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# LEACHING TESTS FOR NON-VOLATILE ORGANIC COMPOUNDS – DEVELOPMENT AND TESTING

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**Title:**

# Leaching Tests for Non-Volatile Organic Compounds – Development and Testing

**Abstract:**

The main objective of this project was to develop a leaching test method suitable for organic non-volatile compounds. The project was performed in two parts. The first part of the project focused on solving problems concerning separation of solid and solute in the batch test and to evaluate the batch test versus the equilibrium column test. In the second part of the project the test methods were implemented on different Nordic laboratories and an impression of repeatability and reproducibility were obtained.

Based on the knowledge from previous investigations and results obtained in this study an equilibrium column leaching test is recommended for testing the leachability of non-volatile organic compounds from contaminated soils and waste products at compliance level (routine control purposes). This recommendation is primarily based on lack of understanding the inconsistent results of the batch test. In addition the results of the implementation of the test methods in Nordic laboratories showed that only the equilibrium column test provided reproducible results, which is a major demand for tests used for routine control purposes.

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## *APPENDICES*

# 1 SUMMARY AND CONCLUSIONS

This project was based on knowledge and experiences concerning leaching tests for non-volatile organic compounds obtained in a previous project (Miljøstyrelsen, 2003). Within that project a batch leaching procedure and an equilibrium column leaching procedure for organic compounds were developed. However, some problems remained unsolved. The project has aimed at solving these problems and in addition to obtain an impression of the repeatability and reproducibility of the test methods. Based on the results of this project recommendations regarding choice of test methods for estimating leaching of non-volatile organic compounds from soils and waste products have been given.

The project was performed in two parts. The first part of the project focused on solving problems concerning separation of solid and liquid in the batch test and on evaluating the batch test versus the equilibrium column test. In the second part of the project the test methods were implemented at different Nordic laboratories and an impression of repeatability and reproducibility was obtained. The particle size was measured in all eluates produced in the second part of the project to help clarifying differences observed between batch and column tests.

Based on experiments performed in this project the following conclusions can be drawn regarding leaching of non-volatile organic compounds from contaminated soils and waste residuals:

- The results from these experiments supported findings reported in the literature concerning generating inorganic colloids in a batch leaching test during agitation. In order to obtain consistent and reliable results from a batch test these artificially generated colloids must be separated from the solution before chemical analysis.

- The solid and liquid in the batch leaching test was separated by centrifugation at two different centrifugation forces (27000 g for 30 minutes and 6200 g for 60 minutes). The results obtained for 2 soils and 2 waste products indicated that centrifugation at 6200 g for 60 minutes was sufficient to separate solid and liquid in a batch leaching procedure. In addition centrifugation of 200 ml of eluate at 27000 g for 30 minutes resulted in technical problems. The centifugation vessels of steel were slowly deformed and they became difficult to remove from the centrifuge.

- Comparing results obtained in batch leaching test with results obtained in the equilibrium column leaching test showed that in some cases leaching of the smaller PAH (2-3 rings) was underestimated in the batch leaching test. Based on the results this could not be explained.

- Results from column and batch leaching tests indicated that centrifugation at 6200 g for 60 minutes seemed sufficient to remove colloids generated in the batch tests. No indications of overestimation of the leaching concentrations of the larger PAH (4-6 ring) due to insufficient separation of solid and liquid were found for these materials.

- Data from development and validation in the previous project, as well as from the literature demonstrate that there is no method available “off the shelf” for determination of total petroleum hydrocarbons in leaching tests that satisfy the performance requirements for this purpose. It is suggested to devote further method development and validation efforts to improving a SPE and GC-MS-SIM based method, but two alternatives are presented as well.

The batch leaching procedure and the column leaching procedure were tested in 2 and 3 different Nordic laboratories respectively. One soil contaminated with pieces of clay pigeons was distributed to the participating laboratories. Evaluating the results of this minor round robin it should be kept in mind that the participating laboratories carried out the specific test procedure for the first time. In addition information concerning sample stability and homogeneity is available. The results of the ring-test were analysed according to ISO 5725-2 providing estimates of the repeatability and the reproducibility for each test method.

- The column test was set up at DTU, DHI and VTT and a good agreement between leached concentrations of 16 PAH obtained by all three laboratories was observed. For the column test the repeatability (within laboratory variation) for the 16 PAH were in the range of 21% –59%. The repeatability was lowest for the smaller PAH and highest for the larger PAH. The reproducibility (between laboratory variation) was between 32% and 59%. The testing of the column leaching test at 3 different Nordic laboratories showed promising results for the column test indicating that it is a relative robust test once it has been established.

- The batch test was set up at NGI and twice at DHI (treated in the evaluation as two different laboratories). Comparing the results obtained there was at least a factor of 10 and up to a factor of 100 between the leached concentration of naphthalene, acenaphthene, fluorene, phenanthrene and anthracene obtained by DHI and NGI. Several of these compounds were below the analytical detection limit in eluates produced by NGI. The repeatability for the 16 PAH were in the range of 10% – 43% highest for the smaller PAH and lowest for the large PAH, which was contrary to the observation for the column test. The reproducibility was between 17% and 104%, reflecting large deviations between of the results obtained for some of the compounds at the participating laboratories.

- Results obtained in this project indicated that during the batch leaching test the material was grinded, which resulted in a higher content of inorganic colloids in the eluates from the batch leaching procedure. Also the size of the colloids were affected during the batch testing as smaller colloides were observed in the batch test than in the column tests.

**Recommendation of test method for leaching of non-volatile organic compounds:**
Based on the knowledge from previous investigations (Miljøstyrelsen 2003) and results obtained in this study, an equilibrium column leaching test is recommended for testing the leachability of non-volatile organic compounds from contaminated soils and waste products at compliance level (routine control purposes). This recommendation reflects the lack of understanding the results of the batch test and the concerns related to generation of colloids in the batch procedure. In addition the results of the implementation of the test methods in Nordic laboratories showed that only the equilibrium column test provided reproducible results, which is a major requirement for tests used for routine

control purposes. The results of an equilibrium column test provides information on the expected concentration of non-volatile organic compounds in the porewater in a contaminated soil under equilibrium conditions.

The equilibrium column method is recommended for testing of leaching of non-volatile organic compounds such as polycyclic aromatic hydrocarbons (PAH) and non-volatile petroleum hydrocarbons. Full benefits of the test require development of an analytical method for total petroleum hydrocarbons (TPH) in eluates that is applicable at lower concentrations than those analytical methods currently available.

# 2 INTRODUCTION

## 2.1 Background

Most of the Nordic countries are currently implementing legislation on utilisation and / or landfilling of waste and contaminated soil in which determination and evaluation of the leaching properties of the materials plays and important role. The major advantage of leaching-based criteria is that they may be directly related to the potential risk to groundwater and surface water caused by the utilisation and landfilling of waste and contaminated soil. Unfortunately, today only criteria based on leaching of inorganic compounds and DOC is included in legislation despite the fact that many of the contaminants of concern are organic compounds. This is mainly due to the fact that no standardized leaching methods for organic compounds are available at present.

For regulatory use a leaching test for organic compounds on compliance level (according to the test hierarchy defined by CEN TC 292) should be developed. The most obvious test method for this purpose would be a batch leaching method analogous to the batch test method known for inorganic compounds (EN 12457). Organic compounds, however, have some physical and chemical properties that differ very much from the properties of inorganic compounds and in a suitable leaching test method for organic compounds these properties must be taken into account.

During the last 10 years development of leaching test methods for organic compounds has been ongoing (Comans et al., 2001; Nordtest 2000; Miljøstyrelsen, 2000, and 2003) and this project is based on the knowledge and experiences obtained in these works.

Recently DHI and DTU in Denmark conducted a large project founded by Centre of Waste Research (C-RES) in Denmark and the Danish EPA (Miljøstyrelsen, 2003). It was the aim of that project to develop test methods suitable for testing the leaching of volatile as well as non-volatile organic compounds from soils. Two test methods were developed aiming at equilibrium between organic compounds distributed between solid and liquid. One method was a column test with re-circulation of eluate until equilibrium was obtained. The other method was a batch test agitated until equilibrium was obtained. However, some major problems concerning the applicability of the batch test for non-volatile, strongly sorbing compounds as for example PAH and heavy petroleum hydrocarbons turned up and could not be solved within that project. The main problem appeared to be generation of colloids during batch leaching and removal of these “artificial” particles from the eluate before analysis.

The present project aims at solving these problems if possible and the work is a continuation of the results obtained in Miljøstyrelsen (2003).

## 2.2 Objectives

The overall objective of this project has been to be able to recommend a leaching test method for non-volatile organic compounds. The recommended test method should be suitable for regular control purposes (compliance testing). It is a requirement of such a method that the test is consistent, robust and reproducible.

In order to fulfil this purpose the following intermediate aims had to be addressed:

- To evaluate suitable techniques for analysis of petroleum hydrocarbonss in eluates
- To evaluate different procedures for centrifugation of eluates from a batch leaching procedure in order to find a useful method for centrifugation
- To evaluate the batch leaching test against an equilibrium column leaching test
- To test the batch leaching – and/or the equilibrium column leaching procedures at different Nordic laboratories.

Based on the results of this project recommendations concerning choice of test method for non-volatile organic compounds will be given.

This project has been carried out in co-operation between DHI in Denmark, E&R at DTU in Denmark, VTT in Finland, SGI in Sweden and NGI in Norway.

# 3 PHYSICAL AND CHEMICAL PROCESSES CONTROLLING THE LEACHING

The physical and chemical processes controlling the leaching of non-volatile organic compounds have been described already in several reports (Comans et al. 2001, Miljøstyrelsen 2000, Nordtest 2000). Nordtest (2000) provides a comprehensive overview of the most important issues. Thus, parts of this chapter have been adopted from Nordtest (2000) with only minor changes.

For organic compounds three major processes control the concentration in the aqueous phase in batch or column test systems (or natural soil systems): dissolution, sorption, and the presence of dissolved organic matter and colloids (organic and inorganic). If there is a free organic phase in the contaminated soil or in the waste product, dissolution of the organic compounds from the free phase into the aqueous phase controls the concentration in the aqueous phase. If there is no free phase, the concentration in the aqueous phase is controlled by sorption and by the dissolved organic carbon and colloids.

## 3.1 Dissolution

Dissolution of organic compounds from an organic phase into an aqueous phase is only important in contaminated soils with a free phase. If the free phase only contains one organic compound, the concentration in the aqueous phase or in the pore water corresponds to the aqueous solubility. If the free phase contains more than one organic compound, the equilibrium concentration in the aqueous phase or in the pore water can be estimated using Raoult's law:

$$C_i = x_i \cdot S_i$$

where

$C_i$ is the equilibrium concentration of compound i in the aqueous phase
$x_i$ is the mole fraction of compound i in the free phase
$S_i$ is the aqueous solubility of compound i.

In a batch leaching test it is important to know how long time it takes to obtain equilibrium. In the literature studied, only two detailed reports on experiments were found where the aqueous concentration has been measured as a function of time (Poulsen et al., 1991, Burris and McInture, 1985). One of the experiments dealt with the solubility of BTEX from gasoline in water mixed with either methanol or MTBE. It was performed in 60 ml glass bottles with approximately 55 ml water and approximately 5 ml of gasoline. The bottles were agitated 0,5 hours to 50 hours at 10°C, and it turned out that 1 hour was almost enough to obtain the equilibrium concentration. In another experiment (Burris and McInture, 1985) the concentration in water as a function of time was examined in a system containing a mixture of 1-methylnaphthalene and methylcyclohexane. The experiments were carried out in a 500 ml glass bottle with 400 ml water and 0.5-3 ml free phase. Magnetic stirring agitated the bottle. Equilibrium was achieved within 24 hours, and more than 90% of the equilibrium concentration was achieved within 12 hours. A contact time of 12-24 hours is often applied in dissolution experiments with some form of agitation. In an experiment without agitation to measure the solubility of trichloroethylene, equilibrium was achieved within 5 and 19 days in experiments containing 3 ml trichloroethylene and 14 ml water.

The above mentioned contact times to achieve equilibrium are from experiments without soil. The presence of soil does not necessarily result in longer times to achieve equilibrium if the system is agitated sufficiently effectively to keep the soil in suspension. The presence of large aggregates or lumps of soil that may contain free phases may prolong the time needed to achieve equilibrium since sorption equilibrium has to be obtained, too. A detailed description of dissolution processes is given in Miljøstyrelsen (2000).

## 3.2 Sorption

Sorption controls the aqueous concentration of organic compounds in contaminated soils without free organic phases. An extensive review of sorption and desorption has been given in Miljøstyrelsen (2000).

Sorption of organic compounds to soils is often described in very simplified manner. However, that simplification makes it easier to quantify sorption on the basis of only a few parameters. The simplified method is described in the following.

The traditional description is based on some simplifying assumptions:

- The adsorption isotherm is a standard tool for characterization of the partitioning of the organic compounds between the soil and sediments and the aqueous solution, basicly describing how solute concentration is related to the adsorbed concentration. The simplest isotherm model is the linear adsorption isotherm that has been used frequently (e.g. Bouchard et al. 1990; Larsen et al. 1992; Kan et al., 1994), and is based on the principle that the sorption capacity of the sorbent is infinite. This means that there always is a fixed ratio between the concentration in the aqueous phase ($C_w$) and the concentration on the soil ($C_s$). That ratio is called the distribution coefficient ($K_d$ and its unit is l/kg) and is independent of the concentration of the organic compound.

- Generally, it has been recognized that sorption of organic compounds from aqueous solution to soil is dominated by the fraction of natural organic carbon in the soil unless this fraction is extremely small (e.g. Karickhoff et al., 1979; Pignatello, 2000). Consequently, the partitioning of organic compounds between solute and natural organic carbon has been intensively investigated during the past decades. It is, however, still not fully understood and most transport models in soils use simple linear equilibrium expressions. Sorption onto minerals (clay, metal oxides, and metal hydroxides) is normally considered negligible unless the fraction of natural organic carbon is extremely small (Grathwohl, 1998; Pignatello, 2000). The type of natural organic carbon is not taken into account.

- The distribution coefficient is proportional to the content of natural organic carbon in the soil ($f_{oc}$) and the distribution coefficient between the organic carbon and water ($K_{oc}$):

$$K_d = f_{oc} \cdot K_{oc}$$

where $K_{oc}$ is the partitioning coefficient between water and organic carbon (l/kg) estimated from the widely used $K_{oc}$-$K_{ow}$ (octanol water partitioning coefficient) relations as proposed by Karickhoff et al. (1981), Abdul et al. (1987) or others.

- Sorption is reversible, e.g. the sorption process where an organic compound is adsorbed to the solid phase from aqueous phase and the process where an organic compound is desorbed from the solid phase to the aqueous phase can be described by the same $K_d$-value.

- Sorption is instantaneous, e.g. the mass transfer of an organic compound from the aqueous phase to the solid phase (or the reverse) to obtain equilibrium is so fast that it can be considered instantaneous.

- The effects of other organic compounds or colloids on sorption are negligible. Thus there are no competition for sorption sites between different organic compounds when more than one organic compound is present simultaneously.

The simple approach to describe sorption is often not valid and it has been shown frequently that sorption is a slow continuing process (e.g., Wu and Gschwend, 1986; Ball and Roberts, 1991a; Pignatello and Xing, 1996; Grathwohl, 1998; Valsaraj and Thibodeaux, 1999, Gamst et al., 2004). The sorption process is believed to be slow because the particles in the soil may contain an internal structure, in which the organic compounds diffuse and adsorb (referred to as intraparticle diffusion). This diffusion process is slow because the pores are narrow and the diffusion process thus becomes hindered by the size of the pores. Diffusion in and out of an internal structure of soil particles thus slows down the apparent sorption. Many hypotheses regarding slow sorption kinetics have been proposed, although hindered intraparticle diffusion through the narrow pore network of the soil particles and/or through the soil organic matter seems to be the dominating theories (Wu and Gshwend, 1986; Ball and Roberts, 1991a and b; Miller and Pedit, 1992; Grathwohl and Reinhard, 1993; Grathwohl, 1998; Brusseau et al., 1991; Pignatello and Xing, 1996; Weber and Huang, 1996). These explanations have been shown to fit experimental results.

The reversibility of sorption is another assumption that is not always fulfilled. Lower mass transfer rates are often observed for desorption than for adsorption. This is usually even more apparent in older than in more recently contaminated soils. This observation is often explained as being caused by non-attainment of sorption equilibrium (Pignatello, 2000; Gratwohl, 1998; Allen-King et al., 2002). Some researchers have claimed that irreversible bindings to the soil organic matrix may also be the explanation (Alexander, 1995).

Nonlinear sorption has been observed frequently (e.g., Kishi et al., 1990; Weber et al., 1992; Gamst et al., 2001), and some studies have shown that nonlinearity increases with increasing sorption time (Pignatello and Xing, 1996; Weber and Huang, 1996; Huang and Weber, 1998; Gamst et al., 2004).

Problems with contaminants associated with colloids and dissolved organic carbon in the solute (e.g. Knabner et al., 1996) sometimes results in concentration measurements that exceed the solubility (Weiß, 1998, Comans, 2001; Gamst et al., 2004). Problems with insufficient seperation of the aqueous phase from the soil phase appear to be the dominating reason for these observations in batch techniques (Gamst et al., 2004).

## 3.3 Colloids

Colloids are microscopical or submicroscopical organic or inorganic particles that are suspended in an aqueous phase. Colloids in porous media of interest in relation to leaching tests may be both particles of biological origin (bacteria, viruses, and organic material), minerals (clay minerals, mineral precipitation, metal oxides, metal hydroxides), and combinations of those, e.g. clay minerals with humic substances adsorbed to the surface. Usually colloids are defined on the basis of their size. Particles with a diameter larger than 1 µm sediment fast and are considered as the upper size limit for colloids. The lower size limit for colloids is on the borderline of soluble molecules at approximately 1 nm (Stumm and Morgan, 1995).

Thus, colloids constitute an additional separate phase in a water-saturated porous media, which usually is regarded as consisting of only two phases, water and solids (in the absence of air and a free phase). Due to the relatively large surface area pr. mass unit the capacity for sorption of organic compounds is often much larger than for the porous media. A contributing cause may also be that the colloids generally have a larger content of natural organic carbon. The naturally occurring colloids may have the following effects on transport and leaching of organic compounds:

- A larger fraction of the organic compounds than theoretically assumed is present in the aqueous phase due to the binding to the colloids.

- The organic compounds are potentially more mobile, because they are transported with the pore water sorbed to the colloids. This process is called colloid facilitated transport.

A review of colloids has been given in Miljøstyrelsen (2000) and in Nordtest (2000).

As far as the strongly sorbing organic compounds (e.g. PAH and PCB) are concerned, the presence of colloids have to be taken into consideration when performing leaching tests (batch or column tests). It is very important to define the objective of the test. If the colloids are considered as contributing to the leachable portion from a contaminated soil, the colloids should be measured as part of the aqueous phase. If the colloids are not considered as contributing to the leachable portion from a contaminated soil, the colloids should be separated from the aqueous phase to obtain the concentration in the real aqueous phase.

# 4 RELEVANT ORGANIC COMPOUNDS

## 4.1 General considerations

The organic compounds or groups of compounds that are of primary interest in relation to a leaching are:

- Petroleum hydrocarbons
- PAH
- PCB (not discussed in detail)

PAH, petroleum hydrocarbons and PCB have all been widely used in industrial processes as for example in asphalt production, gas production, in gasoline and diesel, for wood treatment and wood preserving, etc. Depending on the activities on a site, these compounds can be found in contaminated soils and in waste products. Some of these compounds are not easily degraded and thus persistent in the environment. In addition processes such as ageing play an important role in the behaviour of many of the components in the environment, and these processes can not be predicted by theoretical considerations. These aspects make the above compounds relevant for a leaching test. Phenols could also be of interest but they are readily degraded and thus in most case not relevant in relation to leaching tests. Volatile organic compounds such as chlorinated solvents and BTEX may also in some cases be of interest but mostly, a trustworthy pore water concentration can be obtained from theoretical estimation methods. Recently, leaching of brominated flame retardants from landfilled waste material has become a new field of interests (STF, 2004).

In this project non-volatile compounds will be defined as compounds with a boiling point above the boiling point of the hydrocarbon $C_{10}H_{22}$ (e.g. above 174 °C) and the leaching procedures for non-volatile compounds will be discussed for petroleum hydrocarbons ($C_{10}$ –$C_{35}$) and PAH including naphthalene. PCB's are not included in this work but based on the hydrophobicity they are expected to behave similarly to hydrophobic PAH in a leaching test. The experimental work has only comprised the leaching of PAH.

For petroleum hydrocarbons, $C_{10}$ –$C_{35}$ corresponds roughly to the diesel range organics (DRO) as defined by the American Environmental Protection Agency (US EPA) and the range of compunds would be termed semivolatiles in standards such as those published by US EPA ) (EPA 8015B).

## 4.2 Petroleum hydrocarbons

The major, high volume petroleum products are gasoline, kerosene and jet fuel, diesel and gas oil, heavy fuel and lubricating oils. Almost all petroleum products are derived from crude oil, which is a complicated mixture of hydrocarbons. The products are produced in industrial processes including distillation, cracking, alkylation and hydrogenation in order to provide mixtures of the desired properties for each product. The composition of the petroleum products is regulated with respect to *e.g.:* contents of aromates and sulphur (EU Directive 2003/17/EF) and meet technical requirements with respect to properties such as vapour pressure, boiling point, distilation residue and viscosity (EN 228 and EN 590).

As can be seen from table 4.1, petroleum components cover a broad range of boiling points, volatility, water solubility and hydrophobicity. In addition, each product will contain a very large number of individual components. The composition of the petroleum products differs among products, production methods, crude origins, added additives/blending components and even time of the year and distribution country.

Common major groups of components include alkanes and iso-alkanes (paraffins), alkenes (olefins), cycloalkanes (naphtenes), monoaromatics, di- and polyaromatics and heteroaromatics. Table 4.1 presents physiochemical properties of selected representatives of the major component groups.

