

BRIEF SUMMARY

November 10th 2017

BRIEF SUMMARY

Electrokinetic remediation of soil and groundwater



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1.0 INTRODUCTION

This paper briefly presents results obtained by use of electrokinetic, EK, for remediation of organic contaminants in soil and sediments.

1.1 Background

The terms Electrokinetic remediation, Electrokinetics, or simply EK covers a number of remediation methods based on the utilization of a passing electric current in a body of soil

The pioneering field works, eventually leading to electrokinetics, took place during the first half of the 20th century. These works mainly focused on consolidation of soft clays through electroosmosis; i.e. partial drying of clay in-situ by removal of water in an electrical field, thereby increasing the carrying capacity of the soil.

In the eighties, a number of works aimed on remediating soil contaminated with radioactive elements and/or metals utilizing the electroosmotic moved water as a carrier of the contaminants. In some of cases, removal of organic compounds was observed as a side effect.

These side effects have been developed into the presently used methods of electrokinetic remediation of organic contaminant and thus the results presented in this paper.

1.2 Technical description

A basic electrokinetic remedial system consists of a number of electrodes surrounding the soil contamination in question, a special power supply, and connecting cables.

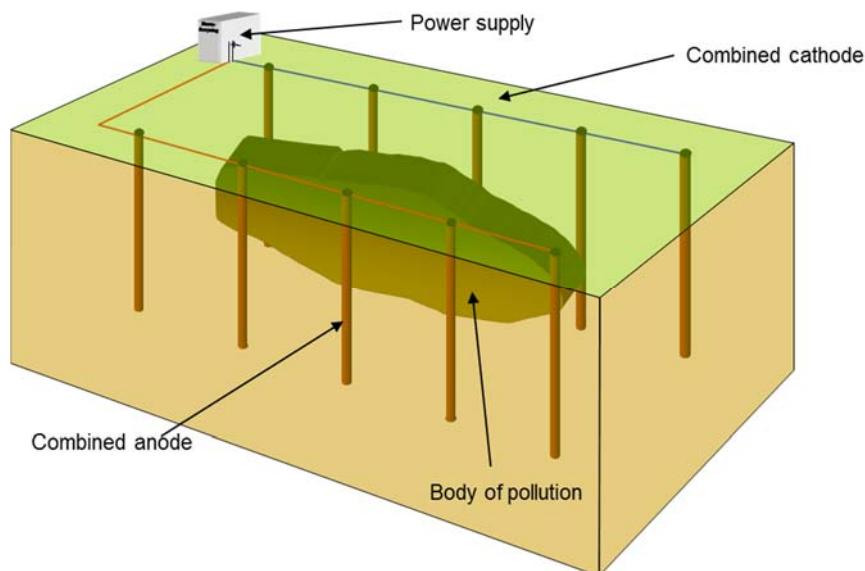


Figure 1: Basic EK-setup with distributed series connected electrodes typically used at sites up to 10 x 45 m.



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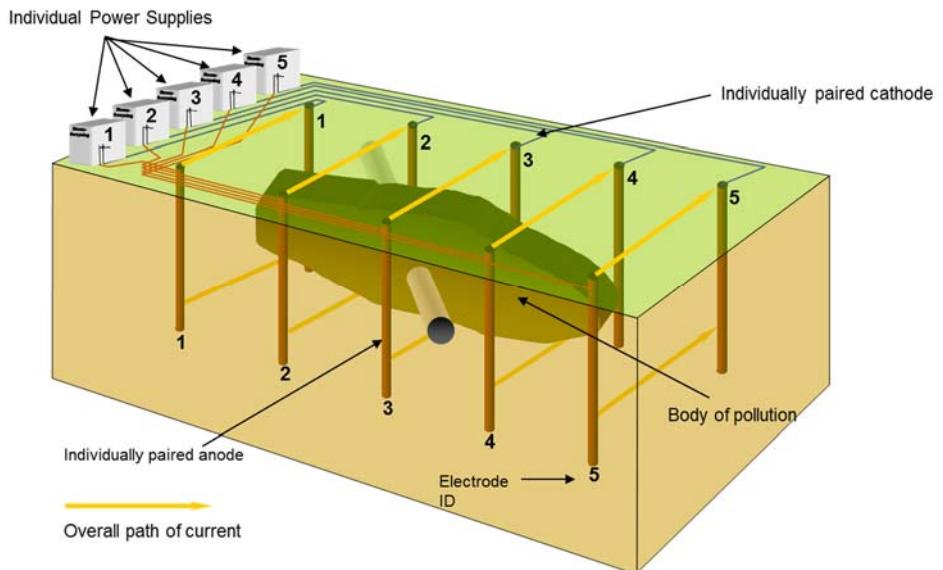


