Theory and Application of Landfarming to Remediate Polycyclic Aromatic Hydrocarbons and Mineral Oil-Contaminated Sediments; Beneficial Reuse

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ABSTRACT

When applying landfarming for the remediation of contaminated soil and sediment, a fraction of the soil-bound contaminant is rapidly degraded; however, a residual concentration may remain, which slowly degrades. Degradation of polycyclic aromatic hydrocarbons (PAHs) and mineral oil can be described using a multi-compartment model and first-order kinetics, in which three degradable fractions are distinguished; (1) rapid, (2) slowly, and (3) very slowly degradable. Using this model populated with data from long-term experiments (initiated in 1990), it is shown that time frames from years to decades can be necessary to clean the soil or sediment to obtain a target below regulatory guidelines. In passive landfarms without active management, three principal potentially limiting factors can be identified: (1) availability of appropriate microorganisms, (2) supply of oxygen for the biodegradation process, and (3) bioavailability of the pollutants to the microorganisms. Bioavailable PAHs and mineral oil are readily biodegradable contaminants under aerobic conditions, and presence and activity of microorganisms are not problems. The other two factors can be limiting and are theoretically described. Using these descriptions, which are in agreement with field experiments of 10 to 15 yr, it is shown if and when optimization of the biodegradation process is an option. Because a long time period is necessary to degrade the slowly and very slowly degradable fractions, passive landfarming should be combined with beneficial use of the land area. Examples include the development of natural environments, use in constructions, growing of biomass for energy production, including biofuels, and use as cover for landfills.

S EDIMENTS function as sinks for many contaminants entering the water phase. Serious pollution has occurred in harbors and industrial areas, but sediments in rural areas may also be polluted. The main contaminants present are polycyclic aromatic hydrocarbons (PAHs), mineral oil, and heavy metals. Anaerobic conditions in sediments are responsible for the persistence of PAHs and mineral oil, and for strong binding of heavy metals and accumulation of all these compounds in sediments. In a delta area such as the Netherlands, new sediments are deposited continuously. As long as contaminants are discharged into the environment, these new sediments may become polluted. Model studies have shown that in the Netherlands, discharge of the main contaminants (PAHs and heavy metals) will remain at such a level that

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polluted sediments are to be expected for the next hundred years (Kramer et al., 1997).

It is frequently necessary to dredge water systems to assure accessibility to harbors and proper functioning of smaller channels and ditches for supply and discharge of water. According to AKWA (2001), approximately 250 million cubic meters of dredged sediment will require treatment from the current time until the year 2010 in the Netherlands, with PAHs and/or mineral oil as the qualifying contaminants in part of this amount.

Bioremediation (in aerobic conditions) is a suitable treatment technology to remove PAHs and mineral oil from soil and sediments. Several methods are available, ranging from intensive treatment in bioreactors to passive landfarms in which external process interventions are minimized to reduce costs and use of energy (Bortone and Palumbo, 2007). Remediation of the millions of cubic meters of polluted sediments in the coming years, however, can only be achieved if inexpensive technologies are available. Landfarming is considered as a promising technology (AKWA, 2001) to remediate PAH- and mineral oil-contaminated sediments. Landfarming was first used in the 1970s, when oil-containing waste from the U.S. oil industry was disposed by mixing it with soil to stimulate biodegradation of mineral oil (Dibble and Bartha, 1979). Based on this experience, landfarming has been developed, taking into account money, space, time, energy emission, use of raw material, depletion of material reuse, and public acceptance to create sustainable remediation methods for contaminated soils and sediments (Sims and Harmsen, 2001). The relatively low costs of passive landfarming are a reason that there is an increasing tendency in the Netherlands to apply this system in practice. Thus it is important to know when passive landfarming can be used and to what extent the method can be optimized. In passive landfarms, three principal potentially limiting factors can be identified:

(1) Availability of appropriate microorganisms.
(2) Bioavailability of the pollutants.
(3) Supply of oxygen (aerobic conditions) for the biodegradation process.

Polycyclic aromatic hydrocarbons are readily biodegradable contaminants under aerobic conditions as follows from many publications (Sims and Overcash, 1983; Cerniglia and Heitkamp, 1989; Cerniglia, 1992; Van Achteren et al., 1998). Hydrocarbon-utilizing bacteria are widely distributed (Schlegel, 1992) and the ability to utilize mineral oil as an energy source is not

Abbreviations: PAHs, polycyclic aromatic hydrocarbons; DOM, dissolved organic matter; DOC, dissolved organic carbon; SOM, solid organic matter.

restricted to a few specialists among microorganisms. Therefore, presence and activity of microorganisms are not problems. In soils, presence of nutrients (N, P, and K) can be a limiting factor for the activity of the microorganisms, but this factor is not limiting in sediments. This is caused by the degradation of organic matter in the sediment, which results in availability of nutrients.

Microorganisms are present within pores in the soil or sediment matrix, but cannot be present in pores smaller than their own size. This explains that in a properly functioning landfarm, (bio)availability of pollutants for degradation is limited by microbial access to pores. The rapid degradable fraction is the fraction of the contaminant present in the larger pores and the fraction that can be transported to these pores in a year of landfarming treatment. Contaminants adsorbed to or absorbed (also referred to as sequestered) into organic matter are not directly available for the degrading organisms and this fraction results in a residual concentration. The contaminants must be transported by diffusion to the microorganism to be degraded. This is a slow process for adsorbed compounds due to sorption retarded diffusion, and will be even slower for absorbed compounds, because the stability of the organic matter is involved. Both factors limit bioavailability and therefore biodegradation. It has been demonstrated to be possible to increase the degradation rate of the rapid desorbable fraction, but it is difficult to increase the availability of the slow and very slow desorbable fractions and thereby the degradation rate in a landfarm (Harmsen, 2004; Bortone and Palumbo, 2007).

Proper functioning of microorganisms implies sufficient oxygen, because the degrading microorganisms need aerobic conditions to degrade PAHs. Oxygen is not present in the original in situ saturated sediment, but becomes available when the sediment is dewatered. This allows oxygen to enter and aerate the sediment. Both contaminant diffusion and the aeration process are described in this paper using a mechanistic model. The results of the model are supported by data from a landfarm at Kreekraksluizen (The Netherlands), where sediments have been passively landfarmed for a period of 10 to 15 yr (Harmsen, 2004).

