones. Upon their passage, they absorb mineral hydrocarbons from the ground. The mixture is then pumped from the groundwater level to the surface. This removal step is followed by oil/water separation on the surface, where non-wovens were tested. For the experimental setup, see [41,42]. The second stage in the project is an "enzymatic degradation", where an enzyme suspension is added to the saturated and non-saturated zones in order to cleave the remaining hydrocarbons. These enzymes are introduced in solution and adsorbed onto non-wovens. That second stage is not part of this paper but described elsewhere [43]. After stage two, the native microorganisms should be able to degrade the broken-down, remaining hydrocarbons. Stage two hence makes the aged hydrocarbons "accessible" for natural attenuation/degradation.

The site was cleared of vegetation in an area of approx. 500 m^2, and five wells were prepared for the experiments. The central well was used to continuously suck groundwater so that a "funnel" approx. 0.5 to 0.75 m deep was produced, in order to avoid any mobilized contaminants leaving the site. The well located most downstream was used as a "security well", to pump off mobilized contaminants in case anything went wrong in the experiments. The other three wells had openings in both the saturated and the unsaturated zone, so the emulsion could be supplied as desired. Prior to starting the trials, approval was obtained from the local authorities, and the state of the groundwater was monitored by a third party before and after the field trials.

2.1. Preparation of Oil-in-Water Emulsions

In this work, rapeseed oil in water was chosen as the extraction medium. Rapeseed oil is a low-cost, local product, which is also biodegradable and a proper solvent for various mineral hydrocarbons. Other plant oils such as sunflower oil of local origin could also have been used. The main idea was to use a completely biodegradable, natural solvent, of which residues in the ground would not pose an environmental problem.

For the lab experiments during process development, deionized water and tap water were used. For the field trials, groundwater was taken. An amount of 5% plant oil in water (by weight) was used as the default emulsion, with different emulsifiers. A higher oil content resulted in higher viscosity and slower wetting/permeation of the soil.

The emulsions were found to be stable for a maximum of 50 h thanks to systematic screening with surfactants and co-surfactants. The approach of increasing the density of the emulsions by adding salt did not work because the salts greatly reduced the stability of the emulsions. Lab trials were performed with ultrasonic mixers. For the field trials, a 300 L vessel with a disk stirrer was used. A surfactant/emulsifier is required to stabilize an emulsion of oil in water (O/W emulsion). This addition prevents coalescence of the disperse phase (here: oil). Surfactants have a hydrophilic and a hydrophobic/lipophilic part; a co-surfactant may also be necessary. The so-called HLB value (hydrophilic–lipophilic balance) is decisive. It indicates the mass ratio between the polar and non-polar parts on a scale of 0–20, where the range of 0–8 describes lipophilic materials and 9–20 hydrophilic ones. For water-in-oil emulsions, emulsifiers with an HLB value of 3–6 are recommended, and for oil-in-water emulsions, 8–18 has proven advantageous. Trials were performed with the following surfactants: Sodium laurethyl sulfate SDS), sodium dodecyl sulfate (SDS), polysorbates (Tween™ 20 to Tween™ 80), various vegetable lecithins, polyethylene glycole (PEG 400), glycerol stearate and sucrose stearate. As co-tensides, n-pentanol and n-propanol were tested.

Whole milk, condensed milk and coconut milk were tested as ready-made emulsions with 3.5 to 10% oil-in-water content, but showed slow permeability. These are the most stable emulsions (Table 2):

Table 2. Emulsions with stabilities in excess of 50 h.

Rapeseed Oil [g]	Deionized Water [g]	Tenside [g]		Cotenside [g]	
25 (5%)	465	SSL	10 (2%)	-	-
25 (5%)	450	SSL	25 (5%)	-	-
17.5 (5%)	297.5	Lutensol TO 5	35 (10%)	-	-
17.5 (5%)	262.5	Emulan A	35 (10%)	Lutensol	35 (10%)
25 (5%)	465	SSL	5 (1%)	Sucrose stearate	5 (1%)
25 (5%)	455	Sucrose stearate	15 (3%)	Glycerine stearate	5 (1%)
25 (5%)	460	Lecithine	15 (3%)		
25 (5%)	455	Lecithine	20 (4%)		
25 (5%)	450	Lecithine	25 (5%)		

