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Evaluation of quicklime mixing for the remediation of petroleum contaminated soils

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Abstract

Quicklime mixing is an established solidification/stabilization technique to improve mechanical properties and immobilise contaminants in soils. This study examined the effects of quicklime mixing on the concentrations and leachability of petroleum hydrocarbon compounds, in two natural soils and on a number of artificial sand/kaolinite mixtures. Several independent variables, such as clay content, moisture content and quicklime content were considered in the study. After mixing the soils with the quicklime, pH, temperature, moisture content, Atterberg limits and concentrations of petroleum hydrocarbon compounds were determined on soil and leachate samples extracted from the treated soils. Significant decreases in concentrations of petroleum hydrocarbon compounds were measured in soils and leachates upon quicklime mixing, which may be explained by a number of mechanisms such as volatilization, degradation and encapsulation of the hydrocarbon compounds promoted by the quicklime mixing.

The increase in temperature due to the exothermic hydration reaction of quicklime when in contact with porewater helps to volatilize the light compounds but may not be entirely responsible for their concentration decreases and for the decrease of heavy aliphatics and aromatics concentrations.

Keywords: Remediation; Solidification; Stabilization; Quicklime; Clay; Petroleum; Hydrocarbons

1. Introduction

The recent implementation of the Landfill Directive (Council Directive 1999/31/EEC) in the UK has substantially increased the costs for disposal of contaminated soils. On-site remediation or pre-treatment prior to disposal may offer a more viable and economical alternative to direct disposal of contaminated soil.

Solidification/stabilization with addition of cement-based binders is an established treatment technology for soils contaminated with inorganic compounds [1] whereas a relatively limited experience exists for its applications to organic compounds, in particular petroleum hydrocarbons.

The mixing of contaminated soils with calcium oxide (quicklime) promotes a number of reactions in the soil/porewater including flocculation, ion exchange, lime carbonation, dissolution of clay minerals and pozzolanic reactions [2–8]. A cation linking mechanism, in which Ca ions link clay particles through their negative edges, or binding of the clay particles by the silicate hydrates gels produced by the pozzolanic reactions may result in formation of clay macroaggregates [9,6,10]. The macropores of these aggregates may encapsulate large volumes of porewater.

The hydration reaction of lime in the porewater is highly exothermic and generates significant amounts of heat energy, which results in evaporation of porewater and drying of soil [11].

As a result of the above reactions, lime mixing, brings about significant time-dependent changes in soil physico-chemical properties such as pH, cation exchange capacity [8,12,13] specific surface area [5] and Atterberg limits [9,14,15].

The effects of the above reactions may be useful to remediate soils contaminated with organic compounds such as petroleum hydrocarbons, whereby the more volatile compounds may be removed from the soils primarily by volatilization during the CaO exothermic reaction and the less mobile compounds may

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be immobilised by encapsulation in the clay/pozzolanic products aggregates. Furthermore, introduction of oxygen into the soil together with the heat generated during the quicklime mixing may lead to destruction of the hydrocarbon compounds [16]. Therefore, the mixing of soils contaminated with petroleum hydrocarbons with quicklime appears to be a promising remediation as well as pre-disposal treatment technique for soils contaminated with organic compounds.

A relatively limited number of studies exist in the literature, to the authors' knowledge, about quicklime remediation of soils contaminated with organic compounds. A laboratory study on the treatment of PCB contaminated soils with calcium oxide has been carried out by USEPA [17]. Temperatures of 180–200 °C were measured in the soils after mixing them with quicklime. PCB removal was mostly attributed to dusting, vaporization and steam stripping and about 7% of removal attributed to chemical dechlorination and destruction. Marion and Payne [18] and Marion et al. [19] evaluated the mixing of quicklime for remediating soils contaminated with pesticides and petroleum hydrocarbons. The soils were mixed with quicklime in large on-site treatment units. The quicklime was pre-treated using natural fatty acid to make it hydrophobic and oleophilic. The authors observed a major decrease in the concentration of many hydrocarbons. They explained the removal of volatile BTEX constituents as due to volatilization and that of higher molecular weight constituents as the result of encapsulation in a $Ca(OH)_2$ matrix. Dean [20] mixed quicklime to treat about 10,000 cubic yards of deep clayey soils. Trichloroethene and 1,1,1-trichloroethane soil concentrations were reduced to below the leachability soil cleanup target levels.

The aim of the present study was to assess the feasibility of quicklime mixing as a viable technique to remediate soils contaminated with low and high levels of petroleum hydrocarbon compounds and identify the different mechanisms responsible for reducing the concentration and the leachability of the compounds in soils. The study examined the effects of quicklime mixing on the concentrations of petroleum hydrocarbon compounds in two natural soils and a number of artificial sand/kaolinite mixtures. Several independent variables, such as clay content, mixing moisture content and quicklime content were considered in the study.

2. Materials and methods

2.1. Materials

Natural samples of a clayey sandy silt of the London clay formation from Hampshire, UK and a clay of the Lower Coal Measures from Sheffield, UK and a number of artificial mixtures of sand and kaolinite were used in the experiments.

The silt and clay samples were taken from trial pits in disused petrol filling station sites. Due to the previous use of the sites, the soils were contaminated with petroleum hydrocarbon compounds. Composition, moisture content and Atterberg limits were determined on a number of soil samples from the sites. The composition of the silt samples was approximately 45% sand, 35% silt and 20% clay. The silt had moisture contents ranging between 36% and 27%, liquid limits between 43% and 61% and plastic limits between 22% and 17%.

The composition of the clay sample was approximately 25% sand, 35% silt and 40% clay. The clay had moisture content of 32%, liquid limit of 57% and plastic limit of 27%.

Dry blasting silica sand (Goonvean Ltd.) with size in the range 212–600 μm and kaolinite (Opal Alpha, Goonvean Ltd.) were used in this study to prepare a number of artificial mixtures. The mineralogical composition of the kaolinite reported by the manufacturer was: 82% Kaolin, 12% Mica, 3% Feldspar, 1% Quartz and 2% Smectite. The kaolinite had a reported specific surface area of $10\,m^2/g$. Liquid limit and plastic limit of the kaolinite were determined in the laboratory. Liquid limit was determined to be 60% and plastic limit 34%. Commercially available gasoline and diesel fuel were used to contaminate the sand/kaolinite mixtures. The quicklime (Limbase 60, Buxton Lime Industries Limited) contained >90% calcium oxide and small quantities of calcium carbonate, magnesia and trace elements. Quicklime was stored in a sealed plastic container at room temperature.

2.2. Methods

The experimental work on the clay and sand/kaolinite samples was carried out in the laboratories of the Department of Earth Science and Engineering of Imperial College. The work on the silt sample was carried out in the field. Chemical analyses were carried out by ALcontrol Geochem (Chester, UK), a UKAS accredited commercial laboratory.

Moisture content, liquid and plastic limit of soils were determined using the BS1377:1990 Part 2(3), 2(4.3) and 2(5) methods [21–23], respectively. Moisture contents were determined on duplicate samples. The pH measurements were carried out with a Willheim WTW 315i pH meter provided with a SenTix 41electrode. The soil pH was determined on slurry samples made of 2/1 water to soil weight ratio using a procedure adapted from Head [24] and BS1377:1990 Part 3 [25] The pH meter was routinely calibrated using the two-point calibration with pH 7 and 10 standard buffers. Temperatures were measured by inserting a thermometer (HANNA-EITH WP) into the soil samples. Soil samples were placed in standard sealed glass jars and sent inside coolboxes with ice packs to Alcontrol Geochem Laboratory for the chemical analyses immediately after mixing. Only the samples of silt were retained for 2 days before being sent to the lab. The samples received by the laboratory were stored in temperature-controlled room at 4 °C and tested within 24 h from receipt. Total petroleum hydrocarbon working group compounds (TPH) and 16 speciated polynuclear aromatic hydrocarbon (PAH) analyses were carried out. TPH as measured according to the Total Petroleum Hydrocarbon Working Group is split between aliphatic and aromatic hydrocarbon species and banded by carbon number. The aliphatic hydrocarbons generally have lower volatility than the aromatic hydrocarbons and require the use of an extraction method to prepare for analysis. The aromatic range compounds, are typically found in gasoline and are extracted by using a volatilization method. The gasoline range hydrocarbons (GRO) (C4–C10), including benzene, toluene, ethylbenzene, xylenes (BTEX) and MTBE, concentrations were determined by gas chromatography–flame ionisation detection using a method based on US EPA Methods 8021b & 602 [26,27]; the Extractable Petroleum Hydrocarbon (EPH) (C10–C40) concentrations by gas chromatography–flame ionisation detection Massachusetts Department of Environmental Protection, 1998 Method [28]; the PAH by gas chromatography–mass spectrometry US EPA Method 8100 [29]. EPHs and PAHs were extracted using accelerated solvent extraction system (ASE) followed by solvent reduction using a Zymark Turbovap. The soluble organics were extracted from the soil sample using hexane as the solvent. Leachates were extracted from soil samples using the DIN 34 414 Part 4 1984 [30] Method. The soil samples were agitated in a slurry state (water to solid ratio 10:1) for 24 h inside new sterilized glass vessels with PTFE lids were used. Distilled water saturated with CO_2 and with a pH of 5.6 was used to prepare the slurry samples. The slurry samples were filtered and centrifuged and the extract water submitted for further analyses. Glass fiber filters (Whatman 1.6 μm) and centrifuge glass vials with PTFE lids were used to minimise adsorption of hydrocarbons. All vials and vessels were discarded after use.

The QA/QC procedures for this study consisted of the standard Alcontrol laboratories QA/QC procedures, that is one reagent-blank leachate sample is analysed for every 20 leachate samples, one certificate reference material tests and one reagent-blank test are analysed for every 20 soil samples. In addition Arcadis GMI included a duplicate for the clay sample mixed with 15% quicklime.