*Table 4.1 Physical and chemical properties for selected petroleum components, PAH see table 4.2. From Miljøstyrelsen (1996 and 2004)*

| **Compound** | **Boiling point (°C)** | **Vapour pressure (Pa)** | **Solubility (mg/l)** | **Distribution coef. between air/ water $K_H$ (-)** | **Octanol-water distribution coef. log $K_{ow}$ (-)** |
|---|---|---|---|---|---|
| *Paraffins* | | | | | |
| Heptane | 98 | 6.200 | 3,1 | 84 | 4,66 |
| 2-Methylhexane | 90 | 8.800 | 2,5 | 140 | 3,16 |
| Octane | 126 | 1.800 | 0,7 | 126 | 5,18 |
| Dodecane | 216 | 16 | 0,005 | 317 | 7,24 |
| Pentadecane | 270 | 1,5 | 0,000075 | 520 | 8,63 |
| Eicosane | 344 | 0,023 | 0,0019 | 80 | 11,3 |
| Pentacosane | 402 | $2,0*10^{-4}$ | $2,9*10^{-8}$ | $1,5*10^{4}$ | 12,6 |
| Pentatriacontane | 491 | $7,2*10^{-10}$ | $2,5*10^{-13}$ | $2,5*10^{5}$ | 17,5 |
| *Olefins* | | | | | |
| 1-Octene | 121 | 2.300 | 2,7 | 39 | 4,57 |
| *Cycloalkanes* | | | | | |
| Cyclooctane | 151 | 750 | 7,9 | 4,2 | 4,47 |
| *Monoaromatics* | | | | | |
| Benzene | 80 | 12.700 | 1.760 | 0,23 | 2,13 |
| m-Xylene | 139 | 1.100 | 160 | 0,30 | 3,2 |
| *Di- and polyaromatics* | | | | | |
| Biphenyl | 256 | 1,3 | 7,5 | 0,012 | 5,52 |
| *Heteroaromatics* | | | | | |
| Dibenzothiophene | 332 | 0,027 | 10 | 0,0013 | 4,12 |

Besides common, in many countries now obsolete, additives such as alkylleads and MTBE, added non-petroleum components may represent a variety of chemical structures with polymers, tensides and metal compounds frequently used.

Futhermore, spilled petroleum products will change composition (“weather”) due to preferential degradation, vaporisation and leaching of some components. Accordingly, the composition of petroleum hydrocarbon components present in a soil or a waste is not related to the original petroleum product components in a simple and straightforward manner. Typically, an old spill of a petroleum product will consist mostly of highboiling branched alkanes and be enriched in PAH and heterocyclic aromatic compounds (NSO compounds).

An inventory supporting the development of Danish quality criteria for soil, air and groundwater at contaminated sites identified monoaromatics, di- and polyaromatics and selected additives/blending components (1,2-dichloroethane, 1,2-dibromoethane and MTBE) as the petroleum constituents of primary concern (Miljøstyrelsen, 1993). The WHO monography on selected petroleum hydrocarbons (IPCS, 1982) identified benzene, hexane and aromatic compounds as potential risks to human health.

Soils may contain organic compounds resembling petroleum hydrocarbons with respect to many structural features and properties, where the origin of these compounds is plant remains: biogenic hydrocarbons. Furthermore, soil organic matter is largely humic substances which also share structural features and properties with part of the petroleum hyrdocarbons. Distinction between petroleum hydrocarbons and biogenic hydrocarbons and humic substances is not straightforward.

## 4.3 PAH

A literature review on processes and factors governing PAH mobility in soil, aquifers and waste materials, with special focus on colloid-facilitated transport and ageing phenomena is given in Nordtest (2000). In this study, it was concluded that the mobility and leachability of PAH in porous media are governed by retention of the contaminants through poorly characterised sorption processes. Principal factors in predicting the influence of sorption in specific cases are the content of organic matter in the soil and the hydrophobicity of the compounds. However, complicating conditions and factors related to the heterogeneity and the physico-chemical sorption mechanisms make the assessment of PAH leachability a non-trivial task.

In summary, complicating factors include:

- the potential presence of dissolved and/or colloidal organic matter which may enhance the PAH leachability.
- kinetics or non-reversible sorption of PAH (e.g. ageing).

A suitable leaching test method for PAH must incorporate and account for these important processes in a consistent and reliable manner. Table 4.2 contains physical and chemical data relevant to the leaching and mobility of the PAH. As can be seen from the data in table 4.2, PAH are large hydrophobic compounds with low water solubilities and high affinities for surfaces and organic phases.

*Table 4.2 Physical and chemical properties of PAH (16 EPA). From Miljøstyrelsen (1996)*

| **Compound** | **Boiling point (°C)** | **Vapour pressure (Pa)** | **Solubility (mg/l)** | **Distribution co-efficient between air and water $K_H$ (-)** | **Octanol-water distribution coefficient log $K_{ow}$ (-)** |
|---|---|---|---|---|---|
| Naphthalene | 218 | 10,4 | 31 | 0,17 | 3,36 |
| Acenaphthylene | 275 | 0,9 | 3,93 | $4,8*10^{-3}$ | 4,1 |
| Acenaphthene | 279 | 0,3 | 3,42 | $6,0*10^{-3}$ | 3,92 |
| Fluorene | 295 | 0,09 | 1,98 | $4,1*10^{-3}$ | 4,18 |
| Phenanthrene | 339 | 0,016 | 1,2 | $1,6*10^{-3}$ | 4,57 |
| Anthracene | 340 | $1,4*10^{-3}$ | 0,041 | $2,4*10^{-3}$ | 4,54 |
| Fluoranthene | 375 | $1,3*10^{-3}$ | 0,21 | $5,0*10^{-3}$ | 5,22 |
| Pyrene | 393 | $6,1*10^{-4}$ | 0,14 | $4,4*10^{-4}$ | 5,18 |
| Benz(a)anthracene | 435 | $2,7*10^{-5}$ | 0,014 | $3,3*10^{-4}$ | 5,61 |
| Chrysene | 448 | $8,4*10^{-7}$ | $2,0*10^{-3}$ | 3,9*10-4 | 5,91 |
| Benz(b+j+k)fluoranthene | 480-481 | $5*10^{-3}$ – $1,3*10^{-4}$ | $1,5*10^{-3}$ – $8,0*10^{-4}$ | $3,0*10^{-5}$ - $1,6*10^{-6}$ | 6,4 – 6,84 |
| Benzo(a)pyrene | 496 | $7,3*10^{-7}$ | $3,8*10^{-3}$ | $2,0*10^{-5}$ | 6,50 |
| Indeno(1,2,3-cd)pyrene | - | - | $6,2*10^{-2}$ | - | 7,66 |
| Dibenz(a,h)anthracene | 524 | $3,7*10^{-10}$ | $5,0*10^{-4}$ | $8,3*10^{-8}$ | 6,50 |
| Benzo(g,h,i)perylene | 525 | $1,3*10^{-8}$ | $2,6*10^{-4}$ | $5,5*10^{-6}$ | 6,90 |

# 5 ANALYSIS OF PETROLEUM HYDROCARBONS IN ELUATES

Petroleum hydrocarbons in environmental matrices cannot be analysed by adding up the sum of all single compononts in the mixtures, simply because the number of components is too big. Therefore, petroleum hydrocarbons are analysed using a combination of methods specific for individual components and sum parameters, mostly with subdivision in component groups according to boiling point of the components or the chain length of straight chain alkanes. The ideal method for analysis of petroleum hydrocarbons in eluates (and soils) should include all hydrocarbons of petroleum origin (“total petroleum hydrocarbons”, TPH), but no biogenic hydrocarbons and humic substances.

In the current context of non-volatile organic compounds (>C10, boiling point above 174°C), simple volatile components such as BTEX, MTBE and halogenated ethanes are not considered. Heavier alkylbenzenes ($C_9$- and $C_{10}$-aromates, trimethyl-, tetramethyl, methylethyl- and diethylbenzenes) are generally analysed and evaluated with the BTEX components and are thus not included as non-volatile components here.

The selection of an appropriate analytical method depends upon the analytical quality (performance characteristics of the method) required and the information on individual components needed. Behind these requirements are the quality criteria or maximum contaminant concentrations enforced for the investigations in question.

## 5.1 Quality criteria for petroleum hydrocarbons in groundwater and drinking water

The quality criteria for petroleum hydrocarbons that are relevant to leaching tests on wastes and soils are summarised in table 5.1. The end points considered are groundwater at contaminated sites and drinking water, as specific criteria have not yet been given for leachates from soils and wastes.

The drinking water guidelines for total petroleum hydrocarbons (TPH) are 5 µg/l, and 10 µg/l in Denmark and Norway, respectively. No drinking water guideline has been given for TPH in Finland.

*Table 5.1 Petroleum hydrocarbon relevant quality criteria relevant to leaching tests*

| **Non-volatile components** | **EU drinking water guideline[1]** | **Groundwater quality criteria** | | | |
|---|---|---|---|---|---|
| (µg/l) | | Denmark[2] | Sweden[3] | Norway[4] | Finland[5] |
| Naphthalene | - | 1 | - | - | - |
| Sum of PAH | 0,1[1] | 0,2[2] | 0,2[3]/10[4] | 0,1 | 0,1[1] |
| Benzo(a)pyrene | 0,01 | - | - | 0,01 | 0,01 |
| Total hydrocarbons | - | 9[5] | 100[6] | 10 | - |

1) Rådets direktiv 98/83/EF, 2) Miljøstyrelsen, 1998b, 3) www.naturvaardsverket.se, 4) helsedepartementet, 2001, 5) social og hälsovervågningsministeriet, 2001

## 5.2 Analytical quality criteria

In the Nordic countries, there are no specific quality criteria for analytical methods used in association with leaching tests. Generally, it is recommended or required in the Nordic countries to use laboratories accredited according to the international standard ISO 17025 {EN ISO/IEC 2000 52 /id}.

The Danish Environmental Protection Agency (DEPA) has defined quality classes for analysis to be used in environmental monitoring and control, but analysis for organic contaminants are not included in the requirements stated {Miljøstyrelsen 1997 45 /id}). It is generally required that the analytical detection limit is below 1/10 of the criteria and the precision better than 10-20% relative standard deviation (%RSD) (Miljøstyrelsen, 1998a) in investigations of Danish contaminated sites.

In the Drinking Water Directive (Rådets direktiv 98/83/EF), a trueness of 75-125%, a precision better than 25% RSD and an analytical detection limit below 25% of the criteria are required.

A statistically based calculation of analytical detection limits is frequently used accepting a risk of false negatives of 5% or below (detection limit equal to 4-5 times the standard deviation of blank determinations or determinations close to blank samples). In the measuring range close to the detection limit, the RSD is best described including both the blank standard deviation and a standard deviation contribution proportional to the component concentration (Wilson et al., 2004). For this approach, the relation between detection limit, component concentration, precision as %RSD and the width of the 95% confidence interval of measurements is given in table 5.2 (Håndbog i metodevalidering, 1994, Wilson et al., 2004).

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[1] Benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene

[2] Benzo(a)pyrene, benzo(b+k)fluoranthene, fluoranthene indeno(1,2,3-cd)pyrene and benzo(ghi)fluoranthene

[3] Benz(a)anthracene, chrycen, benzo(b+k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene

[4] Naphtalene, acenaphtalene, acenaphtene, fluorene, phenathrene, anthracene, fluoranthene, pyrene and benzo(ghi)perylene

[5] Defined as $C_5$-$C_{35}$, C7-C12 and C9-C16 hydrocarbons

[6] Criteria separate for apolar aliphatic and total extractable aromatic hydrocarbons at gas stations

*Table 5.2 Relationship between limit of detection, component concentration, precision and confidence interval of measurements assuming a 10% RSD at high concentrations (Håndbog i metodevalidering 1994, Wilson et al., 2004).*

| **Concentration** | **Relative standard deviation (%)** | **95% confidence interval for analytical result (%)** |
|---|---|---|
| 1* detection limit | 24 | 48 |
| 2* detection limit | 15 | 30 |
| 3* detection limit | 12 | 24 |
| 4* detection limit | 11 | 22 |
| 5* detection limit | 11 | 22 |

Table 5.2 shows that for component concentrations above 3 times the analytical detection limit, little is gained by improving the detection limit with respect to precision. Above 3 times the analytical detection limit, the relative standard deviation is better than 12% and the risk of being more than 25% wrong below 5%. It should be noted that if the proportional %RSD at high concentrations is increased to above 12,5%, the confidence interval will increase accordingly to above 25%.

Based upon these considerations, a requirement for an analytical detection limit of 25% of the lowest Nordic quality criteria (concentration to be controlled 4 times the detection limit) is adapted for the current work (*e.g.:* ≈2,5 µg/l total petroleum hydrocarbons). A requirement for a precision (repeatability, within series relative standard deviation) better than 12,5% and a trueness (relative recovery of true value, when appropriate) better than 75-125% is enforced as well.

## 5.3 Standard methods

A selection of standard methods used for analysis of total petroleum hydrocarbons in water samples is compiled in table 5.3. Methods aiming at volatile petroleum fractions (*e.g.:* gasoline range organics, GRO, determined with purge and trap GC or similar) and methods evidently too crude for the purpose (very high detection limit or very non-specific, *e.g.:* gravimetric determination of oil and grease, immuno assay methods for total hydrocarbons or thin layer chromatography for petroleum compound group analysis) are not considered.

*Table 5.3 Selected standard methods used for analysis of total petroleum hydrocarbons in water samples*

| **Method** | **Analytical steps** | | | **Performance characteristics** | | |
|---|---|---|---|---|---|---|
| | **Enrich-ment** | **Separation** | **Quantita-tion** | **Detection limit µg/l** | **Precision %** | **True-ness %** |
| EPA 418.1 | LLE[7] | LC[8] removal of grease | IR[9] | 100 | - | - |
| EPA 8015B | LLE | GC[10] | FID[11] | - | - | - |
| EN ISO 9377-2 | LLE | LC + GC | FID | 100 | 3,0-14 | 71-100 |

Method EPA 418.1 based upon LLE has been used in Denmark (DS/R 209) in a modified version with detection limits reported close to 1 µg/l, but a sample volume of 4 l and an advanced IR detector (FT[12]-IR) are required to obtain this. Furthermore, the IR detection is non-specific, *e.g.:* it does not distinguish between different petroleum components or fractions and is susceptible to bias from non-petroleum components in the water samples analysed. Procedures have been established that allow for reduction of bias of TPH by humic substances using IR at two wave lenghts, but these do not mask the bias of aliphatic structures in the humic substances. The IR method generally requires the use of solvents (freons or chlorinated solvents) that are in the process of being phased out as ozone depleting substances.

Method 8015B is a generic method for detemination of non-halogenated organics in solid and liquid matrices using GC/FID. Performance characteristics are not given for TPH or DRO, but single component detection limits recorded were in the range of 10 µg/l, precision in the range of 5-30% and trueness in the range of 90-140% (100 µg/l level) (EPA 8015B).

The Danish version of method EN ISO 9377-2 (extraction and determination of all extracted hydrocarbons, $C_{10}$-$C_{40}$, with GC-FID) states that the method is not applicable for drinking water due to the high detection limit and that a suitable method for detemination of TPH in this matrix is currently not available.

The overall conclusion is that the standard TPH methods available are not suitable for analysing petroleum hydrocarbons in eluates from leachings tests. The detection limits are too high (GC-FID), or the methods require to large sample volumes (IR), are of insufficient specificity (GC and IR) or require use of solvents in phase-out (IR).

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[7] LLE: liquid liquid extraction, transfering and concentrating apolar organic compounds from a water sample into an organic solvent

[8] LC: liquid chromatography of extract, separating organic compounds accoridng to polarity

[9] IR: infra detection, a non specific detection method for aliphatic organic compounds

[10] GC: gas chromatography, separating organic compunds according to boiling point

[11] FID: flame ionization detection, a non specific detection method

[12] FT: Fourier transform, method that allows for recording of multiple spectra in a short time interval and thus for improvement of detection limits

## 5.4 Dedicated methods

### 5.4.1 Petroleum fractionation methods

In order to qualify the bulk sum parameter “total petroleum hydrocarbons”, TPH, several methods have been suggested that break the lump sum result down into fractions reflecting boiling point (number of carbon atoms) or polarity (aliphatic or aromatic hydrocarbons). All methods are based upon LLE combined with GC-FID. Photo ionization detection (GC-PID) has been suggested to detect volatile aromatic compounds.

The method used in Denmark for analysing total petroleum hydrocarbons in soil subdivides TPH into hydrocarbon fractions $C_6$-$C_{10}$, $C_{10}$-$C_{25}$ and $C_{25}$-$C_{35}$ and is based upon liquid extraction and GC-FID (VKI, 1998).

The American Petroleum Institute (API) has developed a method with LC fractionation of extracted hydrocarbons into aliphatics and aromatics, combined with a GC subdivision into 5 (aliphatics) or 7 (aromatics) boiling point fractions (API, TPHCWG). The method can be applied to both soil and water samples, but the limit of detection for water samples is stated as 5.000 μg/L and for soil samples as 50 mg/kg. These fractions have been interpreted in terms of fate and transport properties in order to enable risk assessment based upon properties averaged over each fraction. The interpretation approach has been refined and adjusted to reflect Danish risk assessment procedures (Miljøstyrelsen 2004).

The overall conclusion is, that fractionation TPH methods may be useful for risk assessment but will not be able to comply with the detection limit requirement for leaching test application.

### 5.4.2 GC-MS based sum parameters

Mass spectrometry (MS) is a detection method that allows for distinction between different organic compounds in the detector; *e.g.:* it can be used as a specific detection method. Combining the separation of different compounds in the GC with specifi detection in the MS reduces noice in analysing complicated mixures and thus enables lower detection limits. For specific quantification purposes, the MS detector is operated in selected ion monitoring mode (SIM) detecting sets of ions specific for each anlyte in question.

The MS detector can also be operated as a non-specific detector in total ion current mode (TIC) where al ions formed in the MS are recorded. In this mode, the sensitivity of the MS as detector for GC is comparable to that of GC-FID, and estimated at the least 10 times lower than for GC-MS-SIM (Minear and Keith, 1984).

A combination of crude sum parameters (LLE, followed by LC fractionation and gravimetry) and GC-MS-SIM determination of selected petroleum components (alkanes, PAH and alkylated PAH) has been suggested for the purpose of source identification and risk assessment (Miles et al, 1999, Wang and Fingas, 1997). This method provides information on components of human health concern and of markers of origin and degradation. The major drawback is that it does not give an estimate of the total concentration of petroleum hydrocarbons with the required detection limit (gravimetry too high detection limit, GC-MS-SIM determines only part of the TPH).

For determination of total petroleum hydrocarbons in soils, an intermediary mode has been suggested (SIMFAB), where aliphatic hydrocarbons are recorded as the common ion with m/z[13] = 57 and aromatic hydrocarbons with the common ion m/z = 91. A method applying SPE extraction and GC-MS- SIM detection at m/z = 71 and 85 (aliphatic hydrocarbons detected only) has also been suggested (SINTEF). Performance characteristics are not available, but the detection limit was estimated of 5 µg/l. Experimentally, a similar approach was developed for use with leachates from leaching tests with separation/concentration of petroleum hydrocarbons with SPE[14] and GC-MS-SIM using the ions with m/z = 71 and 85 (Miljøstyrelsen, 2003). A detection limit of 50 µg/L, a trueness of 60% and a highly unsatisfactory precision were obtained. For this method, it was concluded that the extraction method (SPE), detection (MS-SIM) and calibration required further development in order to acchieve performance characteristics adequate for the purpose (see section 5.2). Further development should also address the fact that the response factor in the MS will vary among components, in particular with boiling point and betweeen aliphatic and aromatic compounds.

It should be emphasized here, that TPH is a method dependent parameter, *e.g.:* that the analytical results obtained are defined by the method used. Therefore, TPH obtained with a GC-MS-SIM based sum parameter will and can not be equal to results obtained with a GC-FID based sum parameter. Similarly, data obtained after SPE will and can not be equal to data obtained with LLE, although the data differences may be less here. Comparison of data will require recalculation based upon experimentally based data for both TPH methods for a represenative selection of samples.

The overall conclusion is that the SPE and GC-MS-SIM based method may be developed into a method complying with the performance requirements, but that no suitable GC-MS based method is available “off the shelf”.

### 5.4.3 Indicator component methods

An alternative approach would be to select indicator components that are considered either the critical components with respect to human health and environmental risk, or representatives allowing for calculation of of leached TPH from their concentration. The analytical advantages of such an approach would be that low detection limits could be obtained combining GC-MS-SIM quantification of the indicator components with calibration based upon deuteriated internal standards for each component.

Health based, non-volatile indicator components would be the aromatics, *e.g.:* the polycyclic aromatic hydrocarbons (PAH). Heterocyclic aromatic compounds (NSO) and some additives may have to be included.

Representative indicator components and calculation alegoritms that allow for TPH from all sources and all matrices can not be developed. The reason for this can be seen in figure 5.1 giving gas chromatograms for different petroleum products in soil, in addition to an old and weathered diesel contamination.

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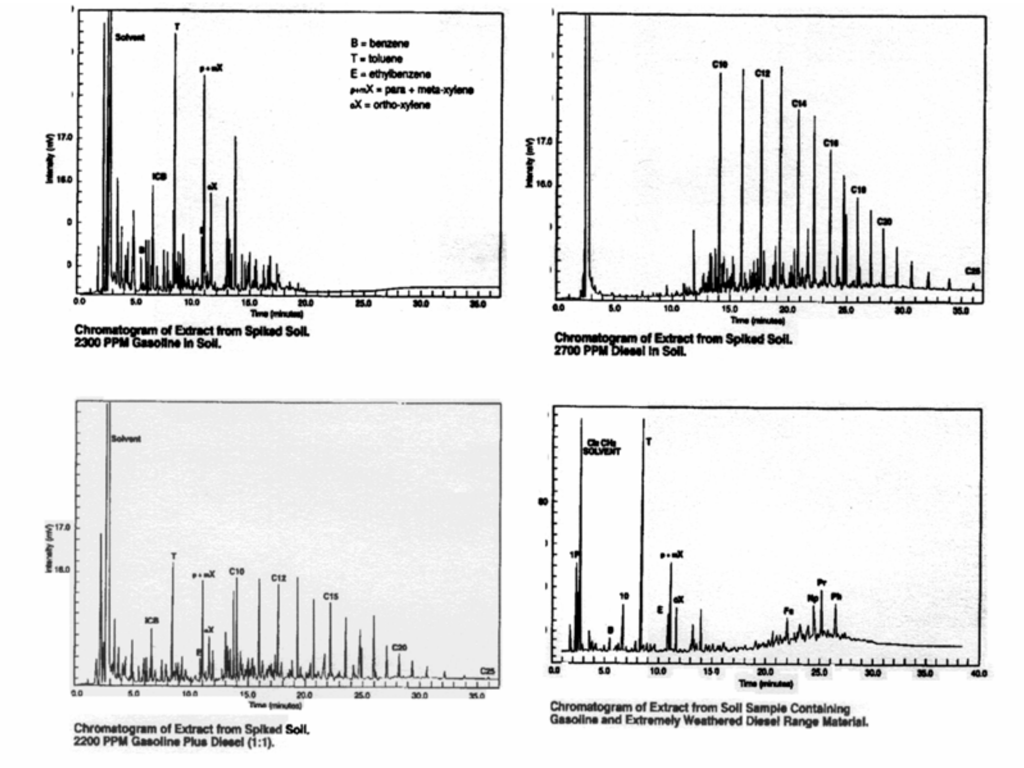
[13] m/z: mass divided by charge

[14] SPE: solid phase extraction, a method to extract and concentrate organic compounds from water into an organic extract



Chromatogram of Extract from Spiked Soil.
2300 PPM Gasoline in Soil.