The last three formulations from Table 2 were used in the field trials. The lecithine was purchased from Lasenor (Barcelona, Spain; Giralec HE-60). This is a highly enzymatically hydrolyzed sunflower lecithin (E-322). The advantages of lecithines are their availability, biodegradability and good separability, since the emulsions have a stability that hardly exceeds 50 h. The hydrolysis of the lecithin leads to a better water solubility so that less energy is required for mixing. In Figure 4, the setup of the field trials is shown.
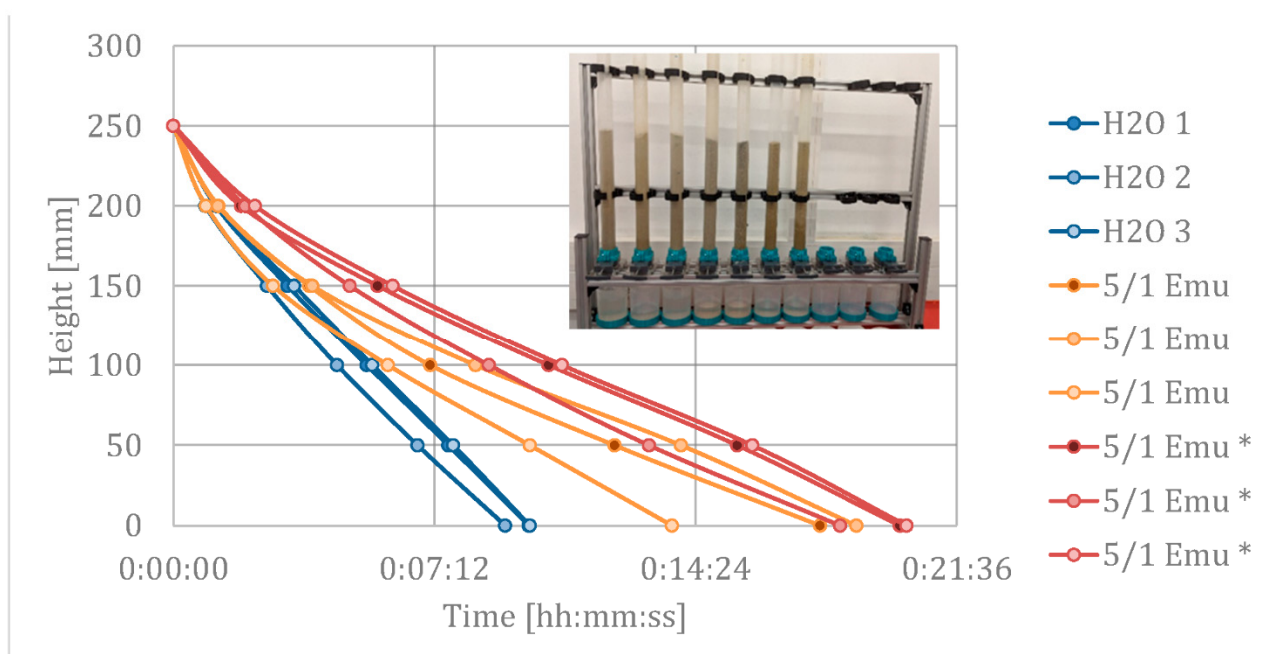
Figure 4. Setup of the field trials. **Left**: 300 L stainless steel mixer. **Right**: Close-up of the emulsion. It was colored for better visibility.

2.2. Flushing of Soils with Oil-in-Water Emulsions

The oil-in-water emulsions prepared as described above were tested in various soils in order to flush them and remove the contained mineral hydrocarbons.

In Figure 5, a lab experiment is shown where water and emulsions were allowed to travel through glass columns (250 cm) to determine the k_f values.

Figure 5. Lab trials to determine the speed with which water and emulsions travel through the soil. Sand from the brownfield N77 was used as a substrate. It was compressed in the glass columns to obtain comparable conditions. The three curves are the first, second and third passages, with dry and wetted sand. The insert shows the experimental setup. Emu = emulsion; The * stands for trials where the sand was wet.