MATERIALS AND METHODS

Experimental Landfarm

Landfarms were started on a semi-field scale in an experimental field at Kreekraksluizen, (The Netherlands). Initial experiments started in 1990 on fields with a drainage layer of 30 cm. Each field was 20 × 7 m. A layer of approximately 50 cm of dredged sediment was applied to each field; the layers were reduced to about 30 cm after dewatering. The sediment layer was intensively treated to stimulate biodegradation during the first few years using either: cultivation (tillage) or no cultivation, and addition of wood chips and sludge from a sewage treatment plant containing PAH-adapted microorganisms. The sediments originated from the Geul Harbor in Rotterdam and the Zierikzee Harbor, Zeeland. Biodegradation was observed to occur in all field plots, but there were no significant differences between the treatments (de Groot and van Lierop, 1995). It was found that between 1990 and 1993

the concentration of PAHs (Dutch National List) in Geul Harbor and Zierikzee sediment decreased from 52 to 3.7 and from 65 to 18 mg kg^{-1} dry matter, respectively.

In 1993 the sediments from the different experimental fields were combined and used to start two new experimental fields containing the Geul Harbor and Zierikzee sediment, with a layer of approximately 60 cm dewatered sediment. These sediments were further treated passively (passive landfarming). Passive landfarming implies minimal management activities and is especially suitable for reduction of residual concentrations. The fields were not cultivated, no nutrients or other substances were added, and natural succession of developing vegetation was allowed. In intensive landfarming, processes are optimized using active management activities to reduce contaminants to residual concentrations as quickly as possible.

In June 1994, the landfarm was extended by adding two fields for the treatment of sediment from the Petroleum Harbor in Amsterdam and sediment from the harbor in Wemeldinge, also situated in the province of Zeeland. In these fields an original layer of sediment of approximately 1 m was used. In one replicate field of each sediment, dewatering was stimulated with vegetation (passive landfarming), while two other replicate fields were intended for intensive cultivation in the first period of intensive landfarming. In this period of cultivation, no vegetation could develop. After construction of the landfarms it was required by regulation that due to the high PAH concentrations in the Petroleum Harbor sediment, this had to be classified as chemical waste and thus special permission was necessary before continuing the experiments. Activities on the landfarm like cultivation could only be started after receiving all necessary permissions (November 1994). During the first summer only a crust of about 10 cm was dewatered. The crust prevented further dewatering by evaporation. In November 1994, the sediments were completely saturated again and covered with water, because in autumn, the amount of precipitation exceeds the amount of evaporation. Cultivation to stimulate dewatering and degradation, in combination with the facilitation of surface runoff to remove rainfall were started in late 1994. As a result, the first period (June through November 1994) was not an effective period for dewatering and bioremediation throughout the entire depth of the sediment layer. The different treatments are summarized in Table 1.

The extent of dewatering and resulting aeration was followed by observations in small freshly dug trial pits. Three distinct conditions could be distinguished: (1) anaerobic conditions where the sediment was still black, (2) aerobic conditions where the sediment was visible as a brown aerobic soil, and (3) partly aerobic conditions where black aggregates were visible in the developing brown soil.

In a field experiment it is not possible to homogenize a complete field, therefore the heterogeneity of the polluted sediment has to be considered. To be able to construct reliable biodegradation curves, all fields were sampled intensively. At least five random samples were taken each time a field and layer were sampled. Samples composed of five subsamples taken within 1 m around the sampling point were transported to the laboratory in 300-mL containers for further analysis. At the initiation of the landfarms, additional samples were necessary to achieve the desired confidence. The cultivated landfarm was sampled over the entire depth. In the vegetated landfarm, a rapidly dewatering upper layer and a slower dewatering lower layer could be distinguished. The whole oxidized brown layer was considered as upper layer and the black and partly black layer as lower layer. Due to ripening, the depths of these layers changed during the experiment. Layers were sampled separately. Samples were analyzed for PAHs (high performance liquid chromatography [HPLC]/Fluores-

Table 1. Sediments investigated at Kreekraksluizen.

Type of sediment and treatment	Start	Intensive landfarming (period)	Passive landfarming since	Vegetation present since	PAHs†		Mineral oil	
					Start	2004	Start	2004
					mg kg^{-1} dry matter			
Petroleum Harbor					550	22	13 500	1300
Cultivated	1994	1994–1996	1996	1996				
Vegetated	1994		1994	1995				
Wemeldinge					45	25	2000	500
Cultivated	1994	1994–1996	1996	1996				
Vegetated	1994		1994	1995				
Geul Harbor	1990	1990–1993	1993	1993	52	2	8100	<200
Zierikzee	1990	1990–1993	1993	1993	65	15	630	<200

† PAH, polycyclic aromatic hydrocarbon.

cence) and mineral oil (gas chromatography [GC]/flame ionization detection [FID]), after extraction with acetone and petroleum ether (respectively ISO 13877 and ISO 16703; ISO, 1998; ISO, 2005).

The solid phase method using TENAX described by Cornelissen et al. (1997) was used to measure the rapid desorbable fraction of pollutants. This method allows prediction of the organic contaminant fraction that can be degraded in 1 yr on a landfarm (Harmsen and Ferdinandy, 1999), and the desorption rate constants for rapid and slow desorption.

After dewatering, a rich vegetation (mostly herbaceous species) developed spontaneously, and no special measures were necessary. Because plant seeds are stored in the sediment, the variation of vegetation in the first years was high. After 5 yr there was vigorous growth of vegetation, with the locally growing grass (*Calamagrostis epigeios*) emerging as the dominant species. Introduction of special plants was not found to be effective. Salt-tolerant reed could not survive in Petroleum Harbor (brackish origin) and Wemeldinge (saline origin)sediments in the dry summer of 1994. Because the observed root formation of the spontaneous vegetation was finally over the whole depth and intensively in the first 50 cm, no further special measures were taken. Creation of an intensive root system is the main task of vegetation in passive landfarming, thereby increasing the evaporation and the volume of air-filled pores. In the last part of this article the beneficial application of landfarming with special vegetation is described.

MODELS

Availability for Degradation

Equilibrium Approach

Polycyclic aromatic hydrocarbons are strongly adsorbed to the soil or sediment organic matter (SOM). In an equilibrium situation the adsorption of the contaminant can be expressed with a partition coefficient. The partition coefficient between organic matter and water, present outside the particle or in the pores, is often expressed as K_{oc}. In this constant, organic matter is expressed as organic carbon. In modeling adsorption equilibrium the partition coefficient between soil (or sediment) and water (K_d) is often used. K_d is assumed to be constant and is defined as:

$$K_d = 1000 fr_{oc} K_{oc} = 580 fr_{om} K_{oc} \qquad [1]$$

where: K_d = adsorption coefficient in m^3 kg^{-1}, fr$_{oc}$ = mass fraction of organic carbon in kg kg^{-1}, and fr$_{om}$ = mass fraction of organic matter in kg kg^{-1}.