Figure 2: EK-setup with individually powered pairs of electrodes typically used at sites large areas and/or obstacles in the ground.

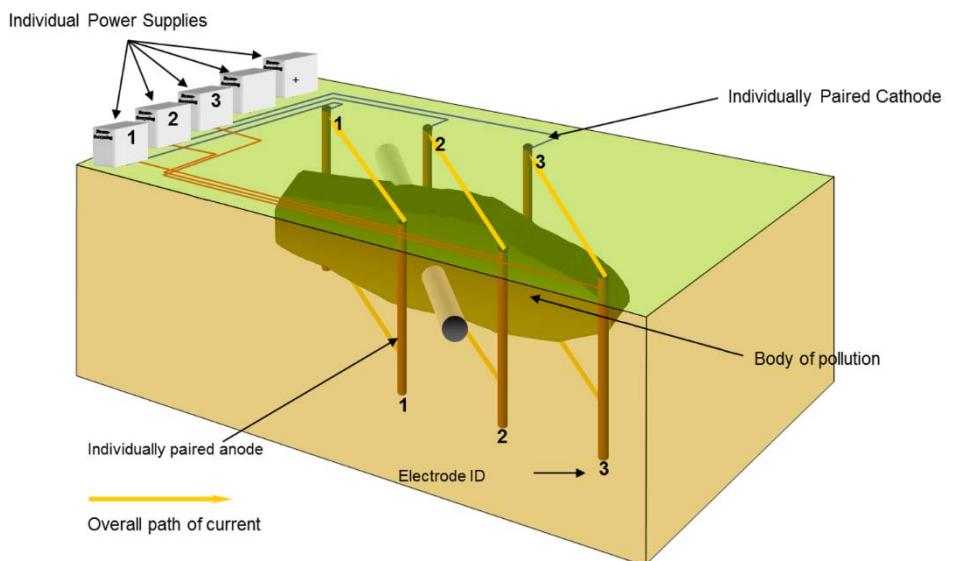


Figure 3: EK-setup modified from Figure 2 with only three but individually powered pairs of electrodes. The path of current is modified due to an obstacle in the ground.

EK works in all soils. The only requirement is that the water content does not fall below 3-5 % W/W. The fastest remediation rates are found in clayey soils below the groundwater table. During EK organic contaminants in both soil and groundwater are removed. No increased water solubility or increased groundwater concentrations have been observed.

There are no known limits to the depth of possible operation.

During remediation, a voltage of 6-10 V/m between electrodes is required



1.2.1 Duration of remediation

Remediation duration depends largely on the contaminants and the agreed target concentrations.

Contaminant decay follows a first order kinetic with $T_{1/2}$ ranging from a few weeks to 1½ year.

1.2.2 Power supply

One power supply typically delivers between 800 and 1.200 W with a working voltage of 6-12 V/m at 10 – 20 Ampere. The power supplies connect to 3 x 400 V from the main grid.

1.2.3 Energy consumption

Depending on properties of soil, groundwater and contaminants energy consumption ranges between three and five kWh per ton of soil treated. This applies to both remediation In-Situ and On-Site. Large amounts of soil On-Site requires less energy than small batches.