From Figure 5, the following k_f values can be read: 4.6×10^{-4} m/s for water and 3.2×10^{-4} m/s to 2.1×10^{-4} m/s for oil-in-water emulsions. For clay, virtually no permeability of either water or emulsion could be measured, with estimated k_f values on the order of 10^{-9} m/s.

In the next step, the maximum extraction yields of the soil flushing were estimated by lab experiments. A total of 500 g of soil were intensely mixed with 500 g of solvent (water and emulsions). Table 3 presents the results for sand, and Table 4 for clay.

Table 3. Extraction experiments with sand from Droesing.

Sand, Untreated			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	96.9
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	1020
Sand, extracted with milk (3.6% fat)			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	92.3
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	1050
Sand, extracted with emulsion (50% rapeseed oil in water)			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	87.9
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	468
Sand, extracted with pure rapeseed oil			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	98.2
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	820
Sand, extracted with pure coconut milk (19% fat)			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	89.9
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	704

Table 4. Extraction experiments with clay from Droesing.

Clay, Untreated			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	97.7
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	12,100
Clay, extracted with milk (3.6% fat)			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	82.4
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	10,800
Clay, extracted with emulsion (50% rapeseed oil in water)			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	88.1
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	2090

Table 4. *Cont.*

Clay, Untreated			
Clay, extracted with pure rapeseed oil			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	97.8
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	7820
Clay, extracted with pure coconut milk (19% fat)			
Parameter	Method	Unit	Value
Dry matter	EN 14346:2006	%	69.4
Hydrocarbons (C10–C40)	EN 14039:2004	mg/kg	4860

The experiments were repeated three times and the results were averaged. The sand sample contained 1020 ppm of hydrocarbons prior to the flushing experiments. With milk, no reduction could be achieved, and with pure rapeseed oil and coconut milk there was hardly a reduction in the hydrocarbon content of the sand. The emulsion of 50% rapeseed oil in water, however, yielded a reduction to 468 ppm, which is a flushing of 54%. There were some fluctuations in the results, which can be attributed to inhomogeneities in the sample. The trials were performed at room temperature and ambient pressure. Agitation was performed for 30 min.

As Table 4 shows, the initial hydrocarbon contamination of the clay was as high as 12,100 ppm. Flushing with milk yielded a very low reduction. Likewise, pure rapeseed oil did not wash out much of the hydrocarbons. Coconut milk was better in this matrix, and the best result was achieved with a rapeseed-oil-in-water emulsion (50%). The residual hydrocarbon contamination was 2090 ppm, which means that 83% of the contamination was washed out.

In the next step, it was investigated how much plant oil remains in the soil after flushing (see Table 5).

Table 5. How much plant oil stays in the ground after flushing with the emulsion?

Medium	Solvent [g]	Captured [%]	Captured after flushing w. water once [%]	Captured after flushing w. water twice [%]
Pebbles	Water/oil 900/100	84	91.37	97.64
Pebbles	Water/oil 900/100	90.85	99.35	99.71
Medium	Solvent [g]	Captured [%]	Captured after flushing w. water once [%]	Captured after flushing w. water twice [%]
Coarse sand	Water/oil 900/100	63.15	71.67	78.75
Coarse sand	Water/oil 900/100	57.77	71.21	76.77
Medium	Solvent [g]	Captured [%]	Captured after flushing w. water once [%]	Captured after flushing w. water twice [%]
Clay (dry)	Water/oil 900/100	56.11	73.26	79.83
Clay (dry)	Water/oil 900/100	53.9	67.82	74.67
Medium	Solvent	Captured [%]	Captured after flushing w. water once [%]	Captured after flushing w. water twice [%]
Clay (wet)	Oil	81.5	86.37	89.7
(Clay (wet)	Oil	80.89	87.56	89.61

As Table 5 shows, the experiments were performed with three model matrix materials: pebbles, coarse sand and clay. The clay was tested dry and wet. A quantity of 10% of rapeseed oil in water was added to the solids, and the amount of oil that could be captured after passage through a column on a net was determined. Additionally, the flushing of that column with water (same mass as the solids) was performed once and twice in order to further reduce the amount of rapeseed oil in the material. It can be seen that by the washing activity, the residual oil is reduced. Additionally, it can be seen that dry clay retains more plant oil than wet. With a very coarse ground (pebbles), almost all plant oil can be extracted, whereas clay will retain approx. 10–20% of the plant oil.