Equation [1] is valid if PAHs only interact with SOM. There is, however, also an interaction with dissolved organic matter (DOM) present in the water phase (Roskam et al., 2002), which is stronger for the highly insoluble PAHs. Dissolved organic matter is mostly expressed as dissolved organic carbon (DOC). Also the interaction of the contaminant with DOC can be described with a partition coefficient between dissolved organic carbon and water: K_{oc}^{DOC}. In that case the expression for K_d becomes:

$$K_d = \frac{1000 fr_{DOC} K_{oc}}{(1 + fr_{DOC} K_{oc}^{DOC})} \qquad [2]$$

where: fr_{DOC} = mass fraction of organic carbon dissolved in water in kg kg^{-1}; K_{oc}^{DOC} = partition coefficient between dissolved organic matter (expressed as organic carbon) and water.

K_{oc}^{DOC} can be described similarly as the K_{oc} for solid organic matter *SOM*, using data from literature (Lüers and Ten Hulcher, 1996; Poerschmann and Kopinke, 2001; Mackay and Gschwend, 2001; Laor and Rebhun, 2002). Reported values differ by a factor up to 6. The correlation can be described as:

$$\log K_{oc}^{DOC} = 1.20 \log K_{ow} - 1.04 \qquad [3]$$

where: K_{ow} = octanol/water partition coefficient.

Dissolved organic carbon values measured in the drainage water of the landfarms on Kreekraksluizen are between 0.05 and 0.10 kg m^{-3}. The presence of DOM in the water phase results in a smaller variation in the K_d values at higher DOC values, as shown in Fig. 1. Mackay and Gschwend (2001) have reported an increase in the solubility of PAHs at a coal tar site, which is in agreement with these calculations.

It can be concluded that if diffusion is the limiting factor for degradation, the degradation rate for individual PAHs will become comparable.

Nonequilibrium Approach

The rate of desorption can be limited by internal diffusion processes, which control the transfer of compounds from the interior of the sediment aggregate to the external surfaces. A large variety of diffusion controlled transport models have been proposed in the literature to describe non-equilibrium desorption, ranging from relatively simple first order kinetic rate equations,
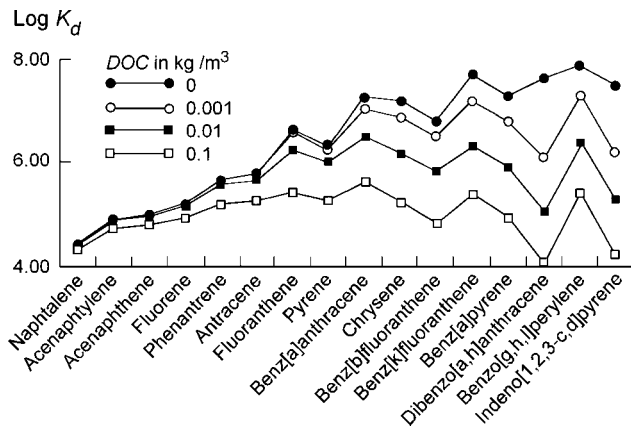
Log K_d

Fig. 1. The effect of dissolved organic matter (DOC in kg m^{-3}) on the calculated distribution coefficient K_d of polycyclic aromatic hydrocarbons (PAHs) in sediment (m^3 kg^{-1}). Fraction organic matter in the sediment amounts to 0.05 kg kg^{-1}.

multi-compartment desorption models, to transport models involving contaminant exchange between a region with a high mobility of the pollutants and a region with a low mobility of the pollutants. van Genuchten and Šimůnek (1996) give an extended discussion of the different transport equations that can be used. One of the simplest models for transport of a pollutant out of sediment aggregate is given by Rolston et al. (2003):

$$\frac{\partial c}{\partial t} = -k \times c \qquad [4]$$

where: k = first order kinetic rate constant in d^{-1} and c = average contaminant concentration in the aggregate in kg m^{-3}.

Assuming no mass transfer limitation outside the particle, Eq. [4] can be integrated, resulting in:

$$\frac{c_t}{c_0} = e^{-k \times t} \qquad [5]$$

in which: c_o = average concentration of contaminant in the aggregate at $t = 0$ and c_t = average concentration of contaminant in the aggregate at $t = t$.

If different adsorption sites are present like expended and condensed organic matter (Pignatello, 1998) or black carbon (Koelmans et al., 2006), Eq. [5] can be expended to a sum of first-order decreases. In this article a sum of three first-order decreases is used: (1) rapid, (2) slow, and (3) very slow, each decrease expression having its own rate coefficient.

The rate constant k in Eq. [5] has to be considered as an empirical rate constant. It includes physical factors like the size and shape of the sediment aggregate and the moisture content. For a structured soil, which is the result of landfarming a sediment, the first-order transport process can be modeled more realistically. It is assumed in this model that the transport of a contaminant in a single aggregate, containing pores that are partially filled with water, occurs via the water-filled pores in the aggregate and can be described by a general diffusion equation (Rijtema et al., 1999). In this model, the shape of the aggregate (sphere, cylinder, or plate) is represented by the shape factor m. The diffusion equation can

be solved numerically, which results in an equation like Eq. [5], in which the rate constant k is expressed as:

$$k = \frac{2(m + 1)D_s^w}{[\theta + \rho_s(1 - \varepsilon)K_d]r^2} \qquad [6]$$

where: θ = internal aggregate moisture content in m^3 m^{-3}, ε = volume fraction of total pore space in the aggregate (water and air-filled) in m^3 m^{-3}, r = distance from the surface to the center of the aggregate in m, m = shape factor for the aggregate structure (0 for plate aggregate; 1 for cylindrical aggregate; 2 for spherical aggregate), ρ_s = specific weight of the wet soil sediment in kg m^{-3}, and D_s^w = average contaminant diffusion coefficient in sediment/soil pore water in m^2 d^{-1}.

The internal aggregate moisture content has to be considered in unsaturated soils as the immobile moisture fraction and depends on clay content and organic matter content. In aerobic unsaturated soils, its value varies from 0.02 in sandy soils with very low organic matter content to about 0.50 in soils high in clay and organic matter content. In sediments, the moisture content will be much higher and may reach values of 0.7. The contaminant diffusion coefficient in soil pore water D_s^w can be approximated by:

$$D_s^w = \eta\theta D^w \qquad [7]$$

where: η = tortuosity factor and D^w = diffusion coefficient of contaminant in water.

The value of η depends on the clay and the internal moisture content and is given by Rijtema et al. (1999) as:

$$\eta = -0.00389\text{fr}_{cl} + 1.28\theta \qquad [8]$$

where: fr_{cl} = weight fraction of clay.