2.3. Preparation of samples

2.3.1. Natural soil samples

Experiments were carried out on the silt and clay samples using different quicklime contents. The silt samples were tested at moisture contents equal to and twice the natural moisture content. A summary of the samples used in the experiments is presented in Tables 1a and 1b. Two samples of contaminated silt ($LC1_0$ and $LC2_0$), approximately 1 kg each, were initially thoroughly mixed and homogenised at their natural moisture contents using a steel rod into a 250 ml polyethylene plastic tub. Quicklime was then added at once and mixed for about 60 min using a stainless steel spatula. The amount of quicklime used corresponded to 5% (samples $LC1_5$, $LC1_{5\text{-w64}}$, $LC2_5$ and $LC2_{5\text{-w64}}$), 10% (sample $LC2_{10}$) and 20% ($LC2_{20}$) on a dry weight percentage basis (w/w). Two samples with higher moisture content ($LC1_{5\text{-w64}}$ and $LC2_{5\text{-w64}}$) were prepared by adding tap water after the lime had been added to the soil and the samples had been mixed for few minutes. The samples were sent to the laboratory immediately after the quicklime mixing; the chemical analyses were carried out within 72 h from mixing.

Table 1a
Silt samples

Sample	w (%)	CaO (%)	pH
$LC1_0$	32	0	7.71
$LC1_5$	32	5^*	11.37
$LC1_{5\text{-w64}}$	64^*	5^*	11.51
$LC2_0$	32	0	7.75
$LC2_5$	32	5^*	11.35
$LC2_{10}$	32	10^*	11.67
$LC2_{20}$	32	20^*	12.72
$LC2_{5\text{-w64}}$	64^*	5^*	11.34

Note: w = moisture content; *: estimated value.

Table 1b
Clay samples

Sample	w (%)	CaO (%)	pH
SC_O	32	0	7.54
SC_5	32	5	–
SC_{10}	32	10	–
SC_{15}	32	15	–

The sample of Sheffield clay, which weighed approximately 20 kg, was obtained from four sub-samples taken from areas on site where petroleum hydrocarbons impacts had been identified. The different sub-samples were mixed in an attempt to produce a homogeneous sample. However, due to the plasticity of the clay the hand-mixing procedure used was not completely successful and intact lumps of clay were observed in the sample. The clay was tested at its natural moisture content. Quicklime was added to the clay and mixed on a glass plate using a stainless steel spatula. The amount of quicklime used corresponded to 5% (sample SC_5), 10% (sample SC_{10}) and 15% (sample SC_{15}) on a dry weight percentage basis.

After thoroughly mixing to uniformly disperse the quicklime, the samples were placed in standard sealed glass jars and sent to Alcontrol Geochem Laboratory for the chemical analyses. Additional details on the preparation methods for the clay sample are discussed in [31].

2.3.2. Artificial sand/kaolinite samples

The sand and kaolinite were initially mixed dry using sand:kaolinite ratios of 90:10 (sample $(S_{90}K_{10})_{0\text{-w24}}$), 75:25 (sample $(S_{75}K_{25})_{0\text{-w29}}$) and 50:50 (samples $(S_{50}K_{50})_{0\text{-w40}}$, $(S_{50}K_{50})_{0\text{-w60}}$ and $(S_{50}K_{50})_{0\text{-w20}}$) as summarized in Table 2.

To contaminate the sand/kaolinite mixtures, distilled water was mixed with 3000 mg/kg of gasoline and diesel fuels each and the resulting mixture gradually added to the dry sand/kaolinite mixtures. The resulting wet mixtures were thoroughly mixed using a stainless steel spatula in open containers. In order to obtain samples with a good workability, a moisture content approximately equal to the mixtures liquid limit, was selected for the different samples. Moisture contents of samples $(S_{50}K_{50})_{0\text{-w60}}$ and $(S_{50}K_{50})_{0\text{-w20}}$ were, respectively, 1.5 and 0.5 times the liquid limit of the 50:50 sand:kaolinite mixture. After mixing, the samples were stored either in sealed polyethylene containers or in sealed polyethylene bags in a refrigerator. The samples were stored for 1 week to allow for complete hydration of the clay minerals. During this period of time the samples were periodically mixed to obtain a more uniform distribution of the hydrocarbons. Quicklime was added and mixed on a glass

Table 2
Sand/kaolinite samples composition

Sample	Sand (%)	Kaolinite (%)	*w* (%)	CaO (%)	G + D (mg/kg)
$(S_{90}K_{10})_{0\text{-w}24}$	90	10	24	0	6000
$(S_{75}K_{10})_{0\text{-w}29}$	75	25	29	0	6000
$(S_{50}K_{50})_{0\text{-w}40}$	50	50	40	0	6000
$(S_{50}K_{50})_{0\text{-w}60}$	50	50	60	0	6000
$(S_{50}K_{50})_{0\text{-w}20}$	50	50	20	0	6000
$(S_{90}K_{10})_{5\text{-w}24}$	90	10	24	5	6000
$(S_{90}K_{10})_{10\text{-w}24}$	90	10	24	10	6000
$(S_{90}K_{10})_{20\text{-w}24}$	90	10	24	20	6000
$(S_{75}K_{25})_{10\text{-w}29}$	75	25	29	10	6000
$(S_{50}K_{50})_{10\text{-w}40}$	50	50	40	10	6000
$(S_{50}K_{50})_{10\text{-w}60}$	50	50	60	10	6000
$(S_{50}K_{50})_{10\text{-w}20}$	50	50	20	10	6000
$(S_{100})_{15\text{-w}5}$	100	0	5	15	0
$(S_{100})_{30\text{-w}10}$	100	0	10	30	0
$(S_{100})_{45\text{-w}15}$	100	0	15	45	0
$(S_{90}K_{10})_{0}$	90	10	–	0	0
$(S_{75}K_{10})_{0}$	75	25	–	0	0
$(S_{50}K_{50})_{0}$	50	50	–	0	0

Note: G + D = gasoline and diesel.

plate using a stainless steel spatula. The amount of quicklime used corresponded to 5% (sample $(S_{90}K_{10})_{5\text{-w}24}$), 10% (samples $(S_{90}K_{10})_{10\text{-w}24}$, $(S_{75}K_{25})_{10\text{-w}24}$, $(S_{50}K_{50})_{10\text{-w}40}$, $(S_{50}K_{50})_{10\text{-w}60}$ and $(S_{50}K_{50})_{10\text{-w}20}$) and 20% (sample $(S_{90}K_{10})_{20\text{-w}24}$) on a dry weight percentage basis, as summarized in Table 2.

Quicklime was added at once in all samples but $(S_{90}K_{10})_{10\text{-w}24}$, where it was added more gradually. As the moist soil samples immediately dried up upon addition of quicklime, thus making the mixing hard, the mixing was done with no more than 2 kg of wet soil at a time.

After preparation, the treated sand:kaolinite samples as well as the remainders of untreated sand:kaolinite samples were placed in sealed polyethylene containers and stored at ambient temperature. Both treated and untreated mixtures were periodically sampled for determination of pH, Atterberg limits and moisture contents and to carry out the chemical analyses.

Mixtures $(S_{100})_{15\text{-w}5}$, $(S_{100})_{30\text{-w}10}$, and $(S_{100})_{45\text{-w}15}$ were prepared using 100% sand with different moisture and quicklime contents to evaluate the effects of quicklime mixing on soil temperature. The samples were prepared at 5%, 10% and 15% moisture content. The stoichiometric equivalents of quicklime for complete hydration reaction were added to the samples, that is 15%, 30% and 45%. For samples $(S_{100})_{15\text{-w}5}$ and $(S_{100})_{30\text{-w}10}$ the mixing took place in a 1000 ml glass beaker, for sample $(S_{100})_{45\text{-w}15}$ in a flat enameled metal tray.

Samples $(S_{90}K_{10})_0$, $(S_{75}K_{25})_0$ and $(S_{50}K_{50})_0$ were prepared using sand:kaolinite ratios of 90:10, 75:25 and 50:50 only to determine the Atterberg limits of uncontaminated sand/kaolinite mixtures to be compared to those of contaminated samples $(S_{90}K_{10})_{0\text{-w}24}$, $(S_{75}K_{25})_{0\text{-w}29}$ and $(S_{50}K_{50})_{0\text{-w}4}$ prepared with same sand:kaolinte ratio. The sand/kaolinite samples used in the experiments are summarized in Table 2.

3. Results

3.1. Temperature measurements

Temperature measurements were carried out to evaluate the magnitude and rate of change of temperature upon quicklime mixing.

Plots of temperatures measured during the quicklime mixing of sand samples $(S_{100})_{15\text{-w}5}$, $(S_{100})_{30\text{-w}10}$, and $(S_{100})_{45\text{-w}15}$ and clay samples SC_5, SC_{10}, and SC_{15} are presented in Fig. 1a and b. The temperature increased rapidly during the first few minutes of mixing, then reached a maximum value and eventually decreased gradually.

Temperatures were also measured in the sand/kaolinite samples during the mixing with quicklime. The temperature changes with time were consistent with the trend shown in Fig. 1.

The maximum temperatures recorded were: 24 °C (SC_5), 28 °C (SC_{10}), 31 °C (SC_{15}), 100 °C ($(S_{90}K_{10})_{5\text{-w}24}$), 74 °C ($(S_{90}K_{10})_{10\text{-w}24}$), 107 °C ($(S_{90}K_{10})_{20\text{-w}24}$), 100 °C ($(S_{75}K_{25})_{10\text{-w}29}$), 67 °C ($(S_{50}K_{50})_{10\text{-w}40}$), 41 °C ($(S_{50}K_{50})_{10\text{-w}60}$), and 42 °C ($(S_{50}K_{50})_{10\text{-w}20}$). Temperatures were not measured in the silt samples. However, heat generated during the quicklime mixing in these samples was significant and enough to melt the polyethylene tubs.