Chromatogram of Extract from Spiked Soil.
2700 PPM Diesel in Soil.

Chromatogram of Extract from Spiked Soil.
2200 PPM Gasoline Plus Diesel (1:1).

Chromatogram of Extract from Soil Sample Containing
Gasoline and Extremely Weathered Diesel Range Material.

*Figure 5.1 Gas chromatograms of fresh petroleum products added to soil and to a soil with an aged diesel contamination (from API, TPHCWG)*

An attempt to calculate TPH (all peaks) from one or a few indicator components (one or a few peaks peaks) in diesel based upon an alegoritm set up for gasoline would evidently fail. The same goes for two different diesel products and, as can also be seen from figure 5.1, for calculation for a weathered diesel from an alegoritm set up for a fresh diesel.

Furthermore, the leachability of petroleum components vary with chain length (boiling point) and chemical structure (aromatic or aliphatic), see figure 5.2. Therefore, the petroleum hydrocarbon profile in a leaching test will differ considerably from that of the original soil. It should further be noted from figure 5.2, that whereas aromatic dissolved concentrations can exceed 0,01 µg/l (groundwater quality criterium for the carcinogenic benzo(a)pyrene) for all equvalent carbon numbers, aliphatics with equivalent carbon lenght above 17 will not exceed this concentration due to solubility limitation.

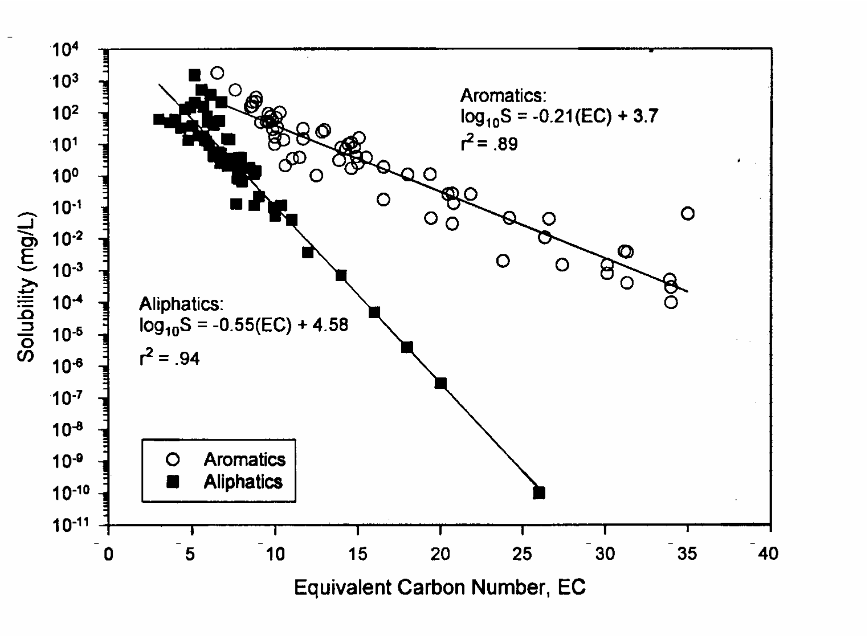


*Figure 5.2 Water solubility of petroleum components against equivalent carbon number (from API-TPHCWG)*

Therefore, calculation of TPH from indicator components should be done for fractions of aliphatic and aromatic hydrocarbons, using one indicator component for each fraction. The fractions should be sufficently narrow to allow for selection of one representative for each. A set of fractions has been suggested for both analytical purposes and for fate and transport calculations (API-TPHCWG), where the non-volatile fractions are presented in table 5.4 with suggestions for indicator components of each fraction. It should be noted that the indicator components each should reflect intermediary leaching properties for their fraction.

*Table 5.4 Suggested fractions of TPH (from API-TPHCWG) and tentative suggestions for indicator components*

| Aromatics | | Aliphatics | |
|---|---|---|---|
| **Equivalent carbon number** | **Indicator component** | **Equivalent carbon number** | **Indicator component** |
| $C_{10}$-$C_{12}$ | Naphtalene | $C_{10}$-$C_{12}$ | Undecane |
| $C_{12}$-$C_{16}$ | 1,5-Dimethylnaphtalene | $C_{12}$-$C_{16}$ | Pentadecane |
| $C_{16}$-$C_{21}$ | Anthracene | $C_{16}$-$C_{21}$ | Nonadecane |
| $C_{21}$-$C_{35}$ | Benz(a)anthracene | - | - |

Determination of TPH in soils and leachates should then be accomplished using extraction of petroleum hydrocarbons, GC-MS-SIM detection of fraction indicator components and calculation of corresponding TPH contents and fractions. Algoritms for calculations (*e.g.:* "calibration") are developed using generic or site specific factors for the relation between indicator components determined as described and the TPH fractions obtained after LC separation into aliphatic and aromatic extracts and GC-FID detection. Calibration factors should be established seprately for fresh and weathered products.

This approach would be a combination of the fractionation approach (API TPHWG) and the selected petroleum components approach (Mills et al., 1999, Wang and Fingas,

1997) and could be extended to include more single components for providing also information on human health risks, fate and transport or origin/source.

In summary with respect to indicator component methods for determination of petroleum hydrocarbons in leaching tests, either a human health based selection of indicators (PAH only, possibly NSO and selected additives) disregarding all other petroleum hydrocarbons, or the suggested combined indicator component/fractionation method may be developed into suitable methods.

## 5.5 Evaluation of methods for leaching tests

No methods are currently available “off the shelf” for determination of total petroleum hydrocarbons (TPH) as part of a leaching test satisfying the performance requirements set up for this application. The methods currently available either require too large sample volumes, are to non-specific, have to high detection limits or uses solvents in phase-out.

Three methods may be developed into suitable methods for determination of total petroleum hydrocarbons (TPH) in leaching tests:

- SPE and GC-MS-SIM based TPH analysis
- indicator component/fractionation TPH analysis
- human health based indicator selection analysis

Both the SPE and GC-MS-SIM and the indicator component/fractionation methods require further method development, refinement and validation, but both are likely candidates for a suitable method.

The SPE and GC-MS-SIM based method has the advantage of being a simple method the use of which may be extended to other applications such as drinking water analysis.

The indicator component/fractionation method has the advantage of providing data that can be used directly in the fate and transport calculations used in risk assessment.

For both methods, comparison with data obtained with previous GC-FID methods will require recalculation based upon experimentally obtained data because TPH is a method dependent parameter, *e.g.:* that the analytical results obtained are defined by the method used.

The prerequisite for using analysis of human health based indicators of petroleum hydrocarbon contamination is a revision of the current regulatory approach to establish quality criteria based upon these indicators only. Full identification of the appropriate indicator components must be accomplished (in particular with respect to NSO compounds and additives) and for some components, analytical method development and validation may be required (again: for NSO and additives). Also, it should be ensured that developed indicators are protective woth respect to environmental hazards.

Based upon these considerations, it is suggested to work with the SPE and GC-MS-SIM based method (short-term), with the indicator component/fractionation method as a valid alternative requiring a more extensive development and validation effort (also short-term), and finally with the human health based indicator component approach as the long-term objective.

# 6 LEACHING TESTS

## 6.1 Batch test

A batch leaching test for organic compounds was developed in Miljøstyrelsen (2003). However, some specific problems concerning separation of solid and liquid for non-volatile organic compounds remained unsolved. This project focuses on these problems.

The batch test for non-volatile organic compounds is a technically fairly simple test which is conducted in a glass container (~680 mL) at a liquid to solid ratio (L/S) of 2 l/kg and with a maximum headspace of 5 %. The eluent consists of a solution of 0,005 M $CaCl_2$ in demineralised water. The container is rotated end over end for 24 hours and subsequently centrifuged in order to separate solid and liquid. The centrifugation is performed in two steps. The first step includes centrifugation at 720 g for 15 minutes to separate the bulk part of the solids from the solution. It is an advantage if the leaching bottle could be used directly in the centrifuge in order to avoid loss of organic compounds by sorption onto new equipment. After the first centrifugation the eluate is transferred to a centrifugation vessel of steel by applying nitrogen pressure to the leaching bottle (see figure 6.1). Using this method of transferring eluates will separate floating materials with a density less than that of water from the the liquid phase. In the second centrifugation step the eluates are centrifuged at high forces. After centrifugation the eluates are characterised physically and chemically. This test method provides a determination of the "equilibrium" concentration of non-volatile organic compounds in the eluate. The main advantages of this batch test method are:

- It is simple and easy to perform.
- The main principles in this test are well known from testing of inorganic compounds.

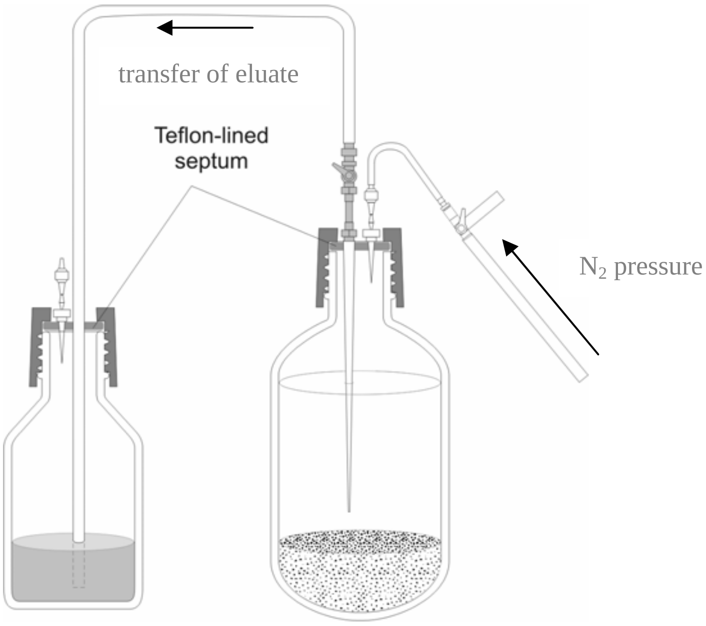


*Figure 6.1 Sketch of a batch leaching test for organic compounds.*

## 6.2 Column test

A column test was also developed in a previous study conducted by DHI and E&R, DTU in co-operation (Miljøstyrelsen 2003), and as the batch test it was designed to assess the equilibrium distribution of non-volatile organic compounds between solid and liquid.

- The column test is performed in a glass column (size: (~15 cm length and ~6 cm diameter, ~425 $cm^3$) at a fixed L/S depending on the properties of the test material (for most soils the L/S will be between 0,5 and 1,5 l/kg). A continuous vertical up-flow is used, so that the column is water saturated. The eluent that consists of 0,005 M $CaCl_2$ containing 0,5 g/l $NaN_3$ (to prevent degradation) is recirculated in the test system for 7 days to obtain equilibrium. The flow velocity is approximately 0,7cm/h (darcy velocity). The eluate is collected as one single fraction after 7 days of recirculation. The eluate is not further treated by centrifugation nor filtration after the leaching has ended. The eluate is characterised physically and chemically. For analysis of organic compounds the extraction is performed directly in the receiving vessel from the test system. The set-up of the column test is illustrated in figure 6.2.

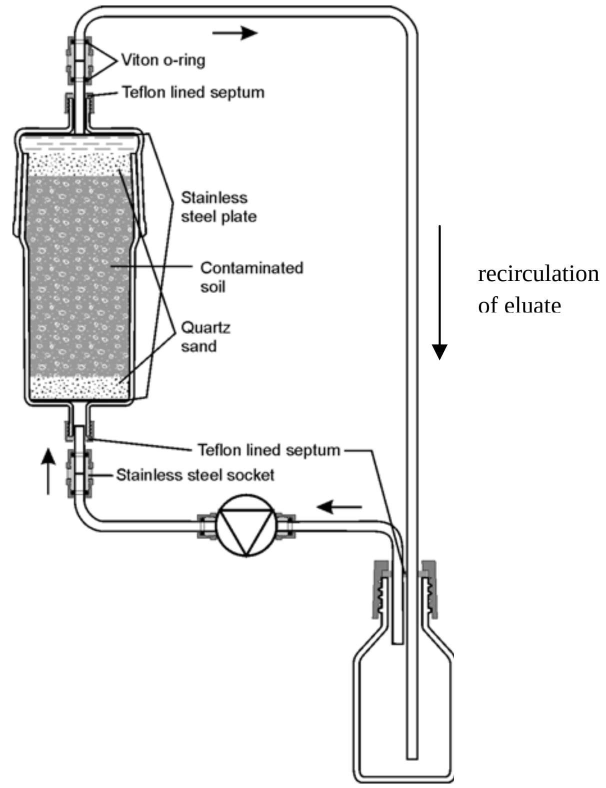


*Figure 6.2 Sketch of the equilibrium column test for organic compounds. The eluate is recirculated through the column for 7 days.*

The main advantages of this column test method are:

- No additional treatment of the eluate is needed after leaching before it can be characterised. Colloids present in the eluate after leaching are expected also to be mobile in a natural situation. Thus, the concentration of organic compounds in the eluate represent an equilibrium concentration taking into account the potential influence of dissolved organic carbon and colloids on the leachability.

- The test material is treated very gently during testing and no grinding of the material will occur during leaching.
- It is a fairly simple test method, which is easy to operate once it has been established.

# 7 CRITICAL TEST CONDITIONS

## 7.1 Sorption of organic compound to equipment

PAH in water solutions are known to adsorb strongly to materials in contact with the solution (Bauw et al., 1991; Reemtsma and Mehrtens, 1997).

The total loss of PAH during testing (in this case diffusion tests were used) has been estimated, based on parallel loss test (Larsson, 2002). The total loss of PAH in the leachates of the diffusion tests was estimated to be between 0,2 % (w/w) and 20 % (w/w). The percentage loss depended mostly on the concentration and probably also on the pH in the leachate. The highest percentage of loss was seen at high pH and at the lowest original concentration in leachate. The upper interval of the total loss-% of PAH was mostly influenced by a major loss of naphthalene. In another test (Larsson, 2004), the adsorption of PAH on glass surfaces during diffusion leaching was about 2 % (w/w). The results from these two studies are not directly comparable as the concentration in the leachates differed significantly between the two tests. However, the results clearly showed that the concentration of PAH in the leachate strongly influence the percentage of loss. Increased percentages of loss were found with decreasing total concentration in eluate. These results indicated that the loss of larger PAH happened more rapidly than losses of the smaller PAH. It took much longer time to reach maximum loss of the small PAH.

For a harbor area soil Gamst et al. (2005) found that the amount of PAH adsorbed to equilibrium column leaching test materials corresponded to 9% of the totally leached amount of PAH. The total leached amount of PAH from the soil was, however, less than 1% of the total soil content of PAH and therefore it must be expected that material sorption will increase the desorption rate of contaminants from the soil. The minor effect on the totally leached amount of PAH may, however, alter the PAH composition in the leachate, because less than 3% of the total leached 2-ring PAH and 0%-11% of the 3-ring PAH where sorbed to materials. In comparison 19%-49% of the leached 4-ring and 49%-53% of the leached 5- and 6-ring PAH were sorbed to materials. These results illustrate how larger PAH sorb more strongly to most materials, which is in accordance with others (Bauw et al., 1991; Reemtsma and Mehrtens, 1997; Comans, 2001). Sorption to glass and steel materials is likely to be a fast surface reaction that changes the concentration gradient between leachate and soil particles and within the contact time used in the equilibrium column setup, leachate PAH and PAH sorbed to materials is likely to be in equilibrium. The fraction of PAH removed from the soil particles is diminutive and material sorption will consequently increase the desorption rate from the soil particles because of the changes in concentration gradient between soil and liquid and, the effect on the measured leachate concentration will likely be insignificant when equilibrium is obtained.

To minimise losses of the organic compounds by sorption onto the equipment, transfer of the eluates to new glasses or containers should be avoided after leaching equilibrium is obtained.

## 7.2 Generation of colloids in the batch test

Many studies have been conducted to determine sorption equilibrium parameters for organic compounds, and most often batch leaching techniques have been used for that purpose. In many ways the experiences from these investigations can be used in this context as the leaching test methods presented in this project basically are aiming at determining equilibrium desorption parameters. Several investigations have focused on comparison of different techniques for the determination of sorption rates. Some researchers have observed good agreement between different techniques and others have observed a disagreement up to an order of magnitude (Maraqa, 2001). However, none of the techniques used have been standardised, including the batch test. Different test conditions for the batch sorption test as for example centrifugation force and time have been used (e.g. Gamst et al., 2004, Maraqa, 2001, Bowman et al., 2002) which resulted in different particle cut-offs, that might affect the results of the tests for hydrophobic compounds. Gamst et al. (2004) observed in a study for naphthalene that results obtained from batch sorption experiments conflicted with observations from gas diffusion experiments on the same soil (Gamst et al., 2003). It was suggested that the different observations might be due to the intra-aggregate diffusion of naphthalene in soil aggregates in the column experiment, whereas such aggregates are predominantly destroyed by physical disruption in the batch experiment. Thus, Gamst et al. (2003) suggested that the very different conditions in column and batch experiments must be considered when comparing sorption kinetic data.

Further, Bergendahl and Grasso (1998) have tried to quantify the production of, and the mechanisms behind the release of, colloids in a batch leaching test of a coal tar contaminated soil. The study quantified the generation of colloid fractions during testing and particle count data indicated that the concentration of 0,72 – 0,83 μm diameter colloids in the filtrate increased with agitation time. It was concluded that colloid generation during batch testing resulted in an increase in total colloidal surface area in the filtrate. An increase in colloidal surface area may result in an overprediction of the aqueous phase concentration of hydrophobic contaminants.

In a literature survey, Larsson et al. (2000), presented results from batch tests of a tar-containing road construction material which indirectly indicated production of “soluble” PAH, hypothetically either in the form of PAH contaminated small particles or as dissolved PAH. The survey addressed the need for further studies that could reveal the potential production of soluble PAH/particles containing PAH during batch tests.

Miljøstyrelsen (2003) also obtained indirect indications of the generation of colloids during agitation of batch tests (see Figure 7.1). For two different soils increasing eluate concentrations of selected PAH-compounds were found as a function of contact time. At the same time increases in the turbidities were detected indicating the production of colloids during agitation by grinding of the soil materials. These results demonstrated that with increasing presence of colloids higher concentrations of PAH in the eluates can be found. A similar picture can be found in the results obtained by Nordtest (2000).

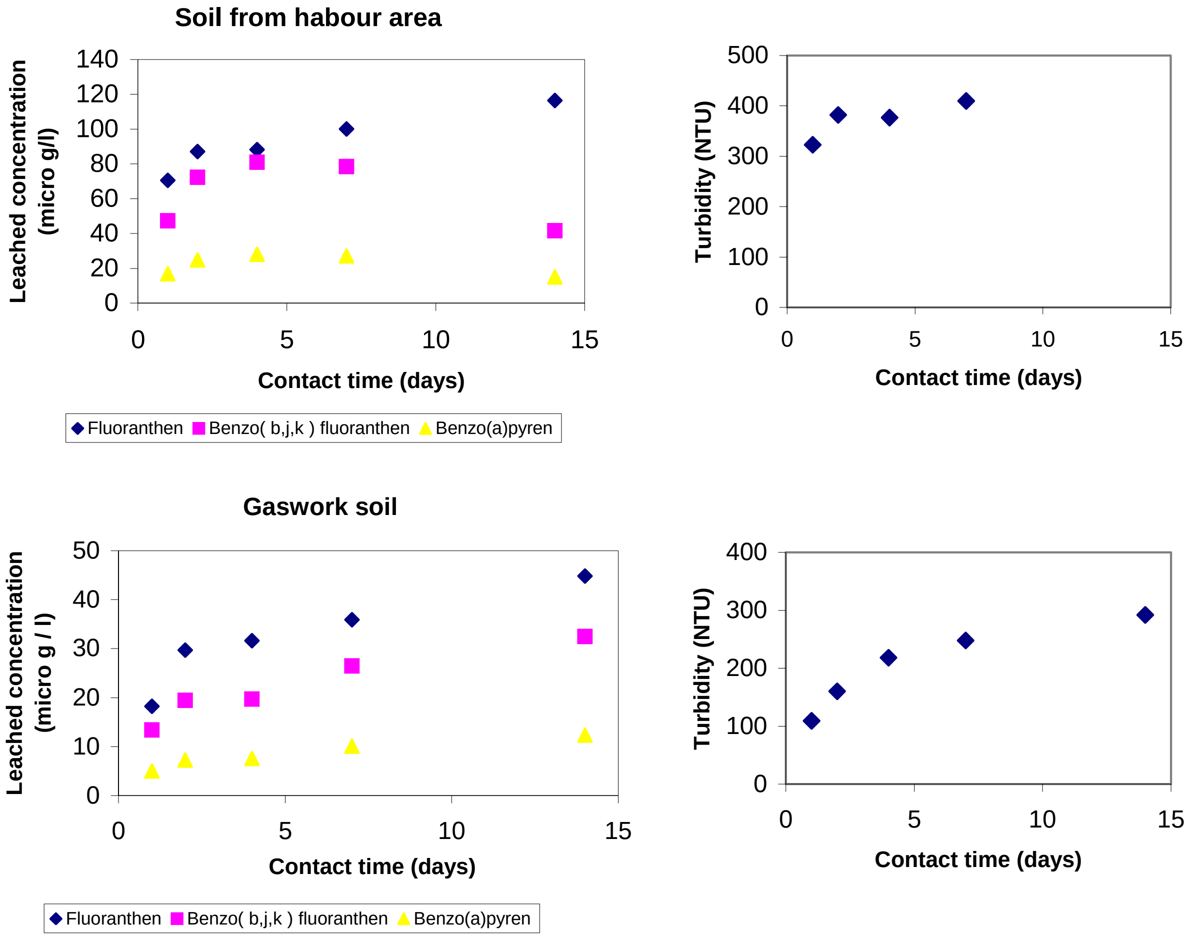


*Figure 7.1* *Results obtained by batch test procedures. Eluate concentration of PAH as a function of contact time compared to the turbidity of the eluates. The gaswork soil is a loamy soil and the harbour soil is a sandy soil. The results are from Miljøstyrelsen (2003).*

## 7.3 Separation of solid and liquid

In the batch leaching procedure the solid and the liquid have to be separated by either filtration or centrifugation. Both filtration and centrifugation techniques yield operationally defined particle cut-offs.