Using the values of D^w from the literature, the values of D_s^w can be calculated. However, the DOM also influences the diffusion coefficient. The associated molecule is much larger and will consequently diffuse more slowly in the water phase than the individual PAH molecule. The diffusion coefficient of the associated DOM-PAH molecule can be estimated using the expression (Trapp and Matthies, 1997):

$$D^w(\text{DOM} - \text{PAH}) = 1.728 \times 10^{-4} \times \sqrt{\frac{32}{M}} \qquad [9]$$

where: M = molar mass.

Using the relations for D_s^w (Eq. [7]) and η (Eq. [8]), and limiting the application to components with high K_d values, the expression for the rate constant as given in Eq. [6] can be simplified as:

$$k \sim \frac{\theta^2}{(1 - \varepsilon)r^2} \qquad [10]$$

Because the moisture fraction is a variable, this equation can be used to compare unsaturated conditions (landfarm) and saturated conditions, as found in laboratory desorption studies. The simplification is not valid in situations with high clay content and low moisture content, which only occur under extremely dry conditions.

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Presence of Oxygen

A sediment is anaerobic directly after dredging and placement in a landfarm. The presence of oxygen is the limiting factor for biodegradation, because oxygen must diffuse through the water, which is a slow process. During dewatering and ripening (formation of physically stable soil aggregates), dredged sediment is changed into a structured soil, in which part of the water (moisture) in the pores between soil particles is replaced by air and oxygen can reach greater depths. It is possible to predict the air-filled fraction of the soil using basic soil properties (silt, sand and clay content, organic matter content) and the soil water potential. In landfarming systems the depth containing sufficient oxygen is an important parameter, because this determines the thickness of the layer of sediment that can be applied. Rijtema et al. (1999) developed theories to describe aeration in soils. These theories have been used to model oxygen present in sediment during dewatering. The Petroleum Harbor sediment treated on the Kreekraksluizen landfarm has been used as an example. During dewatering and ripening of dredged sediment the following visible processes occur:

(1) Compaction of the sediment layer,
(2) Development of cracks between large soil aggregates,
(3) Aeration of smaller aggregates (color changes from black to brown),
(4) A soil that supports vegetation is developed.

Aeration has been modeled, taking into account the following physical processes (Harmsen, 2004):

(1) Formation and aeration through cracks as a result of shrinking,
(2) Soil moisture profile as a function of properties of the developed soil and time of the year, including the water balance,
(3) Size of aggregates as a function of moisture potential,
(4) Oxygen consumption due to degradation of organic matter (rapid, slow and very slowly degradable fractions),
(5) Oxygen diffusion in aggregates,
(6) Temperature,
(7) Temperature-dependent activity of microorganisms.

The soil moisture profile is not a constant factor. It depends on the soil type, water table, amount of rainfall, and evaporation. Figure 2 gives an example of a soil moisture profile. With excess rainfall the sediment can be saturated, and after physical equilibration, gas-filled pores are present (difference between saturation and equilibrium in Fig. 2). This describes the situation in the winter period. In summer evaporation increases as temperature increases and vegetation grows. As a result, the air-filled pore volume further increases.

RESULTS AND DISCUSSION

Degradation

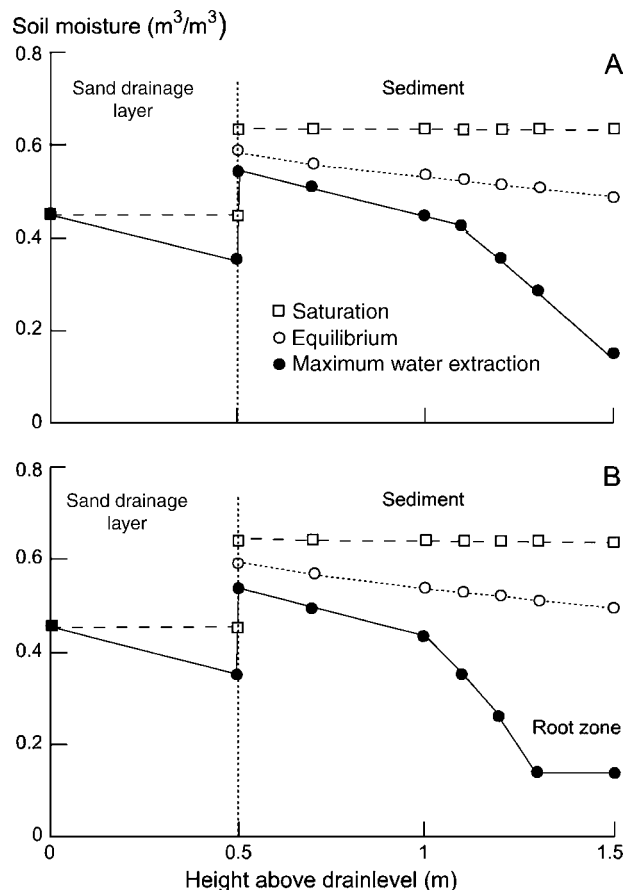Both PAHs and mineral oil have been degraded during the course of 10 to 15 yr of landfarming. Table 1

Fig. 2. Soil moisture distributions as a function of the depth below the soil surface in Petroleum Harbor sediment. Above the drains (at −1.5 m below surface) a sand drainage layer of 0.5 m is present. (A) bare sediment; (B) sediment covered with vegetation with an effective root zone of 0.2 m. The maximum supply rate from the deeper layers by capillary rise equals 0.01 m d^{-1}, when the maximum water extraction rate has been reached.

shows the original concentrations and the concentrations present in October 2004 in the different sediments. In one case (Geul Harbor), values have been decreased to almost background values, but in the other landfarms residual concentrations were still present. Residual concentrations in the different treatments of Petroleum Harbor and Wemeldinge sediments were the same in 2004.