1.2.4 Activity restrictions during operation

At the cases presented in this summary, no restrictions were imposed on any activity taking place at the sites.



2.0 IN-SITU EK REMEDIATION CASES

2.1 Case 1: Remediation of gasoil release partly under buildings

An erroneous installed oil pipe returning unused oil from an oil-heated industrial stove caused a release of ca. 3.5 m^3 of gasoil contaminating an area of 250 m^2 to a depth of 2,5 m.b.g. Groundwater was situated 1,5 - 2 m.b.g in a clayey till.

All together two m^3 of oil was removed by excavation of the oil tank and connected pipelines and by a temporary pump and treat system operating for a year.

Complete removal by excavation was hindered by the fact that the contamination partly was situated under parts of buildings housing boiler room, kitchen and bathrooms.

An EK-remediation system comprising three pairs of electrodes were installed 15 months after the spill.

The remediation was monitored by quarterly soil sampling at four sampling areas situated around the four sites with the highest concentrations identified during initial site assessments.

End documentation consisted of 24 evenly distributed soil samples. A maximum of 39 mg TPH/kg was identified.

The EK remediation was performed without any restrictions on site activities.

Heating pipes running through the remediated area was electrically insulated in order to prevent corrosion and unwanted diversion of the current.

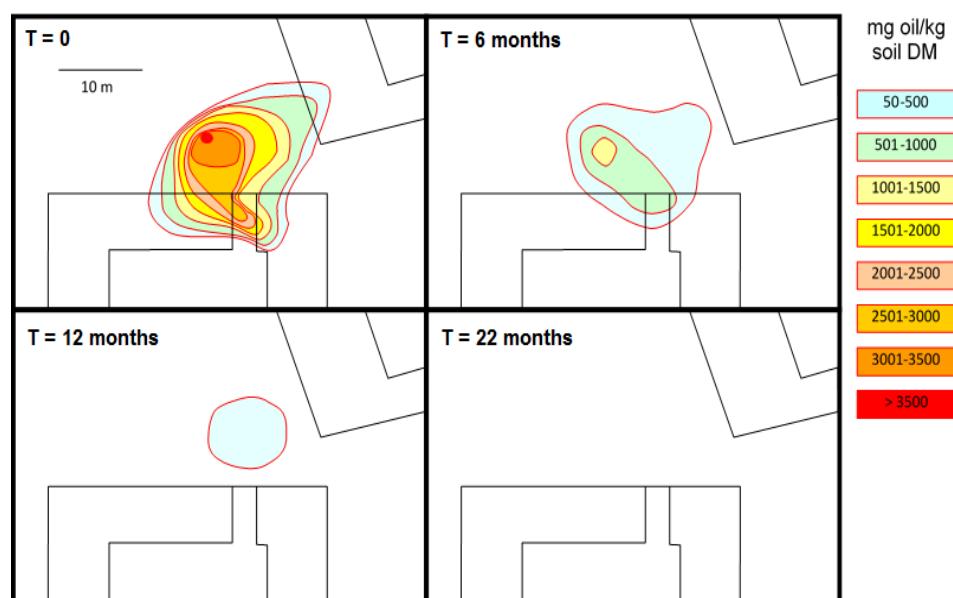


Figure 4: Spatial development of oil concentrations during EK remediation



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Over a period of two years, concentrations decreased from an average of 2.172 to 23 mg TPH/kg. $T\frac{1}{2}$ for TPH was 99 days.