### 7.3.1 Separation by filtration

Previous investigations have focused on separation of solid and liquid by filtration in relation to organic compounds (Comans et al., 2001, Miljøstyrelsen 2000, working document ISO/TC 190/SC 7/WG6). Many different filters are commercially available but not all filters if any are suitable for organic compounds such as PAH and heavy hydrocarbons as these compounds may sorb strongly to the filter materials.

VTT (2001) has tested the suitability of a range of different filters in relation to filtration of eluates containing chlorophenoles and PCB. The results indicated that PCB were lost by sorption on filters made of cellulose nitrate. However due to very low leaching concentrations of PCB it was not possible to draw further conclusions in relation to sorption on to filters. For chlorophenoles the filter material did not seem to affect the results significantly except for filters made of cellulose nitrate. Rood et al. (1994) also observed losses of PCB due to filtration.

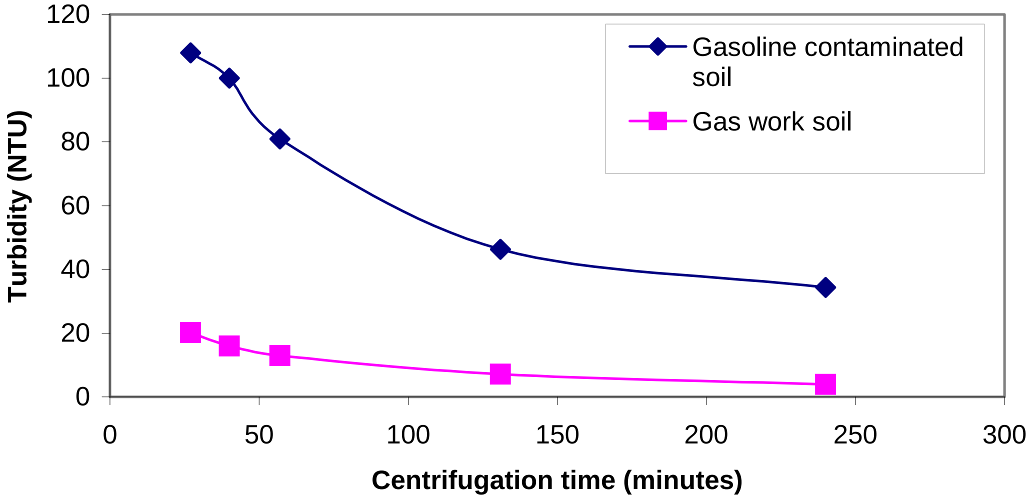
Bauw et al. (1991) showed that filtration was very critical to PAH and there were significant differences in PAH sorption to different kinds of filters all made of glass fibres and with comparable particle cut-off. Miljøstyrelsen (2000) observed similar results. Spiked samples were filtered through a glass fibre filter and for 2-ringed PAH the recover was typically 80%, whereas the recover of the larger PAH in some cases was less than 10%. However, these findings are not consistent with findings presented in a working document from ISO/TC 190/SC 7/WG6 N0058. This document presents data from comparison of separation of solid and liquid by decantation, centrifugation and filtration. These results show that only for one soil eluate (out of 4 soils tested) a significantly reduced concentration of PAH was found after filtration with a nitrate cellulose filter.

Rødsand and Rike (1999) found a recovery of 60-95% of 3-ring PAH whereas 20–81% for 4-ring PAH and 5-20% for 5+6-ring PAH using Teflon filters and spiked water samples.

### *7.3.2 Separation by centrifugation*

Separation of solid and liquid by centrifugation has often been used to investigate sorption and desorption of non-volatile organic compounds. However, no standards or guidelines exist on how to centrifuge the sample, e.g. specifying centrifugation force and time. This has resulted in the use of numerous different centrifugation settings (e.g. Bouchard et al., 1990; Kan et al., 1994; Gamst et al. 2003, Hwang and Cutright, 2004). It is well known that different centrifugation force and time yields different particle cut-off in the solution and thus the content of colloids in the solutions are different. This may affect the content of hydrophobic compounds in the eluates and the results of the tests may thus be biased by such test specific differences.

A previous study has indeed shown that the centrifugation time and the centrifugation force strongly influenced the results of the batch leaching tests (Miljøstyrelsen 2003). Figure 7.2 and 7.3 show some of the results obtained in that study. As an indicator of the effect of varying centrifugation time on separation of solid and liquid, the turbidity was determined (Figure 7.2). The results showed a clear decrease in turbidity as a function of increasing centrifugation time, indicating that colloids were removed from the eluates with increasing centrifugation time. The eluates from batch tests performed on a soil from a former gas production facility were analysed for PAH and these results are shown in Figure 7.3.



*Figur 7.2 Turbidity determined in eluates as a function of time of centrifugation. Two different test materials were used; A soil collected from a petrol station and a soil from a former gas production facility (data from Miljøstyrelsen, 2003).*

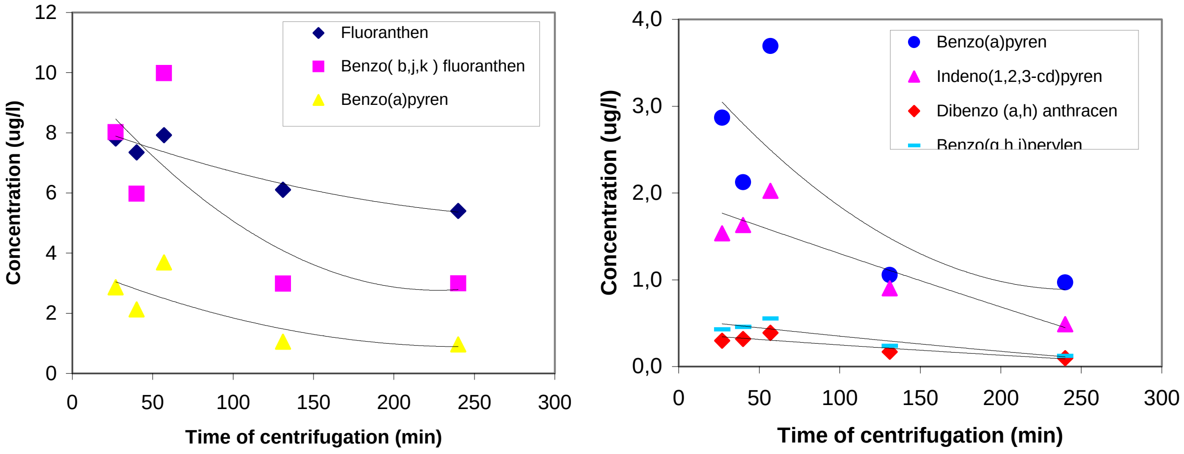


*Figure 7.3 Effect of centrifugation on the concentration of PAH in eluates from batch leaching tests. The eluates are centrifuged at 720 g at varying time. The test materials originated from a former gas production facility (unpublished data)*

In Figure 7.3 it can be seen that the concentration of PAH in the eluate from a batch leaching test decreases with increasing centrifugation time. These results illustrate that a technical procedure (e.g. centrifugation) may have an influence on the result of the batch leaching test and it is thus important that the method for centrifugation is specific (e.g. centrifugation force and time) in a test procedure for a batch leaching test.

By comparing results from a batch test and an equilibrium column-leaching test it was also shown by Miljøstyrelsen (2003) that centrifugation at only 720 g was far to little to remove the colloids built up in the batch test.

In Appendix C formulas for calculating the actual centrifugation force can be found together with a description of the relationship between centrifugation force and time.

## 7.4 Degradation of organic compounds during leaching

When focusing on organic leachable compounds, it is of major importance to minimise any degradation of such compounds both during the leaching test and before analysis.

Degradation by light may easily be minimised by covering the test equipment and sample bottles with aluminium foil. However, microbial degradation may not be avoided as easily. Chemical agents such as sodium azide ($NaN_3$) or mercury chloride ($HgCl_2$) (normally 0,2 g/l $NaN_3$ or 2 %(w/w) $HgCl_2$) have been used to reduce/minimise biodegradation (e.g. Jørgensen 1992). However, the influence or bias such additives may have on the leaching procedure is not well understood. For example, it is known that $NaN_3$ may increase the pH in soil (Skipper and Westermann, 1973; Wolf et al., 1989). Changes of pH to very low or very high pH may increase the content of leached PAH as a result of an increase in leaching of dissolved humic substances (Wahlström et al., 1994).

The introduction of non-oxic conditions by phycical pre-treatment of the eluent may possibly be an alternative to the application of chemical additives (experiences from SGI, DHI and DTU). However, such measures will only prevent aerobic degradation. Potential anaerobic degradation processes will not be affected, but anaerobic degradation is often slower and may need significantly longer lag-phase time, compared to aerobic degradation. Results from Larsson (2002) and Larsson (2003) hypothetically indicate that the heavier PAH may have less tendency to be degraded in anaerobic leaching test than the lighter PAH. Also here, more research is needed to quantify the potential biodegradation rates of the organics as a function of different circumstances of the leaching test.

Studies of PAH degradation have shown that the smaller PAH (2-4 ring) are readily degradable (Hestbjerg et al., 2003; Muncnerova and Augustin, 1994) while the larger PAH remain recalcitrant (Hestbjerg et al., 2003; Schneider et al., 1996). However, degradation in these studies is very slow.

# 8 TEST MATERIALS

## 8.1 Soils

Two Danish soils and two types of waste products were in present project used for the experiments in this project. Both soils were contaminated with PAH. The clay pigeon contaminated soil originated from a former military shooting range and pieces of clay pigeons could be found to a depth of more than one meter. The soil was sieved through a 9,5 mm sieve in order to remove large stones and roots. Oversize pieces of clay pigeons were crushed in a jaw crusher and sieved through a 4 mm sieve. Finally the material was homogenised with the soil.

The soil from an industrial site (B&W soil) originated from a former shipyard site, which had also earlier been used as dumpingsite for waste from early industrial activities in Copenhagen. The soil was homogenised and large stones and roots were removed. The particle size distributions of the soils are given in table 8.1 and the total contents of PAH-compounds can be found in table 8.2.

*Table 8.1 Particle size distribution of the soils used for experimental work.*

| **Materials** | **Clay Pigeon contaminated soil** | **B&W soil** |
|---|---|---|
| Short description | Soil from a former military shooting range | Soil from a former shipyard and industrial waste disposite |
| Clay (< 2 μm) (g/100 g) | 14,8 | 7,1 |
| Silt (2 – 63 μm) (g/100 g) | 23,9 | 7,3 |
| Sand (63 – 2000 μm) (g/100 g) | 55,3 | 64,1 |
| Humic substances (g/100 g) | 4,4 | 21,6 |
| $CaCO_3$ (g/100 g) | 1,54 | n.a. |
| Total C (g/100 g) | 2,79 | n.a. |

*n.a: not analysed*

*Table 8.2 Total content of PAH in the soils*

| **Compound** | **Unit** | **Clay pigeon contaminated soil** | **Industrial soil (B&W soil)** |
|---|---|---|---|
| Content of dry matter | % | 84 | 85 |
| Naphthalene | mg/kg dw. | 2,8 | 2,7 |
| Acenaphthylene | mg/kg dw. | 0,027 | 0,014 |
| Acenaphthene | mg/kg dw. | 7,9 | 5,5 |
| Fluorene | mg/kg dw. | 9,6 | 7,7 |
| Phenanthrene | mg/kg dw. | 61 | 40 |
| Anthracene | mg/kg dw. | 15 | 9,2 |
| Fluoranthene | mg/kg dw. | 74 | 62 |
| Pyrene | mg/kg dw. | 64 | 55 |
| Benz(a)anthracene | mg/kg dw. | 53 | 49 |
| Chrysene/Triphenylene | mg/kg dw. | 64 | 62 |
| Benz(b+j+k)fluoranthene | mg/kg dw. | 131 | 100 |
| Benzo(a)pyrene | mg/kg dw. | 73 | 58 |
| Indeno(1,2,3-cd)pyrene | mg/kg dw. | 12 | 9,6 |
| Dibenz(a,h)anthracene | mg/kg dw. | 3,5 | 2,6 |
| Benzo(g,h,i)perylene | mg/kg dw. | 10 | 8,7 |
| Sum PAH (16 EPA) | mg/kg dw. | 583 | 470 |

## 8.2 Waste products

Two waste products were chosen for the experimental work. Clay pigeons used for shooting practice were crushed in a jaw crusher to < 4 mm using the same procedure as described in EN 12457 part 1-4. Road sweeping were obtained from RGS 90 in Copenhagen. The road sweepings, which were collected during the springtime in Copenhagen area, were homogenised. The total contents of PAH compounds in the waste materials are given in table 8.3.

*Table 8.3 Total content of PAH in the soils*

| **Compound** | **Unit** | **Crushed clay pigeon** | **Road sweepings** |
|---|---|---|---|
| Content of dry matter | % | 99,9 | 97,1 |
| Naphthalene | mg/kg dw. | 54 | < 0,05 |
| Acenaphthylene | mg/kg dw. | 0,87 | 0,089 |
| Acenaphthene | mg/kg dw. | 280 | < 0,05 |
| Fluorene | mg/kg dw. | 190 | < 0,05 |
| Phenanthrene | mg/kg dw. | 1400 | 0,34 |
| Anthracene | mg/kg dw. | 330 | 0,11 |
| Fluoranthene | mg/kg dw. | 2500 | 0,82 |
| Pyrene | mg/kg dw. | 2300 | 0,82 |
| Benz(a)anthracene | mg/kg dw. | 2000 | 0,36 |
| Chrysene/Triphenylene | mg/kg dw. | 1700 | 0,36 |
| Benz(b+j+k)fluoranthene | mg/kg dw. | 3300 | 0,73 |
| Benzo(a)pyrene | mg/kg dw. | 2400 | 0,69 |
| Indeno(1,2,3-cd)pyrene | mg/kg dw. | 1500 | 0,59 |
| Dibenz(a,h)anthracene | mg/kg dw. | 0,56 | 0,15 |
| Benzo(g,h,i)perylene | mg/kg dw. | 1200 | 0,73 |
| Sum PAH (16 EPA) | mg/kg dw. | 19000 | 6,3 |

All test materials were stored in airtight metal buckets at 4 °C until they were used for the experiments.

All analyses of eluates and solid materials were done by Eurofins A/S in Denmark.

PAH in solid materials was analysed after extraction with dichloromethane by GC/MS-SIM (gas chromatography with mass spectroscopy detections with ion selective monitoring).

PAH in eluates was analysed after extraction with dichloromethane by GC/MS-SIM (gas chromatography with mass spectroscopy detections with ion selective monitoring).

# 9 BATCH LEACING METHOD: SEPARATION OF SOLID AND LIQUID BY CENTRIFUGATION

In order to improve the technique for separation of solid and liquid in the batch test method a number of experiments were performed. For each of the four materials described above the following experiments were performed: 6 batch tests were performed on each material according to a protocol given in Appendix B. The eluates were decanted into a large vessel and mixed by stirred for several minutes before separation of solid and liquid by centrifugation. Three of these eluates were centrifuged at 6200 g for one hour and the rest at 27000 g for 30 minutes. The experimental set-up is illustrated in Figure 9.1. It allows for comparison of two different centrifugation techniques excluding the heterogenity of the test materials. All equipment's used for experiments were made out of glass or stainless steel.

**Batch tests**

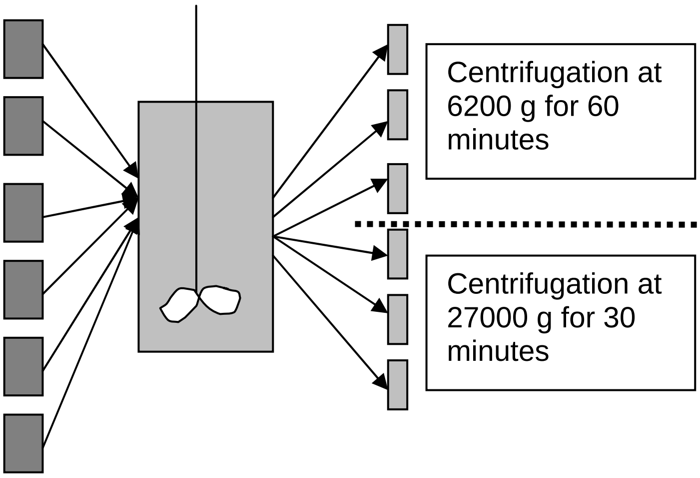


*Figure 9.1 Illustration of the experimental set-up for improving the technique used for separation of solid and liquid in the batch test.*

One of the most critical steps in a batch leaching procedure is the separation of the liquid from the solid phase as discussed in chapter 7.3. Based on our experiences and knowledge concerning the availability of suitable filters it was chosen to separate solid and liquid by centrifugation. Thus two different settings for centrifugation were investigated;

1. Centrifugation at 6200 g for 60 minutes (this will correspond to centrifugation at 12100 g for 30 minutes). These requirements for centrifugation can be fulfilled by centrifuges that common analytical laboratories can be expected to have as a standard devices.

2. Centrifugation at 27000 g for 30 minutes. These specifications may be hard to fulfil for a common laboratory as it requires an ultra-centrifuge. In addition most ultra-centrifuges are only capable of treating a few ml in each vessel and these centrifuges

can not be use for this purpose. The ultra centrifuge used for this purpose should be capable to centrifuge minimum 200 ml in a single vessel.

These two centrifugation settings thus represent 1) a procedure that can be met at a common laboratory and 2) a procedure that requires special equipment.

The results of the batch leaching tests conducted to investigate the effect of centrifugation are shown in detail in appendix D. Average values of the concentrations of PAH in the eluates and the relative standard deviations of 3 replicates are summarised in table 9.1 and 9.2. The relative standard deviations obtained express the uncertainty of centrifugation, sampling of centrifuged eluate and of analysis of PAH.

*Table 9.1 Effect of centrifugation on results of batch leaching tests performed on two different soils. Results are given as an average value and relative standard deviation based on triplicates.*

| | **Clay pigeon contaminated soil** | | | | **B&W soil** | | | |
|---|---|---|---|---|---|---|---|---|
| | 27000 g, 30 min | | 6200 g, 60 min | | 27000 g, 30 min | | 6200 g, 60 min | |
| | Average | rel. std. | Average | rel. std. | Average | Rel. std | Average | Rel. std |
| | µg/l | % | µg/l | % | µg/l | % | µg/l | % |
| Naphthalene | 2,2 | 101 | 0,66 | 66 | 0,012 | 66 | 0,032 | 49 |
| Acenaphthylene | 0,016 | 35 | | - | 0,084 | 15 | 0,099 | 11 |
| Acenaphthene | 0,55 | 13 | 0,23 | 68 | 0,028 | 22 | 0,016 | 11 |
| Fluorene | 0,41 | 10 | 0,21 | 38 | 0,019 | 24 | | |
| Phenanthrene | 0,73 | 10 | 0,37 | 6 | 0,053 | 18 | 0,022 | 26 |
| Anthracene | 0,16 | 54 | 0,055 | 5 | 0,082 | 6 | 0,092 | 10 |
| Fluoranthene | 1,1 | 13 | 0,54 | 5 | 0,14 | 11 | 0,10 | 6 |
| Pyrene | 0,78 | 15 | 0,30 | 4 | 0,18 | 12 | 0,12 | 5 |
| Benz(a)anthracene | 0,42 | 36 | 0,10 | 0 | 0,037 | 15 | 0,031 | 16 |
| Chrysen/Triphenylene | 0,57 | 33 | 0,16 | 4 | 0,06 | 15 | 0,068 | 10 |
| Benz(b+j+k)fluoranthene | 0,86 | 45 | 0,16 | 4 | 0,14 | 15 | 0,23 | 25 |
| Benzo(a)pyrene | 0,40 | 48 | 0,061 | 7 | 0,083 | 18 | 0,16 | 30 |
| Indeno(1,2,3-cd)pyrene | 0,26 | 52 | 0,037 | 4 | 0,12 | 14 | 0,26 | 35 |
| Dibenz(a,h)anthracene | 0,071 | 48 | 0,013 | 15 | 0,021 | 24 | 0,037 | 41 |
| Benzo(g,h,i)perylene | 0,25 | 52 | 0,034 | 4 | 0,14 | 11 | 0,30 | 38 |
| Sum PAH (16 EPA) | 7,73 | 32 | 2,47 | 23 | 1,20 | 7 | 1,60 | 23 |

*Table 9.2 Effect of centrifugation on results of batch leaching tests performed on two different waste materials. Results are given as an average value and relative standard deviation based on triplicates.*

| | **Clay pigeons** | | | | **Road sweepings** | | | |
|---|---|---|---|---|---|---|---|---|
| | 27000 g, 30 min | | 6200 g, 60 min | | 27000 g, 30 min | | 6200 g, 60 min | |
| | Average | rel. std. | Average | rel. std. | Average | Rel. std | Average | Rel. std |
| | µg/l | % | µg/l | % | µg/l | % | µg/l | % |
| Naphthalene | 9,6 | 4 | 9,8 | 10 | 0,050 | | 0,051 | - |
| Acenaphthylene | 0,08 | 5 | 0,072 | 13 | | | | |
| Acenaphthene | 14 | 4 | 7,1 | 11 | 0,033 | 6 | 0,039 | 8 |
| Fluorene | 8,1 | 1 | 3,5 | 12 | 0,017 | 23 | 0,023 | 29 |
| Phenanthrene | 44 | 3 | 13 | 13 | 0,12 | 0 | 0,15 | 4 |
| Anthracene | 10 | 0 | 4,1 | 13 | 0,024 | 27 | 0,027 | 11 |
| Fluoranthene | 27 | 2 | 5,6 | 14 | 0,10 | 14 | 0,10 | 10 |
| Pyrene | 22 | 0 | 4,3 | 16 | 0,10 | 18 | 0,093 | 6 |
| Benz(a)anthracene | 4,6 | 11 | 1,1 | 17 | 0,021 | 56 | 0,016 | 22 |
| Chrysen/Triphenylene | 4,5 | 4 | 1,2 | 17 | 0,035 | 53 | 0,025 | 17 |
| Benz(b+j+k)fluoranthene | 1,9 | 16 | 1,1 | 26 | 0,037 | 80 | 0,026 | 23 |
| Benzo(a)pyrene | 0,93 | 19 | 0,58 | 30 | 0,020 | - | 0,013 | 20 |
| Indeno(1,2,3-cd)pyrene | 0,30 | 39 | 0,39 | 50 | 0,016 | - | 0,013 | 12 |
| Dibenz(a,h)anthracene | 0,08 | 43 | 0,09 | 49 | | - | | |
| Benzo(g,h,i)perylene | 0,23 | 43 | 0,31 | 51 | 0,013 | - | 0,011 | |
| Sum PAH (16 EPA) | 147 | 4 | 52 | 13 | 0,52 | 28 | 0,54 | 15 |

Only in a few cases the relative standard deviations are above 50 % and generally they are between 10 and 40 %. These results were partly unexpected because of the uncertainty arising from the inhomogeneity of the test materials, which was believed to be a major source of uncertainty, was eliminated from the test results. Comparing the relative standard deviations obtained for each centrifugation method and for each test material, no systematic variations could be found. However, for most compounds the relative standard deviations obtained for the clay pigeon contaminated soil are significantly higher in the 27000 g – centrifugation due to the results from one of the replicates. Leaving the results of that replicate out, the relative standard deviations obtained by different centrifugation methods are comparable (data not shown).

