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Hydrocarbon-Contaminated Soil in Cold Climate Conditions: Electrokinetic-Bioremediation Technology as a Remediation Strategy

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8.1 Introduction

8.1.1 Hydrocarbon Contamination

Soil contamination refers to reduced soil quality and is considered a global issue. Health risks and environmental impacts associated with exposure to petroleum hydrocarbons have led to soil contamination being considered a major concern. There are more than 3 000 000 potentially contaminated sites worldwide, and they may represent a loss of economic opportunities and a threat to human health and the ecosystem [1]. If the current trend continues, the number of potentially contaminated sites is expected to increase by 50% by 2025 [2]. The leading causes of contamination vary widely across Europe but include past and present industrial and commercial activities ~~and~~ the disposal and treatment of waste.

In Europe, heavy metals and mineral oil are the most frequent soil contaminants (37.3 and 33.7%, respectively~~, at the investigated sites)~~ [2]. Each year, thousands of oil spills occur on land and in water as the result of various types of incidents, including transportation and facility releases. The sources of petroleum hydrocarbons entering the environment are numerous as the number of individual hydrocarbon components is quite large [3]. Petroleum hydrocarbon contaminants can be characterized as the vast majority of organic compounds and byproducts classified as priority environmental pollutants, such as persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) due to their persistence and recalcitrant nature [3]. Long exposure to oil-containing waste may lead to the migration of hydrocarbons in the environment, resulting in secondary contamination sites [4, 5]. Moreover, petroleum hydrocarbons impose a significant ecological risk: they can inhibit plant

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growth, damage soil structure and groundwater quality, and pose serious threats to human health [5].

Soil is a non-renewable resource and the basis for life and supporting livelihoods. The need to restore the natural quality of affected soil by the restitution of its functions and elimination or reduction of actual or potential risks to human health and the environment calls for the development of efficient remediation technologies. The physico-chemical properties of oil, such as its hydrophobic nature with low water solubility and a high octanol-water partition coefficient, make the development of a remediation strategy a challenge because oil adsorbs tightly to soil organic matter and thus is less susceptible to degradation [6]. Moreover, certain environments make the remediation challenge even more difficult.

8.1.2 Oil Spills in Arctic Environments

A broad range of new chemicals of emerging Arctic concern have been identified, and PAHs are included in the list [7]. Some researchers pointed out that residents in Arctic regions are exposed to high concentrations of POPs and heavy metals [8, 9]. Epidemiological studies established in the circumpolar area to investigate the link between exposure to contaminants and health outcomes showed links between exposure to contaminants and neurobehavioral, reproductive, cardiovascular, endocrine, and carcinogenic effects [10]. In addition, the bioaccumulation of hydrocarbons in the food chain of Arctic mammals was also reported [11], which represents a real threat as such hydrocarbons are mutagenic and carcinogenic [5].

Human activities in polar regions are oil-dependent, and in the future, the industry probably will expand, which increases the risk of adding more oil-contaminated sites. Hydrocarbon fuels are used extensively as the primary energy source for heating, transportation, power generation, and operating vehicles, aircraft, and ships. Generally, oil spills are related to accidental leaks during transport, management, or storage; and as a result of accidental spills and past disposal practices, petroleum contamination can be found in soils, especially around settlements [12]. Spills and releases include crude oil, oil byproducts (e.g. heating oil, refined fuels, and lubricants), and oil–chemical mixtures of various kinds [13].

The Arctic environment is very fragile to anthropogenic disturbances due to slow recovery times [14], and treating contamination is difficult due to suboptimal environmental conditions with a very short treatment season, remote sites, and limited local infrastructure [15].

Polar environments present significant challenges to oil spill mitigation. Extreme cold, snow and ice cover, frozen ground, variably wet and organic-rich soils, undulating surface cover (e.g. tundra, muskeg, and tussocks), and short summers hamper recovery and remediation of oil spilled in the Arctic.

Soil in the Arctic has specific characteristics that are different from other soil environments. Polar soils have unique periglacial features, including permafrost and numerous types of patterns, primarily due to freeze-thaw effects [16]. Permafrost environments are sensitive to heat and slow to recover from impacts. Thus, oil spills in permafrost environments are difficult to mitigate and clean up [13]. These soil features might affect hydrocarbon remediation, as the activity of indigenous hydrocarbon-degrading microbes is limited, likely due to a combination of unfavorable conditions, cold and fluctuating temperatures, low nutrient levels, and low moisture [12, 15]. In addition to the growing interest and advances in environmental science in cold regions, much remains to be learned about spill response and remediation and how to manage spills in these cold, harsh environments [13].

8.1.3 Remediation of Petroleum-Contaminated Soil

Considerable efforts have been made to remediate petroleum-contaminated sites [17]. Remediation technologies for contaminated environments are site specific, and the variables are associated with the nature and composition of the contaminants together with the physical, chemical, and biological conditions of the environment [13].

Hydrocarbon soil remediation technologies can be mainly classified into two types: physical–chemical and biological [3, 18, 19]. The US EPA has documented inadequate performance of various remediation technologies, which may be attributed to (i) matrix characteristics (e.g. clayey soils are difficult to remediate because of their low permeability and organic content); (ii) heterogeneous conditions of the site (e.g. clayey within sand formation); (iii) physical and chemical characteristics of the contaminants; and (iv) co-existing inorganic and organic contamination. Very few technologies (e.g. washing/flushing soil and solidification/stabilization) have been successful in removing mixed contamination; most failed due to long treatment times and high cost [20, 21].

