Soil flushing by surfactant solution: Pilot-scale demonstration of complete technology

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ABSTRACT

This paper mainly relates to the real polychlorinated biphenyl (PCB)-contaminated soil flushing process, in which an aqueous solution of anionic surfactant was passed through sandy soil having an average concentration 34.3 mg/kg of dry matter. The goal of the treatment was to decrease the PCB concentration in the soil to less than 10 mg/kg, which is a limiting value if the soil is to be used in the field of civil engineering. The laboratory part was focused on the demonstration of the suggested method for estimating the CMC value of the surfactant used for leaching the PCBs from the soil to the solution. The estimate was based on a set of batch experiments carried out with the same soil as the soil used for the pilot-scale experiments. Theoretically, all effects affecting the CMC should be considered in an estimated value.

The experimental facility used for the pilot-scale demonstration consisted of a steel column (3 m in length, 1.5 m in diameter) containing 1.7 m^3 of polluted soil and a liquid circulation system, by which an aqueous solution of a surfactant was supplied to the soil. Spolapon AOS 146 (anionic surfactant) solution (40 g/L) was passing through the soil column for 2.5 months. The concentration of the surfactant and PCBs in the aqueous soil extract was monitored during this time period. The final PCB concentration profile in the soil was determined after stopping the liquid flow. After passing through the soil, the PCBs containing the aqueous extract was pumped out from the steel column bottom to a treatment unit, where it was processed by coagulation. The final PCB concentration profile in the soil was compared with the results of the theoretical model, which is also described in the paper. The time necessary to reach the limit demanded was estimated to move within the range from 6 to 12 months.

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1. Introduction

Proposals for remediation of soils polluted by polychlorinated biphenyls (PCBs) compounds have included incineration, solidification/vitrification, electrokinetic approaches and some other special methods [1,2]. However, mainly due to costs, environmental constraints and efficacy, many of these approaches have never been applied in the field-scale system, except very expensive incineration. That is why other more efficient methods for treating PCB contaminated soils continue to be proposed, optimized and evaluated [3].

Significant attention is devoted to the process in which the PCBs are leached out from the soil by using surfactant solutions [4,5]. This technique is mostly called soil flushing when used as an in situ process or soil washing for an ex situ batch arrangement [6–8].

The positive effect of the surfactant presence in the aqueous phase in contact with the PCB contaminated soil to the PCBs solubility has been known for many years [9]. A treatment technique based on surfactant solution flushing/washing has been found to be able to reduce the hydrophobic hydrocarbon content in solid contaminated materials [5]. It can be expected, that leaching with a surfactant can effectively and cheaply substitute very expensive thermal methods (the only methods able to remove the PCBs and other persistent pollutants from soils), at least for less-contaminated soils [10].

Many scientific studies from recent years deal with the principles of the surfactants effects on the solubilization of non-polar species in aqueous solutions as well as with surfactant behavior in aquifers, with the possibilities of increasing the surfactant efficiency, etc. As the main condition for reaching a high enough pollutant solubilization efficacy in an aqueous solution, the necessity of an excess of critical micellar concentration of the surfactant in the leaching solution is usually mentioned [9]. Particularly, many studies related to the suitable types of surfactants and their interactions with the pollutants [3,9,11–16], suitable composition

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of flushing solutions [4,17–19], sorption behavior of surfactants [9,20–24], biodegradability of surfactants [25,26], as well as to a processing of soil extracts with high content of both the contaminant and surfactant [27–29] have been published. In addition to these studies, some works describing practical technological applications of surfactants are also available [10,30]. Many studies have been published [31,32], in relation to the persistent organic pollutants (POPs) or particularly PCBs. This provides quite a sufficient amount information about these species.

In this study we want to extend the number of such practically oriented studies. We would like to present the integrated results of the pilot-scale demonstration of the PCB-polluted soil flushing by use of a simple anionic surfactant without any additives and in this way, to share our experience with practical questions of surfactant application for PCB removal from polluted soils. To make the study more integrated, we also suggest a method for estimating the CMC value of the surfactant based on laboratory batch experiments, which is demonstrated and a simple mathematical model of the flushing process is described. The study also contains results of processing the soil extract with a high content of both PCBs and surfactant.

2. Theory

The theoretical part consists of the description of the simple "semi-empirical" mathematical model of the process, in which the soil layer is flushed by the aqueous surfactant solution. The model is based on our previously published model related to metal-polluted soil flushing [33]. In the present article, we disclose only a new part of the model which is specific to the soil flushing by the surfactant solution (this is the only thing in which the model differs from the model published before). The new part of the model consists in the description of PCB solubilization from the soil to the solution.

The theory of the micellar solubilization of the PCBs on the molecular scale is in scope with a few models already suggested [34]. In general, such models try to describe the PCB solubilization/flushing process in a very exact way, but it is difficult to use it for a simple simulation of the flushing process if we only want a fast and simple estimate, sufficient for a decision about continuing the particular remediation project of applied research (for example). In contrast to these exact models, the simple model suggested in this work describes the flushing process in a "semi-empirical" way, which should be simple and fast to use. The "semi-empirical approach" means, that model input data is obtained from a set of simple laboratory experiments carried out with the particular polluted soil.