During the experiments some technical difficulties were recognised, which can influence the test results as seen above. During the high-speed centrifugation at 27000 g it was noted that it became more and more difficult to remove the steel centrifugation vessels carefully from the centrifuge without disturbing the contents. The steel containers were slowly deformed by the very high pressure, which occurred during centrifugation of 200 ml. Thus, removing the vessels from the centrifuge may have caused re-suspension of small particles and through that affected the results.

In Figure 9.2 – 9.5 the average values obtained for each compound by using different centrifugation settings are compared.

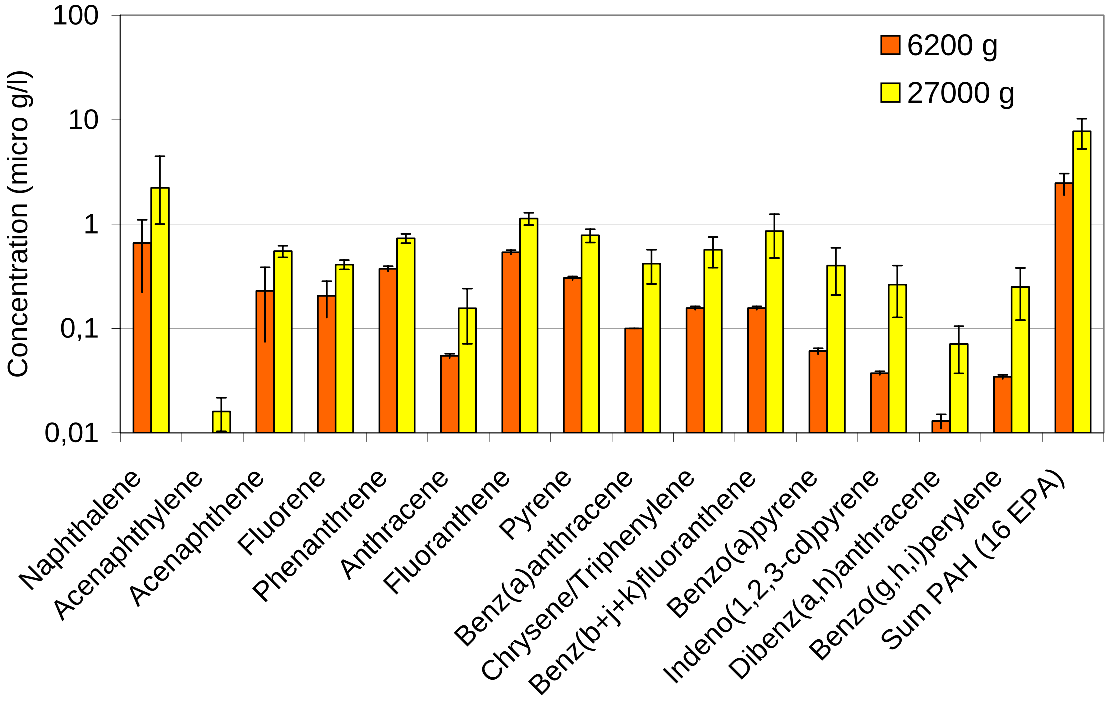


*Figure 9.2* *Average leached concentration (µg/l) of PAH from a clay pigeon contaminated soil. Average values (n=3) obtained by using different centrifuge settings are compared for each compounds.*

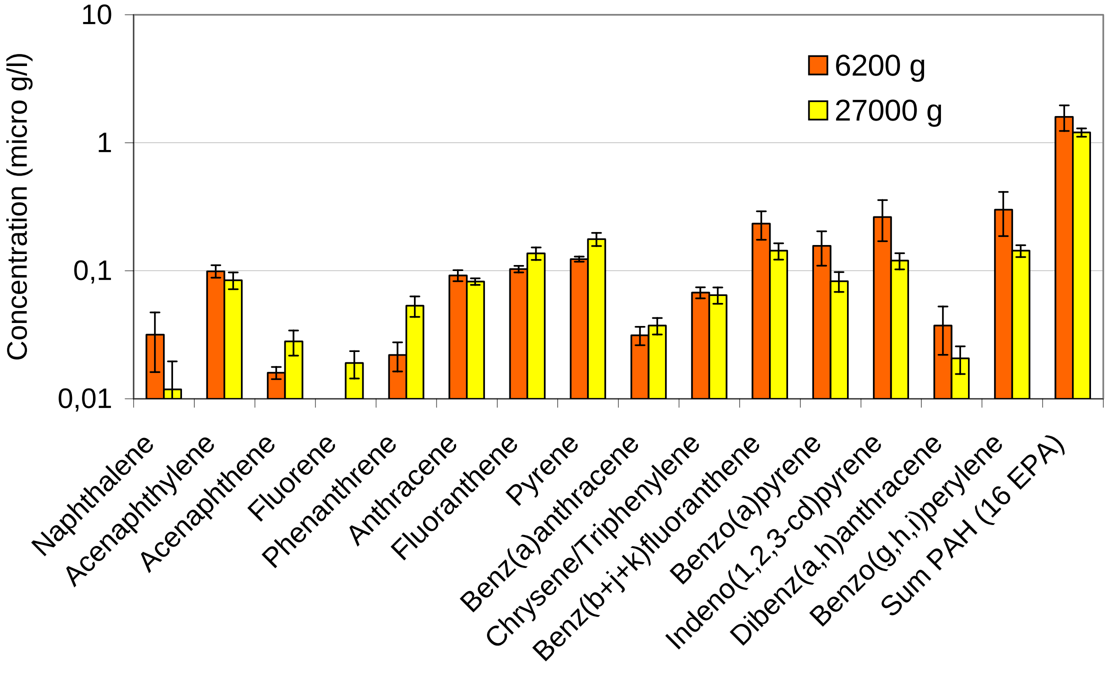


*Figure 9.3* *Average leached concentration (µg/l) of PAH from an industrial contaminated soil (B&W soil). Average values (n=3) obtained by using different centrifuge settings are compared for each compounds.*

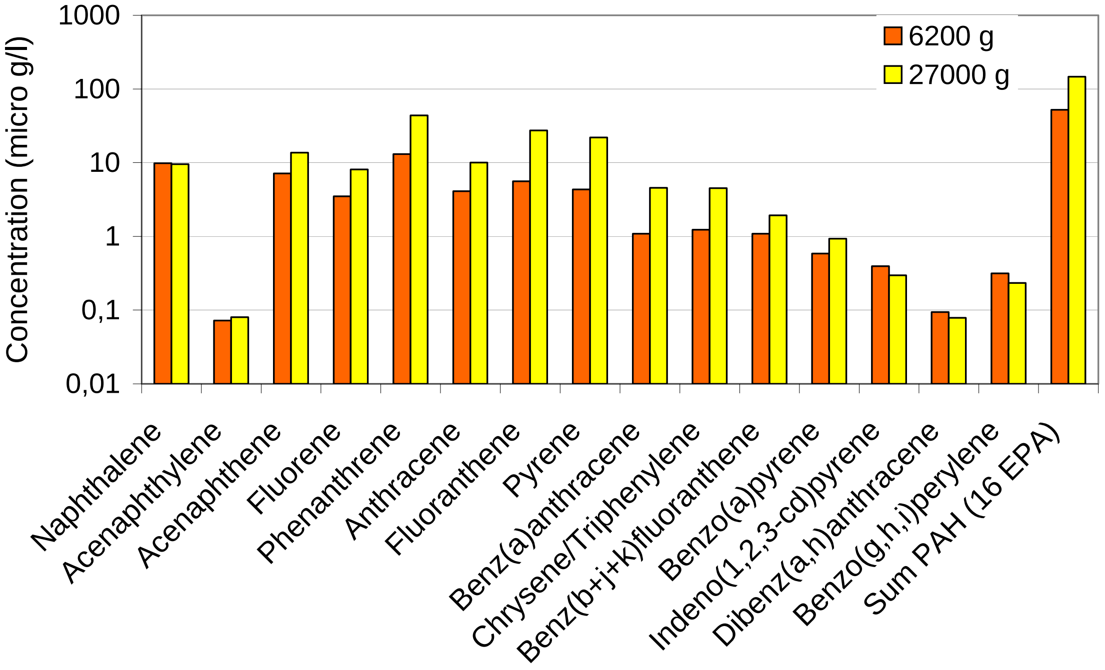


*Figure 9.4* *Average leached concentration (µg/l) of PAH from crushed clay pigeons. Average values (n=3) obtained by using different centrifuge settings are compared for each compounds.*

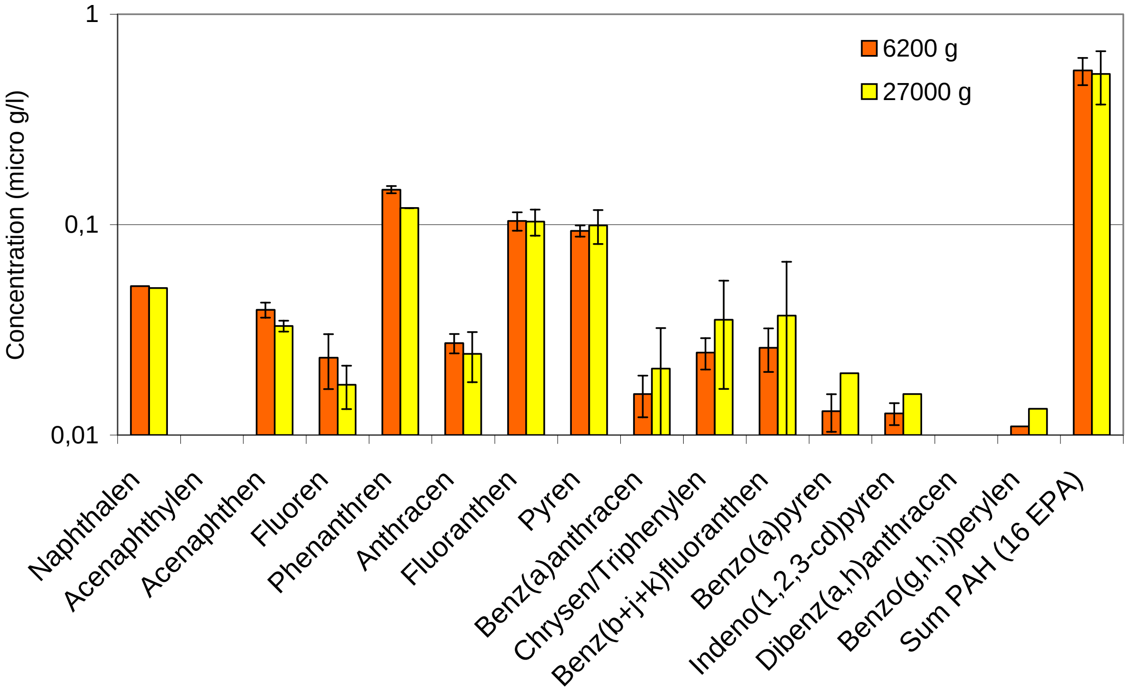


*Figure 9.5* *Comparison of average leached concentration (µg/l) of PAH from road sweepings. Average values (n=3) obtained by using different centrifuge settings are compared for each compounds.*

Comparing the average eluate concentration obtained by different centrifugation settings does not lead to a simple and clear picture. It can be seen that centrifugation at 27000 g for 30 minutes does not seem to remove more particles containing PAH from the solution than centrifugation at 6200 g for 60 minutes does for any of the materials. However, this picture might be disturbed by the fact that in some cases the concentrations of PAH in the eluates centrifuged at 27000 g for 30 minutes were higher than obtained for samples centrifuged at 6200 g for 60 minutes (confer Figure 9.2). This would be absolutely unexpected unless the eluates were disturbed after centrifugation.

Overall, these results indicate that centrifugation at 6200 g for 60 minutes is sufficient to separate solid and liquid in a batch leaching procedure. Looking at the practical circumstances, this is a nice result as most laboratories are expected to be able to centrifuge at 6200 g for 60 minutes without being forced to buy new and expensive high-speed centrifugation equipment.

# 10 COMPARISON OF RESULTS FROM COLUMN TESTS AND BATCH TESTS

An important part of the development of a separation technique for the batch leaching test would be to compare the results obtained from the batch procedure to results obtained from an equilibrium column procedure. The results from this column test are believed to represent the distribution of an organic compound between solid and solution at equilibrium, taking into account compounds sorbed to natural mobile colloids. It should be a requirement of a batch leaching procedure that the results are comparable to the results of the equilibrium column test.

To compare the results obtained by batch test to results from a column test, each test was performed in triplicats (or more). The eluates from the batch test were centrifuged at 27000 g for half an hour. This method of centrifugation was chosen at a time when the results from the previous study were still unknown. The averages of the leached concentrations and the relative standard deviations for each compound and each test material are given in table 10.1 – 10.4, and the results from batch and column tests are compared in Figure 10.1 – 10.4.

The results of the column test and the batch test may in this case be compared on the basis of the concentrations of organic compounds in the eluates. This can and must only be done when the amount of an organic compound removed from the solid material by leaching is very small (less than a few percent of the total content). By comparison based on concentration it is assumed that the content of the solid material is the same before and after leaching. If this assumption cannot be justified, the comparison between test methods should be based on the distribution of each compound between solid and solution (e.g. concentration in solid after leaching / eluate concentration, also called a distribution coefficient).

*Table 10.1 Results of column and batch leaching tests performed on a soil contaminated with clay pigeons.*

| **Clay pigeon contaminated soil** | **Column test** | | **Batch test** | |
|---|---|---|---|---|
| | Average (n=4) µg/l | rel. std. % | Average (n=1-3) µg/l | Rel. std % |
| Naphthalene | 12 | 5 | 0,88 | - |
| Acenaphthylene | <0,03 | - | <0,01 | - |
| Acenaphthene | 4,1 | 6 | 0,31 | - |
| Fluorene | 3,5 | 6 | 0,25 | - |
| Phenanthrene | 7,4 | 5 | 0,27 | 4 |
| Anthracene | 1,3 | 6 | 0,064 | 11 |
| Fluoranthene | 1,8 | 13 | 0,50 | 2 |
| Pyrene | 1,2 | 20 | 0,28 | 0 |
| Benz(a)anthracene | 0,17 | 23 | 0,087 | 13 |
| Chrysen/Triphenylene | 0,22 | 24 | 0,14 | 11 |
| Benz(b+j+k)fluoranthene | 0,12 | 38 | 0,11 | 18 |
| Benzo(a)pyrene | 0,054 | 44 | 0,043 | 28 |
| Indeno(1,2,3-cd)pyrene | 0,029 | 42 | 0,023 | 39 |
| Dibenz(a,h)anthracene | 0,016 | | 0,013 | 22 |
| Benzo(g,h,i)perylene | 0,024 | 47 | 0,021 | 28 |
| Sum PAH (16 EPA) | 31 | 6 | 2,0 | 37 |

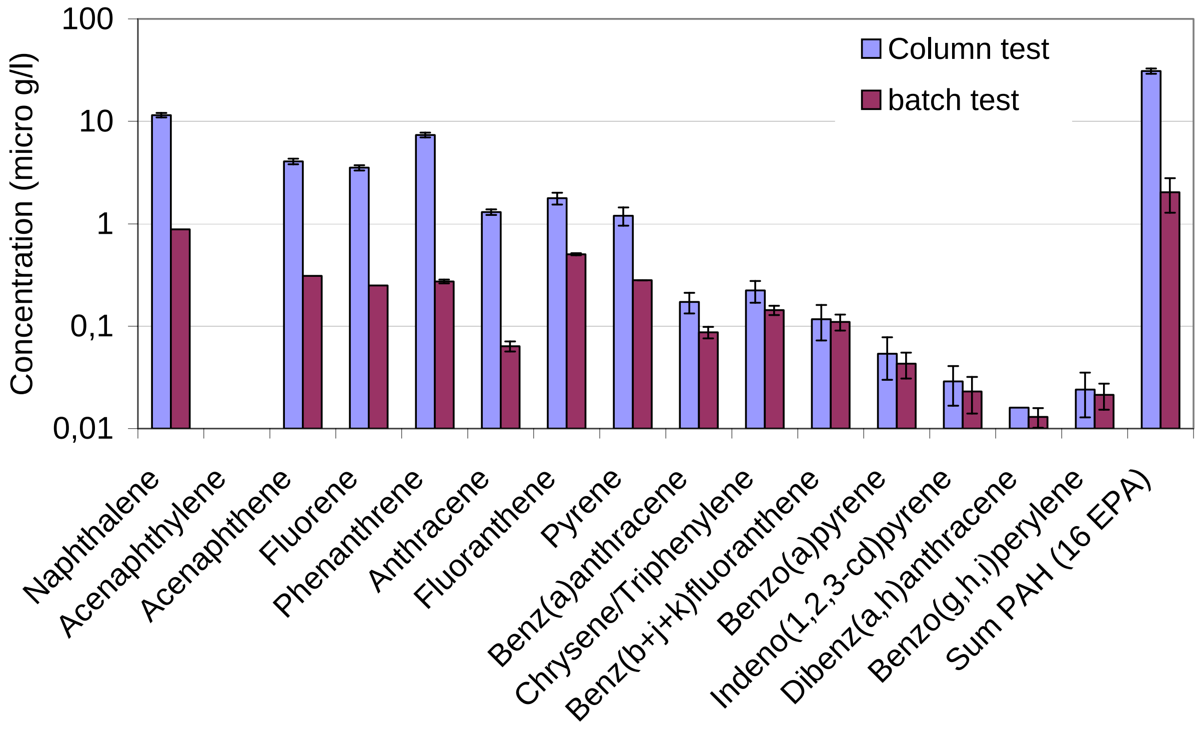


*Figure 10.1 Leached concentrations (average value n=3-4) of PAH obtained from column and batch leaching tests, respectively. The test material was a clay pigeon contaminated soil.*

*Table 10.2 Results of column and batch leaching tests performed on an industrial soil (B&Wsoil).*

| **Industrial soil**<br>**B & W soil** | **Column test**<br>Average (n=4) µg/l | <br>rel. std. % | **Batch test**<br>Average (n=3) µg/l | <br>rel. std. % |
|---|---|---|---|---|
| Naphthalene | 0,11 | 13 | 0,014 | 16 |
| Acenaphthylene | 0,12 | 54 | 0,061 | 30 |
| Acenaphthene | 0,046 | 30 | 0,018 | - |
| Fluorene | 0,036 | 33 | <0,01 | - |
| Phenanthrene | 0,069 | 10 | 0,020 | 15 |
| Anthracene | 0,13 | 60 | 0,054 | 7 |
| Fluoranthene | 0,076 | 15 | 0,073 | 9 |
| Pyrene | 0,10 | 13 | 0,11 | 13 |
| Benz(a)anthracene | 0,017 | 31 | 0,016 | 0 |
| Chrysen/Triphenylene | 0,031 | 22 | 0,031 | 28 |
| Benz(b+j+k)fluoranthene | 0,045 | 44 | 0,054 | 73 |
| Benzo(a)pyrene | 0,023 | 29 | 0,033 | 66 |
| Indeno(1,2,3-cd)pyrene | 0,030 | 52 | 0,060 | 86 |
| Dibenz(a,h)anthracene | <0,01 | - | 0,014 | - |
| Benzo(g,h,i)perylene | 0,033 | 57 | 0,063 | 93 |
| Sum PAH (16 EPA) | 0,88 | 27 | 0,60 | 40 |

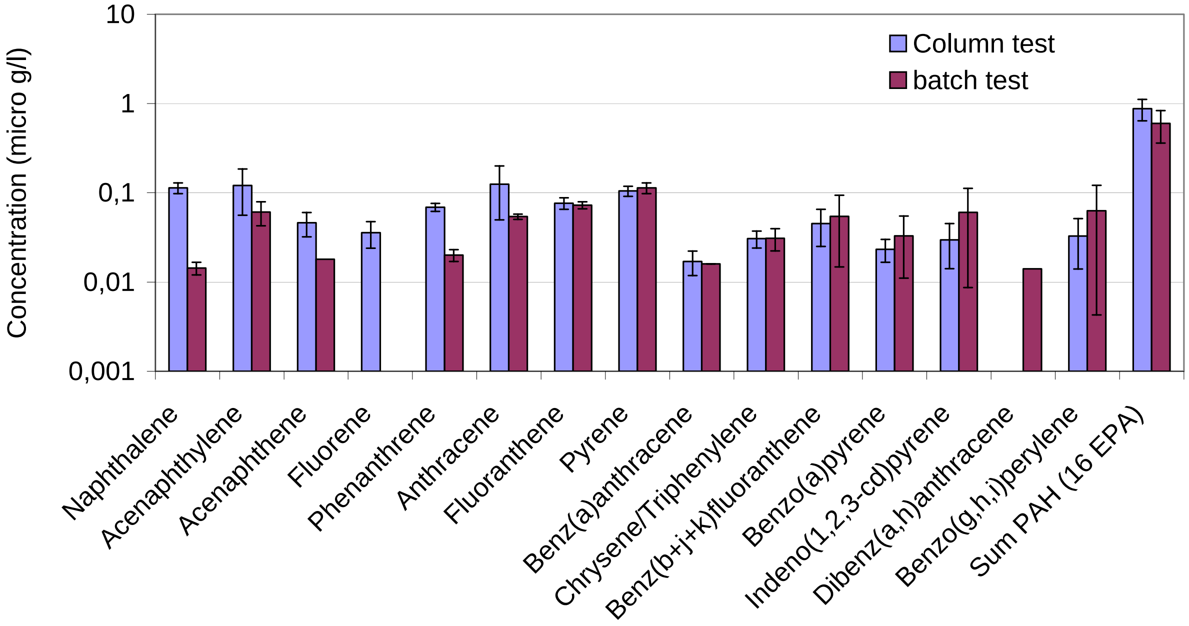


*Figure 10.2 Leached concentrations (average value n=3 - 4) of PAH obtained from column and batch leaching tests, respectively. The test material was an industrial soil (B&W soil).*

From the results of testing two different soils using two different leaching test methods it can be seen that there is a tendency towards underestimation of the leaching of smaller PAH (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene) in the batch test. This is most pronounced for the clay pigeon contaminated soil and less for the industrial soil. The reason for these findings is not known but might partly be explained by looking at the test procedures. During the separation of the solid and the liquid according to the batch procedure the eluates are handled several times, being transferred from the leaching vessel to a centrifugation vessel and further on to a bottle for chemical analysis. During these transfers of the eluates the compounds might be lost by evaporation and sorption onto the centrifugation vessels and analysis bottles. It would, however, be expected that also the large PAH would be sorbed to the materials, which is not the case here. Alternatively, the small PAH are lost due to degradation while tumbling the batch in 24 hours. In the batch test degradation is not inhibited by sodium azide as in the column test. However, the eluent used in the batch tests was purged with $N_2$ for 24 hours in order to remove most of the oxygen. Such a fast degradation of the small PAH is not expected from degradation rates reported in the literature (Miljøstyrelsen, 1996).