Some remediation actions involve the excavation and removal of the polluted soil, which causes site disturbance and adds to the cost of remediation treatment [17]. Research efforts have been focused on finding economic and suitable non-invasive methods for the remediation of oil-contaminated soil. Several in situ technologies have been investigated, such as bioremediation and phytoremediation, in which living bacteria, fungi, or green plants are used to clean up contaminated lands. Bioremediation, as a primary remediation technology to treat a wide range of hydrocarbons, has been a topic of considerable research interest over the last couple of decades, since it is effective and economical in removing oil with less undue environmental damage. Some studies have already proved that enrichment of oil-degrading microbial communities occurs soon after oil contamination, showing that cold-adapted indigenous microorganisms play an essential role in decontaminating cold climates [22, 23]. Nevertheless, successful bioremediation of petroleum hydrocarbons in soil has remained a challenge. It is a relatively slow process, and the degree of success depends on a number of factors such as soil type and structure, pH, association with co-pollutants, and temperature [24]. The temperature has been studied to accelerate the natural biodegradation rate during soil remediation [25]. Laboratory studies have demonstrated that mineralization can occur at low temperatures, but the rate of degradation is higher at elevated temperatures as they increase the degradation and volatilization rates of hydrocarbons. Given the low temperatures in subsurface soils and the short season during which soils are thawed (one to two months) there is a need to control temperature, pH, nutrient levels, and moisture to optimize degradation rates [26, 27]. For example, the results from the study carried out by Fritt-Rasmussen [28] with soil from Greenland showed that oil degradation is greater at elevated temperatures and even more so when heat and nutrients are combined. Other studies have also shown the importance of coupling technologies to enhance hydrocarbon removal, such as biostimulation with active heating [25].

8.1.3.1 Electrokinetic Remediation (EKR)

Electrochemical remediation or electrokinetic remediation (EKR) is an emerging technology that consists of the controlled application of a low-intensity direct current through the soil between electrodes. A direct current is imposed on the contaminated soil to extract contaminants by the combined mechanisms of electroosmosis, electromigration, and/or electrophoresis. During electroremediation, electrolysis reactions at the inert electrodes produce protons at the anode and hydroxyl ions at the cathode. As a consequence, large pH gradients are caused by the transport of the generated protons and hydroxyl ions [29].

EKR is an effective and flexible technology that is versatile enough to be applied to different soil textures with moisture ranging from unsaturated to saturated [20, 30, 31]. However, the technology's effectiveness may be diminished by the sorption of contaminants on soil particle surfaces and various effects induced by the hydrogen ions and hydroxide ions generated at the electrodes.

Like all the remediation techniques, EKR also has drawbacks, including the limited desorption of some contaminants from the matrices, making it necessary to apply e.g. an enhancing solution. To improve EKR removal efficiency, many studies have been conducted using, for example, surfactants, enhancement solutions, pH control, desorbing agents, and pulse and alternating currents to facilitate the mobility of contaminants and test different variables [32].

EKR has been applied to a wide variety of pollutants including organic, inorganic, and mixed contaminants. EKR showed high efficiency in removing heavy metals (e.g. chromium, cadmium, copper, uranium, mercury, and zinc) [33], PAHs [34], polychlorinated biphenyls [35], atrazine [36], molinate, and bentazone from soil [37]. Regarding metals, the acid environment promotes metal extraction/dissolution, keeping metals in solution as cations that migrate toward the cathode end under the effect of the electric field. On the other hand, organic pollutants are transported by electromigration, electroosmosis, and electrophoresis if the organic molecules are ionizable during EKR [29]. The different nature of both types of contaminants (inorganic and organic) and their possible interactions make it challenging to optimize the operating conditions for their simultaneous extraction and transport out of the matrix [20, 31, 38].

EKR technology can be flexibly applied to soil remediation using in situ or ex situ treatment schemes. To overcome the isolated technology drawbacks and enhance removal, the application of EKR alone or combined with other techniques such as Fenton, surfactants, or biotechnologies has been demonstrated to be effective in reducing hydrocarbons in soil [39–42]. The combination of EKR with bioremediation has been increasing over the years and demonstrates multiple advantages [42]. For example, using an alternating technology instead of simultaneous application has been shown to prevent competition between the isolated processes that would lower their efficiency in removing *n*-hexadecane from soil [43]. However, to the best of our knowledge, the effect of EKR coupled with bioremediation simulating in situ treatment aiming at removing hydrocarbons from ~~polar soils~~ was never studied. Hydrocarbon/oil remediation by EKR has been demonstrated, but studies have been focused primarily on ex situ bioremediation [25, 44–46]. Thus, treatment effectiveness in cold climate conditions and the development of strategies for in situ remediation in cold climates with limited environment disturbance is of great importance for the decontamination of oil spills.

8.2 Case Study

The present case study [47] examined the potential of EKR to stimulate biological degradation of oil pollution in soil in a simple setup with electrodes placed directly in the soil, applicable for in situ remediation strategies. Tests were done at two different temperatures resembling temperate and Arctic climates, and with three different current strategies: polarity-reversal at two different intervals and continuous application.

8.2.1 Description of the Site

The soil samples were collected in Sisimiut (66°56′ N, 53°40′ W), a town on the west coast of Greenland, approximately 75 km north of the Arctic Circle (Figure 8.1).

Figure 8.1 Map of Greenland, indicating the site where the soil was sampled.

This is the second-largest town in Greenland, with about 5230 inhabitants who use oil products for transport and heating buildings (www.qeqqata.gl).

The climate of polar regions is characterized by short, cold summers and extremely cold winters. Temperatures in Sisimiut range between −16 °C and 16 °C. The coldest months are January–March, with average maximum and minimum daily temperatures for the coldest day of –16 °C and –10 °C, respectively. The warmest months are July and August, with average daily low and high temperatures of 6 °C and 16 °C for the warmest day, respectively. The relative humidity ranges from 49% to 97% in a year, with the driest times in March and the most humidity around August (https://pt.weatherspark.com).

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8.2.2 Soil Sampling

The soil samples were taken at a Sisimiut dump site where barrels of waste oil are stored prior to incineration at the local waste incineration plant. Oil spills were visible (Figure 8.2). The soil was impacted as a result of leakage from an above-ground storage tank.