2.1. PCB solubilization description

Equilibrium distribution of species (e.g. PCBs) between the solution and the soil can be generally described by a distribution coefficient l/s, which is defined as [35]

$$K_{ws} = \frac{C_w^*}{C_s^*} \tag{I}$$

where K_{ws} means the distribution coefficient of the PCBs between the solution and the soil and C_w^* and C_s^* are the equilibrium concentrations of the PCBs in the solution and the soil, respectively.

The description of the PCBs distribution coefficient dependence on the amount of the surfactant present in the solution is an important part of the model suggested. This "semi-empirical" approach is similar to other kinds of problems, although it is obvious from the theoretical knowledge it is not quite correct to describe the solubilization of the organic pollutants in an aqueous surfactant solution by distribution coefficient (because PCBs are present inside the

structures known as surfactant micelles—it is not the same mechanism as the dissolution of inorganic salts in water, for example). The distribution coefficient only has to be understood in the model as a tool for quantification of the amount of the pollutant solubilized in the flushing solution without any interpretations. However, a similar approach to the model description of the systems with surfactants has already been published [16].

Two effects affecting the surfactant concentration in the solution, which is efficient towards the PCBs solubilization from the soil, are included in the model. The first is the adsorption of the surfactant by the soil particles. The second is the existence of a critical micellar concentration (CMC).

Adsorption of the surfactant by the soil is described by the Langmuir isotherm in the model:

$$C_{ads.(surf.)}^* = C_{max} \times \frac{C_{w(surf.)}^* \times \alpha}{1 + C_{w(surf.)}^* \times \alpha} \tag{II}$$

where $C_{ads.(surf.)}^*$ is the surfactant equilibrium concentration adsorbed onto the soil, while $C_{w(surf.)}^*$ is the residual equilibrium surfactant concentration in the aqueous solution. C_{max} means the maximal sorption capacity of the soil and α is the Langmuir adsorption coefficient.

The surfactant concentration efficiency toward the PCB solubilization is then the residual surfactant concentration in the solution after adsorption onto the soil lowered by the CMC:

$$C_{eff.(surf.)} = C_{w(surf.)}^* - CMC \tag{III}$$

where $C_{eff.(surf.)}$ represents the concentration of the surfactant in the solution, which is efficient toward the PCB solubilization from the soil.

Finally, the PCB solubilization efficacy description included in the model is based on K_{ws} dependence on $C_{eff.(surf.)}$. It is considered that one shall know both this functional dependence and sorption isotherm of the surfactant onto the soil from a set of simple laboratory batch experiments carried out on the sample of the same soil which the flushing technology is considered to be used upon.

3. Experimental

3.1. Materials and methods

Simple laboratory experiments which provided the input data for the flushing model suggested and which was briefly introduced in the theoretical part as well as the pilot-scale demonstration of the flushing are described in the experimental part of this paper.

3.1.1. Chemicals, solvents and surfactants

A sample of the technical anionic surfactant with trade name Spolapon AOS 146 was provided to the study by Enaspol Velvety Co. (Czech Republic). The product contains 38 wt.% of the active surfactant component. The structure of the surfactant is based on the linear sodium alkene sulfonates and hydroxyalkanesulfonates (C12–C16). This product was chosen due to its low price (about 0.8€/kg) and with respect to the results of the preliminary laboratory tests with the various surfactants, in which Spolapon AOS 146 proved similar PCB solubilization efficiency from the soil as the other tested products (which were more expensive). The CMC value of this surfactant in water was determined by various methods about 2–3 g/L [36].

Hexane for PCB extractions from the samples was supplied by Pestapur while Florisil for the extracts purification by Sigma–Aldrich. Methylene blue was also supplied by Sigma–Aldrich. Chloroform was supplied by Penta (CZ). Ferric chloride (39 wt.% solution) used for flocculation was supplied by Kemi-

floc (CZ) as well as calcium hydroxide for neutralization. The sample of Septonex (volumetric agent for anionic surfactant determination) was bought in a pharmacy. The systematic name of Septonex is (1-(ethoxycarbonyl)pentadecyl)trimethyl ammonium bromide. It is similar to Hyamine 1622 (*N*-benzyl-*N,N*-dimethyl-*N*-(4-(1.1.3.3-tetramethylbutyl)-phenoxyethoxyethyl)ammonium chloride), which is also commonly used for surfactant analysis by the volumetric method [37].