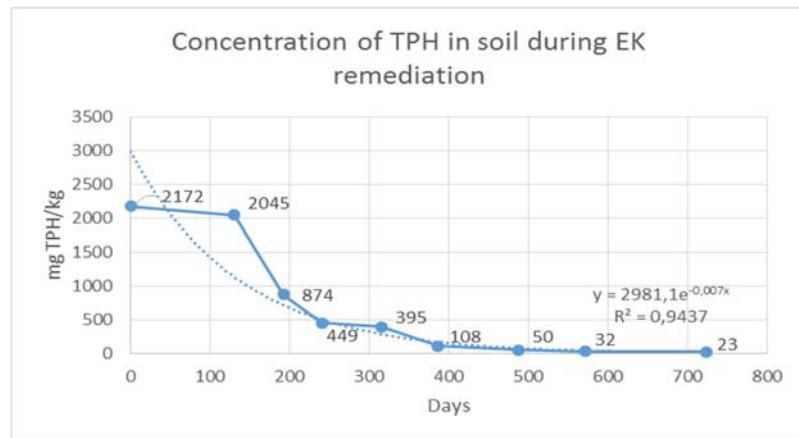


Figure 5: Development in oil concentrations during EK remediation

2.2 Case 2: Indoor climate abatement of petroleum vapours

A spill of 900 litres of petroleum at a small farm in the southern part of Jutland caused highly elevated indoor petroleum vapour concentrations.

Within weeks of the spill, an excavation removed most product. However, the remaining product situated under the farmhouse caused indoor petroleum vapour concentrations exceeding Danish EPA quality criteria more than 100 times.

In order to abate indoor petroleum vapours installation of an EK system comprising two sets of electrodes took place a year later

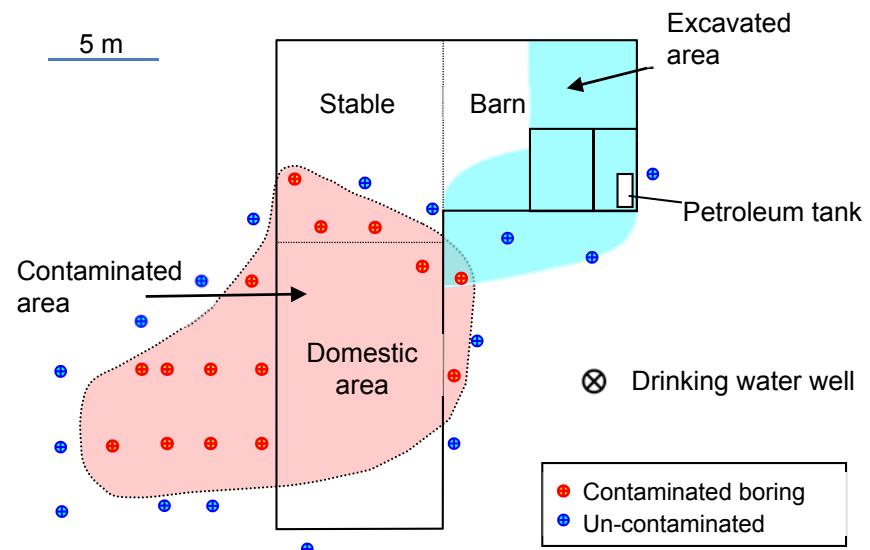


Figure 6: Situation plan over indoor petroleum vapour EK abatement



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The local lithology consisted of firm moraine clay with bands of sandy clay. During remediation the groundwater table was situated at 1-1,5 m.b.g. but varied more than a metre over the year.

Due to insurance coverage limitations, no soil- or groundwater samples were collected during the project

Over a period of 9 months soil vapour concentrations were lowered from ca. 540 mg TPH/m³ to 56 µg TPH/m³. T_½ for soil vapour TPH was 20 days and ca. 1 day for BTEX.

The abatement was performed without any restrictions on site activities.

Compound	Day 0 Soil vapour concentration	Day 130 Calculated indoor concentration	Day 260 Calculated indoor concentration	Calculated indoor concentration	Soil vapour concentration	T _½ Days
TPH ³	540.500	3980 / 40 x	1200	88 / -	56	1 20
Benzene	1550	12,4 / 99 X	0,4	0,003 / -	0,05	1 1
Toluene	4650	36,7 / -	4,3	0,03 / -	1,08	1 1
Ethylbenzene	2615	20 / -	3	0,02 / -	0,45	1 1
m- and p-xylene	2100		9,4		0,45	1 1
o-xylene	1070	24 / - ²	11,3	0,2 / - ²	0,45	1,2 1

All values are in µg/m³

1: Marks that the soil vapour concentrations do not exceed Danish EPA quality criteria for indoor air, why calculations are not made.