The soil under study was sampled from one of the identified spills in August 2017. During sampling, there was a strong odor of oil products, and free-phase oil was observed on the surface. The soil was dug up from a depth of 0 to 30 cm using a shovel and transported to Denmark in a polyethylene bucket. The EKR experiments took place at the Technical University of Denmark. In the laboratory, the soil was carefully homogenized by turning it continuously and removing larger particles such as stones, bricks, clinkers, and fibrous roots.

8.2.3 Electrokinetic Remediation (EKR) Experiments

Four strategies were tested at the laboratory scale: single bioremediation (Bio-control) performed as a control test; application of direct electric current to assess the influence of EKR as a combination of electrokinetic and biological (EKR-continuous); EKR with daily polarity reversal of the electric field (EKR-REP); and EKR with the current switched on/off every six hours (EKR-ON/OFF).

The influence of temperature was tested by comparing remediation at 6 °C and 22 °C (6 °C represented the summer temperature in the Arctic). The 6 °C

Figure 8.2 Soil sampling site.

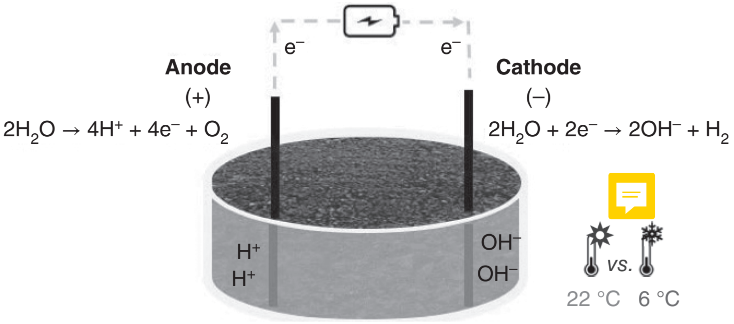

Figure 8.3 Experimental setup for EKR.

experiments were placed inside a refrigerator; 22 °C was the room temperature in the laboratory. The impact of the technology on soil properties was also assessed.

The experiments were carried out in a Plexiglas box (inner Ø = 8 cm; height = 4 cm) filled with 250 g of soil (Figure 8.3). The experiments lasted 14 days with an applied current intensity of 5 mA. The soil was initially weighed, and its moisture content was determined; to maintain an identical amount of water in the soil during EKR, the soil was weighed once a day in a digital balance, and deionized water was added if needed.

Mixed metal oxide (MMO) coated titanium electrodes 3 mm in diameter and 5 cm long (provided by FORCE® Technology, Denmark; Cathodic Protection) were used, and the power supply (Hewlett Packard E3612A) maintained constant direct current. The distance between the two electrodes in the EKR experiments was 4.5 cm.

8.2.4 Analytical Procedures

8.2.4.1 Soil Characterization

The studied soil was characterized in terms of oil content, phosphorus and metals, pH, conductivity, organic content, water content, and soil morphology. After EKR, the soil was divided in half – anode side and cathode side – and the same parameters were assessed.

- *General parameters*
  Dried soil (5.0 g) was agitated with KCl (1 M, 12.5 ml) for an hour, and pH was measured using a radiometric analytical electrode. For conductivity measurements, dried soil (10.0 g) was agitated with distilled water (25 ml) for an hour, and a radiometric analytical electrode was used. Organic matter was based on loss of ignition of dried soil (2.5 g) heated at 550 °C for an hour. Carbonate content was measured by treating dried soil (5.0 g) with HCl (3 M; 20 ml), and the developed CO_2 was measured volumetrically in a Scheibler apparatus calibrated with $CaCO_3$. Water content was calculated as weight loss at 105 °C for 24 hours.
  Laser and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) analysis was also carried out.

8.3 Determination of Metals and Phosphorus

The metals and major elements were measured after digestion: 20.0 ml (1:1) HNO_3 added in 1.0 g of dry soil were autoclaved (200 kPa, 120 °C for 30 minutes). Solid particles were subsequently removed by vacuum filtration through a 0.45 μm filter, and the liquid was diluted to 100 ml. The concentrations in the filtrate samples were analyzed with a Varian 720-ES inductively coupled plasma-optical emission spectrometer (ICP-OES). The digestion method is described in Danish Standard (DS) 259 [48].

- *TPH analysis*
  The soil samples were prepared with an internal standard consisting of three stock solutions with monobrobenzene, o-terphenyl, and squalan in pentane. The concentration was 10 000 mg l^{-1}. 1000 μl of each stock solution were added to a 100 ml volumetric flask filled with pentane. The concentrations of the internal standards were 100 mg l^{-1}.
  For oil extraction, 60 g of soil was shaken with 20 ml pentane in a 100 ml redcap glass; shaking stopped after a liquid suspension was reached (after about 30 s of handshaking). 20 ml of pentane with internal standard was added to the sample, and it was placed on a shaking table at 150 rpm for 24 hours. The organic phase was transferred into a vial from which further analyses were carried out. The oil content of the polluted soil was determined by gas chromatography using a flame ionization detector (GC-FID). Pentane controls and blinds were run randomly in the line sequence.
  The quantification of initial total petroleum hydrocarbons (TPH) in the range of C10–C40 was measured externally at a licensed laboratory following ISO/DIS 16703.

8.3.1 Results and Discussion

8.3.1.1 Soil Characteristics

The soil characteristics are summarized in Table 8.1. The soil has a sandy loam texture, ~~which allows good drainage;~~ a neutral pH (pH = 7.43); and both low buffer capacity (low content of carbonate, 1.9%) and organic matter (4.4%).