3.1.2. Analytical methods used

The PCB content in the soil was analyzed in the following way: a known mass of the soil sample between 0.8 and 1.5 g (precisely measured on an analytical balance) was extracted for 4 h by hexane on the temperature of its boiling point (the soil was placed between the boiling test-tube and back flow condenser of hexane, in this way, soil extraction by fresh solvent was achieved). Then, the soil extract in the boiling test-tube containing the whole PCB content of the soil was then passed through a column with length of 10 cm and diameter of 3 mm filled with an activated Florisil. The extract was filled up to the volume of 10 mL by the hexane and PCB concentration was measured on the gas chromatograph with the ECD detector (Hewlett Packard 5890). Only six congeners (number 28, 52, 101, 153, 138, and 180) of the PCBs were quantitatively evaluated due to Czech law. The PCB content in the sample was then the sum of those six congener concentrations.

The PCB concentration in the aqueous samples was determined after extraction with 10 mL of hexane for 2 h with shaking, separation of the hexane phase sample and purification of it by use of the same column of Florisil as in the case of the soil samples extracts.

The analysis of anionic surfactant content in the liquid aqueous samples was done by the volumetric method in a two-phase system chloroform–water [37]. The methylene blue solution was used as indicator while the solution of cationic substance Septonex was a volumetric agent. At the beginning of the titration, in the presence of anionic surfactant, the color blue remains in the chloroform phase. As titration (in term of addition of the volumetric solution) continues, the color blue passes into the water phase. The point of equivalence was determined as decolorizing of the chloroform phase.

3.1.3. Soil sample pre-treatment

Real PCB-contaminated soil used for the experiments in this study was sampled on the site situated in the central area of the Czech Republic, where an incinerator plant was planned to be built but has never been realized. The soil sample for a laboratory part of the research was taken from the same place on the site as the sample for the future pilot-scale demonstration (see Fig. 1).

The laboratory sample of the soil was air-dried and sieved through a sieve with a mesh of 1.6 mm. For the experiments, only the undersieve fraction was used due to the desired condition of homogenous sample. The soil sample (about 5 kg) was then homogenized by rotation in a barrel for 30 min. The soil pH was measured in a 1:2.5 (m/v) ratio of soil and 0.01 M CaCl$_2$ water solution suspension. The soil sample was analyzed for its total carbon content by an Elementar Vario EL III analyzer while carbonates were determined gravimetrically after reaction with phosphoric acid. The difference between these values was considered as the soil organic carbon content (after calculation of the soil carbon content in the form of carbonates). Granulometric analysis, soil texture, the soil particle's density and hydraulic permeability were determined according to the Czech/European/International norm CSN CEN ISO/TS 17892-4 "Geotechnical investigation and testing—laboratory testing of soil". Bulk density was simply determined in a volumetric cylinder and porosity was calculated from the densities (particles and bulk). Finally, the PCB concentration in the soil sample for the labora-

Fig. 1. Polluted site where the soil sample for laboratory experiments as well as for pilot-scale demonstration was taken (sampling by use of small loader).

tory experiments was determined (11 samples were taken from the barrel). The whole soil characteristics are presented in Table 1 including PCB concentration in the soil used for the pilot-scale demonstration. The PCB concentration in the pilot-scale sample was lower than in the laboratory sample although the sample was taken at the same place on the polluted site as the sample for the laboratory experiment. It could be caused (among other reasons) by sieving of the laboratory sample which causes the removal of bigger fractions of the soil which are usually less-contaminated due to its lower surface area (finally, the sieving process causes pre-concentration of the contaminant in the undersieve fraction).

3.2. Laboratory experiments

The equilibrium batch leaching experiments were carried out in frame of the laboratory part of the project presented. These experiments were focused on description of both the sorption behavior of Spolapon AOS 146 onto the soil and the solubilization efficacy of it towards the PCBs present in the soil. Both of these aims were achieved by two sets of the equilibrium batch experiments carried out in the following manner: first, 100 mL of the Spolapon AOS solution with various concentrations was shaken for 24 h with 40 g of soil. The concentrations of Spolapon AOS 146 used were

Table 1
Selected physical and chemical characteristics of the homogenized soil sample used for experiments

pH (CaCl$_2$)	7.2
Organic carbon (%)	1.5
CO$_3^{2-}$ (mg/kg$_{dry\,soil}$)	30,000
Sand (%)	80
Silt (%)	17
Clay (%)	3
Gravel (%)	0
Texture	Sandy silt
Particles density (kg/m^3)	2650
Bulk density (kg/m^3)	1630
Porosity (%)	40
Hydraulic conductivity (m/s)	5.7×10^{-6}
Total PCBs (mg/kg$_{dry\,soil}$), laboratory part[a]	78 ± 23
Total PCBs (mg/kg$_{dry\,soil}$), pilot-scale demonstration[b]	34 ± 3

The data relates to the laboratory sample (fraction <1.6 mm), if not pointed differently.

[a] Means and standard deviations (*n* = 11) are presented.

[b] Means and standard deviations (*n* = 4) are presented; not sieved, sampled after homogenization before introducing it into flushing tank (1.7 m^3).

1.01, 2.55, 3.56, 4.48, 5.29, 7.97, and 10.08 g/L. After equilibrium in the mixtures was reached by shaking for 24 h, the concentration of Spolapon AOS 146 in the aqueous phase was determined. For this purpose, the sample of the liquid phase was filtered through a membrane filter with pore diameter 0.45 μm.