In the upper layer of the vegetated landfarms, aerobic conditions had been achieved in the first summer. Therefore, the fastest initial degradation occurred in this layer. The degradation curves can be fitted to two exponential curves. In Fig. 3A the degradation curve obtained from the Petroleum harbor sediment for the sum of PAHs on the Dutch National List, (Phenanthrene, Anthracene, Fluoranthene, Benz[a]anthracene, Chrysene, Benz[k]fluoranthene, Benz[a]pyrene, Benzo[g,h,i]perylene, and Indeno[1,2,3-c,d]pyrene) is presented. Naphthalene was not included because the accuracy of the measurement, especially at low concentration, was poor. Similar degradation curves were obtained with individual PAHs. Also high molecular weight PAHs showed rapid degradation, although the rapid degradable fraction was smaller compared to the low molecular ones. After 1 yr, aeration was no longer
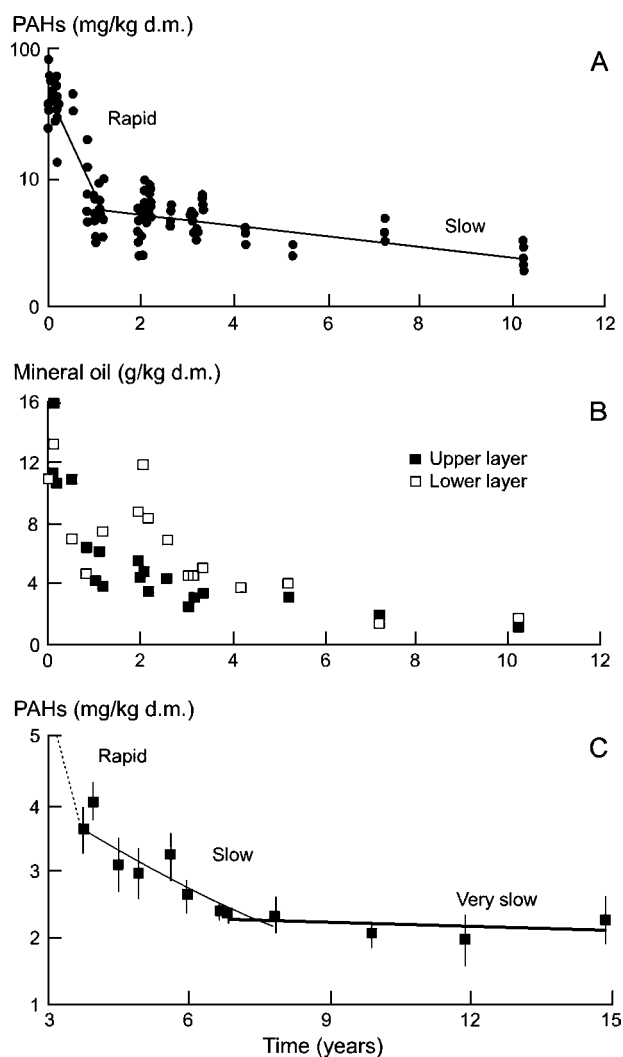
Fig. 3. Degradation curves measured on the landfarm Kreekrakslui-zen. (A) Polycyclic aromatic hydrocarbons (PAHs) (Dutch National List) in Petroleum Harbor sediment (upper layer of vegetated sediment). Individual measurements, fitted with two exponential functions (rapid and slow degradation). Mind the logarithmic scale. (B) Mineral oil in the vegetated Petroleum Harbor landfarm (upper layer and lower layer). Presented data are the average concentration per sampling date. (C) PAHs in Geul Harbor sediment. 95% confidence values are given, fitted with two exponential functions (slow and very slow degradation).

the limiting factor in the upper layer, and the initial rapid degradation was followed by a slower phase.

In the cultivated field, which was sampled over the whole depth (90 cm), more time was necessary to obtain aerobic conditions. Cultivation mixed the aerated upper layer with anaerobic sediment from the lower layers. Because cultivation was started in November 1994 instead of June 1994, 2 yr were necessary to obtain a field aerated over the entire depth of 90 cm. This was reflected in the degradation curve. Rapid degradation lasted for 2 yr, followed by a slower degradation rate in succeeding years. In the cultivated landfarm as well as in the upper layer of the vegetated landfarm, the first rapid degradation period corresponds with the time required to produce a fully aerated sediment.

In the lower layer of the vegetated landfarm, approximately 4 yr were necessary for dewatering, resulting in a slower degradation rate. However, this did not have a long-term influence on residual concentrations. Optimal dewatering in the upper layer and slow dewatering in the lower layer gave the same results after 5 yr of treatment. This is illustrated in Fig. 3B for mineral oil. During biodegradation, the composition of the mineral oil changed, leaving predominantly high molecular weight components.

In the Wemeldinge sediment, the proportion of rapidly degrading PAHs was much lower, and the different treatments did not affect the results obtained in the landfarm. Very similar results were obtained from both the intensive cultivated landfarm and the upper and lower layers of the vegetated landfarm.

Both PAH and mineral oil concentrations stabilized in the Petroleum Harbor and Wemeldinge sediments at the end of the measurement period. Possibly a third, very slow degrading fraction is present. Further analysis of measurements over an extended period is necessary to establish the proper degradation rate coefficients for the slow degrading fractions in these sediments. Data from the Geul Harbor sediment was used to determine these coefficients. This series of data is long enough to derive degradation rate coefficients. In Fig. 3C the average PAH values (Dutch National List) are presented, including the 95% confidence value for every measurement date.

After 7 yr of slow degradation Fig. 3C shows a subsequent period of very slow degradation. Fitting the data representative for very slow degradation results in a rate constant of 0.013 yr^{-1}. However, because changes are very small and the measurements are over a period of more than 7 yr, accuracy is low. After degradation of the rapidly degradable fraction, a new subsequent rapidly degradable fraction is created from the very slow available fraction. PAHs from this fraction are transported by diffusion to sites were microorganisms are active and this can be measured using the TENAX-method. Therefore, results of TENAX measurement can also be used to calculate the rate constant. In 2004 this rapid degradable fraction (measured as the rapid desorbable fraction with TENAX) was 5.9% with no significant differences between individual PAHs. Assuming that this fraction will be degraded in 1 yr and will follow first-order degradation, this value gives a rate constant of 0.061 yr^{-1}. The same fraction in the Zierikzee sediment was 2.2%, which gives a degradation rate constant of 0.022 yr^{-1}.

It was possible to distinguish between rapid degradation (<1 yr), slow degradation (<7 yr), and very slow degradation in the following years. During the period of rapid degradation, differences in degradation rates between the individual PAHs were observed, but during slow and very slow degradation it was no longer possible to distinguish these. Table 2 gives the degradation rate coefficient for rapid degradation k_{rapid} in the Petroleum Harbor sediment, which contained a large fraction of easily degradable PAHs. The rate coefficients were obtained by fitting the part of the curve responsible for

Table 2. Degradation rate constants of PAHs in the investigated sediments.†

PAHs	k_{rapid} Petroleum Harbor, vegetated upper layer	k_{slow}					$k_{very\ slow}$
		Petroleum Harbor, cultivated	Petroleum Harbor, vegetated upper layer	Wemeldinge, cultivated	Wemeldinge, vegetated upper layer	Geul Harbor	Geul Harbor
					yr^{-1}		
Fluorene	3.99	0.20	0.13	0.17	0.14	0.15	0.097
Phenanthrene	3.68	0.12	0.04	0.11	0.055	0.08	0.048
Anthracene	3.37	0.13	0.16	0.070	0.077	0.23	0.044
Fluoranthene	2.48	0.19	0.15	0.078	0.019	0.26	0.071
Pyrene	2.13	0.17	0.15	0.062	0.030	0.09	–
Benz[a]anthracene	1.55	0.15	0.14	0.071	0.029	0.15	0.072
Chrysene	1.22	0.17	0.13	0.054	0	0.25	0.044
Benz[b]fluoranthene	0.73	0.16	0.12	0.055	0.028	0.18	0.041
Benz[k]fluoranthene	0.89	0.15	0.13	0.054	0.029	0.12	0.048
Benz[a]pyrene	0.51	0.18	0.11	0.053	0.038	0.15	0.018
Benzo[g,h,i]perylene	0.21	0.01	0.04	0.028	0.13	0.12	0.028
Indeno[1,2,3-c,d]pyrene	0.44	0.08	0.01	0.053	0.012	0.08	0.026