For the larger PAH that sorb strongly on to colloids it can be seen that for these soils the batch tests and the column tests provided comparable results. Results for larger PAH do not indicate any losses of compounds to equipment as seen for lighter PAH. This is not in agreement with results obtained by Larsson (2004); Gamst et al. (2005).

The relative standard deviations of both column and batch tests performed on these soils are generally between 10% and 50%. For some of the smaller PAH compounds the relative standard deviations are in a few cases lower than 10% and for some of the larger PAH the relative standard deviations are above 50% but below 100%. The concentrations of the larger PAH are, however, closer to the detection limit of the chemical analysis, which also might affect the repeatability.

The relative standard deviations obtained for larger PAH (benz(b+j+k)fluaoranthene, benzo(a)pyren, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene) leached from the industrial soil by the batch procedure are relatively large, between 66% and 93%.

*Table 10.3 Results of column and batch leaching tests performed on crushed clay pigeons.*

| **Clay pigeons, crushed** (< 4mm) | **Column test** Average (n=3) µg/l | rel. std. % | **Batch test** Average (n=3) µg/l | rel. std. % |
|---|---|---|---|---|
| Naphthalene | 10,20 | 7 | 9,23 | 33 |
| Acenaphthylene | 0,09 | 14 | 0,061 | 38 |
| Acenaphthene | 7,57 | 5 | 9,8 | 31 |
| Fluorene | 3,43 | 7 | 5,4 | 32 |
| Phenanthrene | 10,67 | 11 | 28 | 30 |
| Anthracene | 4,27 | 3 | 7,1 | 32 |
| Fluoranthene | 5,80 | 17 | 18 | 29 |
| Pyrene | 4,73 | 16 | 14 | 29 |
| Benz(a)anthracene | 1,77 | 38 | 2,7 | 33 |
| Chrysen/Triphenylene | 1,63 | 43 | 2,5 | 34 |
| Benz(b+j+k)fluoranthene | 2,25 | 70 | 1,2 | 36 |
| Benzo(a)pyrene | 1,04 | 69 | 0,58 | 40 |
| Indeno(1,2,3-cd)pyrene | 0,74 | 84 | 0,22 | 58 |
| Dibenz(a,h)anthracene | 0,14 | 78 | 0,056 | 56 |
| Benzo(g,h,i)perylene | 0,62 | 88 | 0,18 | 60 |
| Sum PAH (16 EPA) | 55,33 | 12 | 100 | 31 |

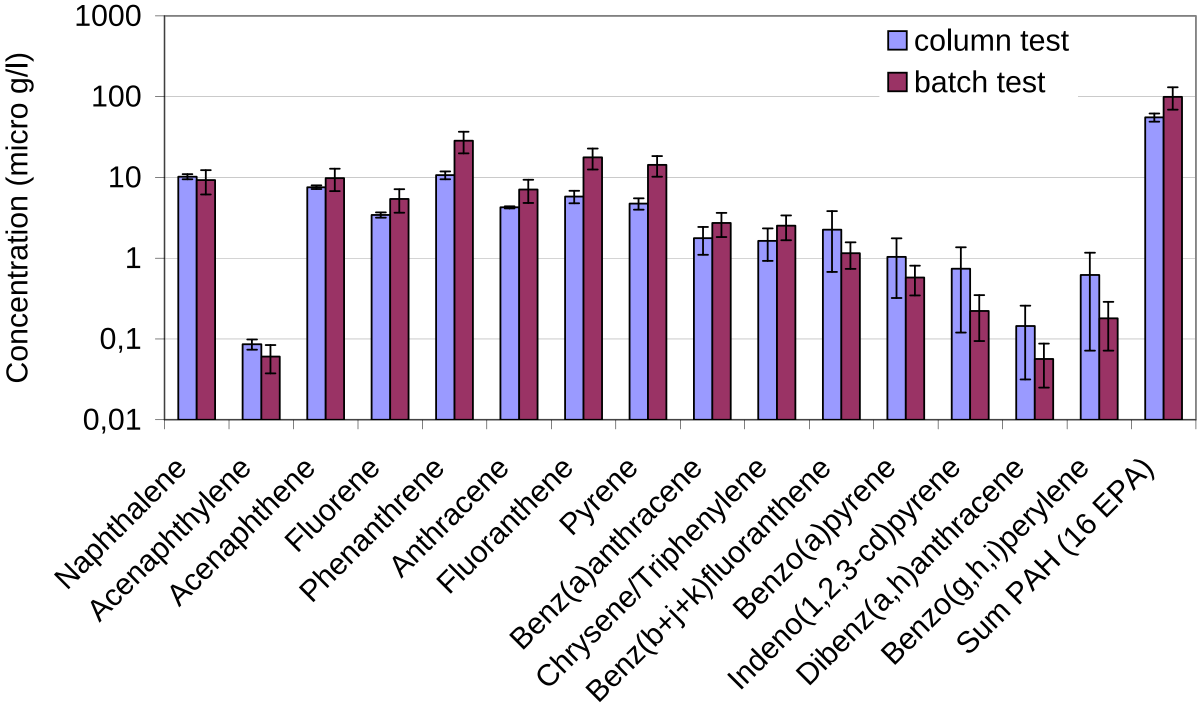


*Figure 10.3 Leached concentration (average value n=3-4) of PAH obtained from a column and batch leaching test, respectively. The test material was crushed clay pigeons.*

*Table 10.4 Results of column and batch leaching tests performed on road sweepings.*

| **Road sweepings** | **Column test**<br>Average (n=3)<br>µg/l | <br>rel. std.<br>% | **Batch test**<br>Average (n=3)<br>µg/l | <br>rel. std.<br>% |
|---|---|---|---|---|
| Naphthalene | 0,090 | 19 | 0,088 | 2 |
| Acenaphthylene | <0,01 | - | <0,01 | - |
| Acenaphthene | 0,044 | 19 | 0,037 | 23 |
| Fluorene | 0,037 | 21 | 0,027 | 31 |
| Phenanthrene | 0,15 | 18 | 0,118 | 27 |
| Anthracene | 0,039 | 21 | 0,031 | 7 |
| Fluoranthene | 0,10 | 34 | 0,085 | 26 |
| Pyrene | 0,092 | 29 | 0,078 | 25 |
| Benz(a)anthracene | 0,027 | 52 | 0,014 | 10 |
| Chrysen/Triphenylene | 0,026 | 53 | 0,024 | 15 |
| Benz(b+j+k)fluoranthene | 0,047 | 57 | 0,027 | 8 |
| Benzo(a)pyrene | 0,023 | 66 | 0,011 | 0 |
| Indeno(1,2,3-cd)pyrene | 0,021 | 52 | 0,011 | 7 |
| Dibenz(a,h)anthracene | <0,01 | - | <0,01 | - |
| Benzo(g,h,i)perylene | 0,019 | - | <0,01 | - |
| Sum PAH (16 EPA) | 0,68 | 30 | 0,550 | 18 |

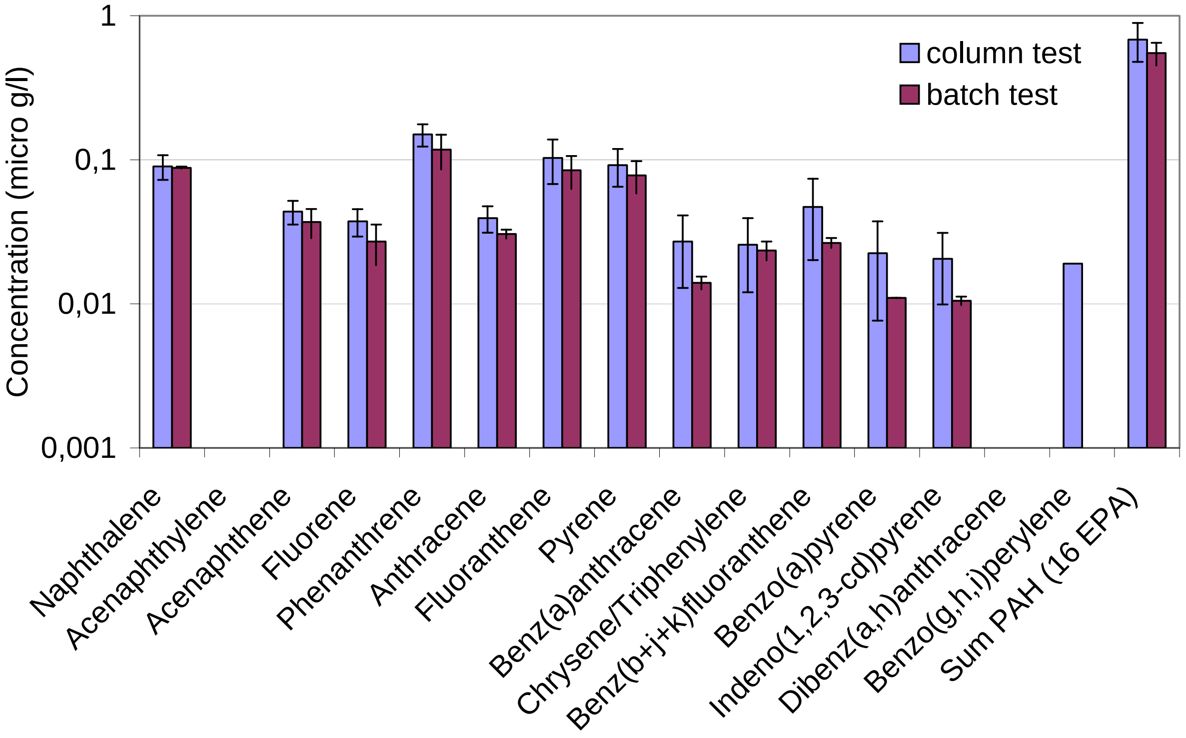


*Figure 10.4 Leached concentration (average value n=3-4) of PAH obtained from a column and batch leaching test, respectively. The test material was road sweepings.*

The results obtained from column and batch leaching tests on the two waste materials show a fairly good agreement between the results for all PAH, although Figure 10.3 and 10.4 indicate a minor tendency of lower concentration of larger PAH obtained from the batch tests.

The relative standard deviations of both column and batch test are also for waste materials generally between 10% and 50%. In a few cases the repeatability for some of the smaller PAH compounds is lower than 10% and for some of the larger PAH with strong sorbing tendency the repeatability is above 50% but below 90%. The relative standard deviations obtained for larger PAH (benz(b+j+k)fluaoranthene, benzo(a)pyren, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene) leached from the industrial soil in column tests are relatively large, between 70% and 88%.

Based on the results obtained from testing of 4 different materials in an equilibrium column leaching test and a batch leaching test it is not simple and straight forward to conclude whether or not a batch leaching procedure is suitable for the determination of the leaching of non-volatile organic compounds from soils and waste materials.

The results, however, indicate that in some cases the leached concentrations are lower in the batch test than in the column test. In these cases the column test would provide the most conservative estimate of the leached concentrations.

# 11 TESTING OF LEACHING METHODS AT NORDIC LABORATORIES

Based on the results presented in chapter 10, the project group decided to set up both the column leaching test and the batch leaching test in participating Nordic laboratories. This was decided in order to get experiences from the implementation of the test methods at laboratories that have not been deeply involved in the development of the test methods. Such experiences are very valuable as a part of the evaluation of suitable test methods.

The results obtained by the different laboratories can be used as a first indication of the reproducibility of the test methods. It should however be kept in mind that normally in a round robin testing the participating laboratories have experiences in performing the tests, which is not the case in this study. Also, a test of sample homogeneity and stability is missing.

## 11.1 Ring testing set-up

One soil was chosen (clay pigeon contaminated soil) for testing of both the column and the batch leaching methods in Nordic laboratories (DHI, VTT, NGI). Representative samples (min. 5 kg) of the soil were obtained after careful homogenisation of the soil using a riffle splitter. Samples for leaching tests were sent to VTT and NGI and a sample for analysis of particle size distribution was sent to SGI. Protocols describing the leaching test methods to be used were also distributed to the participating laboratories.

As a first and minor evaluation of the performance of the column and batch test method the programme given in table 11.1 was followed.

*Table 11.1 Programme for a minor testing of leaching tests methods at different Nordic laboratories.*

| Laboratory | Column test | Batch test |
|---|---|---|
| DTU | triplicates<br>(conducted in October 2003) | - |
| DHI | triplicates<br>(conducted in May 2004) | triplicates (conducted in May 2004)<br>triplicates (conducted October 2003) |
| VTT | triplicates<br>(conducted one by one in May/June 2004)* | - |
| NGI | - | triplicates (conducted in May 2004) |
| SGI | Determination of the particle size distribution in all eluates conducted in May 2004<br>Determination of particle size distribution of the B&W soil | |

* It was only possible to perform these tests one at the time due to high initial costs of the equipments. Eluate from one of the triplicates was lost during shipping of the samples and thus only two replicates from VTT are included in the evaluation

As shown in table 11.1 some of the tests have been performed in october 2003, but are also included in this ring testing in order to increase the number of laboratories and data. This might allow a statistical evaluation according to ISO 5725 keeping these deviations in mind.

The particle sizes and concentrations were assessed by photon correlation spectroscopy (PCS), using a BI-90 (Brookhaven Instruments Corp.) with a Lexel 2 W Ar-laser, using a wavelength of 488 nm and a laser effect of 300 or 600 mW. The measurements were performed in closed polystyrene cuvettes.

## 11.2 Results of the ring test

### 11.2.1 Equilibrium column test

Column leaching tests according to the method described in appendix A were performed at DHI, DTU and VTT in triplicates. However one of the eluates from the column tests performed by VTT was lost during shipping and thus only two replicates were used for VTT. The results of the tests are given in detail in appendix E together with average values, standard deviations and relative standard deviations. In Figure 11.1 the average values obtained of each laboratory are compared for each of the 16-PAH components.

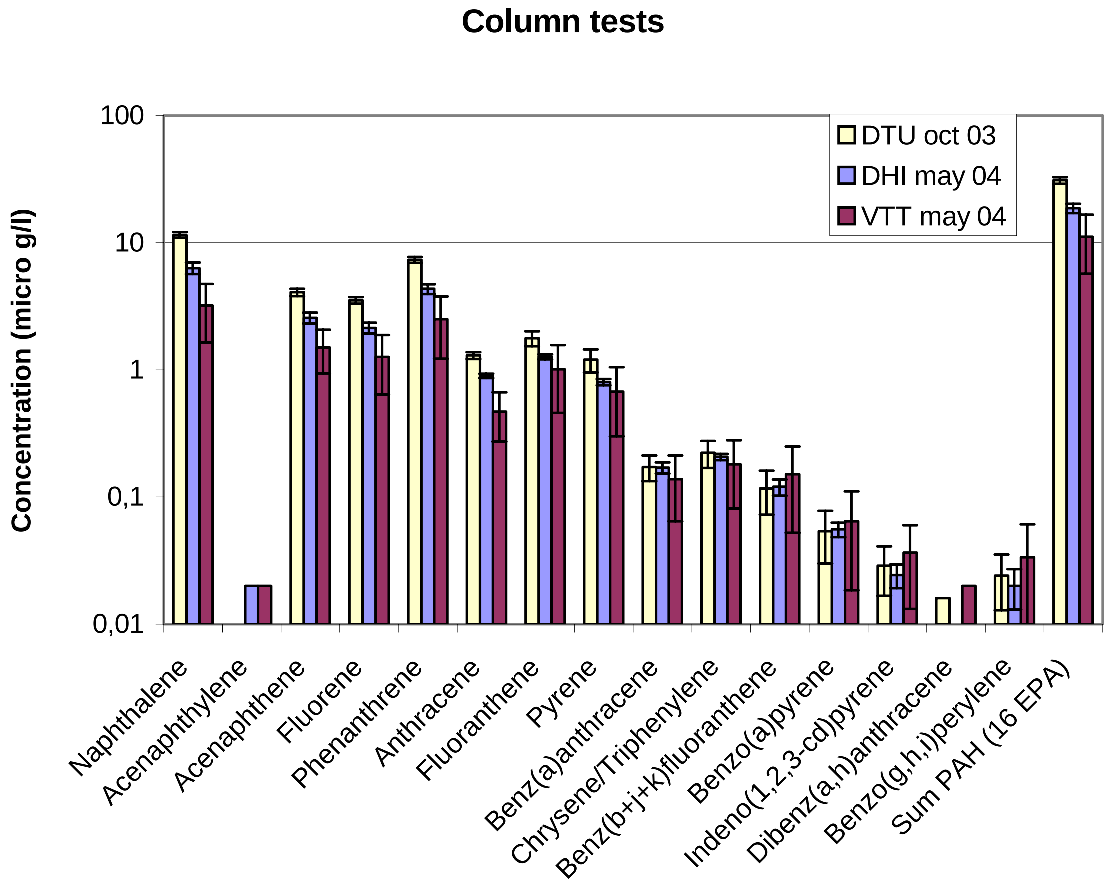


*Figure 11.1 Comparison of results from equilibrium column tests obtained at different laboratories. The tests were performed as duplicates or triplicates on the clay pigeon contaminated soil.*

From the results shown in Figure 11.1 it can be seen that there is a reasonable agreement between the results obtained by DTU, DHI and VTT, and especially the level of each compound is very comparable between the three laboratories. The maximum deviation of a factor of 3 was found for naphthalene determined by DTU and VTT. The relative standard deviations vary between 4% and 47% for DTU and DHI. For VTT the relative standard deviations, based on 2 replicates, lies between 38% and 82% but these replicates have also not been performed on the same time, which probably increase the relative standard deviations.

The statistical evaluation is conducted according to ISO 5725-2. The average values, the repeatability standard deviation ($s_r$) and the reproducibility standard deviation ($s_R$) are obtained (Table 11.2). When evaluating these data according to ISO 5725 it should be remembered that:

- Two of the laboratories were setting up the test for the first time, and had only limited test routine if any.

- No data on sample homogeneity is available.

- No data on sample stability is available.

The results of the statistical analysis should be seen as a first guess on the repeatability and reproducibility of the test method.

*Table 11.2 Data analysis of batch leaching tests performed at 3 Nordic laboratories in triplicates.*

| | **Average** | **Within laboratory variability (Repeatability)** | | **Between laboratory variability** | **Reproducibility** | |
|---|---|---|---|---|---|---|
| | **m (µg/l)** | **Sr** | **Sr (%)** | **SL** | **SR** | **SR (%)** |
| Naphthalene | 8,1 | 1,9 | 24 | 3,9 | 4,3 | 53 |
| Acenaphthylene | - | - | - | - | - | - |
| Acenaphthene | 3,1 | 0,56 | 19 | 1,2 | 1,4 | 44 |
| Fluorene | 2,6 | 0,58 | 22 | 1,0 | 1,2 | 46 |
| Phenanthrene | 5,4 | 1,2 | 22 | 2,3 | 2,6 | 48 |
| Anthracene | 0,99 | 0,18 | 19 | 0,38 | 0,42 | 43 |
| Fluoranthene | 1,5 | 0,31 | 21 | 0,35 | 0,47 | 32 |
| Pyrene | 0,98 | 0,24 | 25 | 0,26 | 0,35 | 36 |
| Benz(a)anthracene | 0,16 | 0,046 | 28 | - | 0,046 | 28 |
| Chrysene/Triphenylene | 0,21 | 0,060 | 29 | - | 0,060 | 29 |
| Benz(b+j+k)fluoranthene | 0,13 | 0,057 | 44 | - | 0,057 | 44 |
| Benzo(a)pyrene | 0,058 | 0,028 | 48 | - | 0,028 | 48 |
| Indeno(1,2,3-cd)pyrene | 0,030 | 0,014 | 46 | - | 0,014 | 46 |
| Dibenz(a,h)anthracene | - | - | - | - | - | - |
| Benzo(g,h,i)perylene | 0,026 | 0,015 | 59 | - | 0,015 | 59 |
| Sum PAH (16 EPA) | 23 | 4,7 | 21 | 9,4 | 11 | 46 |

The repeatability for the 16 PAH are in the range of 21% –59%, which should be regarded as a reasonable result taking the above mentioned circumstances into account. The repeatability is lowest for the smaller PAH and highest for the large PAH. The reproducibility lies between 32% and 59%. It should be noted that for the compounds from benz(a)anthracene to benzo(g,h,i)perylene the reproducibility is identical to the repeatability, which means that the reproducibility is dominated by the repeatability.