The differences in maximum temperatures in the different samples can be explained in terms of the procedure adopted for the quicklime mixing. A rapid addition of quicklime, a larger

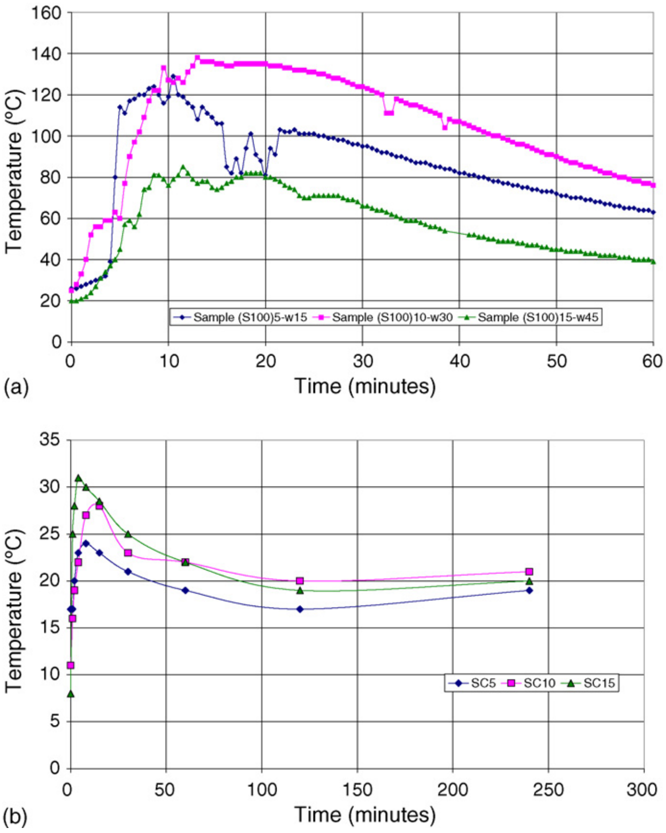

Fig. 1. Temperatures (a) in treated sand samples $(S100)_{5\text{-w}15}$, $(S100)_{10\text{-w}30}$, and $(S100)_{15\text{-w}45}$ and (b) in treated clay samples SC_5, SC_{10} and SC_{15}.

exposure area for the quicklime hydration reaction and a confined mixing environment, which minimises heat losses, result in higher temperatures. Therefore, confined mixing in a small diameter beaker (samples $(S_{100})_{15\text{-w5}}$ and $(S_{100})_{30\text{-w10}}$) resulted in higher temperatures than mixing in open tray or glass plate (samples SC_5, SC_{10}, SC_{15} and $(S_{100})_{45\text{-w15}}$). Rapid addition of lime (samples $(S_{90}K_{10})_{5\text{-w24}}$ and $(S_{90}K_{10})_{20\text{-w24}}$) resulted in higher temperatures than a gradual addition (samples SC_5, SC_{10}, SC_{15} and $(S_{90}K_{10})_{10\text{-w24}}$). Presence of clay lumps during mixing in high clay content samples (SC_5, SC_{10}, SC_{15}, $(S_{50}K_{50})_{10\text{-w40}}$, $(S_{50}K_{50})_{10\text{-w60}}$ and $(S_{50}K_{50})_{10\text{-w20}}$) resulted in a reduced surface available for quicklime hydration reactions, and thus in lower temperatures than in samples with lower clay contents.

3.2. pH, moisture content and Atterberg limits

The time-dependent effects of quicklime mixing on pH, moisture content, liquid limit and plastic limit were determined on the clay and on the sand/kaolinite samples. Pozzolanic reactions start immediately upon addition of lime to the wet soils, therefore, the reference time, $t = 0$, for determining the time effects is considered to be the time at which lime is added and mixing is started.

For comparison purposes liquid limit and plastic limit were also determined on the samples prior to quicklime mixing (clay sample SC_0, and sand/kaolinite samples $(S_{90}K_{10})_{0\text{-w24}}$, $(S_{75}K_{25})_{0\text{-w29}}$ and $(S_{50}K_{50})_{0\text{-w40}}$) and on uncontaminated sand/kaolinite samples ($(S_{90}K_{10})_0$, $(S_{75}K_{25})_0$ and $(S_{50}K_{50})_0$). The results are presented in Fig. 2 and Tables 3, 4a and 4b.

The magnitudes of the liquid limits of the uncontaminated and contaminated sand/kaolinite samples are comparable; plastic limits of the uncontaminated samples are slightly smaller than those of the contaminated samples.

Therefore, the addition of hydrocarbons did not have a significant effect on the Atterberg limits of the sand/kaolinite samples.

The results in Fig. 2 show that liquid limit and plastic limit of the treated Sheffield clay samples, increased immediately upon quicklime mixing and then either remained constant or slightly decreased with time. Moisture content decreased immediately upon quicklime mixing and then, after an increase possibly due to the soil taking up moisture from the surrounding environment, slightly decreased with time. Post-treatment moisture content decreased with increasing quicklime content, as expected, while the magnitude of post-treatment liquid and plastic limits were not significantly affected by quicklime content.

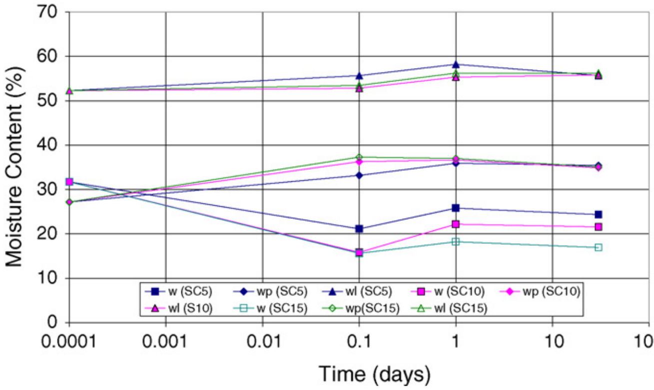

Fig. 2. Moisture content (w), plastic limit (w_p) and liquid limit (w_l) before (t assumed = 0.0001) and after mixing (t = 0.1, 1 and 30 days) in treated clay samples SC_5, SC_{10} and SC_{15}.

Table 3
Properties of untreated clay and sand/kaolinite samples

Sample	T (°C)	pH	w (%)	w_l (%)	w_p (%)
SC_0	–	7.54	32	57	27
SC_5	17	7.54	32	57	27
SC_{10}	11	7.54	32	57	27
SC_{15}	8	7.54	32	57	27
$(S_{90}K_{10})_{0\text{-w24}}$	10	5.5	24	23	18
$(S_{75}K_{10})_{0\text{-w29}}$	11	5.6	29	23	16
$(S_{50}K_{50})_{0\text{-w40}}$	13	5.5	40	34	23
$(S_{50}K_{50})_{0\text{w-60}}$	10	5.4	60	34	23
$(S_{50}K_{50})_{0\text{-w20}}$	10	5.3	20	34	23
$(S_{90}K_{10})_0$	–	–	–	22	15
$(S_{75}K_{10})_0$	–	–	–	23	15
$(S_{50}K_{50})_0$	–	–	–	35	19

Note: * = estimated; w = moisture content; w_l = liquid limit; w_p = plastic limit.

The results in Tables 4a and 4b show that in both clay and sand/kaolinite samples the pH increased rapidly upon quicklime mixing. In the sand/kaolinite samples the pH continued to increase more gradually over the 30-day study period while in the clay decreased slowly with time after the initial increase.

Liquid limit and plastic limit of the treated sand/kaolinite samples increases upon addition of quicklime and then remained approximately constant with time. Moisture content in both clay and sand/kaolinite samples decreased at first and then remained constant or slightly decreased with time.

For samples $(S_{90}K_{10})_{5\text{-w24}}$, $(S_{90}K_{10})_{10\text{-w24}}$ and $(S_{90}K_{10})_{20\text{-w24}}$, which were identical except for the amount of quicklime with which they were mixed, it can be observed that moisture content decreased and liquid limit increased with quicklime content whereas the plastic limit appears to be independent of quicklime content.

Comparing the results on samples $(S_{90}K_{10})_{10\text{-w24}}$, $(S_{75}K_{25})_{10\text{-w29}}$ and $(S_{50}K_{50})_{10\text{-w40}}$, which had similar consistency (i.e. moisture content approximately equal to liquid limit) and were mixed with same lime content but had different clay content, it can be observed that the percent change in moisture content, defined as $(w_{\text{untreated}} - w_{\text{treated}})/w_{\text{untreated}}$, increased with decreasing initial moisture content and that the largest percent increase in liquid and plastic limit occurred in the sample with the highest clay content (sample $(S_{50}K_{50})_{10\text{-w40}}$).

Comparing the results on samples $(S_{50}K_{50})_{10\text{-w40}}$, $(S_{50}K_{50})_{10\text{-w60}}$ and $(S_{50}K_{50})_{10\text{-w60}}$, which had same clay and lime

Table 4a
Post-treatment properties of clay samples

Sample time, t (days)	SC_5	SC_{10}, pH	SC_{15}
0	7.54	7.54	7.54
0.1	12.60	12.58	12.45
1	12.54	12.52	12.54
30	12.24	12.29	12.33

Table 4b
Post-treatment properties of sand/kaolinite samples

Sample time, *t* (days)	$(S_{90}K_{10})_{5\text{-w}24}$	$(S_{90}K_{10})_{10\text{-w}24}$	$(S_{90}K_{10})_{20\text{-w}24}$	$(S_{75}K_{25})_{10\text{-w}29}$	$(S_{50}K_{50})_{10\text{-w}40}$	$(S_{50}K_{50})_{10\text{-w}60}$	$(S_{50}K_{50})_{10\text{-w}20}$
pH							
0	5.5	5.5	5.5	5.6	5.5	5.4	5.3
1	12.3	12.3	12.3	–	–	–	–
3	–	–	–	12.3	12.1	12.8	12.2
7	12.3	12.3	12.5	12.6	12.5	12.5	12.5
15	12.6	12.5	12.5	12.2	12.4	12.4	12.6
30	12.6	12.6	12.7	12.6	12.6	12.6	12.7
Moisture content, *w* (%)							
0	24	24	24	29	40	60	20
1	20	13	7	–	–	–	–
15	19	13	8	18	29	48	12
30	19	13	8	18	28	45	12
Liquid limit, w_l (%)							
0	23	23	23	23	34	34	34
1	24	27	29	–	–	–	–
3	–	–	–	36	52	57	–
7	26	28	29	37	52	51	47
15	26	29	30	38	52	60	48
30	26	28	29	36	52	61	44
Plastic limit, w_p (%)							
0	18	18	18	16	23	23	23
1	19	21	21	–	–	–	–
3	–	–	–	25	31	34	28
7	22	22	22	22	30	32	28
15	21	20	20	23	31	34	28
30	18	20	19	24	31	35	28

content but different initial consistency, it can be observed that the largest percent changes in liquid and plastic limit and moisture content occurred in sample $(S_{50}K_{50})_{10\text{-w}60}$, which had the largest initial moisture content.