† PAH, polycyclic aromatic hydrocarbon.

rapid degradation. Differences are caused by the size of the fraction (higher for the low molecular weight ones) and not by the degradation time (comparable for all). Degradation rate coefficients of slow degradation k_{slow}, for those situations where no limiting conditions for degradation were present in the period of slow degradation, are also given in Table 2. Situations with no limiting conditions included the upper layer of the vegetated landfarm, the cultivated landfarm, and the passive landfarm with Geul Harbor sediment. The difference in magnitude of the degradation coefficients is caused by the size of the very slow degradable fraction. This size was unknown for Petroleum Harbor and Wemeldinge sediment. For Geul Harbor, values for the degradation coefficient for very slow degradation $k_{very\ slow}$ are presented. The observed degradation rate in the Zierikzee sediment was too small to distinguish the slow degradable fraction from the very slow degradable fraction.

When the TENAX method was used to establish desorption rate constants, the same trend was visible, i.e., large differences for the individual PAHs during rapid desorption and small differences during slow desorption. TENAX experiments were performed with the fresh Petroleum Harbor sediment and with the culti-

vated sediment as present on the landfarm in 1997 (Table 3). There is a logical order in the presented values, except for the underlined values. There is no explanation found for these high values. The sizes of the rapid desorbable fractions did follow the logical order and these fractions were small (28 and 19%) for the two (6-ring) PAHs, this compared to approximately 90; 75 and 55% for respectively 3-ring, 4-ring, and 5-ring PAHs. The rapid desorbable fractions were degraded during the rapid degradation phase.

The observation of comparable slow degradation and slow desorption rate coefficients for all PAHs in a specific landfarm is in agreement with the theory of the equilibrium approach, where (Fig. 1) it was shown that due to the presence of DOM, the K_d values and consequently diffusion rates of the individual PAHs becomes comparable. During slow desorption, diffusion is the rate-limiting process.

Tables 2 and 3 show greater differences in the values of desorption and degradation rate coefficients. If desorption curves are compared with degradation observed in a bioreactor, similar values are obtained (Cornelissen et al., 1998; Braida et al., 2004). As long as there are other limiting conditions (absence of oxygen during dewatering in the first period of landfarming), the supply of

Table 3. Desorption rate constants k_{rapid} and k_{slow} of PAHs in fresh and cultivated (1997) sediment of Petroleum Harbor, measured with the TENAX method.

PAHs†	Fresh sediment				Cultivated sediment			
	k_{rapid}		k_{slow}		k_{rapid}		k_{slow}	
				yr^{-1}				
Fluorene	10237	(2556)‡	42	(7)	1545	(1357)	3.9	(2.0)
Phenanthrene	6701	(980)	33	(2)	2103	(1792)	9.7	(5.1)
Anthracene	6246	(798)	38	(7)	3558	(3191)	4.8	(2.6)
Fluoranthene	2686	(443)	83	(17)	2204	(2709)	6.9	(3.9)
Pyrene	701	(156)	22	(7)	1550	(1936)	9.9	(5.8)
Benz[a]anthracene	426	(84)	25	(8)	793	(374)	1.9	(1.3)
Chrysene	426	(99)	17	(13)	1198	(827)	2.9	(1.4)
Benz[b]fluoranthene	262	(33)	37	(11)	337	(211)	5.1	(4.3)
Benz[k]fluoranthene	268	(29)	40	(11)	629	(587)	7.1	(3.7)
Benz[a]pyrene	231	(38)	31	(12)	197	(52)	6.7	(4.3)
Benzo[g,h,i]perylene	3022§	(176)	21	(3)	461	(918)	10.8	(12.8)
Indeno[1,2,3-c,d]pyrene	3476	(866)	30	(6)	61	(52)	1.2	(0.8)

† PAH, polycyclic aromatic hydrocarbon.
‡ Numbers in parentheses = standard deviation ($n = 5$).
§ Values in italic are not in logical order, no explanation was found.

oxygen will explain the degradation rate. This partly explains the differences for the fast process.

During slow degradation, oxygen is not rate-limiting for degradation, because sediments were dewatered and completely aerobic. It is important to realize the differences in experimental conditions when comparing the rate coefficients. In the landfarm, the soil is unsaturated with water, providing aerobic conditions. The TENAX system is a slurry system and no gas-filled pores are present. Diffusion to the TENAX, which is the driving process for desorption, is faster in a fully water-saturated system and also when soil particles (aggregates) are smaller. As shown in Eq. [10], the rate constant k is proportional to the square of the moisture content (θ, expressed in $m^3 \ m^{-3}$) and inversely proportional to the square of the radius (r in m) of the soil aggregate. Diffusion also depends on the pore volume in the aggregate (ε in $m^3 \ m^{-3}$). In fresh sediment the fraction of the pore volume is about 0.7, which is completely filled with water. In dewatered sediment, a pore volume fraction of about 0.55 and a range of water-filled soil volumes of 0.2 to 0.5 are generally observed. Oxygen is essential for biodegradation and in a landfarm the supply is optimal if about 25% or less of the total sediment/soil volume is filled with water. Comparing the values of the dewatered and fresh sediment, a difference of a factor of 3 to 18 in the rate constant k can be calculated. In the TENAX measurement, as will be the case in bioreactors, the aggregates are partly broken up and mixed in a turbulent fluid environment. This influences the aggregate radius. If this is a factor of 2, differences in the rate constant between a factor of 12 and 76 can be explained. These are also the differences of the values for the slow process as presented in Tables 2 and 3.

Combining the degradation results, the degradation curve on a landfarm can be predicted with a sum of three first-order decreases. Taking into account the sizes of the different available fractions, the rate coefficient k for the rapid, slow, and very slow degradable fractions are respectively 3.5, 0.33, and 0.04 yr^{-1} (Harmsen, 2004). The size of the rapid degradable fraction can be predicted using TENAX. As suggested by Cornelissen et al. (1997), the results of TENAX desorption at 60°C can be an estimate for the slow degradable fraction.