The phosphorus analysis did not show that the soil had a lack of nutrients. The concentration of metals found in the studied soil was below the limit values in soils in Denmark. Environmental quality criteria for oil compounds in soil specific to Greenland do not exist; instead, Danish environmental quality criteria values for health-related use of the soil were used as guidelines in this study. The soil sampled showed contamination of 69 500 ± 500 mg kg^{-1}, with 100 mg kg^{-1} being the quality criteria for soil in areas with very sensitive land use in Denmark [49].

In terms of the type of contamination, Figure 8.4 shows the chromatogram~~s~~ obtained ~~for~~ the soil extraction, from which it is possible to see that the soil contains low- to medium-molecular weight compound mixtures such as diesel fuel.

Table 8.1 Soil characteristics.

Characteristic	Value
pH	7.43 ± 0.02
Conductivity (μS cm^{-1})	574 ± 75
Carbonate (%)	1.9
Organic matter (%)	4.4 ± 0
Water content (%)	10
Grain size	(%)
Clay	4.40
Silt	47.4
Sand	48.2
Metals and elements	(mg kg^{-1})
P	760 ± 24
Pb	37 ± 5
Al	5410 ± 502
Cr	22 ± 1
Cu	43 ± 11
Zn	85 ± 19
Fe	12 702 ± 898
Oil	(mg kg^{-1})
THC	69 500 ± 500

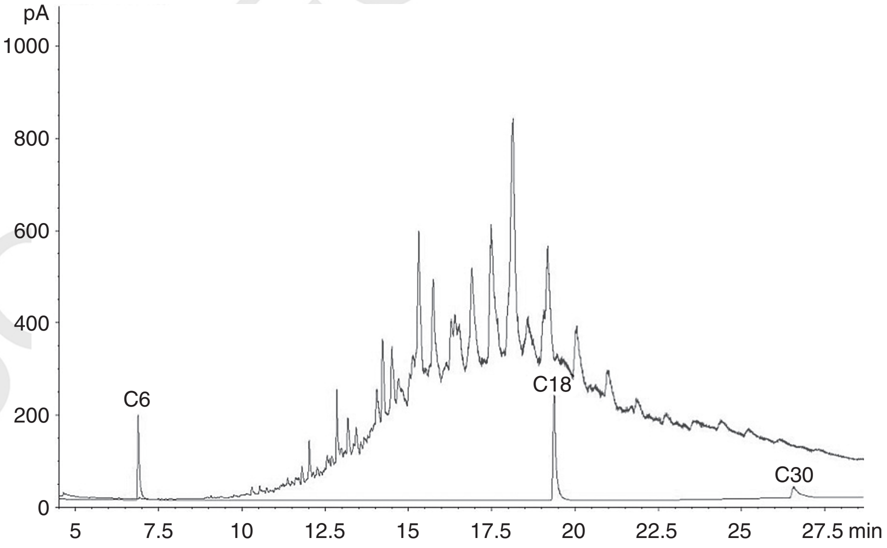

Figure 8.4 Chromatogram obtained from the initial soil extraction and internal standard (monobrobenzene, C6; o-terphenyl, C18, and squalan, C30).

8.3.1.2 EKR Experiments

- *General results*

  To minimize environmental disturbances, it is important to monitor soil characteristics after EKR. The parameters analyzed after the experiments are shown in Table 8.2. After applying a continuous electric field (EKR-continuous), due to the electrolysis of water, the pH became more acidic and alkaline at the anode and cathode side, with values of 6.9 and 10.9 pH, respectively. When the electrode polarization was changed (EKR-REP), it prevented soil acidification and alkalization due to the shifting fronts counteracting each other. For the EKR experiments where the current was switched on/off every six hours, the soil pH changed only on the anode side, possibly due to an oxidation reaction that generated H^+ faster than OH^- and/or precipitation of hydroxides.

  The initial voltage values were similar among the experiments and ranged from 17.2 to 23.2 V. Over time, voltage values fluctuated, and some high voltage levels were registered (up to 66.7 V), which can be explained by an increase in resistance in the soil matrix related to water evaporation. Even though the moisture content in the soil was controlled by adding deionized water, some water losses occurred during the day, which can explain the decrease in soil conductivity and consequent high voltages.

  Soil conductivity increased when a continuous current was applied (except on the cathode side under the cold temperature). This might be associated with a significant increase in proton and hydroxyl ions concentrations as a consequence of the electrolysis of water. When reversed electrode polarization was applied, conductivity did not increase because the acid and basic fronts were partially balanced. Similar results were shown by other authors, e.g. Barba et al. [50].

  Regarding organic content, no differences were found between controls (no applied electric current) and EKR experiments, suggesting that the current did not have any effect on organic matter degradation. The SEM analysis did not

Table 8.2 pH, conductivity, and organic content after EKR (bold values when pH > 8).

Temperature	Remediation strategy	Electrode charge	pH	Conductivity ($\mu S\ cm^{-1}$)	Organic content (%)
Room temperature	EKR-continuous	Anode	6.9	489	2.8
		Cathode	**10.9**	446	2.7
	EKR-REP	Anode	7.7	296	3.0
		Cathode	8.0	200	2.8
	EKR-ON/OFF	Anode	7.8	376	2.6
		Cathode	**10.8**	335	2.8
	Bio-control	*NA*	8.0	311	2.7
Cold	EKR-continuous	Anode	7.2	455	3.0
		Cathode	**10.8**	267	2.7
	Bio-control	*NA*	7.9	256	3.2

NA: not applicable

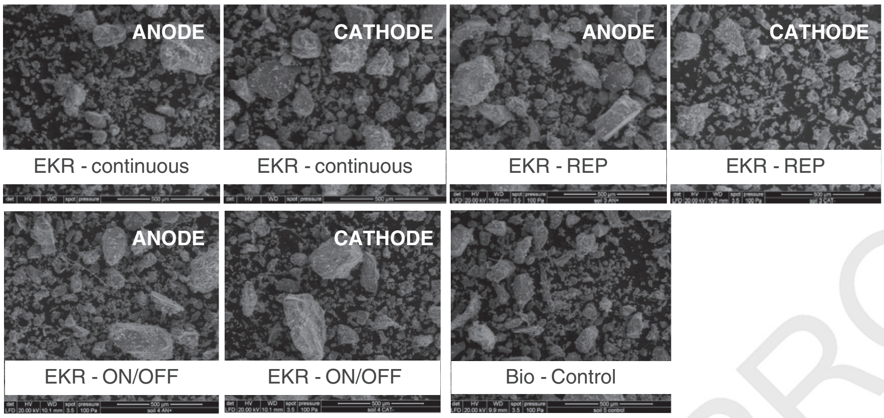

Figure 8.5 SEM analysis for the experimental soil after EKR on both the anode and cathode sides.

show any negative effect regarding physical characteristics when applying electric current (Figure 8.5).