3.3. Concentrations of petroleum hydrocarbons

3.3.1. Silt samples

Concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX), MTBE, total petroleum hydrocarbons (TPH) working groups measured in the silt samples are presented in Fig. 3 and Table 5.

All treated samples present significantly smaller concentrations of hydrocarbons than the untreated samples. Concentrations of BTEX, MTBE and aliphatics with carbon groups in the range >C5–C8 below the analytical method detection limit (<0.01 mg/kg) were measured in the treated samples $LC1_5$, $LC1_{5\text{-w}64}$, $LC2_{10}$ and $LC2_{20}$. Concentrations of heavy aliphatics (>C12–C35) and aromatics (>EC12–EC35) decreased with respect to untreated concentrations in all samples. Concentrations of heavy aromatics below the analytical method detection limit (<0.1 mg/kg) were measured in treated samples $LC1_5$, $LC1_{5\text{-w}64}$, $LC2_{10}$, $LC2_{20}$ and $LC2_{5\text{-w}64}$.

The results in Table 5 show that the post-treatment concentration of total petroleum hydrocarbon (TPH) compounds decreased with increasing quicklime content. Sample $LC2_5$ shows higher concentrations of heavy aromatics (>EC12–EC35) than $LC2_{10}$ and $LC2_{20}$ suggesting that the effect of increasing quicklime content is to decrease heavy aromatics concentrations. However, no apparent effect of quicklime content was observed on heavy aliphatics.

Sample $LC2_{5\text{-w}64}$ show higher concentrations of light aromatics and lower concentrations of heavy aromatics than $LC2_5$ indicating that water addition resulted in an increase of volatile concentrations and in a reduction of heavy hydrocarbon concentrations.

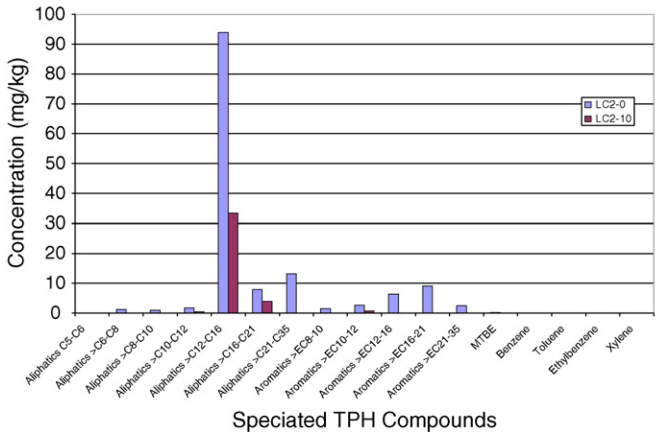

Fig. 3. Concentrations of speciated total petroleum hydrocarbon (TPH), BTEX/MTBE compounds in silt samples $LC2_0$ (untreated) and $LC2_{10}$ (10% quicklime).

Table 5

Concentrations in mg/kg of speciated total petroleum hydrocarbon (TPH), BTEX/MTBE compounds in silt samples $LC1_0$ and $LC2_0$ (untreated) and $LC1_5$, $LC1_{5\text{-w64}}$, $LC2_5$, $LC2_{10}$, $LC2_{20}$ and $LC2_{5\text{-w64}}$ (3 days after treatment)

Compound	$LC1_0$	$LC1_5$	$LC1_{5\text{-w64}}$	$LC2_0$	$LC2_5$	$LC2_{10}$	$LC2_{20}$	$LC2_{5\text{-w64}}$
Benzene	0.03	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.
Toluene	0.03	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.
Ethylbenzene	0.03	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	0.03
Xylenes	0.08	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.
MTBE	0.22	n.d.	n.d.	0.23	n.d.	n.d.	n.d.	0.05
Aliphatics								
C5–C6	0.02	n.d.	n.d.	0.06	0.04	n.d.	n.d.	0.02
C6–C8	1.08	n.d.	n.d.	1.28	0.05	n.d.	n.d.	0.08
C8–C10	0.84	0.03	0.23	0.94	0.01	0.06	0.14	0.50
C10–C12	2.01	0.39	0.66	1.78	0.10	0.51	0.63	1.1
C12–C16	172.5	35.2	25.5	93.9	21.8	33.4	25.6	24.1
C16–C21	20.1	13.2	10.2	7.9	3.5	3.9	3.2	3.9
C21–C35	46.1	25.5	25.9	13.2	12.0	n.d.	n.d.	8.6
Aromatics								
EC8–EC10	1.38	0.04	0.35	1.52	0.02	0.09	0.21	0.86
EC10–EC12	3.01	0.59	0.99	2.68	0.14	0.76	0.94	1.6
EC12–EC16	1.7	n.d.	1.7	6.4	3.2	n.d.	n.d.	1.2
EC16–EC21	1.4	n.d.	n.d.	9.1	3.1	n.d.	n.d.	n.d.
EC21–EC35	0.9	n.d.	n.d.	2.5	1.9	n.d.	n.d.	n.d.
TPH	250.98	74.96	65.56	141.26	45.88	38.69	31.69	42.08

Note: TPH = total petroleum hydrocarbons; n.d. = not detectable.

3.3.2. *Clay samples*

Concentrations of BTEX, MTBE and TPH working groups and polynuclear aromatic hydrocarbons (PAH) measured in the clay samples are presented in Tables 6 and 7, respectively. The results for the clay sample treated with 10% quicklime are also presented in Figs. 4 and 5.

The concentrations measured in duplicate samples SC15 and SC15′ were of comparable magnitude indicating a good consistency in the measurements.

The concentrations of the untreated clay ($SC_{0\,\text{avg}}$ in Tables 6 and 7) are defined using the average of the concentrations measured on a large number of soil samples taken from the site. In particular, the average concentrations of BTEX, MTBE and TPH working groups were computed using the results obtained on 68 samples of untreated clay whereas those of PAH on 40 samples.

All treated samples present significantly smaller concentrations of hydrocarbons than the $SC_{0\,\text{avg}}$ value. The concentrations measured in sample SC_{10} show a decreasing trend with time. Concentrations of aromatics >EC12–EC21 in sample SC_5 and concentrations of aliphatics >C12–C16 and aromatics >EC10–EC16 in sample SC_{15} appear to drop immediately after treatment ($t = 1$ day), then to increase at curing time $t = 2$ days, and eventually decrease again at curing time $t = 30$ days. Concentrations of aliphatics >C12–C35 and aromatics >EC21–EC35 in sample SC_5 and concentrations of aromatics EC16–EC35 in sample SC_{15} appear to initially drop after treatment and then to increase with time.

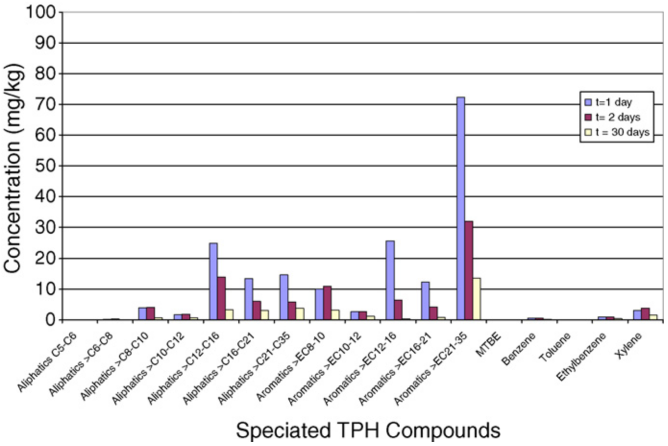

Fig. 4. Concentrations of speciated total petroleum hydrocarbon (TPH), BTEX/MTBE compounds in clay sample S_{10} (10% quicklime) immediately after mixing ($t = 0.1$ day), after 1 and 30 days.

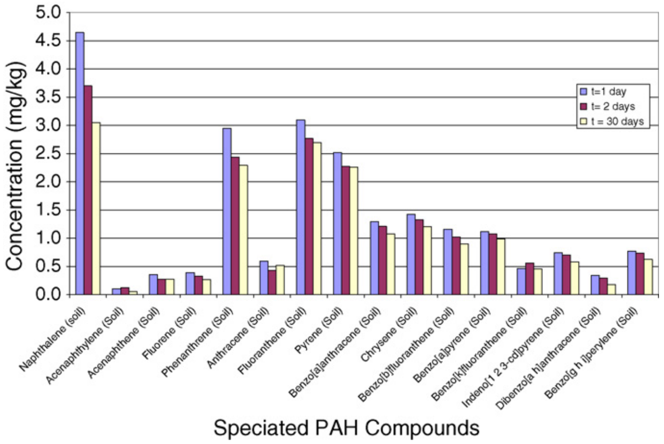

Fig. 5. Concentrations of speciated polynuclear aromatic hydrocarbon (PAH) compounds clay sample SC_{10} (10% quicklime) immediately after mixing ($t = 0.1$ day), after 1 and 30 days.