Aeration

The aeration model has been applied to the following situation where a 1-m layer of sediment has been passively landfarmed; four layers of 25 cm were distinguished. Properties of the sediment were based on the properties of the Petroleum Harbor sediment landfarmed on the Kreekraksluizen landfarm (clay 25.9%, organic matter 9.1%, and dry density after dewatering 947 kg m^{-3}) and the Dutch climate (precipitation and temperature) (Harmsen, 2004). Presence of roots in each layer was one of the variables. The results are presented for every layer (Fig. 4).

The results in Fig. 4A (left figure) simulates the situation of the vegetated landfarm (root depth 25 cm in the first year and 50 cm in the second year) and show that the upper 25 cm was already fully aerated in the first year. The following 25 cm was aerated in the second year. More time will be required to dewater the lower two layers. Results of the model are confirmed by the results of the Kreekraksluizen landfarm (right part of figure). These are the field observations on the aeration (aerobic, partly aerobic, and anaerobic). As explained in the Material and Methods section, the Kreekraksluizen landfarm had a delay of 1 yr caused by legal requirements for permission for treatment. As a result of aeration, the easily degradable organic matter is removed completely together with the easily degradable contaminants in the upper 25 cm in the first year. Two years are necessary for the 25- to 50-cm layer and the degradation rate in the lower layers is smaller. The difference between degradation rates of the upper 25 cm and the lowest layer is confirmed by the result presented in Fig. 3B. One yr is necessary for rapid degradation in the upper layer and 4 yr are necessary to have the same degradation in the lower layer.

Applying intensive landfarming means active soil treatment during dewatering. This will result in both an adequate oxygen supply and degradation of easily degradable organic matter in the first year. If the sediment is cultivated, it is possible to obtain a fully aerated sediment in 1 yr. If intensive landfarming is followed by passive landfarming in the following year, the upper 75 cm of the landfarm will stay fully aerobic (Fig. 4B). This has been confirmed by the results from the Kreekraksluizen landfarm. The setback in aeration after intensive treatment for the lowest layer was also visible.

Increasing the temperature normally affects the degradation rate, not only for degradation of the contaminants, but also for natural organic matter. This results in an extra demand for oxygen. The net effect is that an increase in temperature during the whole year to a summer value (we calculated with an average of 16.8°C from the start of the landfarm), instead of the yearly summer and winter fluctuations, does not affect the degradation. Increasing temperature will only be effective if this is combined with forced aeration. This is only possible in an intensive treatment management system.

CONCLUSIONS AND CONSEQUENCES FOR APPLICATION OF PASSIVE LANDFARMING

Mechanistic Model and Experimental Results

In heavily contaminated sediment PAH and mineral oil degradation becomes limited, following depletion of the fraction that is easily accessible to microorganisms. If this phase is reached, the rate-limiting process can be described by desorption and subsequent transport by diffusion to areas with microbial activity. The formulation of the mechanistic transport model can be simplified to a first-order decrease process in which the rate constant depends on the pore volume, moisture content, and radius of the aggregates in the sediment. Using this approach, it is possible to explain the large differences in
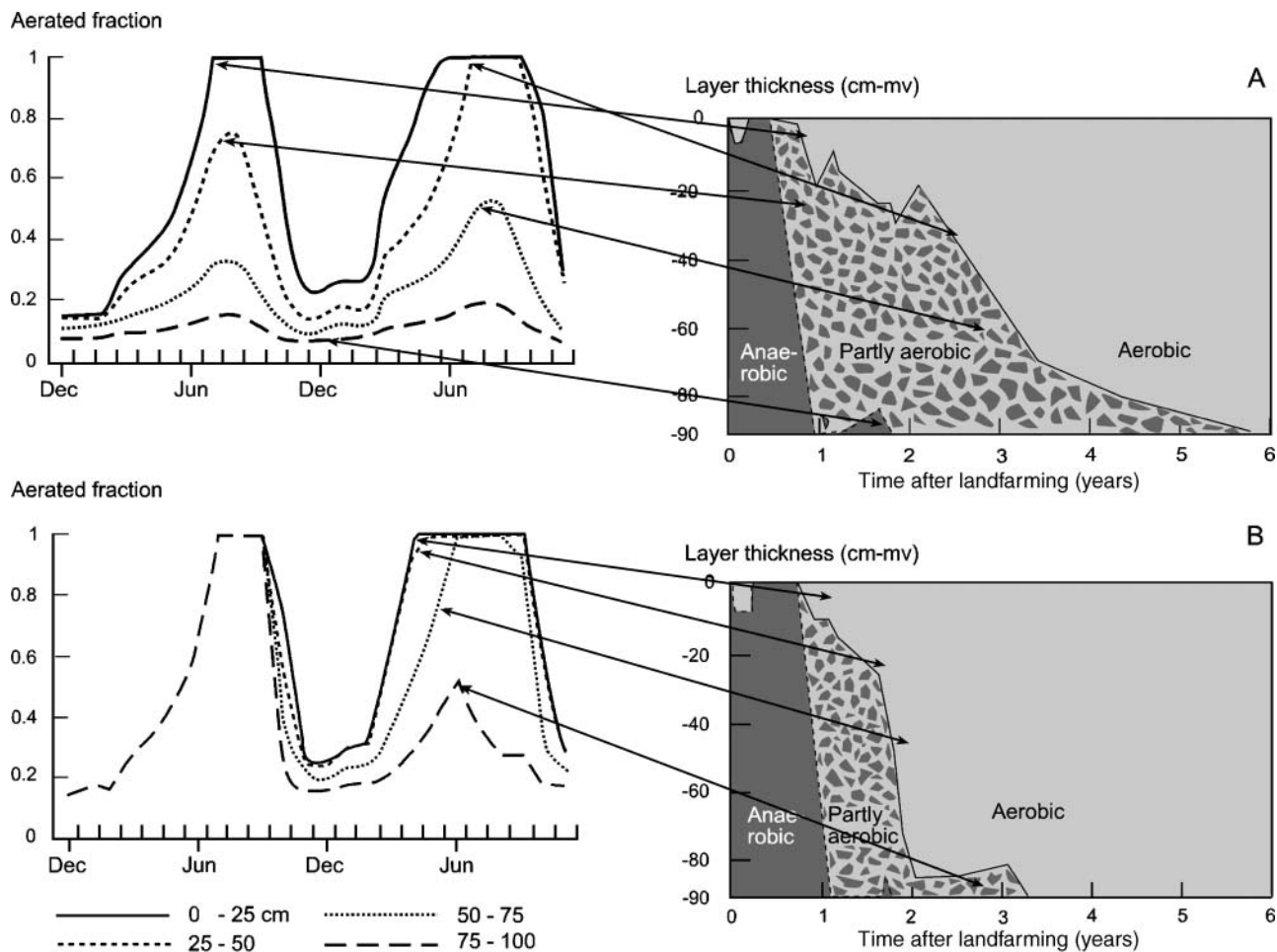
Fig. 4. Aeration, as calculated using the landfarm aeration model (left) and the field observations (right). Arrows connect calculated and observed situations. (A) Landfarm with roots in the upper 25 cm in the first year and roots in the upper 50 cm in the second year. Aeration as observed in the vegetated landfarm of Petroleum Harbor sediment. (B) Active cultivation in the first year and passive landfarming in the second year. Aeration as observed in the cultivated landfarm of Petroleum Harbor sediment.

degradation rate observed between optimized bioreactors and more passive landfarm systems. The diffusion rate of contaminants in the sediment can be increased by increasing the moisture content of the sediment during treatment, but this will limit aeration of the sediment and hence degradation rate.