- *Oil remediation*

  Overall reductions up to 78% were observed for TPH. Figure 8.6 shows the percentage of TPH left in the soil after experiments compared with the initial soil sample.

- *Bio-control* – without *electric current applied*

  Similar TPH removal (71 and 78%) was achieved at both temperatures, suggesting that the tested temperatures (6 °C and 22 °C) did not influence the remediation of oil degradation when current was not applied.

  Compared to the single bioremediation experiment (Bio-control) performed as a control with the initial TPH concentration, it is possible to attribute the loss of TPH to either bio or abiotic factors. Although the presence of indigenous cold-adapted microorganisms that persist in contaminated soils may have influenced oil degradation, hydrocarbon odors were noticed during the soil handling and experiments, suggesting that volatilization might also have played a significant role in TPH removal. Several studies reported that temperature directly affects the chemistry of oil as well as the physiology and diversity of microbial flora in the contaminated matrix [51]. However, the theory about the effect of temperature on microorganisms naturally present in soil is not linear. Some studies have demonstrated that hydrocarbon mineralization occurs in soils at low temperatures, but the rate and perhaps the extent of degradation are higher at elevated temperatures; thus, bioremediation levels are lower at cold temperatures [52, 53]. On the other hand, some studies showed that low temperatures did not influence the removal of hydrocarbons [54]. In the present study, even though no significant differences were found between controls at different temperatures, differences were found when electric current was applied.

- *EKR experiments*

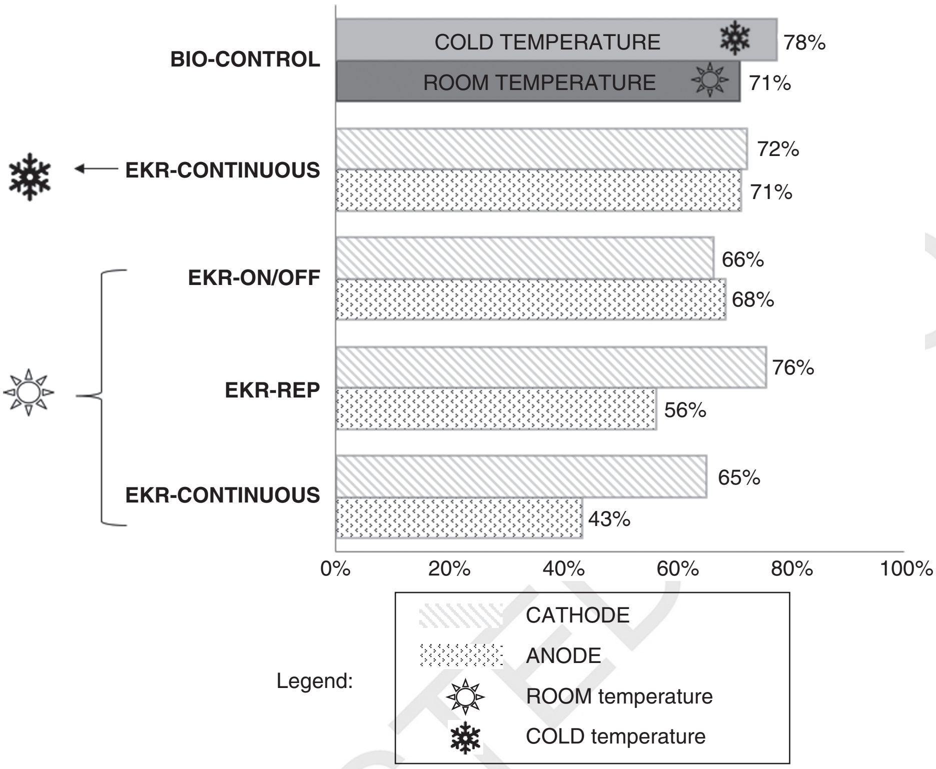

Figure 8.6 Removal of TPH from soil after 14 days of remediation.

Compared to the experiments where no electric current was applied, EKR did not improve oil remediation under the tested conditions (Figure 8.5). However, differences between EKR-continuous carried out at room and cold temperatures were detected, as well as when different electric current strategies were applied.

Among the EKR experiments, homogeneous TPH remediation was achieved when the EKR-ON/OFF current strategy was applied (68 and 66% at the anode and cathode, respectively). For EKR-continuous and EKR-REP, 20% of the difference was found between the anode and cathode sides in terms of TPH removal. The soil temperature was not measured during the experiments because low-intensity current (5 mA) was applied and no large changes in soil temperature were expected [55]. However, it is important to mention that the anode side in these experiments was clearly drier, and differences in the anode and cathode are probably attributed to electrical heating due to ohmic drops. The present results showed approximately 30% of the difference when comparing TPH removal at room and cold temperatures while applying a continuous current (43 vs. 71% at the anode at room and cold temperatures, respectively). Applying electrical current may produce excessive soil heating, which would lead to microbial inactivation [50, 56]. Temperature influences oxygen solubility, which decreases with increasing temperature and reduces the metabolic activity of aerobic microorganisms.