The set of the equilibrium experiments observing the PCB solubilization in the Spolapon AOS 146 solution was carried out in the same way as the previous set for measuring the surfactant sorption, but with the volume of the solution 40 mL and mass of the soil 20 g. Spolapon AOS 146 concentrations in the solutions were 1, 5, 10, 15, 25, and 35 g/L. Samples of the aqueous phase were also filtered through a membrane (0.45 μm) filter before analysis of the PCB concentration.

Based on the results provided by above-described experiments, the sorption behavior of surfactant, the CMC value estimate and the PCB solubilization efficacy dependence on the surfactant concentration in solution were calculated.

Methods for processing the soil extract (containing high concentrations of both PCBs and surfactant) have been also tested in the laboratory part involving flocculation, absorption into an organic solvent and adsorption by carbon black. The best method proved to be flocculation.

A simple reference column experiment was carried out to verify the results obtained from the pilot-scale demonstration. The experimental arrangement, beginning of the experiment, its operation and termination were exactly the same (except for the differences mentioned below) as the experiment described in our previous study (including Fig. 3) [33]. Let us mention the differences to the column experiment in the previous study [33]: the soil was mixed with distilled water before it was poured into the column, the soil layer height was 84 cm, Spolapon AOS 146 solution (15 g/L) was used as the flushing solution and the duration of the experiment was approximately 8 months. Finally, the residual PCB concentration profile in the soil layer was determined.

3.3. Pilot-scale demonstration

The aim of the pilot-scale demonstration was to verify efficacy, time-demands and technology aspects, which are not available in the laboratory scale. The soil used for the pilot-scale demonstration was taken from the same polluted site (and exactly same place) in the Czech Republic as the soil for the laboratory experiments. Sampling of the soil on the site is demonstrated in Fig. 1.

3.3.1. Technological layout

The technological arrangement shown schematically in Fig. 2 was constructed for the purpose of soil flushing demonstration in the area of a toxic waste landfill operated by Dekonta, Ústí nad Labem (northern part of the Czech Republic). A photograph of the facility is shown in Fig. 3. The most important part of the technology was the flushing tank (column) with a diameter of 1.46 m and height of 3 m which was equipped with the filtration bed on the bottom part. It consisted of a layer of the gravel covered by layer of sand and geotextile. The flushing tank was placed in the retaining tank for collecting the soil leachate equipped with a pump. The pump was able to pump the soil leachate either to the tank for waste water (not displayed in Fig. 2) or to the tank to collect the soil extract. The bottom of the retaining tank was equipped with a valve enabling it to discharge the tank completely and then to measure the flushing solution flow through the flushing tank (under the assumption that the flow through the valve and the flushing tank should be equivalent). In the upper part of the flushing tank, an electrode system connected with the control unit and pump of the fresh flushing solution installed near the tank with the flushing solution was installed. This system was able to control
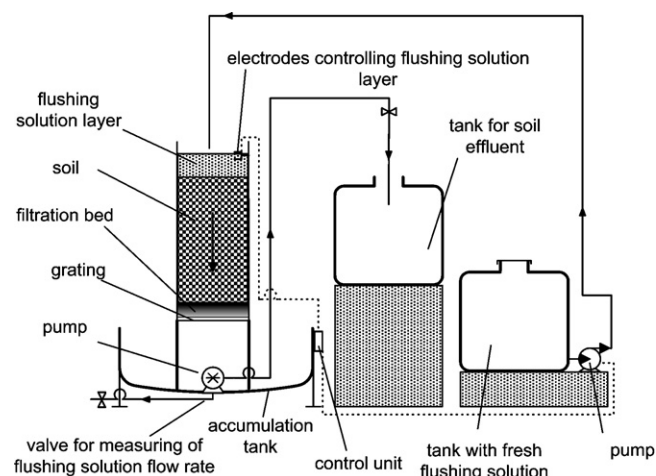

Fig. 2. Pilot-scale demonstration: technical arrangement.

the layer of the flushing solution in the flushing tank on a constant level.

3.3.2. Process description

At the beginning of the pilot-scale demonstration, about 1.7 m³ of the soil was mixed with water to form a dense suspension. Four samples of the soil were taken from the homogenized suspension before introducing it to the flushing tank to know an average initial PCB concentration (see Table 1). Suspension was then introduced into the flushing tank by use of barrels and forklift. After settling, the soil formed a 1-m high layer. The rest of the water set-off from the soil was removed from the flushing tank by the pipe (by use of the effect of water levels difference).

The flushing solution concentration of the anionic surfactant Spolapon AOS 146 was 40 g/L. A relatively high concentration was chosen due to the results of the laboratory experiments and with respect to the expected duration of the pilot-scale demonstration needed to reach some demonstrable changes in the PCB concentrations in soil. The flushing solution was pumped up to the soil in the flushing tank to make a layer of 30 cm. It was kept constant during the flushing process by electrodes connected with the control unit. In fact, by operation, the flushing pilot-scale demonstration was started.