2: Calculations are based on the sum of o, m, and p-xylenes.

3: TPH contribution to the indoor climate is estimated by use of n-Dodecane as model compound.

Figure 7: Soil vapour concentrations development during EK abatement

2.3 Case 3: Harbour sediment

Vordingborg Harbour authorities ordered a pilot EK remediation system in order to evaluate remediation/disposal of harbour sediment.

As is the case with most harbour sediments the sediment contained elevated concentrations of petroleum hydrocarbons, polyaromatic hydrocarbons, heavy metals and organotin compounds.

Organotin compounds in general and tributyltin in particular were of concern due to high aquatic toxicity and high persistence.

Installation of an In-Situ EK plant took place during spring. The operation planned was for six months.



In order to prevent movement of sediment in and out of the 6 x 9 metres test area it was sheet piled with 10 mm HDPE plates in a wooden frame.



Figure 8: EK pilot test area in Vordingborg Harbour during remediation.

The electrodes were connected to a power supply placed on land.

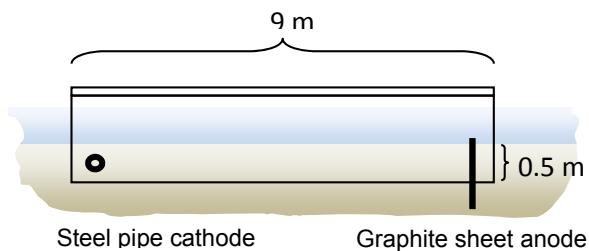


Figure 9: Installation of electrodes in harbour sediment

TBT concentrations were monitored 10 times during 6 months of test. Each monitoring round consisted of 2 pooled subsamples from the whole of the test area to a depth of 0,5 meters below bottom surface.

Local fishermen followed the project with great interest and enthusiasm even placing an inflatable dolphin at the basin.



2.3.1 Organotin compounds

Organotin in the form of tributyltin, TBT, has been used widely as an antifouling agent in ship paint. It degrades slowly, is toxic, and accumulates in sediments.

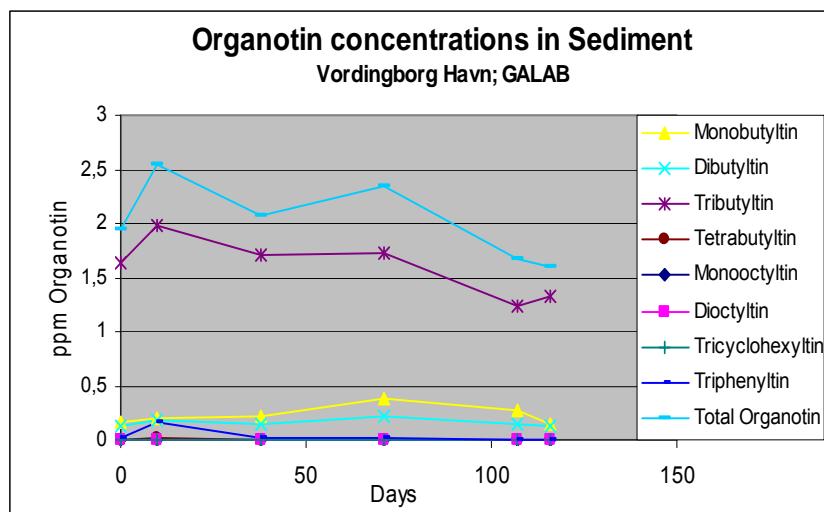


Figure 10: Organotin concentrations in sediment during EK remediation

Organotin concentrations decreased ca. 20 % during remediation corresponding to a $T_{\frac{1}{2}}$ of 230 days.

Also TPH, PAH and metals were followed during the test.

2.3.2 TPH

TPH decreased from a maximum on 1900 to 550 mg/kg during test. The breakdown pattern was similar to what is seen in soil on land.