In EKR-REP, differences between the anode and cathode were also found, but heating phenomena are not expected to be the reason. The differences can be attributed to the electroosmotic flow, which decreased with the REP frequency, making the microbial distribution in soil not uniform [50]. Further studies should optimize the EKR-REP strategy, testing different periods of time. In the EKR-ON/OFF experiment, the effect of heating on the anode side was probably avoided by the current breaks. In addition, the off period has the advantage of less energy expenditure because the current is applied only half the time.

Keeping in mind the characteristics of the Arctic environment, the remediation technology developed must operate under challenging environmental conditions, be easy to operate, have low energy requirements, and have minimal impact on the environment. In addition, it is very important to keep the soil and experimental conditions such as pH and electrical conductivity within proper values for microbial life. When applying electric current, the conditions become more extreme around the electrodes as the experiment progresses, especially with respect to pH values. Negative impacts on microorganisms during EKR cannot be discarded and are most likely attributable to changes in pH rather than the influence of direct current. For example, the results in [57] showed the effect of soil pH on the degradation of PAHs, with a view to manipulating soil pH to enhance the bioremediation of PAHs. The author observed that soil at pH 7.5 was the most suitable for degrading PAHs, suggesting that changing pH using a liming process may be the most effective method to remediate soil contaminated with PAHs [57]. In this sense, the intensity and current strategy applied during soil remediation can be crucial for indigenous microorganisms. Thus, it is critical to control soil changes that may arise due to the application of electric current. One option to control soil pH is to use current strategies like EKR-REP and EKR-ON/OFF [58]. A study conducted by Ramírez et al. [56] showed that biological treatment was improved by the use of electrokinetic soil flushing, but only using the REP strategy. It is important to point out that the influence of applying an electric field on microbial communities is not completely explored yet, and the effect of the electric current is reported to have a limited effect [59] or even stimulate microbial activity [42, 50, 56, 60].

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REP contributed to decreasing the changes that the soil underwent as a consequence of the electrolysis of water because ~~they~~ ions are partially balanced in each polarity reversal. It is assumed that the EKR-REP strategy resulted in suitable conditions for biological processes, as it eliminates soil heating and extreme pH variation due to the acid and basic fronts. In addition, in theory, REP favors the homogenization of the system at a microscopic scale as it acts like a mixer that puts in contact pollutants, microorganisms, and nutrients [55, 56, 61]. Further optimization of EKR applied to oil-contaminated sites in cold regions is needed. Combined remediation between EKR-REP and EKR-ON/OFF could be a strategy to test together to optimize EKR: using less energy without changing soil characteristics or disturbing sites. Moreover, each remediation technology has advantages and limitations, and it is a challenge to find a universal method for oil-contaminated soil that can fulfill all the requirements [17]. Thus, further research on combined technologies (EKR + bioremediation) should also be pursued to optimize the effect of the current application on soil microorganisms in cold climate conditions.

8.4 Conclusions

- The effect of electric current was not observed in the tested conditions, with the experiments showing similar removal for EKR and controls. Removal under cold temperatures was achieved with differences between the anode and cathode sides, probably due to heating phenomena in the anode.
- When applying REP, no changes in soil pH were verified. Switching the current on/off seems to be a feasible practice, as both sides (anode and cathode) showed similar oil remediation.
- Further studies are needed to find a strategy to make te EKR more efficient, and the combination of EKR-ON/OFF and EKR-REP can be a promising remediation strategy.

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References

1 Singh, B.K. and Naidu, R. (2012). Cleaning contaminated environment: a growing challenge. *Biodegradation* 23 (6): 785–786.
2 EEA, European Environment Agency. 2007. http://www.eea.europa.eu
3 Ossai, I.C., Ahmed, A., Hassan, A., and Hamid, F.S. (2020). Remediation of soil and water contaminated with petroleum hydrocarbon: a review. *Environmental Technology and Innovation* 17: 100526.
4 Truskewycz, A., Gundry, T.D., Khudur, L.S. et al. (2019; 19;). Petroleum hydrocarbon contamination in terrestrial ecosystems - fate and microbial responses. *Molecules* 24 (18): 3400.
5 Logeshwaran, P., Megharaj, M., Chadalavada, S. et al. (2018). Petroleum hydrocarbons (PH) in groundwater aquifers: an overview of environmental

fate, toxicity, microbial degradation and risk-based remediation approaches. *Environmental Technology and Innovation* 10: 175–193.

6 Trellu, C., Mousset, E., Pechaud, Y. et al. (2016). Removal of hydrophobic organic pollutants from soil washing/flushing solutions: a critical review. *Journal of Hazardous Materials* 306: 149–174.

7 Arctic Monitoring and Assessment Program (AMAP). (2017). AMAP assessment report: Arctic pollution issues.

8 Weihe, P., Bjerregaard, P., Bonefeld-Jørgensen, E. et al. (2016). Overview of ongoing cohort and dietary studies in the Arctic. *International Journal of Circumpolar Health* 75: 1–12.

9 Dallaire, F., Dewailly, É., Muckle, G., and Ayotte, P. (2003). Time trends of persistent organic pollutants and heavy metals in umbilical cord blood of inuit infants born in Nunavik (Québec, Canada) between 1994 and 2001. *Environmental Health Perspectives* 111 (13): 1660–1664.

10 Abass, K., Emelyanova, A., and Rautio, A. (2018). Temporal trends of contaminants in Arctic human populations. *Environmental Science and Pollution Research* 25 (29): 28834–28850.

11 Andersen, M.S., Fuglei, E., König, M. et al. (2015). Levels and temporal trends of persistent organic pollutants (POPs) in arctic foxes (Vulpes lagopus) from Svalbard in relation to dietary habits and food availability. *The Science of the Total Environment* 511: 112–122.