During the process, once or twice per week, the flow rate of the flushing solution through the soil layer was measured after pumping out the soil leachate from the retaining tank either to the

Fig. 3. Pilot-scale demonstration facility.

tank for wastewater or to the tank for processing it. The content of the retaining tank was pumped to the wastewater tank during the beginning phase of the soil flushing. The soil sorption capacity was not yet saturated and because of it, concentrations of both the surfactant and PCBs were very low. At this moment, in which it was needed to pump the leachate into the tank for processing, we observed visually that the concentrations of both the surfactant and PCBs began to increase from the leachate color and foam. When the retaining tank was empty, the valve at the bottom was opened for at least 1 h to get the same flow through the valve and flushing tank. After that, the flushing solution was measured by use of a volumetric cylinder. The soil leachate collected in the cylinder was then taken as the sample. The flushing process was simulated for approximately 2 months this way.

The flushing process was terminated by removal of the flushing solution layer from the top of the flushing tank. After the predominant part of the flushing solution drained out from the soil layer, the final sampling of the flushed soil was carried out. For this purpose, three holes were made into the soil layer in the flushing tank by use of equipment, which allows one to cut the sample of the whole soil profile. Three sampled profiles were divided into eight sections and then, the mixed sample was prepared from the same sections of each profile. In these eight samples, the final residual PCB concentration was determined.

3.3.3. Model calculations

The flushing process in the pilot-scale demonstration was simulated mathematically by use of the model described in the theoretical part of the article. Data describing the soil properties (bulk density, porosity) used were the same as was presented in the experimental part (Table 1). The flushing solution flow rate used was the same as was observed in the pilot-scale demonstration. The sorption isotherm parameter (sorption of surfactant onto soil) was obtained from laboratory experiments as well as from the description of the PCBs leaching from the soil into solution in dependence on the surfactant concentration after sorption higher than its CMC (e.g. on $C_{\text{eff.(surf.)}}$, see Eq. (III)). The CMC value of the surfactant was also estimated from laboratory experiments.

3.3.4. Soil leachate processing

Soil leachate in the tank for processing it was processed by the patented method based on coagulation, which is named "adsorptive micellar flocculation (AMF)" when anionic surfactant is presented [38,39]. The dose of ferric trichloride was 2760 mg/L. After addition of this agent and neutralization by addition of calcium hydroxide to reach suspension of pH 7, a period of fast mixing (about 600 rpm) for 5 min was followed by a period of slow mixing (about 150 rpm) for approximately 10 min. A simple stirrer (usually used for stirring paints) powered by handheld electric drill was used for mixing the suspension. After sedimentation for 2 days, the filtrate was separated from the sludge by filtration through textile bags, type PM10MY (supplied by Ceske Filtry, Czech Republic). Before filtration, it was possible to directly remove approximately 70–80% of the liquid above the settled sludge.

4. Results and discussion

In this study, the laboratory part and pilot-scale demonstration were carried out. The laboratory part was focused on obtaining the input data for the suggested mathematical model.

4.1. Results of laboratory part

Through the simple batch experiments, the results related to both surfactant sorption behavior and PCB solublization efficacy
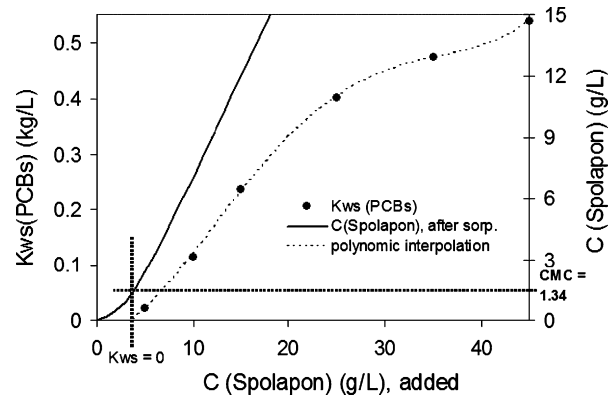

Fig. 4. Diagram for estimation of the CMC value of the surfactant in the soil leachate. The results were obtained through a set of laboratory equilibrium batch experiments with a constant dose of soil and solution under various initial surfactant concentrations in solution. The right y axis represents the equilibrium surfactant concentration after its adsorption onto the soil; Kws(PCBs)—distribution coefficient solution/soil of PCBs in unit $\text{kg}_{\text{soil}}/\text{L}_{\text{solution}}$.

from the soil were obtained. All results are shown in Fig. 4. Surfactant sorption data was interpolated by the Langmuir isotherm and from this, a curve describing the surfactant concentration in the solution after sorption was calculated and marked in Fig. 4 (on right y axis). The Langmuir isotherm parameters were $C_{\text{max}} = 6.3$ g/kg; $\alpha = 2.0$ L/kg (see Eq. (II)).