2.3.3 PAH

Decrease in PAH concentrations during test were limited and in the same order of magnitude as seen in soil, with $T_{\frac{1}{2}}$ on ca 2,5 – 3 years.

2.3.4 Metals

As was to be expected, metals concentrations remained almost stable during the test period.

3.0 ON-SITE EK REMEDIATION

Electrokinetic On-Site remediation of hydrocarbons impacted soils was used extensively for more than a decade.

Due to falling prices on disposal of contaminated soil the last 10 years and steeply decreasing amounts of heavily contaminated soil, On-Site EK remediation has fallen out of favour.

The results presented below represent all 65 parties of soil treated on the plant depicted on Figure 11 and Figure 12. The combined tonnage was ca.137,000 tons.



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Figure 11: EK remediation plant during first loading. Each bay measuring 10 x 30 x 3 metres has a capacity of 2.000 tons



Figure 12: The same EK plant as pictured above after extension to a total of 18 bays and 2 years operation. In addition, the soil heaps outside the bays are treated by EK.

The results obtained showed that TPH and chlorinated solvents are easily treated while treatment of PAH is only viable for higher concentrations. Metals are not affected in any systematic way. Results are summarized in Figure 13.



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Compound	Avg. start concentration. ppm	Avg. Final conc: ppm	% effect	k, d ⁻¹	T½: days	Removal mg/kg	Total removal kg
C5-C10	17 (0-275)	0,21	99	0.00710	98	16	2257
C10-C25	297 (69-1,555)	57	81	0.00266	260	240	32967
C25-C35	208 (0-1,130)	83	60	0.00147	470	124	17071
TPH	512.5 (109-1.875)	138	73	0.00211	328	374	51327
Sum PAH	5.406 (0-55)	3.36	38	0.00077	900	2,1	281
B(a)P	0.974 (0-8.4)	0.66	32	0.00063	1102	0,3	43
D(a,h)A	0.163 (0-1.7)	0.11	33	0.00064	1083	0,1	7
Cd	0,3	0.31	0	-0.000006	-125145	0,0	0
Cr	13	14	-11	-0.00017	-4172	-1.4	-193
Cu	36	39	-7	-0.00012	-6022	-2.7	-369
Ni	10	12	-23	-0.00034	-2060	-2.33	-320
Pb	53	44	16	0.00028	2489	8	1148
Zn	108	103	5	0.00008	9003	5	688
Tonnage; 137248,7 tons (300 – 14,665)		Avg. treatment time: 619 days (108 -1,655)			Number of batches: 62 Energy consumption: < 3,5 kWh/ton		

Figure 13: Results from the total amount of soil treated over ca. 8 years at the plant.

3.1.1 TPH

The results shows that the degradation follows first order kinetics as seen in Figure 5. As with remediations In-Situ degradations rates are higher the lighter the average molecular size T½ ranging from ca. 100 days for C₆-C₁₀ to 470 days for C₂₅-C₃₅.

3.1.2 PAH

Decrease in PAH concentrations were similar to results from In-Situ operations with T½ on ca. 2,5 – 3 years.

3.1.3 Metals

Metals concentrations were not affected in any systematic way.

3.1.4 Chlorinated solvents

Only a few thousand tons of soil impacted with chlorinated solvents were treated. The results were good with T½ on ca. 100 days and average total concentrations around 0,1 mg/kg.

3.1.5 General observations

Routine monitoring of storm water from the EK-plant did not reveal increases in contents of TPH, PAH or metals during the operational period compared to before and after.

During periods of drought watering of the soil around anodes were done in order to maintain effective contact between electrode and soil body.

During initial situation of the site, EK-remediation in this set up was found not to work under overhead high power, 400 kV, electrical cables due to electromagnetic interference. A distance of 100 – 150 m is required.



3.2 Pharmaceuticals impacted groundwater.

A test was performed on 600 litres of groundwater extracted from Kjærgaard Klitplantage. 50 years ago, the site was used for underground disposal of fluid waste from a chemical/pharmaceutical plant.