Compared to the results of the validation of prEN 12457 (van der Sloot et al., 2001), which is a batch leaching test for inorganic compounds, these results obtained for the column test are surprisingly good.

### 11.2.2 Batch test

Batch leaching tests according to the method described in appendix B were performed at DHI in October 2003 and at NGI and DHI in May 2004 – all tests in triplicates. The results of the tests are given in detail in appendix E together with average values, standard deviations and relative standard deviations. In Figure 11.2 the average values obtained by each laboratory are compared for each of the 16-PAH components.

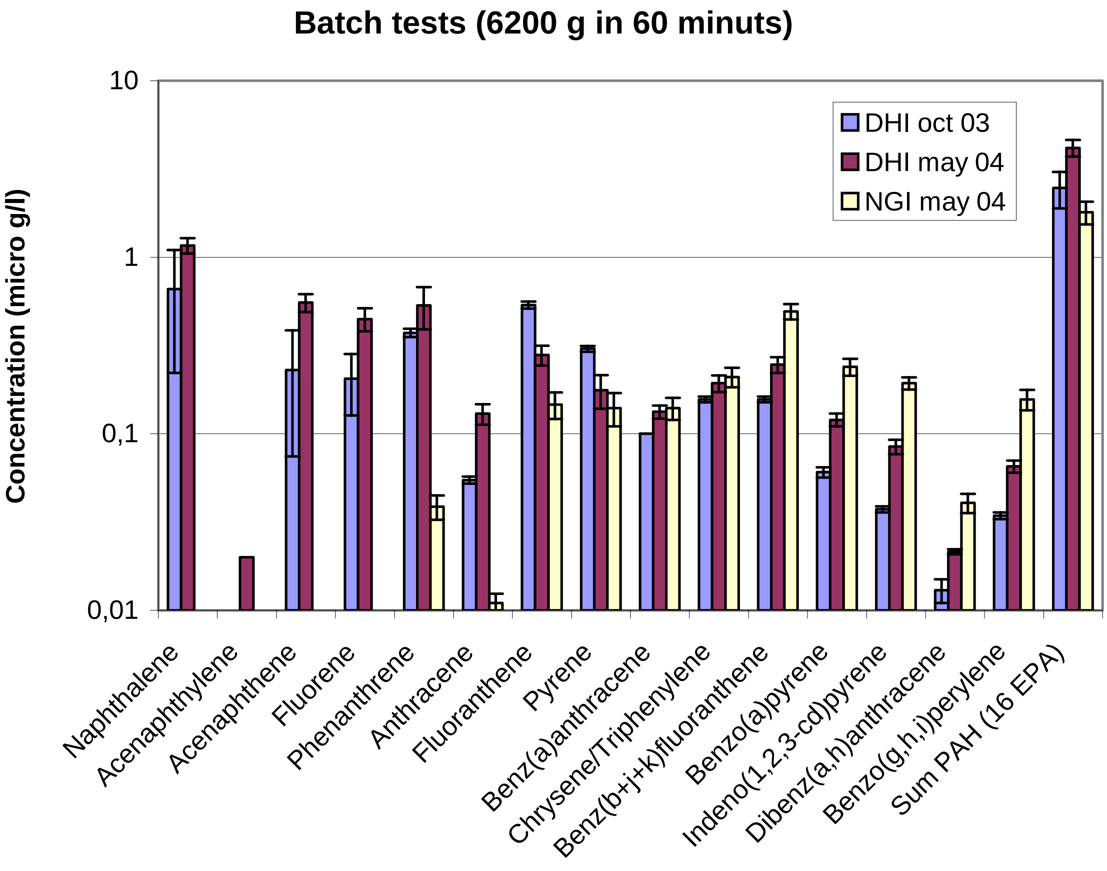


*Figure 11.2 Comparison of results from batch tests obtained at different laboratories. The tests were performed as triplicates on the clay pigeon contaminated soil.*

From the results shown in Figure 11.2 it can be seen that there are large difference between the results obtained by DHI and NGI, especially for compounds between naphthalene and fluoranthene. NGI found that the leaching of these compounds were below the analytical detection limit of 0,01 µg/l whereas DHI found these compounds in concentrations more than 10 times higher. For the largest PAH compounds the leached concentrations found by NGI are higher than the leached concentrations observed by DHI. Deviations between results obtained by DHI in tests performed in October 2003 and in May 2004 can be seen, and for most compounds the concentrations found in May 2004 were highest.

The relative standard deviations obtained by each laboratory are good and lie between 3% and 27%.

The statistical evaluation has been conducted according to ISO 5725-2. The average values, the repeatability standard deviation ($s_r$) and the reproducibility standard deviation ($s_R$) are obtained (Table 11.3). The results that were below detection limits are included (equal to the detection limit) in order to reflect the differences between the results obtained at NGI and DHI.

The repeatability for the 16 PAH are in the range of 10 – 43 %, which is a resonable result taking the circumstances of the ring test into account. The repeatability is in this case highest for the smaller PAH and lowest for the large PAH. The reproducibility lies between 17 and 104 %, reflecting large deviations between results obtained at the participating laboratories. Compared to the results of the validation of prEN 12457 (van der Sloot et al., 2001), these results obtained for the reproducibility are high.

*Table 11.3 Data analysis of batch leaching tests performed at 3 Nordic laboratories in triplicates.*

| | **Average** | **Within laboratory variability (Repeatability)** | | **Between laboratory variability** | **Reproducibility** | |
|---|---|---|---|---|---|---|
| | **m (ug/l)** | **Sr** | **Sr (%)** | **SL** | **SR** | **SR (%)** |
| Naphthalene | 0,61 | 0,26 | 43 | 6,6 | 0,63 | 103 |
| Acenaphthene | 0,27 | 0,10 | 36 | 6,0 | 0,28 | 104 |
| Fluorene | 0,22 | 0,06 | 27 | 5,2 | 0,22 | 99 |
| Phenanthrene | 0,32 | 0,08 | 26 | 5,1 | 0,26 | 83 |
| Anthracene | 0,065 | 0,010 | 16 | 3,9 | 0,06 | 94 |
| Fluoranthene | 0,32 | 0,029 | 9,1 | 3,0 | 0,20 | 62 |
| Pyrene | 0,21 | 0,029 | 14 | 3,7 | 0,089 | 43 |
| Benz(a)anthracene | 0,12 | 0,013 | 11 | 3,3 | 0,024 | 19 |
| Chrysene/Triphenylene | 0,19 | 0,020 | 11 | 3,3 | 0,032 | 17 |
| Benz(b+j+k)fluoranthene | 0,30 | 0,032 | 11 | 3,3 | 0,18 | 59 |
| Benzo(a)pyrene | 0,14 | 0,016 | 12 | 3,4 | 0,092 | 66 |
| Indeno(1,2,3-cd)pyrene | 0,11 | 0,010 | 10 | 3,1 | 0,080 | 76 |
| Dibenz(a,h)anthracene | 0,025 | 0,0032 | 13 | 3,6 | 0,014 | 58 |
| Benzo(g,h,i)perylene | 0,085 | 0,012 | 15 | 3,8 | 0,064 | 75 |
| Sum PAH (16 EPA) | 3 | 0,45 | 16 | 4,0 | 1,3 | 45 |

### 11.2.3 Evaluation of particle size and the amount of colloids in the eluates

To help explaining the differences between leached concentrations obtained in batch and column tests, which were also observed in this ring testing, NVOC (non-volatile organic carbon) and Fe-total were determined in the eluates (Fe only in tests performed at DHI). The results of these analyses are given in table 11.4.

*Table 11.4 Content of NVOC and Fe in eluates from column tests and batch tests. Average values of 2 –3 replicates.*

| | NVOC (mg/l) | Fe (µ/l) |
|---|---|---|
| **Batch tests** | | |
| NGI | 6,5 | - |
| DHI | 6,8 | 210 |
| **Column tests** | | |
| DHI | 46 | 52 |
| VTT | 34 | - |

From the results shown in table 11.4 it can be seen that eluates from the column tests have a higher content of organic matter either dissolved or as colloids than eluates from the batch tests. On the other hand eluates from the batch tests have a higher content of iron indicating a higher content of inorganic colloids in these eluates than observed for the column tests. These results support the theory of generation of inorganic colloids in the batch test during leaching.

The particle size was measured/calculated as a light intensity weighted effective diameter, which often is preferred instead of size distribution, when samples are not filtered. In unfiltered samples a small number of large particles may interfere with the calculated distribution and give an erroneous distribution curve. A relative measure of the amount of particles is given by the count rate, which is an integrated measure of the effect of all particles. The results given in table 11.5 are an average of all measures. Each sample was poured into two cuvettes. Each cuvette was measured for 12 cycles. Each replicate in table 11.5 thus represents exactly 2*12 cycles.

*Table 11.5 Particle counts and effective particle diameters*

| | | 1. Replicate | 2. Replicate | 3. Replicate | Average | STD | Rel. std (%) |
|---|---|---|---|---|---|---|---|
| **Count rate** | | | | | | | |
| VTT column | kc/s | 226 | - | 306 | 266 | 577 | 21 |
| DHI column | kc/s | 200 | 277 | 251 | 242 | 39 | 16 |
| DHI batch | kc/s | 1191 | 1803 | 1912 | 1635 | 389 | 24 |
| NGI batch | kc/s | 673 | 645 | 522 | 613 | 80 | 13 |
| NGI batch (glass vessels) | kc/s | 924 | 960 | 746 | 876 | 114 | 13 |
| **Effective diameter** | | | | | | | |
| VTT column | nm | 1813 | - | 652 | 1232 | 821 | 66 |
| DHI column | nm | 4917 | 2472 | 288 | 2559 | 2316 | 90 |
| DHI batch | nm | 600 | 633 | 470 | 568 | 87 | 15 |
| NGI batch | nm | 454 | 472 | 465 | 464 | 9,3 | 2 |
| NGI batch (glass vessels) | nm | 581 | 902 | 796 | 760 | 164 | 22 |

- Observations during performance of the this leaching test caused rejection of this replicate.

Complementary to the PCS-measurements filtrations were performed through a 1µm polycarbonate filter. This was done as a comparison of separation efficiency in the two leaching tests. Although all separation methods are operational (see 7.3) and should not be expected to give exactly the same results, indications of separation efficiency could still be useful. The amount of particles and the size of particles determined in the samples can be seen from Figure 11.3 and 11.4. From the figures it can be seen that especially the effective diameter determined in filtered samples is smaller than in unfiltered samples and this is most pronounced for eluates from column tests. Also the count rates are lower for filtered samples but in this case it is most pronounced for eluates from batch tests. These results indicate that particles larger than 1 μm are present particullary in eluates from the column tests and these particles might also be mobile under natural conditions.

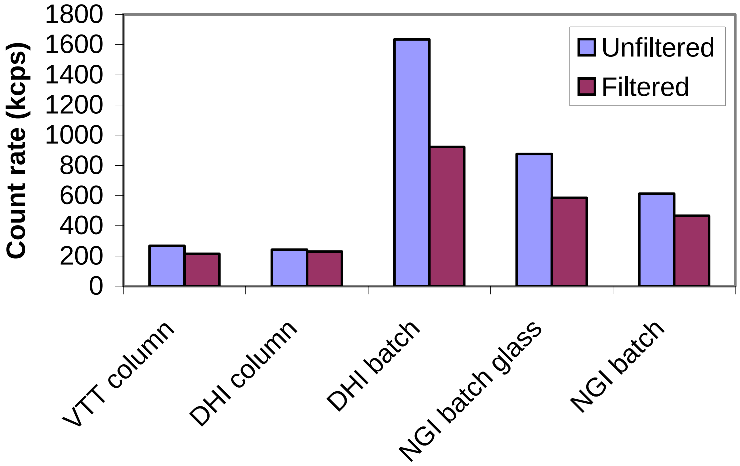


*Figure 11.3 Count rates for column and batch tests unfiltered and filtered.*

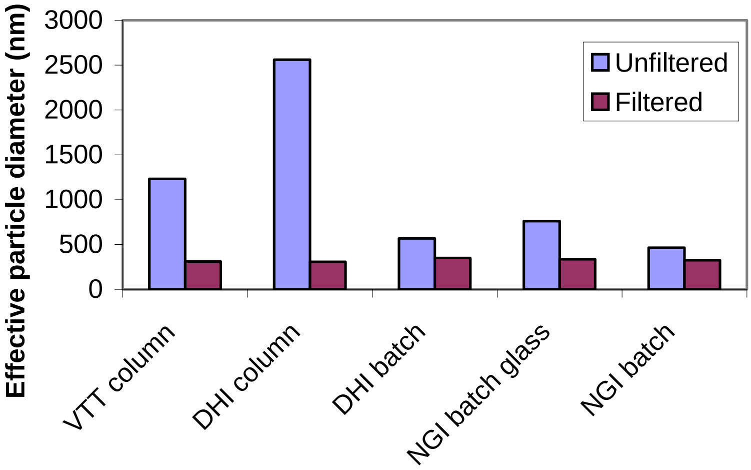


*Figure 11.4 Effective particle diameters for column and batch tests unfiltered and filtered.*

A statistical analysis (t-test) was performed to find differences between the two tests with respect to particle size and amounts of particles. Significant differences for count rates from column and batch tests was observed ($p<0,05$). The count rates were lowest for column tests. For effective diameter no significant differences could be found ($p = 0,11$). It seems, however, as if effective diameter could be higher in eluates from column tests than in eluates from batch tests

Eluates from batch tests produced by NGI were sent in both in plastic bottles and in glass vessels. There were significant differences between the two types of vessels ($p<0,05$) both regarding effective diameters and count rates. The samples stored in plastic generally have lower effective diameters as well as count rates. This indicates that storage in plastic bottles may result in an adsorption of particles and it is therefore not recommended.

Examples of the effects of colloids on the concentration of organic compounds are shown for phenantrene and benzo(a)pyrene in Figure 11.5. The compounds were chosen since they were above detection limits in all replicates and since they are assumed to have different properties regarding volatility and $K_{ow}$-value (see table 4.2). These are factors that may effect their adsorption to particles. Below are shown concentrations of these compounds in all replicates (Figure 11.5) as a function of count rate.

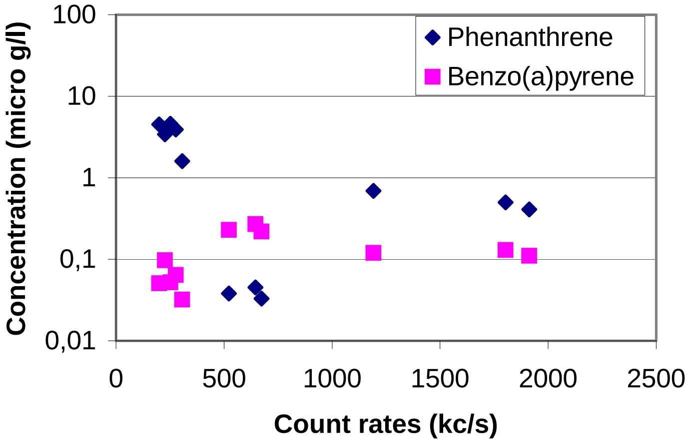


*Figure 11.5 Concentrations in µg/l for phenantrene and benzo(a)pyrene in all replicates from both column tests and batch tests as a function of count rate.*

Phenantrene is presented in higher concentrations in the column test eluates (all dots below 500) than in the batch test eluates, while benzo(a)pyrene seems to have slightly lower concentrations for columns than for batch tests. In order to conclude properly on the effect of colloids on concentrations of different compounds a more thorough statistical investigation is needed. This investigation must take into account the different properties of the organic substances, the inaccuracy in determination of size and distribution of colloids, as well as the inaccuracy in determination of organic compounds.

Overall, these results indicate that during the batch test the test material is ground, resulting in a higher content of colloids in the eluates. Also the size of the colloids are affected during the batch testing as smaller colloides are observed in the batch test than in the column test.

# 12 ASPECTS CONCERNING CHOICE OF TEST METHOD

It is the purpose of this project to be able to recommend leaching test method(s) for determination of leaching of non-volatile organic components from soils and waste products. This test is aimed at routine control testing of soils and waste products, which are utilised or disposed.

In the test hierarchy defined by CEN/TC 292 this test corresponds to a test at compliance level. A test method at this level must provide consistent and reliable results and it must be repeatable and reproducible in different laboratories.

Two test methods are considered for this purpose: a batch test and a column test. Both test methods are aiming at equilibrium of the organic compounds between the solid and the liquid phases. Once equilibrium is obtained the test results will be less sensitive to small changes in the test conditions and the test methods are expected to be more robust than if they were in a state of non-equilibrium stage. In a natural situation an equilibrium situation might not always reflect the real situation, but to do so a specially designed test for the specific situation should be used. An equilibrium concentration in the eluate will, however, in general provide a worst case estimate of leaching of the organic compounds.

The equilibrium column test can basically be regarded as a batch test performed in a column without agitation. The eluate that percolates through the test material several time is believed to be representative of pore water and thus the column test serves as a reference for the batch test.

Aspects of batch and column test methods that are important in relation to the choice of a leaching method for non-volatile compounds are discussed below.

## 12.1 Batch test

The results of previous studies and the results of experiments performed in this project clearly show that during agitation in the batch test inorganic colloids are generated. A larger surface area of colloids may result in an overprediction of the aqueous phase concentration of hydrophobic contaminants. To obtain a reliable and useful result these colloids have to be removed from the eluate before analysis. However, the batch leaching method should somehow be able to include the naturally occurring colloids that potentially enhance the mobility of hydrophobic compounds. These concerns appeared to conflict. Therefore, it is crucial for the batch leaching procedure to find and validate a method that takes these artificially generated colloids into account.

Based on the results of this project it seems possible to separate the solid from the solution by centrifugation and to obtain results for the large PAH which are comparable to results obtained from the equilibrium column test. However analysis of NVOC content and Fe-content in the eluates from both batch and column tests show that the content of inorganic colloids is higher in the eluates from the batch test than in the column eluates. On the other hand the opposite is seen for NVOC, indicating a higher content of dissolved or colloidal organic matter in the column eluates than in the batch eluates. Also the analysis of the amount of particles and the effective particle diameter in the eluates is indicating grinding of test material during the batch test. Knowing that the presence of colloids in solution may have a strong influence on the solute concentration for hydrophobic compounds, it becomes difficult to understand that a column test and a batch test can produce similar eluate concentrations for the most hydrophobic compounds as we actually observed in these experiments.

Comparing results obtained for the smallest PAH in batch and column tests it is unexpected to find that in the batch leaching procedures these PAH are lost. The most plausible explanation would be that these compounds are degraded during testing. However, such a fast degradation is not to be expected with a test duration of 24 hours and after purging the eluaent with $N_2$. The loss of the smallest PAH in the batch leaching procedure remains unexplained.

During the ring test large differences between the batch test results from the participating laboratories were observed for the smallest PAH. The reproducibility is for most compounds slightly higher for the batch test than for the column test. For naphthalene, acenaphthene, fluorene, phenanthrene and anthracene the reproducibility of the batch test was much higher than that observed for the column test.

## 12.2 Column test

The equilibrium column test procedure it is fairly simple and easy to operate once it has been established. The largest challenge is probably finding a pump made of inert material that is suitable for non-volatile and hydrophobic compounds.

As mentioned above, the column test can be regarded as a batch test in a column without agitation. Avoiding agitation is a large advantage of this method. There is no risk that the test results will be biased due to grinding of the materials during testing. In addition, the risk of loosing organic components to the equipment is minimised as the test is performed in a closed system, and during 7 days of contact time the distribution between solid, solution and material surfaces will come close to equilibrium. The eluate is extracted directly in the eluent container (se Figure 6.2) for chemical analysis.

The test method was implemented at 3 different laboratories and results from the ring test show promising results concerning the repeatability and the reproducibility. The column test method seems to be robust and reproducible.

## 12.3 Recommendation of test method for leaching of non-volatile organic compounds:

Based on the knowledge from previous investigations (Miljøstyrelsen 2003) and the results obtained in this study an equilibrium column leaching test is recommended for testing of the leachability of non-volatile organic compounds from contaminated soils and waste products at compliance level (routine control purposes). This recommendation is primarily based on a lack of understanding the results of the batch test and some inconsistency observed for the smallest PAH. In addition, the results of the implementation of the test methods in Nordic laboratories showed that the equilibrium column test provided reproducible results, which is a major requirement of a test to be used for routine control purposes.

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# *APPENDICES*

# *APPENDIX A*

## *Column test protocol*

# Metodebeskrivelse for ligevægtskolonne til ikke-flygtige organiske forbindelser

## Introduktion:

Frigivelse af organiske stoffer fra restprodukter eller jord til vand anses for at være en betydelig proces, som kan føre til forurening af grundvand og overfladerecipienter ved genanvendelse eller deponering. For at sikre, at produkter forurenet med organiske stoffer ikke giver uacceptable påvirkninger af grundvand og overfladerecipienter, er det nødvendigt at bestemme udvaskningen af de forurenende stoffer fra disse materialer. Formålet med denne test er at bestemme udvaskningen af organiske komponenter fra restprodukter og jord. Det skal pointeres, at ikke alle relevante aspekter af udvaskningsegenskaber kan belyses i én udvaskningstest.