Table 6
Concentrations in mg/kg of speciated total petroleum hydrocarbon (TPH), BTEX/MTBE compounds in clay samples $SC_{0\,avg}$ (average measured field concentrations), SC_5, SC_{10} and SC_{15} (treated)

Compound	$SC_{0\,avg}$	SC_5			SC_{10}			SC_{15}			
	–, 0, 32[a]	1, 5, 32[a]	2, 5, 32[a]	30, 5, 32[a]	1, 10, 32[a]	2, 10, 32[a]	30, 10, 32[a]	1, 15, 32[a]	1, 15, 32[a]	2, 15, 32[a]	30, 15, 32[a]
Benzene	2.93	0.58	0.46	0.18	0.60	0.57	0.19	0.32	0.35	0.30	0.16
Toluene	7.90	0.63	0.25	0.05	0.13	0.08	0.05	0.04	0.04	0.05	0.04
Ethylbenzene	5.30	1.20	0.92	0.46	0.97	0.95	0.43	0.50	0.52	0.55	0.37
Xylenes	28.78	5.43	4.0	1.74	3.08	3.90	0.59	1.95	2.01	2.12	1.36
MTBE	4.87	0.05	0.04	0.01	0.06	0.05	0.01	0.03	0.03	0.03	0.01
Aliphatics											
C5–C6	6.89	0.28	0.19	0.05	0.11	0.13	0.04	0.11	0.12	0.13	0.05
C6–C8	23.95	0.40	0.48	0.09	0.29	0.32	0.08	0.23	0.31	0.34	0.09
C8–C10	16.68	4.90	3.45	0.61	4.01	4.07	4.77	0.70	0.77	0.45	0.53
C10–C12	13.89	2.45	2.05	0.73	1.77	1.83	0.77	0.94	1.02	1.30	0.75
C12–C16	93.1	6.1	4.5	8.7	24.9	14.0	3.4	6.2	6.4	7.1	5.1
C16–C21	201.4*	1.4	0.8	9.7	13.4	6.0	3.1	2.4	2.1	3.6	7.0
C21–C35	–	1.3	1.0	20.1	14.7	5.7	3.8	2.0	1.8	1.3	7.2
Aromatics											
EC8–EC10	53.61	13.97	10.09	3.11	10.07	10.95	3.18	3.49	3.68	3.34	2.52
EC10–EC12	19.10	3.67	3.07	1.10	2.66	2.75	1.15	1.41	1.54	1.96	1.13
EC12–EC16	31.5	4.6	5.7	1.5	25.5	6.5	0.4	1.9	1.6	5.9	2.2
EC16–EC21	26.4	2.7	8.5	3.6	12.3	4.2	0.9	1.5	1.5	6.1	8.9
EC21–EC35	79.3	8.2	21.9	32.4	72.3	31.9	13.5	14.0	12.5	30.5	35.2
TPH	565.9	50.0	61.75	81.77	182.28	88.55	31.04	34.88	33.38	62.17	70.75

Note: TPH = total petroleum hydrocarbons; * = C16–C35.

[a] The values are given as time in days, Cao in % and *w* in %.

A progressive decrease of PAH compounds concentration with time was observed only in sample SC_{10}. The concentrations of all PAH measured in all samples at curing time $t = 1$ day curing were smaller than the $SC_{0\,avg}$ values. The concentrations of a number of PAHs at curing times $t = 2$ and 30 days in sample SC_5 were smaller than the $SC_{0\,avg}$ value. However, the concentrations at $t = 2$ days in sample SC_5 were larger than at $t = 1$ day and in some cases even than the $SC_{0\,avg}$ values. Concentrations of PAH in sample SC_{15} were at all times smaller than the pre-treatment concentrations, however, the concentrations of a number of PAHs measured at $t = 30$ days were larger than those measured at $t = 2$ days.

The increases in heavy aliphatics and aromatics and PAH after a short curing time with respect to the initial drop of concentration may be due to desorption of hydrocarbons from soil organic matter resulting from its destruction in the high

Table 7
Concentrations in mg/kg of polynuclear aromatic hydrocarbon compounds in clay samples $SC_{0\,avg}$ (average field concentrations) and SC_5, SC_{10} and SC_{20} (treated)

Compound	$SC_{0,avg}$	SC_5			SC_{10}			SC_{15}			
	–	1	2	30	1	2	30	1	1	2	30
Naphthalene	5.22	2.95	2.58	2.69	4.65	3.70	3.05	3.22	2.74	2.58	2.15
Acenaphthylene	0.39	0.06	0.76	0.06	0.11	0.13	0.06	0.09	0.08	0.09	0.06
Acenaphthene	0.82	0.30	0.44	0.26	0.36	0.28	0.28	0.33	0.30	0.29	0.53
Fluorene	1.21	0.35	1.73	0.23	0.39	0.33	0.27	0.06	0.29	0.29	0.54
Phenanthrene	7.28	2.10	8.37	2.15	2.95	2.44	2.29	2.49	2.27	1.95	5.12
Anthracene	1.74	0.44	2.24	0.43	0.60	0.43	0.52	0.43	0.52	0.51	1.33
Fluoranthene	8.23	2.64	8.07	2.70	3.10	2.77	2.70	2.92	2.74	2.19	5.58
Pyrene	6.72	2.17	5.68	2.29	2.52	2.27	2.26	2.49	2.33	1.85	4.60
Benzo(*a*)anthracene	3.96	1.26	3.59	1.04	1.30	1.21	1.08	1.30	1.16	0.94	2.07
Chrysene	3.35	1.14	2.56	1.15	1.43	1.33	1.21	1.39	1.24	1.04	2.12
Benzo(*b*)fluoranthene	2.82	1.52	3.22	0.82	1.16	1.02	0.90	0.99	0.91	1.17	1.48
Benzo(a)pyrene	1.70	0.96	2.11	0.91	1.12	1.07	0.99	1.19	1.11	1.01	1.72
Benzo(*k*)fluoranthene	1.54	0.57	1.03	0.44	0.46	0.56	0.46	0.53	0.59	0.40	0.62
Indeno(1,2,3)pyrene	2.10	0.59	1.24	0.61	0.74	0.70	0.58	0.82	0.70	0.53	1.08
Dibenzo(*a*,*h*)anthracene	0.74	0.22	0.43	0.20	0.34	0.30	0.18	0.20	0.21	0.17	0.36
Benzo(*ghi*)perylene	2.67	0.75	1.38	0.67	0.77	0.73	0.63	0.86	0.72	0.59	1.10

1, 2 and 30 denote the time in days.

Table 8a
Concentrations in mg/kg of speciated total petroleum hydrocarbon (TPH), BTEX/MTBE compounds in sand/kaolinite sample $(S_{90}K_{10})_{0\text{-w24}}$ (untreated) and samples $(S_{90}K_{10})_{0\text{-w24}}$, $(S_{90}K_{10})_{10\text{-w24}}$ and $(S_{90}K_{10})_{20\text{-w24}}$ (treated)

Compound	$(S_{90}K_{10})_{0\text{-w24}}$			$(S_{90}K_{10})_{5\text{-w24}}$			$(S_{90}K_{10})_{10\text{-w24}}$			$(S_{90}K_{10})_{20\text{-w24}}$		
	1	17	30	1	17	30	1	17	30	1	17	30
Benzene	0.33	0.04	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Toluene	11.64	0.68	0.65	n.d.	0.05	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethylbenzene	2.98	1.08	0.81	0.15	0.04	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Xylenes	17.07	6.57	4.98	1.16	0.28	0.26	0.06	n.d.	0.02	n.d.	n.d.	0.02
MTBE	2.42	0.67	1.07	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Aliphatics												
C5–C6	1.30	0.55	0.26	0.04	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C6–C8	6.54	5.25	12.41	1.64	0.70	0.77	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C8–C10	2.76	3.48	9.30	1.47	1.00	1.66	0.23	0.04	0.08	0.06	0.03	0.06
C10–C12	2.39	1.65	6.62	1.88	1.29	1.61	0.36	0.07	0.11	0.35	0.06	0.04
C12–C16	367.3	712.5	471.5	165.7	570.7	136.6	159.4	556.8	158.0	85.0	359.4	211.7
C16–C21	952.3	1219.6	749.1	431.5	1121.7	379.3	405.4	1367.9	441.7	261.3	1039.9	682.8
C21–C35	302.6	347.0	205.4	158.6	328.1	120.9	120.6	414.4	138.8	84.1	340.9	201.3
Aromatics												
EC8–EC10	24.19	12.87	19.74	3.51	1.81	2.79	0.40	0.06	0.13	0.08	0.05	0.10
EC10–EC12	3.59	2.48	9.93	2.82	1.94	2.42	0.54	0.11	0.16	0.52	0.09	0.06
EC12–EC16	0.6	6.3	68.7	0.3	3.4	3.6	17.2	9.3	4.4	8.3	1.9	6.4
EC16–EC21	4.3	18.0	139.1	0.3	12.8	7.0	48.9	30.2	10.1	29.9	13.5	16.2
EC21–EC35	0.2	34.2	60.5	0.3	4.6	11.9	22.7	49.1	14.3	16.2	8.9	19.7
TPH	1679.96	2364.55	1753.22	768.07	2048.12	668.63	775.63	2427.87	767.65	485.88	1764.68	1138.39

1, 17 and 30 denote the time in days. *Note:* TPH = total petroleum hydrocarbons; n.d. = not detectable.

alkaline post-treatment environment [32]. In the long term, the tendency for increases in concentrations due to desorption may be counteracted by encapsulation of the compounds within the clay/pozzolanic products aggregates.

3.3.3. Artificial sand/kaolinite samples

3.3.3.1. Untreated sand/kaolinite samples. Petroleum hydrocarbon concentrations were measured on the untreated sand/kaolinite samples immediately before and at different times after adding the quicklime. The concentrations measured in samples $(S_{90}K_{10})_{0\text{-w24}}$, $(S_{75}K_{25})_{0\text{-w29}}$, $(S_{50}K_{50})_{0\text{-w40}}$, $(S_{50}K_{50})_{0\text{-w60}}$, and $(S_{50}K_{50})_{0\text{-w20}}$ are presented in Tables 8a and 8b.