The CMC value of the surfactant was estimated based on the theoretical assumption, that the CMC is the surfactant's concentration in the solution in which the contaminant just starts to be substantially solubilized from the soil. Finally, the point of zero value of the Kws(PCB) (e.g. the point where polynomic interpolation of the data crosses the x axis) represents the CMC on the right y axis (e.g. concentration of surfactant actually present in the solution after sorption). The CMC value estimated in this way, from Fig. 4, is 1.34 g/L. Lowering the surfactant CMC by other substances presented in the solution in comparison with the CMC value in distilled water (see above) is in agreement with the theoretical knowledge available.

Finally, the dependence of Kws(PCB) on the surfactant concentration, specifically on the surfactant concentration after sorption—which was lowered about its CMC (e.g. on $C_{\text{eff.(surf.)}}$, see Eq. (III)), was then interpolated by a polynomic function (different from the interpolation in Fig. 4). The interpolation was

$$\text{Kws(PCB)} = 6.4 \times 10^{-7} \times C_{\text{eff.(surf.)}}^4 - 4.9 \times 10^{-5} \times C_{\text{eff.(surf.)}}^3$$

$$+ 8.1 \times 10^{-4} \times C_{\text{eff.(surf.)}}^2 + 1.8 \times 10^{-2} \times C_{\text{eff.(surf.)}} + 9.8 \times 10^{-5}$$

$$\text{(IV)}$$

The coefficients in Eq. (IV) represent the required input data for the application of the model suggested in the theoretical part of the study. The rest of the desired data was made up from the coefficients of the Langmuir isotherm describing surfactant sorption on the soil and the surfactant's CMC value.

The flushing solution flow through the soil layer observed in the column experiment decreased from the initial value of 1.48 L/(h m^2) to the final limiting value of approximately 0.17 L/(h m^2) which remained constant after about 4 months of the experiment. This lowering reflected the settling of the soil layer in the column during the first 4 months of the experiment and it can be extrapolated by the function:

$$Q = 7.7 \times t^{-0.45} \tag{V}$$

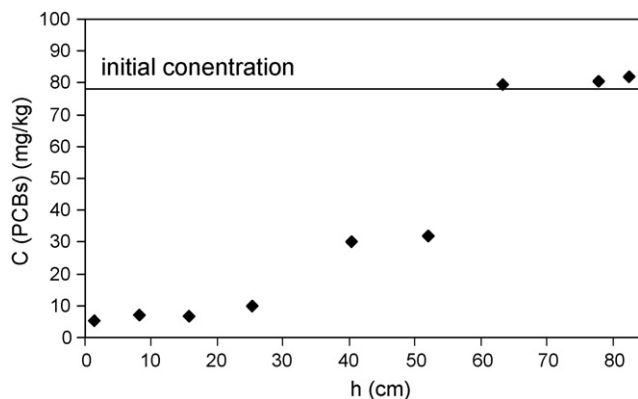where Q is the solution flow and t is the time.

Fig. 5. Residual PCB concentration profile in the soil layer after 8 months of flushing (reference column experiment).

Fig. 5 shows the residual concentration profile of the PCBs in the soil layer after 8 months of flushing (in reference to the column experiment). The results proved that the PCB content in the soil can be lowered to values less than 10 mg/kg (see the first approximate 30 cm of the soil layer, Fig. 5). Such a concentration, perhaps, corresponds with the residual PCB fraction in the soil, which is strongly bound onto the soil particles and is not possible to remove by the flushing process even in the case of a longer duration. It can be reasonably expected that the concentration of PCBs of less than 10 mg/kg would be achieved in whole soil profile in case of longer flushing (our estimate is over the next 5–6 months).

In relation to the PCB concentration in the column leachate: the PCB concentration was very low (the soil sorption capacity towards the surfactant was saturated) within the first 4 months (about 3 pore volumes of soil leachate) of the experiment. During the fifth and sixth month it increased to the final value of 70–80 mg/L which remained constant till the end of the experiment.

4.2. Results of pilot-scale demonstration

The first important result provided by the pilot-scale demonstration was the flushing solution flow rate during the demonstration period. This flow rate was expected to decrease with time according to the theoretical assumption. The resulting flow rate including its interpolation is viewed in Fig. 6. The flow rate, in beginning phase of the flushing, was 1.2 L/(h m^2) and it decreased to 0.38 L/(h m^2) during the period of 2 months. It was possible to interpolate the flow rate lowering by the function (see Fig. 6). This
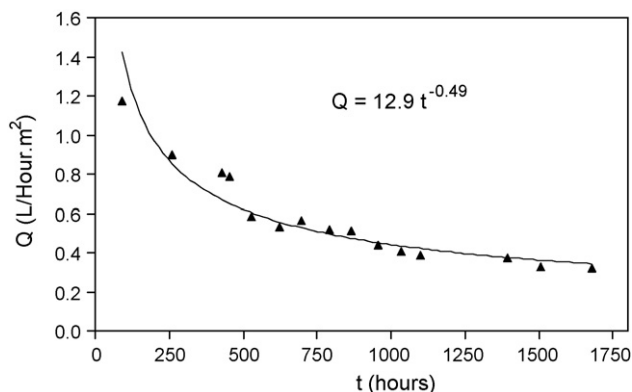
interpolation is very similar to Eq. (V) (laboratory column), so we can expect a subsequent lowering of the flow rate in the pilot-scale demonstration (in case of longer flushing) onto the limiting values similar to those observed in the laboratory. The higher the value of the first coefficient of the interpolation (12.9 in pilot-scale and 7.7 in the laboratory) can be explained by the fact that the soil was not sieved before the pilot-scale demonstration which resulted in a slightly higher hydraulic permeability. The functional equation shown in Fig. 6 was used for the subsequent model simulation of the process.