In Figure 6, one can see an IBC from the field trials in Droesing with two phases: groundwater with a layer of mixed plant oil, and mineral oil floating on top.

Figure 6. Separation of the emulsion after passage through the non-saturated zone and pumping off to the ground: The top layer is a mix of plant oil and mineral oil washed out from the soil.

The main experiments carried out in the non-saturated zone during the field trials are tabulated in Table 6:

Table 6. Flushing and pumping trials in the non-saturated zone.

Date	Emulsion [L]	Contained Plant Oil [L]	Emulsifier	Unit of Emulsifier	Type of Emulsifier	Amount of Total Oil Removed (Estimated *) [L]	Contained Mineral Oil [%]	Plant Oil [L]	% of Oil Captured	Mineral Oil [L]
27 May 2021	190	10	5	kg	Soy lecithine powder	9	65	3.15	63%	5.85
8 June 2021	190	10	5	kg	Soy lecithine powder	8	60	3.2	64%	4.8
9 June 2021	190	10	6	L	Giralec HE	8.5	60	3.4	57%	5.1
17 June 2021	190	10	6	L	Giralec HE	8	55	3.6	60%	4.4
18 June 2021	190	10	6	L	Giralec HE	7	50	3.5	58%	3.5
29 June 2021	190	10	6	L	Giralec HE	7.5	50	3.75	63%	3.75
30 June 2021	190	10	6	L	Giralec HE	8	45	4.4	73%	3.6
	Total	70				56		25		31

* Amount of oil was estimated from the level of the oil in the collection IBC. The oil phase was pumped off after max. 36 h.

The following summary can be given for the non-saturated zone:
Flushing experiments:

- Approx. 50–85% of mineral hydrocarbons from the soil can be washed out in one passage with 10% plant oil in water;
- The method is suitable for permeable soil (gravel, sand), but not for clay;
- Max. 15–50% of the plant oil will remain in the soil, which can be reduced to 10–30% and sometimes 5% by washing with water.

The main experiments carried out in the saturated zone during the field trials are tabulated in Table 7:

Table 7. Flushing and pumping trials in the saturated zone.

Date	Plant Oil [L]	Amount of Total Oil Removed (Estimated *) [L]	Contained Mineral Oil [%]	Plant Oil [L]	% of Oil Captured	Mineral Oil [L]
14 July 2021	30	28	8	25.76	92%	2.24
15 July 2021	30	29	8	26.68	92%	2.32
22 July 2021	30	27	6	25.38	94%	1.62
23 July 2021	30	28	5	26.60	95%	1.40
	120	112		104.42		7.58

* Amount of oil was estimated from the level of the oil in the collection IBC. The oil phase was pumped off after max. 1 h.

As Table 7 shows, a total of 120 L of plant oil were infiltrated into the saturated zone, of which 92–95% were later collected back from the top of the groundwater after max. 1 h. Along with that plant oil, 7.58 L of mineral hydrocarbons were extracted from the ground.

2.3. Separation of Oil and Water Using Non-Wovens

As partly siliconized non-wovens, polypropylene (PP) and polyethyleneterephtalate (PET) with 180 to 320 g/m^2. They were supplied by the company ICS (Thale, Germany). For details on the non-wovens, see [44]. The standard application of these oil-binding materials is capturing oil spills in workshops or after accidents on roads. The underlying idea in the use of oil-binding non-wovens for oil-water separation is to recycle the non-wovens by pressing them out, to achieve a high oil/to non-woven ratio. The prototype for separating oil and water by non-wovens is shown in Figure 7.

Figure 7. Prototype of the non-woven-based oil-and-water separator. **Left**: close-up of a non-woven laden with plant-oil being pressed out. **Right**: IBC installation with the emulsion to be separated in the middle and the pressed-out oil on the right.

When these non-wovens were used for separating plant oil/mineral oil from water, the following performance was found in the field installation:

- Residual mineral-oil content in water: 0.5 to 1.5 mg/L
- Residual water content in the oil (mix of plant oil and mineral oil): max. 2%

The field installation is shown in Figure 8.