It has been shown in the field experiments and with an aeration model that aeration depends on several factors. The highest rate is obtained by intensive treatment (cultivation) during the first year of landfarming. Development of vegetation during passive landfarming is also effective, and the sediment becomes aerated in the rooted layers. The model has also shown that increasing temperature during passive landfarming is not an effective way to stimulate degradation of contaminants.

It is clear that the necessary supply of oxygen in a passive landfarm be provided by creating a significant fraction of air-filled pores. However, this fraction should not become too small, because this will limit diffusion of the contaminants to sites with active microorganisms. Under Dutch climatic conditions this means that the water table on a passive landfarm should be low and any excess of precipitation should be removed during summer by deep-rooted vegetation. Under drier conditions, diffusion can be limited during the latter part of summer. This can be prevented by supplying water or accepting longer cleaning periods.

Combining the two limiting factors, it has been shown that the availability of oxygen is most important during the first phase of bioremediation, followed by the bioavailability of the contaminant. If low residual concentrations are required, the bioavailability of the contaminant determines the time necessary for bioremediation. Lengthy periods of several decades may be necessary to reach regulatory targets, as shown for the experimental Kreekraksluizen landfarm. The extent of biodegradation can be predicted using a model including a summation of three first-order decreases describing the degradation of the rapidly, slowly, and very slowly degradable fractions. Data collected from Kreekraksluizen supports this model. Necessary model parameters are the size of the different fractions and degradation rate coefficients. The sizes of the fractions can be derived from laboratory experiments using TENAX, and degradation rate coefficients on a landfarm are given in this article.

Applications

As already mentioned, vegetation, e.g., growth of biomass on treated sediment, can stimulate degradation. This provides an excellent opportunity to produce non-fossil fuel energy feedstock. Fast-growing species of willow and poplar can be grown and harvested by coppicing on a regular cycle to produce useable wood biomass for a range of applications, including bio-energy. The tree is cut back to just above ground level after the first year of growth causing many new shoots to develop. Harvesting involves the cutting and removal of these shoots at regular (normally 2 to 5 yr) intervals. This practice is called short rotation coppice (SRC) and maximizes the social and economic as well as the environmental benefits of biomass production on marginal land (Paulson et al., 2003).

In the Netherlands, SRC is seen as an opportunity for the reuse and remediation of sediments. Oostwaardhoeve is an experimental farm in northwestern Netherlands where this is practiced (Breteler et al., 2001). Cultivation of willows for biomass energy production has been studied on this farm since 1993. This cultivation has been combined with the remediation (landfarming) of polluted sediments since 1996. In treating sediments, SRC crops have an extra benefit, because they have a positive effect on dewatering. During the treatment the quality of the sediment improves due to biodegradation of PAHs and mineral oil.

In the United States the development of fossil fuel natural resources over large land areas in eastern Utah will require extensive remediation and reclamation of the disturbed land. Remediation using landfarming for production of biomass in the form of energy crops in this area can be applied for producing biofuels as well as for controlling erosion and reclaiming marginal land, thus adding environmental and economic benefits.

A special case has been developed for use in Nizhnekamsk, Tatarstan, Russian Federation (Harmsen and Sims, 2002), where contaminated industrial sludge requires remediation. Although the sludge is highly polluted (almost 50% of the sludge consists of mineral oil and other organic chemicals), landfarming will be effective because (1) microorganisms are present in the sludge and can be activated (Nikitina et al., 2003), (2) effective biodegradation of mineral oil and PAHs has been demonstrated in pilot landfarming experiments (Galukhin et al., 2002), and (3) toxicity has decreased significantly during this treatment (Olsen et al., 2003).

It is proposed to use the dewatered sludge to solve another problem in Nizhenekamsk as cover for a site used for disposal of solid hazardous waste, including spent catalyst, resins, and rubber waste. The site is available for the next 25 yr after which it will be returned to the community. It is expected (using the multicompartment model) that over this period, oil content of the sludge will be reduced to below 1000 mg kg^{-1}.

In 2005 a consortium of different parties (Watervast, 2005) won a competition, where new concepts were solicited for beneficial reuse of large amounts of sediment in the Netherlands. In this concept, reuse of contaminated sediments was combined with construction of dikes to improve safety in the areas between large rivers in the Netherlands. There was serious danger in the high water period of 1995 and, due to climate changes, such events are expected more frequently. A system of low compartment dikes has been designed to reduce the impact of flooding. These dikes can have several functions (e.g., roads, housing, nature), which is important for the social acceptation of the concept. These will be constructed from material from the flood plains, which will create more space for the river in periods of high water, and from dredged sediments from local canals and ditches. Polycyclic aromatic hydrocarbon- and mineral oil-contaminated sediments will be applied to the top of the dikes to ensure aerobic conditions. Use of these materials is not possible in the base of the dike, because of the high water table in the area. The wet conditions are suitable for heavy metal-contaminated sediment to immobilize these contaminants as sulphides (Harmsen et al., 2002).

The beneficial applications described above can all be combined with treatment times of several decades, which can be necessary to reach regulatory targets for landfarming, or even to reach background values for PAHs and mineral oil. In all applications it is possible to achieve and maintain conditions as normally found in a vegetated surface soil with a low water table. Other combinations will be possible and the aeration model provides a tool to predict whether conditions on a site used for landfarming are adequate for aerobic degradation and to optimize these conditions, e.g., lowering of water table, stimulation of vegetation to improve the aeration, and active dewatering. If low residual concentrations of the contaminants are necessary, passive treatment and stimulating vegetation with a well developed root system will probably be the most optimal and cost-effective way of treatment. The degradation model (sum of three first-order decreases) and degradation coefficients given, can show if, and more importantly when, regulatory targets are attained. The combination of passive landfarming with beneficial land use will also have social acceptance aspects that must be addressed. Results and tools presented in this article can be part of this.

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