12 Mohn, W.W. and Stewart, G.R. (2000). Limiting factors for hydrocarbon biodegradation at low temperature in Arctic soils. *Soil Biology and Biochemistry* 32 (8–9): 1161–1172.

13 Filler, D.M., Kennicutt, M.C., Snape, I. et al. (2015). Arctic and Antarctic spills. Cold regions spills. Part XI. In: *Handbook of Oil Spill Science and Technology*, 1e (ed. M. Fingas), 495–512. Wiley.

14 Jorgenson, J.C., Hoef, J.M.V., and Jorgenson, M.T. (2010). Long-term recovery patterns of arctic tundra after winter seismic exploration. *Ecological Applications* 20 (1): 205–221.

15 Schiewer, S. and Niemeyer, T. (2006). Soil heating and optimized nutrient addition for accelerating bioremediation in cold climates. *Polar Record* 42 (1): 23–31.

16 Fitzpatrick, E.A. (1998). Arctic soils and permafrost. In: *Ecology of Arctic Environments* (eds. S.J. Woodin and M. Marquiss). Oxford: Blackwell Science. AQ6

17 Lim, M.W., Lau, E.V., and Poh, P.E. (2016). A comprehensive guide of remediation technologies for oil contaminated soil — present works and future directions. *Marine Pollution Bulletin* 109 (1): 14–45.

18 Alegbeleye, O.O., Opeolu, B.O., and Jackson, V.A. (2017). Polycyclic aromatic hydrocarbons: a critical review of environmental occurrence and bioremediation. *Environmental Management* 60 (4): 758–783.

19 Ranc, B., Faure, P., Croze, V., and Simonnot, M.O. (2016). Selection of oxidant doses for in situ chemical oxidation of soils contaminated by polycyclic aromatic hydrocarbons (PAHs): a review. *Journal of Hazardous Materials* 312: 280–297.

20 Ricart, M.T., Pazos, M., Gouveia, S. et al. (2008). a. Removal of organic pollutants and heavy metals in soils by electrokinetic remediation. *Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances & Environmental Engineering* 43 (8): 871–875.

21 Reddy, K.R. (2013). Electrokinetic remediation of soils at complex contaminated sites: technology status, challenges, and opportunities. *Coupled Phenomena in Environmental Geotechnics*: 131–147.

22 Delille, D., Coulon, F., and Pelletier, E. (2004). Biostimulation of natural microbial assemblages in oil-amended vegetated and desert sub- Antarctic soils. *Microbial Ecology* 47 (4): 407–415.

23 Liu, H., Yao, J., Yuan, Z. et al. (2014). Isolation and characterization of crude-oil-degrading bacteria from oil-water mixture in Dagang oilfield, China. *International Biodeterioration and Biodegradation* 87: 52–59.

24 Bamforth, S.M. and Singleton, I. (2005). Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions. *Journal of Chemical Technology and Biotechnology* 80 (7): 723–736.

25 Couto, N., Fritt-Rasmussen, J., Jensen, P.E. et al. (2014). Suitability of oil bioremediation in an artic soil using surplus heating from an incineration facility. *Environmental Science and Pollution Research* 21 (9): 6221–6227.

26 Chang, W., Akbari, A., Snelgrove, J. et al. (2013). Biodegradation of petroleum hydrocarbons in contaminated clayey soils from a sub-arctic site: the role of aggregate size and microstructure. *Chemosphere* 91 (11): 1620–1626.

27 Naseri, M., Barabadi, A., and Barabady, J. (2014). Bioremediation treatment of hydrocarbon-contaminated Arctic soils: influencing parameters. *Environmental Science and Pollution Research* 21 (19): 11250–11265.

28 Fritt-Rasmussen, J. and Jensen, P.E. (2013). Remediation of oil-contaminated soil in Greenland. In: *ISCORD 2013*, 105–115. Anchorage, Alaska, United States: ASCE.

29 Acar, Y.B. and Alshawabkeh, A.N. (1993). Principles of electrokinetic remediation. *Environmental Science and Technology* 27: 2638–2647.

30 Cameselle, C. and Gouveia, S. (2013). *Advances in Electrokinetic Remediation for the Removal of Organic Contaminants in Soils*. IntechOpen.

31 Maturi, K., Reddy, K.R., and Cameselle, C. (2009). Surfactant-enhanced electrokinetic remediation of mixed contamination in low permeability soil. *Separation Science and Technology* 44: 2385–2409.

32 Moghadam, M.J., Moayedi, H., Sadeghi, M.M., and Hajiannia, A. (2016). A review of combinations of electrokinetic applications. *Environmental Geochemistry and Health* 38: 1217–1227.

33 Ottosen, L.M., Hansen, H.K., Laursen, S., and Villumsen, A. (1997). Electrodialytic remediation of soil polluted with copper from wood preservation industry. *Environmental Science and Technology* 31 (6): 1711–1715.

34 Lima, A.T., Ottosen, L.M., Heister, K., and Loch, J.P.G. (2012). Assessing PAH removal from clayey soil by means of electroosmosis and electrodialysis. *Science of the Total Environment* 435–436: 1–6.

35 Gomes, H.I., Dias-Ferreira, C., Ottosen, L.M., and Ribeiro, A.B. (2014). Electrodialytic remediation of polychlorinated biphenyls contaminated soil with iron nanoparticles and two different surfactants. *Journal of Colloid and Interface Science* 433: 189–195.

36 Ribeiro, A.B., Rodríguez-Maroto, J.M., Mateus, E.P., and Gomes, H. (2005). Removal of organic contaminants from soils by an electrokinetic process: the case of atrazine. Experimental and modeling. *Chemosphere* 59 (9): 1229–1239.

37 Ribeiro, A.B., Mateus, E.P., and Rodríguez-Maroto, J.M. (2011). Removal of organic contaminants from soils by an electrokinetic process: the case of molinate and bentazone. Experimental and modeling. *Separation and Purification Technology* 79 (2): 193–203.