Figure 8. The inclined bed filter (IBF) in the workshop (**left**) and in the field (**right**). In the right picture, two IBCs with mineral hydrocarbons pumped from the ground and separated by the IBF with non-wovens can be seen in the font.

It was not possible to separate mineral oil and plant oil. Selective adsorption trials on zeolithes and activated charcoal failed as well as thermal separation techniques.

In total, 511 m^3 of groundwater was pumped off and treated in the on-site installation to separate water and oil phases. The following performance of the non-wovens could be established (Table 8):

Table 8. Oil removal from water using non-wovens.

Residual Oil Content after the Processes	Groundwater	Emulsion
Classic oil separator (OS)	0.8 mg/L	0.8 mg/L
OS + non-wovens on inclined bed filter (IBF)	0.3 mg/L	0.7 mg/L
Non-wovens (IBF)	0.4 mg/L	0.6 mg/L

3. Results and Discussion

After process development in a controlled lab environment, field trials on an actual brownfield were carried out. There were two fundamental shortcomings of the brownfield "N77 petroleum refinery Droesing":

1. In the groundwater, mineral oil was found to be free-floating. In each of the five novel wells, plus the upstream, already-existing well, a black, oily phase could be pumped from the groundwater. It was approx. 0.5 L during each start of the pump, and the oil phase needed 1–2 days to be present again in a well that had been pumped off. This very high contamination load made quantification of the flushing experiments difficult.

2. The site, to a large extent, is made up of clay, which exhibits a very low water permeability. In fact, the soil was very dry, and it was discovered that both in the saturated and unsaturated zones, easily degradable hydrocarbons were still present, even after 80 years. That observation stresses the difficulty of natural attenuation.

Still, the results show a novel process combination for the remediation of aged brownfields that has a good potential. Below, the main results are discussed.

3.1. Soil Flushing

After the introduction of the oil-in-water emulsions, the liquids from the groundwater level were pumped off. Along with the groundwater, plant oil and washed-out mineral hydrocarbons were pumped off. For the saturated zone, it took up to 36 h for the emulsion to reach the groundwater level. For the non-saturated zone, the passage of the introduced mineral oil to the groundwater top layer took less than 1 h. It can be estimated that the radius of activity is 1–5 m^2 per bore hole in the non-saturated and 5–10 m^2 in the saturated zone. The radius of activity depends on the k_f value of the soil and the depth of the "suction funnel" where the extraction is being carried out. It has proven advantageous to carry out intermittent pumping.

3.2. Cleaning of 500 m^3 of Groundwater

In order to make an on-site demonstration of the capability of non-wovens to separate oil from water in the field, it was decided to run an experiment with 511.3 m^3 of groundwater (Table 9).