As the results in Tables 8a and 8b show, the concentrations of petroleum hydrocarbons were not constant with time. In particular, volatile compounds decreased in all samples but in sample $(S_{50}K_{50})_{0\text{-w60}}$. In sample $(S_{90}K_{10})_{0\text{-w24}}$ heavy aliphatics increased at first and then decreased and heavy aromatics progressively increased with time. In samples $(S_{75}K_{25})_{0\text{-w29}}$ and $(S_{50}K_{50})_{0\text{-w40}}$ aliphatics >C6–C10 measured at 15 days were greater than at 1 day. In sample $(S_{50}K_{50})_{0\text{-w60}}$ volatiles and heavy hydrocarbons measured at 15 days were greater than at 1 day. In sample $(S_{50}K_{50})_{0\text{-w20}}$ heavy aliphatics measured at 15 days were greater than at 1 day.

While the decreases of volatiles can be explained generally in terms of volatilization of the compounds in the storage container headspace and biodegradation, the changes of all hydrocarbons concentrations in $(S_{50}K_{50})_{0\text{-w60}}$ and the changes of heavy aliphatics and aromatics in sample $(S_{90}K_{10})_{0\text{-w24}}$ and heavy aliphatics in sample $(S_{50}K_{50})_{0\text{-w20}}$ are more difficult to explain. A number of concurrent events with different effects on the concentration measurements might have taken place during the storage of the samples. Relatively insoluble heavy aromatics and aliphatics might have been initially present in the samples porewater as an agglomeration of oil droplets or microemulsions [33] and thus might have been initially partially undetected by the GC measurements. The droplets might have progressively dissolved in the porewater thus causing a tendency for higher concentrations measurements. The tendency to concentration increases due to the mechanisms above hypothesized combined with the tendency to concentration decreases due to biodegradation and some degree of volatilization, might explain the changes with time in the measured concentrations of untreated samples.

3.3.3.2. Treated sand/kaolinite samples. Petroleum hydrocarbons concentrations were measured on the sand/kaolinite samples at different times after quicklime mixing. The measured concentrations are presented in Tables 8a, 8b and 9a, 9b.

While most of the treated sand/kaolinite samples show smaller concentrations of petroleum hydrocarbon compounds (TPH) than those of the untreated samples measured at the same time, the same is not true for sample $(S_{90}K_{10})_{10\text{-w24}}$ at $t = 17$ days and samples $(S_{75}K_{25})_{10\text{-w29}}$ and $(S_{50}K_{50})_{10\text{-w40}}$ at $t = 15$ days.

Concentrations of volatiles and heavy aliphatic compounds decreases immediately after treatment. However, after the initial drop, the concentrations of heavy aliphatics increased with time at first and then decreased. Concentrations of heavy aromatics in sample $(S_{90}K_{10})_{5\text{-w24}}$ decreased at first then increased with time, in sample $(S_{90}K_{10})_{10\text{-w24}}$ increased above the pre-treatment concentrations and then decreased, in sam-

Table 8b
Concentrations in mg/kg of speciated total petroleum hydrocarbon (TPH), BTEX/MTBE compounds in sand/kaolinite samples $(S_{75}K_{10})_{0\text{-w29}}$, $(S_{50}K_{50})_{0\text{-w40}}$, $(S_{50}K_{50})_{0\text{-w60}}$ and $(S_{50}K_{50})_{0\text{-w20}}$ (untreated) and $(S_{75}K_{25})_{10\text{-w29}}$, $(S_{50}K_{50})_{10\text{-w40}}$, $(S_{50}K_{50})_{10\text{-w60}}$ and $(S_{50}K_{50})_{10\text{-w20}}$ (treated) at 15 days after treatment

Compound	$(S_{75}K_{10})_{0\text{-w29}}$		$(S_{75}K_{25})_{10\text{-w29}}$	$(S_{50}K_{50})_{0\text{-w40}}$		$(S_{50}K_{50})_{10\text{-w40}}$	$(S_{50}K_{50})_{0\text{-w60}}$		$(S_{50}K_{50})_{10\text{-w60}}$	$(S_{50}K_{50})_{0\text{-w20}}$		$(S_{50}K_{50})_{10\text{-w2}}$
	1	15	15	1	15	15	1	15	15	1	15	15
Benzene	0.32	0.05	n.d.	2.29	0.19	n.d.	0.12	0.72	0.03	3.17	0.04	n.d.
Toluene	6.24	0.51	0.05	42.4	3.89	0.34	7.71	17.84	0.39	53.91	0.71	0.01
Ethylbenzene	1.25	0.56	0.05	6.67	2.61	0.24	2.34	5.22	0.32	7.7	0.17	0.02
Xylenes	7.12	3.31	0.31	36.95	15.17	1.53	14.08	29.12	1.94	40.66	2.52	0.21
MTBE	1.60	1.05	n.d.	17.56	6.37	0.13	0.53	7.82	0.97	19.01	1.77	n.d.
Aliphatics												
C5–C6	1.78	0.84	n.d.	2.66	0.74	0.06	0.82	3.04	0.25	5.66	0.19	n.d.
C6–C8	1.79	2.95	0.33	10.67	12.84	2.03	4.97	12.01	5.03	14.45	9.94	n.d.
C8–C10	1.89	2.38	1.12	1.72	4.12	1.27	2.90	1.91	0.86	0.93	2.68	0.21
C10–C12	2.19	2.30	1.29	2.00	1.81	1.10	2.53	3.06	1.09	1.61	4.30	0.45
C12–C16	693.9	79.1	438.4	499.8	29.1	328.4	595.7	1268.4	786.6	333.2	922.7	487.7
C16–C21	1351.3	119.5	1449.9	800.3	43.1	801.7	1185.5	2044.2	1591.4	467.7	1769.7	1220.6
C21–C35	405.0	225.6	466.9	228.5	82.8	257.8	345.4	645.9	474.5	137.2	524.7	441.7
Aromatics												
EC8–EC10	11.20	7.44	2.03	46.21	23.95	3.68	20.77	37.20	3.55	49.76	6.71	0.55
EC10–EC12	3.29	3.45	1.94	3.00	2.71	1.66	3.80	4.58	1.63	2.42	6.45	0.67
EC12–EC16	0.4	0.3	10.8	0.4	0.4	8.9	0.7	21.8	14.0	0.6	21.8	11.1
EC16–EC21	3.2	0.3	23.8	2.9	0.3	18.9	2.6	45.3	35.6	3.4	43.9	29.9
EC21–EC35	1.2	0.3	26.6	n.d.	0.4	24.0	0.8	14.6	7.3	0.4	13.2	13.7
TPH	2483.8	445.17	2423.27	1643.0	206.41	1450.17	2174.3	4120.62	2922.42	1074.5	3327.39	2206.51

1 and 15 denote the time in days. *Note:* n.d. = not detectable.

ple $(S_{90}K_{10})_{20\text{-w24}}$ increased above the pre-treatment concentrations, then decreased and subsequently started to increase again.

A tendency for concentrations increases of the heavy aliphatics may be produced, as discussed for the untreated sample $(S_{90}K_{10})_{0\text{-w24}}$ in Section 3.3.3.1, by the hypothesized phenomenon progressive dissolution in the porewater initially present as microemulsions. However, while in quicklime treated samples very little biodegradation of hydrocarbons is expected due to the very high pH, a tendency for decreasing concentrations of the heavy aliphatics may be produced by the progressively tighter encapsulation of hydrocarbons in the clay/pozzolanic products aggregates.

The concentrations of volatile petroleum hydrocarbons measured at different times after preparation in samples $(S_{90}K_{10})_{5\text{-w24}}$, $(S_{90}K_{10})_{10\text{-w24}}$ and $(S_{90}K_{10})_{20\text{-w24}}$, which had the same initial clay content and consistency, but different quicklime content, were of comparable magnitude. However sample

Table 9a
Concentrations in mg/kg of polynuclear aromatic hydrocarbon compounds in sand/kaolinite samples $(S_{90}K_{10})_{0\text{-w24}}$ and $(S_{75}K_{10})_{0\text{-w29}}$ (untreated) and $(S_{90}K_{10})_{5\text{-w24}}$, $(S_{90}K_{10})_{10\text{-w24}}$, $(S_{90}K_{10})_{20\text{-w24}}$ and $(S_{75}K_{10})_{10\text{-w29}}$ (treated)

Compound	$(S_{90}K_{10})_{0\text{-w24}}$, 30 days	$(S_{90}K_{10})_{5\text{-w24}}$, 30 days	$(S_{90}K_{10})_{10\text{-w24}}$, 30 days	$(S_{90}K_{10})_{20\text{-w24}}$, 30 days	$(S_{75}K_{10})_{0\text{-w29}}$, 15 days	$(S_{75}K_{25})_{10\text{-w29}}$, 15 days
Naphthalene	0.25	n.d.	n.d.	0.11	0.29	0.07
Acenaphthylene	0.07	n.d.	n.d.	0.01	0.12	0.03
Acenaphthene	0.12	n.d.	n.d.	0.10	0.07	0.04
Fluorene	0.44	n.d.	n.d.	0.02	0.60	0.07
Phenanthrene	0.30	n.d.	n.d.	0.18	0.40	0.34
Anthracene	0.04	n.d.	n.d.	n.d.	0.10	0.05
Fluoranthene	0.07	n.d.	n.d.	n.d.	0.05	0.06
Pyrene	0.12	n.d.	n.d.	n.d.	0.06	0.07
Benzo(*a*)anthracene	0.03	n.d.	n.d.	n.d.	0.01	0.01
Chrysene	0.04	n.d.	n.d.	0.01	0.01	0.02
Benzo(*b*)fluoranthene	0.03	n.d.	n.d.	n.d.	n.d	0.01
Benzo(*a*)pyrene	0.02	n.d.	n.d.	n.d.	n.d.	0.01
Benzo(*k*)fluoranthene	n.d.	n.d.	n.d.	n.d.	n.d.	0.01
Indeno(1,2,3)pyrene	n.d.	n.d.	n.d.	n.d.	n.d.	0.01
Dibenzo(*a*,*h*)anthracene	n.d.	n.d.	n.d.	n.d.	n.d.	0.01
Benzo(*ghi*)perylene	n.d.	n.d.	n.d.	n.d.	n.d.	0.01

Note: n.d. = not detectable.