The site contains high concentrations of mercury, pharmaceuticals, BTEX, and phenols.

The test ran over 24 hours in a tank. The total energy consumption was ca. two kWh and 250 grams of hydrogen peroxide. Results are presented below in Table 1.

3.2.1 1.1.1 TPH

Hydrocarbon degradation rates, including those of BTEX, BTEX range from 79 to 98 %. It is once more seen, that lighter components are removed faster than heavier compounds. Also, BTEX is degraded faster than TPH.

3.2.2 1.1.2 Phenols

Phenol degradation rates range from 82 to 100 %. It is once more seen, that lighter components are removed faster than heavier compounds.

3.2.3 1.1.3 Barbiturates

Degradation rates of barbiturates, a group of tranquilizers now mostly out-phased, are relatively slow and some seems to form as degradation products from other. Degradations rates are up to 50 %.

3.2.4 1.1.4 Sulphonamides

Degradation rates for sulphonamides, a group of antibiotics, ranges from – 10 to 100 %. The negative degradation rate indicates formation of degradation products from other.

3.2.5 1.1.5 Chlorinated solvents

Chlorinated solvents are almost completely degraded with 98 % removal.



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Compound	Start	24 hours	% removal	Amount removed	Unit
Benzene	4400	70	98	4330	µg/l
Toluene	5000	99	98	4901	µg/l
Ethylbenzene	7,9	0,88	89	7	µg/l
m+p-xylene	31	1,4	95	30	µg/l
o-xylene	110	5,4	95	105	µg/l
C ₆ H ₆ -C ₁₀	11000	340	97	10660	µg/l
>C ₁₀ -C ₂₅	1000	210	79	790	µg/l
Total Hydrocarbons	12000	540	96	11460	µg/l
Phenol	1700	140	92	1560	µg/l
2 Methylphenol	2,4	0	100	2	µg/l
2,4 Dimethylphenol	3,1	0	100	3	µg/l
2,5 Dimethylphenol	3,8	0,49	87	3	µg/l
2,6 Dimethylphenol	2,6	0,47	82	2	µg/l
3 Methylphenol	4,3	0	100	4	µg/l
3,4 Dimethylphenol	62	2	97	60	µg/l
3,5 Dimethylphenol	78	0,37	100	78	µg/l
4 Methylphenol	34	0,58	98	33	µg/l
Amobarbital	1200	600	50	600	µg/l
Barbital	2100	1700	19	400	µg/l
Butabarbital	260	190	27	70	µg/l
Pentobarbital	570	340	40	230	µg/l
Secobarbital	3	4	-33	-1	µg/l
Dapson	0	0,002	-	-0,002	mg/l
Sulfaguanidine	4,2	4,6	-10	-0,400	mg/l
Sulfanilamid	48	25	48	23	mg/l
Sulfanilacid	200	96	52	104	mg/l
Sulphadiazin	8,5	0,046	99	8,454	mg/l
Sulphamerazin	0,22	0,003	99	0,217	mg/l
Sulphamethazin	14	0,9	94	13,1	mg/l
Sulphamethiazol	0,91	0,08	91	0,83	mg/l
Sulphathiazol	3,9	0,011	100	3,889	mg/l
Tetrachloroethylene	160	2,9	98	157	µg/l
Trichloroethylene	1200	21	98	1179	µg/l

Table 1: Results from a 24-hour EK / H₂O₂ treatment of pharmaceuticals impacted groundwater.



4.0 CONCLUSION

EK has proven to be a viable technology able to remediate a wide range of soils, sediments and groundwater for an even wider range of contaminants.

There are few limitations to where the process works.

EK requires little energy and has a low environmental impact. It has a very limited influence on site activities and requires only little space for power supplies.

A typical period of remediation of gas oil and heavier petroleum hydrocarbons is one to three years.

Lighter aliphatic components, BTEX, phenols and chlorinated solvents react faster to treatment.



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