Fig. 7 discloses both the PCB and the surfactant concentration in the soil leachate during the process. It is obvious that after 400 h (approximately when 0.8–0.9 of soil layer pore volume of leachate flowed out from soil), the sorption capacity of the soil towards the surfactant became saturated, which caused the increase in both concentrations. There is also an evident relation between the concentration of the surfactant and of the PCBs in the solution. It is clear, that the presence of the surfactant directly determines the higher concentration of the PCBs in the solution in comparison to pure water. It is expected, that the concentration of the PCBs would rise above the final value measured in the pilot-scale demonstration. In accordance with the reference column experiment results, this concentration could be higher (tens of mg/L) in case of a longer duration of the process. It is evident from this fact, that the decontamination is faster and more efficient with time due to increasing the leachate PCB concentration.

It only remains to comment on why the concentrations began to rise before one pore volume of the flushing solution flowed through the soil, especially when the sorption of the surfactant onto the soil particles was known from the laboratory experiments (approx. 6.3 g/kg):

(A) Probably, it was caused by combination of two facts: first, the soil porosity of 40% was estimated but even a little change in the porosity estimate strongly affects the pore volumes of the leachate in which the concentrations began to rise. For example, if we would estimate a soil porosity of 30%, pore volumes of the leachate when concentrations began to rise would increase to approximately 1.1–1.2 (from 0.8 to 0.9 when porosity estimate was 40%).

(B) We can also expect that the flow of the solution through the soil in the pilot-scale experiment was not piston-flow, e.g. some preference pathways could occur in the soil layer. Those two effects probably determines the sorption, from which we expected an increase of both (PCB and surfactant) concentrations later. Finally, it was a positive observation, that the PCBs
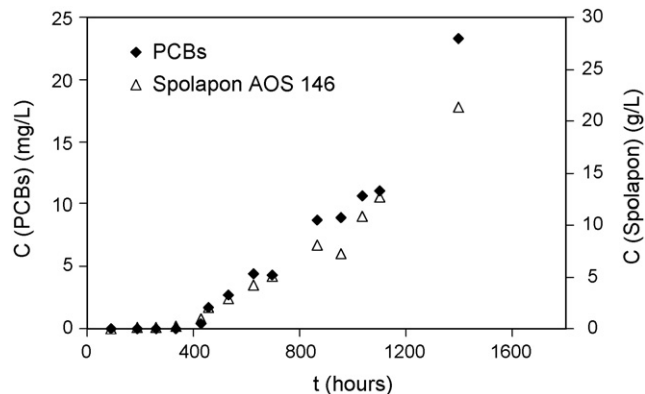

Fig. 6. Flow rate of the solution through the flushing tank during the pilot-scale demonstration.

Fig. 7. Concentrations of the PCBs and of the surfactant in the soil leachate during the flushing in the pilot-scale demonstration.

began to be removed from the soil sooner than was expected from the surfactant sorption behavior.

(C) The third explanation can be that the sorption capacity of the soil towards the surfactant in the pilot-scale demonstration was less than that of the soil in the laboratory part. It could be caused by the fact, that only soil fractions of less than 1.6 mm were used for the laboratory experiments, knowing that fine particles usually have higher sorptivity than the rest of soil (bigger particles). This assumption supports the PCB concentrations found in the laboratory and pilot-scale soil samples (78 and 34 mg/kg of dry soil, respectively). Most probably, the explanation why the concentrations began to rise before one pore volume of the flushing solution had flowed through the soil layer will be a combination of all of the above-mentioned effects (A–C).

The final PCB concentration profile after the flushing was terminated is shown in Fig. 8. For comparison, there is also a theoretical line calculated from the mathematical model included in Fig. 8. The model calculations were done with the above-described input data collected from the laboratory part of the project presented. Other input data for the model were the diameters of the flushing tank, the bulk density of the dry soil ($1.63\,g/cm^3$) and effective porosity of the soil (estimated as 40%).