Table 9b

Concentrations in mg/kg of polynuclear aromatic hydrocarbon compounds in sand/kaolinite samples $(S_{50}K_{50})_{0\text{-w40}}$, $(S_{50}K_{50})_{0\text{-w60}}$ and $(S_{50}K_{50})_{0\text{-w20}}$ (untreated) and $(S_{50}K_{50})_{10\text{-w40}}$, $(S_{50}K_{50})_{10\text{-w60}}$ and $(S_{50}K_{50})_{10\text{-w20}}$ (treated)

Compound	$(S_{50}K_{50})_{0\text{-w40}}$, 15 days	$(S_{50}K_{50})_{10\text{-w40}}$, 15 days	$(S_{50}K_{50})_{0\text{-w60}}$, 15 days	$(S_{50}K_{50})_{10\text{-w60}}$, 15 days	$(S_{50}K_{50})_{0\text{-w20}}$, 15 days	$(S_{50}K_{50})_{10\text{-w20}}$, 15 days
Naphthalene	0.61	0.08	0.29	0.08	0.19	0.13
Acenaphthylene	0.02	0.02	0.07	0.04	0.04	0.04
Acenaphthene	0.03	0.05	0.20	0.16	0.12	0.08
Fluorene	0.41	0.07	0.54	0.31	0.45	0.06
Phenanthrene	0.35	0.27	0.43	0.31	0.31	0.36
Anthracene	0.08	0.06	0.19	0.08	0.10	0.07
Fluoranthene	0.03	0.06	0.15	0.04	0.03	0.23
Pyrene	0.05	0.07	0.16	0.07	0.06	0.22
Benzo(*a*)anthracene	0.01	0.01	0.06	0.01	0.01	0.09
Chrysene	0.01	0.02	0.06	0.01	0.01	0.09
Benzo(*b*)fluoranthene	n.d	0.01	0.03	0.01	0.01	0.06
Benzo(*a*)pyrene	n.d	0.01	0.04	0.01	0.01	0.07
Benzo(*k*)fluoranthene	n.d	0.01	0.04	0.01	0.01	0.08
Indeno(1,2,3)pyrene	n.d	0.01	0.02	0.01	0.01	0.02
Dibenzo(*a*,*h*)anthracene	n.d	0.01	0.01	n.d.	0.01	0.01
Benzo(*ghi*)perylene	n.d	0.01	0.03	0.01	0.01	0.02

Note: n.d. = not detectable.

$(S_{90}K_{10})_{5\text{-w24}}$ showed slightly higher concentrations than the other samples suggesting that a greater quicklime content results in a greater reduction of volatile concentrations.

The concentrations of volatiles measured approximately 2 weeks after preparation in samples $(S_{90}K_{10})_{10\text{-w24}}$, $(S_{75}K_{25})_{10\text{-w29}}$ and $(S_{50}K_{50})_{10\text{-w40}}$, which had the same initial consistency, and quicklime content but different clay content increased in the order of increasing clay content. In the samples $(S_{50}K_{50})_{10\text{-w40}}$, $(S_{50}K_{50})_{10\text{-w60}}$ and $(S_{50}K_{50})_{10\text{-w20}}$, which had the same clay and quicklime content but different initial consistency, the concentrations of volatiles measured approximately 2 weeks after preparation increased in the order of increasing moisture content. Therefore, it can be concluded that the magnitude of moisture and clay contents appear to have an effect on the post-treatment concentrations of volatile compounds. Larger initial clay and moisture contents result in smaller reduction in hydrocarbon concentrations.

Leaching tests were carried out to assess the mass transfer for the lime treated soil samples to a liquid. Petroleum hydrocarbon concentrations were measured in the leachates extracted

Table 10

Concentrations in μg/l of speciated total petroleum hydrocarbon (TPH), BTEX/MTBE compounds in leachates from sand/kaolinite samples $(S_{90}K_{10})_{0\text{-w24}}$ (untreated) and $(S_{90}K_{10})_{5\text{-w24}}$, $(S_{90}K_{10})1_{0\text{-w24}}$ and $(S_{90}K_{10})_{20\text{-w24}}$ (treated)

Compound	$(S_{90}K_{10})_{0\text{-w24}}$	$(S_{90}K_{10})_{5\text{-w24}}$		$(S_{90}K_{10})_{10\text{-w24}}$		$(S_{90}K_{10})_{20\text{-w24}}$	
	30	1	30	1	30	1	30
Benzene	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Toluene	39	n.d	n.d	n.d	n.d	n.d	n.d
Ethylbenzene	146	15	n.d	n.d	n.d	n.d	n.d
Xylenes	958	140	34	n.d	n.d	n.d	n.d
MTBE	41	n.d	n.d	n.d	n.d	n.d	n.d
Aliphatics							
C5–C6	52	n.d	n.d	n.d	n.d	n.d	n.d
C6–C8	849	n.d	n.d	n.d	n.d.	n.d	n.d
C8–C10	1394	318	43	n.d	n.d	n.d	n.d
C10–C12	698	340	36	n.d	n.d	n.d	n.d
C12–C16	n.d.	55	n.d	52	n.d	10	n.d
C16–C21	n.d.	40	n.d	31	n.d	31	n.d
C21–C35	n.d.	13	11	n.d	n.d	1443	n.d
Aromatics							
EC8–EC10	3195	631	99	n.d	n.d	n.d	n.d
EC10–EC12	1048	510	55	n.d	n.d	n.d	n.d
EC12–EC16	14	84	13	74	n.d	30	17
EC16–EC21	n.d.	41	12	48	n.d	49	15
EC21–EC35	17	31	27	33	22	118	12
TPH	7306	2063	296	238	22	1681	44

1 and 30 denote the time in days. *Note:* TPH = total petroleum hydrocarbons; n.d. = not detectable.

Table 11
Concentrations in μg/l of BTEX/MTBE compounds in leachates from sand/kaolinite samples $(S_{75}K_{10})_{0\text{-w29}}$, $(S_{50}K_{50})_{0\text{-w40}}$, $(S_{50}K_{50})_{0\text{-w60}}$ and $(S_{50}K_{50})_{0\text{-w20}}$ (untreated) and $(S_{75}K_{25})_{10\text{-w29}}$, $(S_{50}K_{50})_{10\text{-w40}}$, $(S_{50}K_{50})_{10\text{-w60}}$ and $(S_{50}K_{50})_{10\text{-w20}}$ (treated)

Compound	$(S_{75}K_{10})_{0\text{-w29}}$, 15 days	$(S_{75}K_{25})_{10\text{-w29}}$, 1 day	$(S_{50}K_{50})_{0\text{-w40}}$, 30 days	$(S_{50}K_{50})_{10\text{-w40}}$, 1 day	$(S_{50}K_{50})_{0\text{-w60}}$, 30 days	$(S_{50}K_{50})_{10\text{-w60}}$, 1 day	$(S_{50}K_{50})_{0\text{-w20}}$, 30 days	$(S_{50}K_{50})_{10\text{-w20}}$, 15 days
Benzene	n.d	n.d	n.d	n.d	44	n.d.	n.d	n.d
Toluene	10	n.d.	39	23	1890	17	12	n.d.
Ethylbenzene	87	n.d.	346	47	779	28	n.d	n.d
Xylenes	581	n.d	2229	362	5128	232	116	n.d.
MTBE	n.d	n.d.	314	n.d	660	19	n.d.	n.d.
DRO	180	82	153	121	292	493	527	124

Note: DRO = diesel range organics; n.d. = not detectable.

Table 12a
Concentrations in μg/l of polynuclear aromatic hydrocarbon compounds in leachates from sand/kaolinite samples $(S_{90}K_{10})_{0\text{-w24}}$ and $(S_{75}K_{10})_{0\text{-w29}}$ (untreated) and $(S_{90}K_{10})_{5\text{-w24}}$, $(S_{90}K_{10})_{10\text{-w24}}$, $(S_{90}K_{10})_{20\text{-w24}}$ and $(S_{75}K_{25})_{10\text{-w29}}$ (treated)

Compound	$(S_{90}K_{10})_{0\text{-w24}}$, 30 days	$(S_{90}K_{10})_{5\text{-w24}}$, 30 days	$(S_{90}K_{10})_{10\text{-w24}}$, 30 days	$(S_{90}K_{10})_{20\text{-w24}}$, 30 days	$(S_{75}K_{10})_{0\text{-w29}}$, 15 days	$(S_{75}K_{25})_{10\text{-w29}}$, 15 days
Naphthalene	11871	7539	1279	1941	3343	838
Acenaphthylene	48	561	83	36	18	13
Acenaphthene	179	184	165	116	64	34
Fluorene	1987	2399	1631	99	892	588
Phenanthrene	628	984	1533	1098	225	167
Anthracene	48	51	302	89	19	n.d.
Fluoranthene	65	50	139	63	22	n.d.
Pyrene	73	79	142	116	33	12
Benzo(*a*)anthracene	n.d.	n.d.	n.d.	n.d.	n.d	n.d
Chrysene	n.d.	n.d.	n.d.	n.d.	n.d	n.d.
Benzo(*b*)fluoranthene	n.d.	n.d.	n.d.	n.d.	n.d	n.d.
Benzo(*a*)pyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Indeno(1,2,3)pyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzo(*a*,*h*)anthracene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo(*ghi*)perylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Note: n.d. = not detectable.