38 Pedersen, K.B., Lejon, T., Jensen, P.E., and Ottosen, L.M. (2017). Simultaneous electrodialytic removal of PAH, PCB, TBT and heavy metals from sediments. *Journal of Environmental Management* 198: 192–202.

39 Pazos, M., Rosales, E., Alcántara, T. et al. (2010). Decontamination of soils containing PAHs by electroremediation: a review. *Journal of Hazardous Materials* 177 (1–3): 1–11.

40 Sandu, C., Popescu, M., Rosales, E. et al. (2016). Electrokinetic-Fenton technology for the remediation of hydrocarbons historically polluted sites. *Chemosphere* 156: 347–356.

41 Saichek, R.E. and Reddy, K.R. (2003). Effects of system variables on surfactant enhanced electrokinetic removal of polycyclic aromatic hydrocarbons from clayey soils. *Environmental Technology* 24 (4): 503–515.

42 Gill, R.T., Harbottle, M.J., Smith, J.W.N., and Thornton, S.F. (2014). Electrokinetic-enhanced bioremediation of organic contaminants: a review of processes and environmental applications. *Chemosphere* 107: 31–42.

43 Wang, S., Guo, S., Li, F. et al. (2016). Effect of alternating bioremediation and electrokinetics on the remediation of n-hexadecane-contaminated soil. *Scientific Reports* 6 (1): 1–13. p. 23833 https://www.nature.com/articles/srep23833.

44 Karppinen, E.M., Mamet, S.D., Stewart, K.J., and Siciliano, S.D. (2019). The charosphere promotes mineralization of 13 C-Phenanthrene by *Psychrotrophic* microorganisms in Greenland soils. *Journal of Environmental Quality* 48 (3): 559–567.

45 Cai, Z., Zhou, Q., Peng, S., and Li, K. (2010). Promoted biodegradation and microbiological effects of petroleum hydrocarbons by *Impatiens balsamina L.* with strong endurance. *Journal of Hazardous Materials* 183 (1–3): 731–737.

46 Pedersen, K.B., Lejon, T., Jensen, P.E., and Ottosen, L.M. (2016). Degradation of oil products in a soil from a Russian Barents hot-spot during electrodialytic remediation. *Springerplus* 5 (1): 168.

47 Ferreira, A.R. (2018). Electro-based technologies for contaminants removal from soil and effluent targeting further reuses. PhD thesis, NOVA School of Science and Technology, NOVA University of Lisbon, Portugal.

48 Danish Standards Foundation. (2003). Determination of metals in water, sludge and sediments - General guidelines for determination by atomic absorption spectrophotometry in flame. DS259.

49 Miljøstyrelsen (Danish EPA). (2015). Liste over kvalitetskriterier i relation til forurenet jord og kvalitetskriterier for drikkevand.

50 Barba, S., Villaseñor, J., Rodrigo, M.A., and Cañizares, P. (2017). Effect of the polarity reversal frequency in the electrokinetic-biological remediation of oxyfluorfen polluted soil. *Chemosphere* 177: 120–127.

51 Skupińska, K., Misiewicz, I., and Kasprzycka-Guttman, T. (2004). Polycyclic aromatic hydrocarbons: physicochemical properties, environmental appearance and impact on living organisms. Vol. 61. *Acta Poloniae Pharmaceutica. Drug Research* 61: 233–240.

52 Paudyna, K., Rutter, A., Kerry Rowe, R., and Poland, J.S. (2008). Remediation of hydrocarbon contaminated soils in the Canadian Arctic by landfarming. *Cold Regions Science and Technology* 53: 102–114.

53 Aislabie, J., Saul, D.J., and Foght, J.M. (2006). Bioremediation of hydrocarbon-contaminated polar soils. *Extremophiles* 10 (3): 171–179.

54 Sanscartier, D., Laing, T., Reimer, K., and Zeeb, B. (2009). Bioremediation of weathered petroleum hydrocarbon soil contamination in the Canadian high Arctic: laboratory and field studies. *Chemosphere* 77 (8): 1121–1126.

55 Mena, E., Villaseñor, J., Rodrigo, M.A., and Cañizares, P. (2016). Electrokinetic remediation of soil polluted with insoluble organics using biological permeable reactive barriers: effect of periodic polarity reversal and voltage gradient. *Chemical Engineering Journal* 299: 30–36.

56 Ramírez, E.M., Camacho, J.V., Rodrigo, M.A., and Cañizares, P. (2015). Combination of bioremediation and electrokinetics for the in-situ treatment of diesel polluted soil: a comparison of strategies. *The Science of the Total Environment* 533: 307–316.

57 Pawar, R.M. (2015). The effect of soil ph on bioremediation of polycyclic aromatic hydrocarbons (PAHS). *Journal of Bioremediation and Biodegradation* 6: 291.

58 Harbottle, M.J., Lear, G., Sills, G.C., and Thompson, I.P. (2009). Enhanced biodegradation of pentachlorophenol in unsaturated soil using reversed field electrokinetics. *Journal of Environmental Management* 90 (5): 1893–1900.

59 Mena, E., Villaseñor, J., Cañizares, P., and Rodrigo, M.A. (2016). Influence of electric field on the remediation of polluted soil using a biobarrier assisted electro-bioremediation process. *Electrochimica Acta* 190: 294–304.

60 Shi, L., Müller, S., Loffhagen, N. et al. (2008). Activity and viability of polycyclic aromatic hydrocarbon-degrading Sphingomonas sp. LB126 in a DC-electrical field typical for electrobioremediation measures. *Microbial Biotechnology* 1 (1): 53–61.

61 Huang, D., Xu, Q., Cheng, J. et al. (2012). Electrokinetic remediation and its combined technologies for removal of organic pollutants from contaminated soils. *International Journal of Electrochemical Science* 7 (5): 4528–4544.

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