It is obvious from Fig. 8 that there was a relatively good agreement between the model and experimental outputs, especially when considering the complexity of the system soil–surfactant–PCBs. The correct prediction of the PCBs accumulation in the bottom part of the soil layer which relates with the surfactant adsorption onto soil in the beginning phase of the flushing process was quite positive. Higher residual concentrations achieved at the top part of the soil layer in comparison with the results of the reference column experiment were caused by gravitation separation of the soil particles in the tank which happened during the introduction of the suspension. The finest particles, which are the most contaminated due to their larger sorption surface, remained on the top layer and that was why the residual PCB concentration in the soil (top part of the soil layer) seemed to be unexpectedly high. This observation was confirmed by sieving analysis of the initial soil and the soil from the top part of the soil layer. Finally, there is relevant reason to anticipate that the residual PCB soil concentration will be lower than the observed value at the top part of the soil layer, approximately in units of mg/kg according to the reference column experiment. In case of longer flushing, the attainable decontamination efficacy observed was about 56%, but it can be expected that efficiency could exceed 90% (similar to that in the laboratory column).
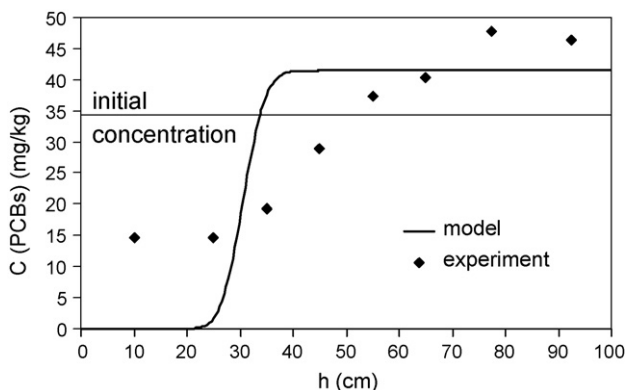

Fig. 8. Residual PCB concentration profile in the soil layer after the pilot-scale flushing was terminated: comparison between results of the analysis and model calculation.

Table 2
Summary of the soil leachate processing

Volume of leachate processed	~900 L
Initial concentration of PCBs	8.1 mg/L
Initial concentration of surfactant	8 g/L
Residual PCBs concentration in filtrate	24×10^{-6} mg/L
Residual surfactant concentration in filtrate	2.2 g/L
Mass of produced sludge	14.2 kg
Moisture of sludge	66%
Concentration of PCBs in sludge	1145 mg/kg (dry sludge)

4.3. Mass balance

The mass balance of the pilot-scale flushing showed the recovery value of the PCBs of 98.8% which was significantly better than could have been expected before. This high recovery was surprisingly better than was expected.

4.4. Processing of soil leachate

The total volume of the soil leachate was $1.4\,m^3$ (about 2.1 pore volumes of the soil layer). Of this volume, about 500 L was directly pumped into the tank for wastewater during the beginning phase of the experiment (see Fig. 7—the first approximate 400 h), because both concentrations (PCB and surfactant) were very low. The rest of soil leachate, 900 L, was collected in the plastic tank with a volume of $1\,m^3$, where it was processed by the above-described patented coagulation method. Information about the processing of the soil leachate is summarized in Table 2. It is obvious that the observed high-PCB removal efficiency allows recirculation of the water in the process in case of the full-scale application.

It remains to refer to the analytical complication caused by the presence of phthalates in the filtrate after coagulation (from the plastic sides of the tank where phtalates are used as plasticizers). Phtalates cause interference, because their peak in chromatogram is on the same retent time as second evaluated congener of the PCBs. Therefore, it was necessary to eliminate this disturbing effect by a modified analytical process in a specialized analytical laboratory. Also from Table 2, the results that the PCBs removed from 2.7 ton of soil were concentrated into 14 kg of sludge. The sludge was then burned in an incinerator (in Ostrava, Czech Republic). We can estimate, that in the case of longer flushing in order to reach the desired remediation efficacy considering the soil leachate of 4 pore volumes (for example), the amount of sludge to be burned should not exceed 50 kg, e.g. approximately 18 kg/ton of soil. This is important from an economical point of view.

5. Conclusions

The pilot-scale demonstration study confirmed that it is technologically possible to remove the PCBs from real contaminated soil by flushing with a surfactant solution. The decontamination efficiency proved to be 56%, but it could be higher than 90% in cases of a longer duration of the flushing process. The time needed to reach this efficiency can be estimated as 6–12 months with approximately 4 pore volumes of flushing solution needed to be passed through the soil. Water consumption can be estimated to be approximately $2\,m^3$ of water per $1\,m^3$ of soil. However, it should be possible to recycle the water in the process due to the residual PCB concentration in the processed soil leachate was very low (24×10^{-6} mg/L). So, the total fresh water consumption should be relatively low due to its recirculation. The costs of decontamination of $1\,m^3$ of soil can be estimated between 250 and 350€/ton (including waste utilization, costs of investments are not included). In principle, it could be possible to operate the technology both in situ and ex situ. We can

expect, that ex situ method should be more efficient, faster and safer towards the surrounding environment, but more cost demanding (due to investments cost which depend on the particular technical solution of the ex situ process). The decision about the technological design of the flushing process has to be made with respect to the particular conditions—soil permeability, hydraulic conditions on locality, local legislation, etc.

The technology of soil flushing by a surfactant aqueous solution could be serious competition to expensive thermal methods especially for less-contaminated soils (up to approximately hundreds mg/kg).

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