Table 9. The 511.3 m^3 groundwater cleanup took place from 21–30 September 2021.
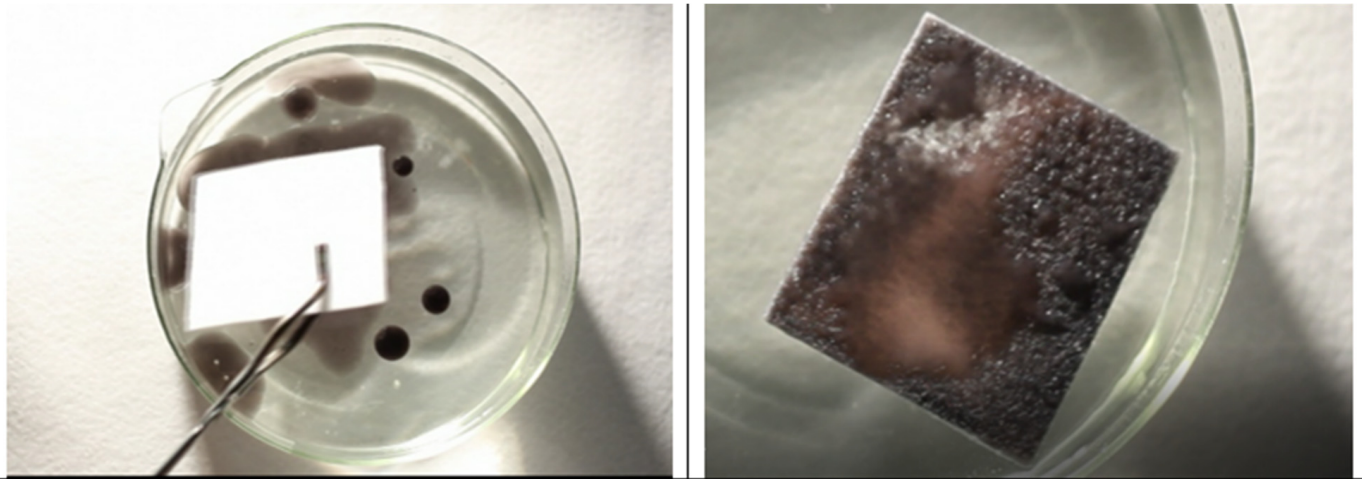
Date	Time	Amount of Water Pumped Up, Cleaned and Re-introduced in the Ground (1.9 L/s)	Cleaning by Classic Oil Separator (OS)	Cleaning by Non-Wovens in the Ihe Inclined Bed Filter (IBF)
21 September 2021	10:35–16:40	41,610	x	-
21 September 2021	11:00–16:40	38,760	-	x
22 September 2021	09:15–16:00	46,170	x	-
22 September 2021	09:15–16:00	46,170	-	x
23 September 2021	10:20–16:15	40,470	x	-
23 September 2021	10:20–16:15	40,470	-	x
28 September 2021	09:35–16:00	37,050	x	-
28 September 2021	10:00–16:00	41,040	-	x
29 September 2021	12:15–17:10	33,630	x	-
29 September 2021	12:30–17:10	31,920	-	x
30 September 2021	09:30–18:20	60,420	x	-
30 September 2021	10:30–18:20	53,580	-	x
Total [L]		511,290	259,350	251,940

The 511.3 m^3 of groundwater contained approx. 3000 L of hydrocarbons, half of which were separated on site by the standard oil separator and half by the inclined bed filter with non-wovens. The trials could have technically been continued, but the permit for the groundwater pumping was exhausted at the end of the experiments.

3.3. Non-Wovens in Brownfield Remediation

To date, oil-binding non-wovens have been extensively used for spill containment, but not yet for brownfield remediation. The idea of using a non-woven material to continuously or intermittently bind hydrocarbons, be pressed out and be reused, has the potential to save adsorbent material and costs. The principle is simple (see Figure 9).

Figure 9. (**Left**): An oil-binding non-woven is brought in contact with oil in water. (**Right**): The material has captured the oil but did not become wet from the water.

The non-wovens in these experiments retained 18 times their own weight in mineral hydrocarbons (and still 17 times their weight after 15 cycles of pressing out and reusing), and were able to retain 8.6 times their weight of rapeseed oil when fresh and 7.8 times their weight of rapeseed oil after 15 loading cycles. The oil-laden non-wovens can be recycled in the processes by pressing them out. A configuration with endless tape could be used. When fully loaded or mechanically overstressed, the oil-laden non-wovens can be incinerated.

4. Summary and Future Directions

In this work, a proof-of-principle for a novel in situ brownfield remediation approach was tested in the field. Plant oil in water could be tested as a solvent for soil-borne mineral hydrocarbons in a landfarming setup, where on-site treatment would allow the well-defined handling and cleanup of large quantities of soil by the new method. The landfarming approach would oversee stepwise excavation of the ground, assessment of its contamination level and on-site treatment of all soil above a certain threshold, with incineration of the most highly contaminated material. In this way, objects that are still buried in the ground can also be found, excavated and disposed of. Particularly for sites like this former petroleum refinery, there will likely be numerous underground installations where no detailed plans are available anymore.

Oil-binding non-wovens can be further developed as reusable hydrocarbon-fixing media, comparable to an oil separator but with potentially lower residual oil concentration in the water. The approach shown in this paper is no mature remediation technology yet; however, it adds one new perspective to the toolkit of brownfield management and cleanup options. In any case, brownfield remediation is a necessity of high relevance, and in situ methods hold interesting environmental and economic promise.

The new in situ technique of extracting aged hydrocarbons from contaminated soil with plant-oil-in-water emulsions combined with oil/water separation by reusable non-wovens could be proven at a technology readiness level (TRL) of 5. It is expected that a new technology for brownfield remediation for petroleum-contaminated, permeable soils can be developed.

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