Table 12b
Concentrations in μg/l of polynuclear aromatic hydrocarbon compounds in leachates from sand/kaolinite samples $(S_{50}K_{50})_{0\text{-w40}}$, $(S_{50}K_{50})_{0\text{-w60}}$ and $(S_{50}K_{50})_{0\text{-w20}}$ (untreated) and $(S_{50}K_{50})_{10\text{-w40}}$, $(S_{50}K_{50})_{10\text{-w60}}$ and $(S_{50}K_{50})_{10\text{-w20}}$ (treated)

Compound	$(S_{50}K_{50})_{0\text{-w40}}$, 15 days	$(S_{50}K_{50})_{10\text{-w40}}$, 15 days	$(S_{50}K_{50})_{0\text{-w60}}$, 15 days	$(S_{50}K_{50})_{10\text{-w60}}$, 15 days	$(S_{50}K_{50})_{0\text{-w20}}$, 15 days	$(S_{50}K_{50})_{10\text{-w20}}$, 15 days
Naphthalene	2979	1424	17184	8531	16072	632
Acenaphthylene	n.d.	14	37	54	76	13
Acenaphthene	22	46	172	118	262	50
Fluorene	386	469	1256	1880	3154	129
Phenanthrene	120	182	783	652	994	292
Anthracene	n.d.	10	200	35	75	53
Fluoranthene	n.d.	n.d	140	24	25	15
Pyrene	n.d.	12	121	33	56	24
Benzo(*a*)anthracene	n.d.	n.d.	n.d.	n.d.	n.d	n.d
Chrysene	n.d.	n.d.	n.d.	n.d.	n.d	n.d.
Benzo(*b*)fluoranthene	n.d.	n.d.	n.d.	n.d.	n.d	n.d.
Benzo(*a*)pyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo(*k*)fluoranthene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Indeno(1,2,3)pyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzo(*a*,*h*)anthracene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo(*ghi*)perylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Note: n.d. = not detectable.

from the untreated and treated sand/kaolinite samples at different times after quicklime mixing. The concentrations measured in the leachates are presented in Tables 10, 11, 12a and 12b. For the sand/kaolinite samples with 90:10 sand:kaolinite ratio the leachate concentrations measured in the treated samples at curing time $t = 1$ and 30 days were compared to those measured in the control sample at $t = 30$ days. For all other samples, the leachate concentrations measured in the treated samples at $t = 1$ day were compared to those measured in the control sample at $t = 15$ days. While the concentrations of hydrocarbons measured in the leachates from the treated samples are generally substantially smaller than those from the untreated sample and decrease progressively with time, concentrations of some PAH compounds in leachates from treated samples are slightly larger than those from untreated samples.

4. Discussion

Decreases in concentrations of petroleum hydrocarbon compounds were generally observed in soil samples contaminated with low (silt samples) and high levels (clay and sand/kaolinite samples) of petroleum hydrocarbon compounds treated with quicklime and in the leachates extracted from them. This observation can be explained as a result of removal of petroleum hydrocarbons from the soils upon quicklime mixing and/or a strong association between the petroleum hydrocarbon compounds and the solid constituents of the samples, which would hinder their extraction and determination by the analytical procedure used.

More specifically, this association mechanism may be explained in terms of encapsulation of hydrocarbons within the clay/lime pozzolanic products matrix. Compounds initially adsorbed on the clay particles surfaces and soil organic matter are released upon quicklime mixing due to the degradation of the silicate minerals and organic matter in the high post-treatment pH environment. These, together with the hydrocarbons dissolved or present as microemulsions in the porewater, are encapsulated in the clay macroaggregates formed as a result of edge to face electrostatic attractive forces and interparticle binding by silicate hydrates gels formed by the pozzolanic reactions. The progressive hardening of these pozzolanic products hinders the release of the compounds in the porewater.

The hypothesized mechanism appears to be supported by the behavior of the Atterberg limits of the treated samples. Liquid and plastic limits of petroleum contaminated samples increased upon lime mixing, consistent with the behavior observed on non-contaminated soils. Increases in liquid limit and plastic limit in clays with low to intermediate plasticity treated with lime have been attributed to a number of processes resulting from the development of pozzolanic reactions [5]. Therefore, it can be concluded that the large initial concentrations of petroleum hydrocarbon compounds present in the clay samples and sand/kaolinite mixtures did not inhibit, nor retard the occurrence of pozzolanic reactions.

The results indicate that largest fraction of the decrease in petroleum hydrocarbons concentrations occurs rapidly upon quicklime mixing. As observed on the clay sample treated with 10% quicklime (Fig. 4) and in the leachates extracted from the treated sand/kaolinite samples, the concentrations continue to decrease progressively with time. This observation suggests that the mechanisms responsible for removal or encapsulation of hydrocarbons have a time-dependent component. However, increases in concentrations of heavy aliphatics and aromatics after the immediate drops were also observed. This time-dependent behavior of heavy hydrocarbons is difficult to explain as it may be the results of several concurrent and counteracting phenomena such as degradation, release in solution of microemulsion oil droplets, desorption from clay particles and organic matter and encapsulation of the compounds. The subsequent decreases of concentrations observed in some cases suggest that progressively tighter encapsulation of the compounds in the clay/pozzolanic products aggregates may become predominant after longer curing times.

While the large increase in temperature observed during the quicklime mixing in the silt and sand/kaolinite samples may contribute to removal of light compounds by a volatilization mechanism, the decreases in concentrations of both volatiles and heavy aliphatics and aromatics in the clay samples, for which small temperature increases were measured during quicklime mixing, may not be related to temperature effects. It is possible that, especially at low temperatures, the decrease in volatiles concentrations may be explained by a significant portion of compounds being mixed at a molecular level with the clay/pozzolanic products matrix, as observed for Toluene in cement matrices [34,35].

The decreases in volatile compounds concentrations observed in all the silt and sand/kaolinite treated samples and heavy aromatics in the silt sample LC2 appear to depend on quicklime content. An increase in quicklime content resulting in larger reduction of compounds concentrations. No effect of quicklime content on concentrations reduction for all other compounds was observed in the silt and sand/kaolinite samples.

Addition of water during quicklime mixing in the silt sample LC2 resulted in an increase of volatile concentrations and in a reduction of heavy aromatics concentrations. The increase in volatile concentration may be explained in terms of water hindering the compounds volatilization. The decrease in heavy hydrocarbon concentrations at higher moisture content may be explained in terms of enhanced mixability of the silt at higher moisture contents resulting in a more homogenous distribution of quicklime and thus enhanced encapsulation of heavy hydrocarbons.

Larger initial clay contents and moisture contents in the sand/kaolinite samples resulted in smaller reductions volatiles concentrations. The first of the above observations may be explained by an increasing difficulty in mixing due to the higher plasticity of the sand/kaolinite mixture and thus a less homogeneous distribution of the quicklime in the samples with larger clay contents. The second observation may be explained, as in the case of the silt samples, by larger initial moisture contents hindering the volatilization process. In addition, a larger initial content of distilled water results in a more dispersed clay fabric, which favours the desorption of hydrocarbons and thus a higher efficiency of extraction during the concentration measurements.

No apparent effect of quicklime content on hydrocarbon concentrations reduction was observed on the clay sample. The largest decreases in concentrations of petroleum hydrocarbons after longer term curing ($t = 30$ days) were observed in the sample treated with 10% quicklime.

Comparing the decrease of hydrocarbon concentrations upon quicklime mixing in the different soil types used in this study, it can be observed that quicklime mixing was equally effective in reducing volatiles in all soil types. However, larger decreases of heavy hydrocarbons were achieved in the natural soil samples. It is possible that the greater concentration reductions achieved for the partially weathered hydrocarbons in the natural samples, as compared to those of fresh hydrocarbons in the spiked sand/kaolinite samples, are due to a greater effectiveness of the mechanisms responsible for the concentration decreases on the degree of weathering of the heavy hydrocarbons.

Concentrations of hydrocarbons measured in the leachates from the treated sand/kaolinite samples were generally substantially smaller than those from the untreated sample and decreased progressively with time. However, concentrations of some PAH compounds in leachates from treated samples were slightly larger than those from untreated samples. As previously discussed in relation to the time dependent behavior of heavy hydrocarbons concentrations in sand/kaolinite samples, mobilisation of PAH hydrocarbons initially present in the soils as droplets might have contributed to the measured increase of PAHs concentrations.

5. Conclusions

The study confirmed that quicklime mixing is a viable technique for remediation and pre-treatment prior to disposal of soils contaminated with either low or high levels of petroleum hydrocarbons.

Mixing soils with quicklime resulted in significant decreases in concentrations and leachability of petroleum hydrocarbon compounds in soils.

Large decreases in petroleum hydrocarbons concentrations occurred rapidly upon quicklime mixing. Smaller decreases may continue to take place progressively with time.

The decreases in petroleum hydrocarbons concentrations may be explained by a number of mechanisms such as volatilization, degradation and encapsulation of the hydrocarbon compounds promoted by the quicklime mixing.

The increase in temperature due to the exothermic hydration reaction of quicklime when in contact with porewater helps to volatilize the light compounds but may not be entirely responsible for their concentration decreases and for the decrease of heavy aliphatics and aromatics concentrations.

An initial high moisture content or addition of water during mixing hindered the volatilization of light hydrocarbons and resulted in higher post-treatment concentrations of volatiles in the silt and sand/kaolinite samples. On the other hand, higher moisture contents in the silt resulted in improved mixability, a more homogeneous distribution of quicklime and therefore enhanced encapsulation and lower concentrations of heavy aromatics in the silt sample LC2.

Additions of larger quicklime contents resulted in a decrease of hydrocarbon concentrations in the silt sample LC2 and volatile hydrocarbons in the sand/kaolinite samples. The effect of quicklime content on the other samples was not evident. In the clay the largest decreases in concentrations of petroleum hydrocarbons after longer term curing ($t = 30$ days) were observed in the sample treated with 10% quicklime.

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