Tests til karakterisering af stofudvaskningen for uorganiske komponenter fra restprodukter og jord kan generelt opdeles i tre kategorier.

(1) "Grundlæggende karakterisering": Tests, der anvendes til at opnå detaljeret information om udvaskningsegenskaber over varierende tidshorisonter samt karakteristiske egenskaber af testmaterialet.

(2) "Overensstemmelsestest" anvendes til at bestemme om testmaterialet er i overensstemmelse med en specifik referenceværdi. Testen fokuserer på kritiske betingelser og udvaskningsegenskaber, som er identificeret gennem en grundlæggende karakterisering.

(3) "On-site verifikation". Tests, der benyttes til en hurtig kontrol af hvorvidt materialet er det samme materiale, som det der er blevet underkastet en overensstemmelsestest.

Ligevægtskolonnetesten til organiske stoffer, som beskrives i denne protokol, bør ses i ovennævnte sammenhæng, og er en test på overensstemmelsesniveau (compliance test).

## Anvendelse:

Metoden anvendes til beskrivelse af udvaskningen af ikke flygtige organiske forbindelser fra granulære affaldsmaterialer, restprodukter og jord.

Metoden retter sig mod vurdering af genanvendelse af mod genanvendelse/deponering af granulære restprodukter og opgravet jord.

Der er tale om en test på overensstemmelsesniveau (compliance test), og den gælder for bestemmelse af udvaskningen af PAH-forbindelser, ikke-flygtige olie-komponenter, phenoler og andre ikke flygtige organiske forbindelser.

## Definitioner*:*

*Udvaskningstest:* Test, hvor et testmateriale (her jord eller granulære restprodukter) bringes i kontakt med et udvaskningsmedium under veldefinerede forhold.

*Udvaskningsmedium*: Væske, som anvendes i udvaskningstesten.

*Eluat:* Væske, som fås fra udvaskningstesten efter separation af væske- og faststof-fasen.

*Væske/faststof-forhold (forkortelse L/S efter Liquid/Solid):* Forhold mellem den totale mængde væske (udtrykt i liter), som under udvaskningen er i kontakt med testmaterialet (udtrykt i kg tørstof).

*Tørstofindhold (forkortelse TS):* forhold udtrykt i procent som andelen af tørstof i testmaterialet.

*Laboratorieprøve:* Prøve eller delprøver, som modtages på laboratoriet.

*Testprøve:* Prøve af passende størrelse, som udtages repræsentativt fra laboratorieprøven.

*Testportion:* Prøve af passende størrelse, som udtages repræsentativt fra testprøven (i nogle tilfælde dog direkte fra laboratorieprøven) og som anvendes i udvaskningstesten.

**Udstyr og reagenser:**

Alt materiale, som kommer i kontakt med jordprøverne, **skal være udført i borasilikatglas eller AISI 316 rustfrit stål**.

(1) Glaskolonne købt hos imw (innovative Messtechnik Weiss) Wilhelmstrasse 107, 72074 Tübingen. Kolonnen skal være syrevasket og skyllet med methanol og placeret i varmeovn ved 200°C i minimum 24 timer. Glaskolonnen består af et 15 cm langt bundstykke med en diameter på 6 cm og et topstykke, der er 6 cm langt med en diameter på ca. 6 cm. De to kolonnedele har begge et ca. 5 cm langt glasslib, hvor de samles. Samlet er kolonnen ca. 16 cm lang med et volumen på 450 ml.

(2) Til kolonnen skal der bruges 2 stk. stålflancer, ca. 12 cm lange (ø = 6 mm) med en gennemstukket og påloddet stålskive (ø =6 cm), 2 stk. rørforskruninger GL12 med plads til indlægning af en teflon coated siliconepakning der lukker tæt om åbningen (gennemføringsdiameter = 6 mm).

(3) Siliconefedt.

(4) Pumpe med keramisk pumpehoved og stålcylinder, pumpekapacitet 0-96 ml / h (Pumpe: QG6 FMI LAB PUMP og pumpehoved: Q1 CSC m. bagskyl). Fås hos Microlab Aarhus A/S)

(5) 250 ml pyrex flaske med teflon coated septum (red cap flasker), flaskerne skal være syrevaskest og glødet ved 550 °C i 2 h.

(6) Stålrør (vasket fra Sandvik) med udvendig diameter på 6 mm (forbinder pumpe og kolonne).

(7) Swagelok (6MO-1-4 Male connector) til samling mellem pumpehoved og stålrør.

(8) Swagelok (6MO-6 Union metric connector) til samling af stålrør.

(9) 1 rulle Teflon tape

(10) Kvartssand 1,0-2,5mm.

(11) 2 stk. gummipropper m. hul (ø = 5 mm) –ikke gennemboret.

(12) 5 ml engangssprøjte m. 20 mm lang silicone (diameter: 5x1 mm)

(13) 2 stk. 4” svensknøgler.

(14) 1 stk. papegøjetang.

(15) 1 stk. niveaubord til pumpemotor

(16) 1 stk. stativ m. kolbeholder arm.

(17) Ledningsevnemåler.

(18) pH-måler

(19) Turbiditetsmåler

(20) Termometer

(21) Teknisk vægt 0-2000 g. eller mere, +/- 0,1 g. nøjagtighed.

(22) Riffelneddeler (til ikke-flygtige stoffer)

(23) Varmeskab til tørstofbestemmelse

(24) Demineraliseret vand (5 < pH < 7,5) og ledningsevne < 0,5 mS/m

(25) 0,005M $CaCl_2$-opløsning i demineraliseret vand, som er tilsat $NaN_3$ (500 mg $L^{-1}$)

(26) $NaN_3$ af analyseren kvalitet (Merck nr. 106688-0100)

(27) $CaCl_2 \times 2H_2O$ af analyseren kvalitet (Merck nr. 102382-0500)

## Testprincip

Testen udføres som en kolonneudvaskningstest med recirkulation af eluatet gennem kolonnen. Eluatet recirkuleres indtil der er opnået ligevægt mellem eluat og testmateriale (I praksis recirkuleres eluatet i 7 døgn). Testen udføres ved stuetemperatur (20 ºC ± 5 ºC).

## Prøveforbehandling:

Testmaterialet vil være homogeniseret af DHI, men skal homogeniseres igen af testlaboratoriet umiddelbart inden testning. Efter homogenisering neddeles laboratorieprøven repræsentativt til en testprøve svarende til ca. 600 g tørstof. Fra testprøven udtages 3 testportioner á mindst 10 g repræsentativt til tørstofbestemmelse. Prøverne opbevares i lukkede glas eller metalbeholdere ved 4 °C.

Homogenisering og neddeling af testmaterialet skal enten foregå på et nedkølet materiale ved 4 °C eller på nedkølet materiale ved stuetemperatur, men hvor opholdstiden ved stuetemperatur minimeres.

## Bestemmelse af tørstofindhold i testprøven:

Tørstofindholdet i hver af de 3 testportioner bestemmes ved 105 ºC ± 5 ºC i henhold til DS 204.

Tørstofindholdet (DR i %) beregnes som:

$$DR = 100 * M_D / M_w$$

hvor

$M_D$ er massen af prøven efter tørring ved 105 ºC (g)

$M_W$ er massen af prøven før tørring ved 105 ºC (g)

Vandindholdet i prøven (MC i %) kan beregnes som:

$$MC = 100 * (M_W - M_D) / M_W$$

## Forberedelse af testportion:

Den resterende del af testprøven (*ca. 500 g tørstof*) anvendes til pakning af kolonnen. Mængden af materiale, der skal til for at fylde kolonnen afhænger af testmaterialets vægtfylde (g/cm$^3$).

## Fremstilling af udvaskningsmedie

Der fremstilles en 0,005M $CaCl_2$–opløsning i demineraliseret vand, hvortil der umiddelbart forinden er tilsat 500 mg $L^{-1}$ $NaN_3$ (natriumazid) for at minimere biologisk nedbrydning i udvaskningssystemet. Der fremstilles udvaskningsmedie efter behov.

## Testprocedure:

### Pakning af kolonne:

Selve glaskolonnen består af to dele – en lang del (bunden) og en kort del (toppen). Før kolonnen pakkes måles taravægt (inklusiv kolonne fittings nævnt under pkt. 2 i afsnit. Udstyr og reagenser) og volumekapaciteten. Procedure for pakning af kolonne er som følgende:

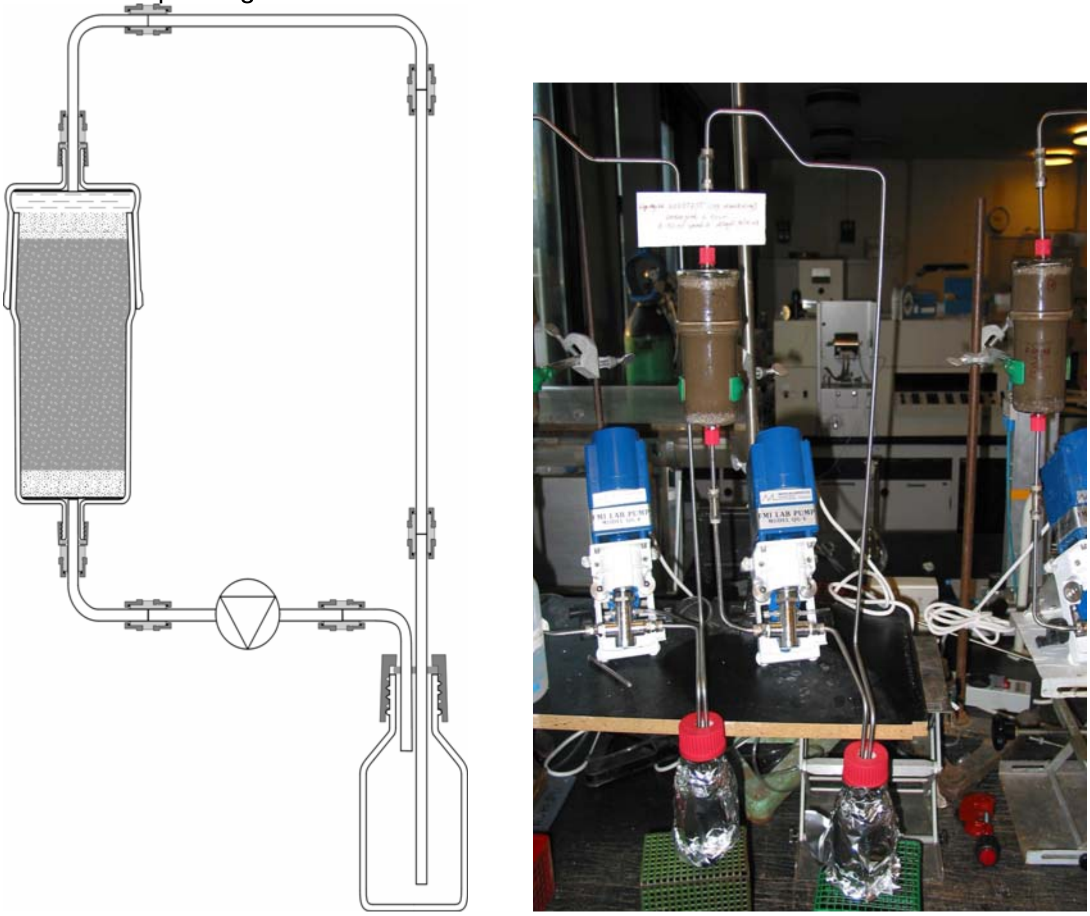
1) En lille tot glasuld placeres med pincet i den ende af flancen hvor pladen er monteret. Pres glasulden lidt sammen i røret.
2) Flancen lægges i kolonnebunden således at rørstudsen stikker ud gennem bunden på kolonnens indløb.
3) Monter rørforskruning og pakning omkring flancerøret og spænd forsigtigt røret sammen med kolonnedelen.
4) Sæt en gummiprop i enden af flancerøret.
5) Placer kolonnen på en vægt således at delene ikke vælter.
6) Tarere vægten.
7) I kolonnen pakkes nu først et filterlag svarende ca. 1 cm kvartssand, som sikrer et jævnt vandflow før udvaskningsmediet ledes gennem den forurenede jord. Højden af sandlaget måles og vægten noteres.
8) Tarere vægten og afvej beholderen med udvaskningsmedie -noter startvægten
9) Med sprøjteflaske tilsættes udvaskningsmediet tilsøjlen, så der er et frit vandspejl på 1-2 cm.
10) Ovenpå filterlaget pakkes et lag af testmaterialet.
11) Testmaterialet komprimeres med en stål genstand (evt. med toppen af den anden stålflance).
12) Ved pakning af testmaterialet fastholdes et lille frit vandspejl og udvaskningsmediet tilsættes efter behov, så det sikres at der ikke er indelukkede luftbobler i kolonnen.
13) Gentag pkt 9-11 indtil kolonnen er fyldt til ca. 1 cm under kanten. Højden af testmaterialet i kolonnen måles og noteres.
14) NB. Tilsæt <u>ikke</u> mere udvaskningsmedie end at der er plads til afslutte med filterlag uden at kolonnen løber over!
15) Tarere vægten med kolonnen
16) Afslutningsvis pakkes et filterlag bestående af ca. 1 cm. kvarstsand for at minimere mobilisering af partikler fra testmaterialet. Højden af sandlaget måles og vægten noteres.
17) Den anden og sidste flance lægges i kolonnetoppen således at rørstudsen stikker ud gennem toppen af kolonnens udløb.
18) Monter rørforskruning og pakning omkring flancerøret men vent med at og spænde sammen.
19) Glasslibet på både kolonnetoppen og –bunden påsmøres et tyndt lag siliconefedt. Dette sikrer, at glasslibet er helt vandtæt, og det er vigtigt, at der ikke efterlades rester af siliconefedt på steder, som er i kontakt med udvaskningsmediet.

20) Gennem toppen af kolonnens udløb tilsættes det sidste udvaskningsmedie indtil kolonnen er helt fyldt.
21) Fortræng alle evt. luftbobler der måtte sidde på over- og undersiden af flancerøret. Dette gøres nemmest ved at bevæge røret lidt.
22) Spænd herefter forsigtigt røret sammen med kolonnedelen.
23) Sæt en gummiprop i topppen af flancerøret
24) Tareres vægten og vej kolonnens totalvægt -noter vægten
25) Afvej herefter beholderen med udvaskningsmedie -noter sluttvægten.

Følgende oplysninger registreres under pakning af kolonnen:

- Mængde filtersand, der er pakket i hhv. top og bund
- Mængde udvaskningsmedie der er tilsat systemet under pakning.
- Mængden af testmateriale der er anvendt i kolonnen.

Bilag A indeholder et skema, som kan anvendes til registrering af nødvendige oplysninger under pakning af kolonnen og testning. Figur 1 viser en principskitse af kolonnetesten samt et billede af testopstillingen.



*Figur 1. Principskitse af ligevægtskolonnetesten, samt billede af testopstillingen*

## Gennemførelse af testen

Efter pakning henstilles kolonnen i stativ med kolbeholder til equilibrering i 24 timer inden testen sættes i gang. I medens samles testsystemet som angivet på figur 1. Kolonne tilsluttes dog først efter endt equlilibrering.

Opstart er som følgende:

1) Placer pumpen på niveaubord og tilslut 220 V.

2) Et Indløbsrør monteres på pumpen vha. en 6MO-1-4 Male connector.

3) Tarere en 250 ml pyrex flaske (forlag) –noter vægten

4) Vip indløbsrøret fra pumpen ned i en 250 ml redcap pyrex flaske (forlag) tilsat ca. 250 ml udvaskningsmedie.

5) Tænd pumpen.

6) Pumpens flow indstilles til en hastighed på 20 mL $h^{-1}$ . Mål flow ved at aflæse ændringen i væskestanden ved hjælp af en 5 ml engangssprøjte monteret på pumpens udløbsrør.

7) Når flowet er indstillet slukkes pumpen igen og udløbsrøret fastgøres til kolonnens indløbsstuds. Fjern derfor først gummiproppen indløbsstudsen og derefter spænd de to rørdele sammen med Swagelok-fitting 6MO-6 Union metric connector.

8) Nu fjernes den sidste gummiprop fra kolonnens udløbsstuds. Det lange rørstykke som går til forlag tilsluttes udløbsstuden v.hj.a en Swagelok-fitting 6MO-6 Union metric connector.

9) Spænd omløberne på swagelokfittings og sikre at der ikke er væsentlige vrid eller spændinger i opstilligen. Dette reguleres vha. niveaubordet og kolonnestativet.

10) Neddyk ind-og udløbsrør i en 250 ml redcap pyrex flaske med teflon coated septum (forlag)

11) Tænd pumpen igen og hold øje med at der kommer små bobler ud fra udløbsrøret i forlaget.

12) Hold øje med kolonnen i 1 times tid for at sikre, at der ikke er tilstopning eller utætheder. Vær opmærksom på at forlaget ikke må være 100 % tæt lukket eller kan evt. overtryk ikke udløses.

13) For at forhindre fotokemisk nedbrydning af de organiske forbindelser i eluatet kan man med fordel pakke forlaget ind i staniol.

14) Eluenten pumpes via recirkulation igennem systemet med en flowhastighed på 20 mL $h^{-1}$ i 7 døgn.

15) Efter 7 døgn er afsluttes testen og det opsamlet eluat i forlaget sendes til analyse. Inden da vejes eluatet i forlaget og flasken tara trækkes fra og vægten noteres.

16) Kolonne, stålrør, stålfittings og pumpe rengøres efter brug.

**Videre håndtering af eluatet:**

Eluatet som er opsamlet i pyrex-beholderen sendes umiddelbart til kemisk analyse for ikke flygtige organiske stoffer. Kan eluatet ikke analyseres umiddelbart efter opsamling opbevares det på køl ved 4 °C

## Beregninger:

Væske/faststofforholdet (L/S-forholdet) i testen kan beregnes, idet testportionens størrelse angivet i tørstof er registreret og mængden af eluent i systemet er kendt.

Resultaterne af de kemiske analyser, som udføres på eluatet fra udvaskningstesten, angives som koncentrationer af de undersøgte stoffer i eluatet, udtrykt i μg/l. Denne koncentration er et udtryk for en den væskekoncentration, som opnås, når der er ligevægt mellem stofferne i testmaterialet og den gennemstrømmende væske.

Mængden af et stof udvasket fra testportionen kan beregnes ved hjælp af følgende formel:

$$A_2 = C_2 *(L_2 + M*MC/100*k) / MD$$

hvor

$A_2$ er den udvaskede mængde af en given komponent ved L/S = 2 l/kg (i mg/kg tørstof)

$C_2$ er koncentrationen af komponenten i eluatet (i mg/l)

$L_2$ er volumenet af udvaskningsmedie i systemet (i ml)

k er en omsætningsfaktor mellem volumen og masse. I temperaturintervallet 15 – 25 °C sættes k = 1.00 ml/g (eller l/kg)

M er mængden af testportion (g)

MD er mængden af testportion (g TS)

## Bilag A: Til registrering af oplysninger for ligevægtskolonnetesten til organiske forbindelser

| | **Kolonne 1** |
|---|---|
| **Oplysninger om testmateriale** | |
| Masse af testportion, M (g) | |
| Tørstofindhold, TS (g/kg) | |
| Vandindhold (g/kg) | |
| | |
| **Pakning af kolonne:** | |
| Vægt af tom kolonne inkl. kolonnefittings | |
| Vægt af tom pyrex-flask uden låg (g) | |
| Tilsat filtersand i bunden af søjlen (g) | |
| Højde af sandlag i bunden (mm) | |
| Tilsat filtersand i toppen af søjlen (g) | |
| Højde af sandlag i toppen (mm) | |
| | |
| Start vægt af udvaskningsmedie incl pyrex-flaske (g) | |
| Vægt af udvaskningsmedie efter pakning af kolonne incl pyrex-flaske (g) | |
| Mængde eluat I pakket kolonne | |
| | |
| Vægt af pakket kolonne incl. prop (g) | |
| Højde af testmateriale i kolonnen (mm) | |
| | |
| **Testforhold** | |
| Mætning af kolonne (start-tid) | |
| Mætning af kolonne (slut-tid) | |
| Pumpe startet (dato) | |
| Pumpe stoppet (dato) | |
| kontakttid (døgn) | |
| | |
| Flowhastighed for udvaskningsmedie (ml/h) | |
| Gennemsnitlig temperatur under hvilken testen er blevet udført | |
| | |
| Vægt af væske i forlag efter testning (g) | |
| Volumen af eluat i rør efter testning (ml) | |
| | |
| Beregnet mængde testprøve i kolonnen (g) | |
| Beregnet mængde testprøve i kolonnen (g TS) | |
| Beregnet samlet mængde udvaskningsmedie (g) | |
| Beregnet L/S-forhold | |
| | |
| **Eluat** | |
| Mængde eluat opsamlet i pyrex-flaske (g) | |
| pH-værdi | |
| Turbiditet (NTU) | |
| Ledningsevne (mS/m) | |
| Mængde eluat sendt til analyse | |
| Dato for afsendelse af eluat til analyse | |
| Analyseparametre | |

# APPENDIX B

## *Batch test protocol*

## Forord

Testprotokollen for batchtesten indeholder testprincipper og -procedurer for testning af ikke-flygtige organiske komponenter. Betegnelserne ikke-flygtige komponenter referer til de i bilag A angivne stofgrupper.

## Introduktion

Frigivelse af organiske stoffer fra jord til vand anses for at være en betydelig proces, som kan føre til forurening af grundvand og overfladerecipienter ved genanvendelse eller deponering af jord. For at sikre at jord forurenet med organiske stoffer ikke giver uacceptable påvirkninger af grundvand og overfladerecipienter, er det nødvendigt at bestemme udvaskningen af potentielt forurenende stoffer fra jorden. Formålet med denne test er at bestemme udvaskningen af organiske komponenter fra jord. Det skal pointeres, at ikke alle relevante aspekter af udvaskningsegenskaber kan belyses i én udvaskningstest.

Tests til karakterisering af stofudvaskningen for uorganiske komponenter fra restprodukter og jord kan generelt opdeles i tre kategorier.

(2) "Grundlæggende karakterisering": Tests, der anvendes til at opnå detaljeret information om udvaskningsegenskaber over varierende tidshorisonter samt karakteristiske egenskaber af testmaterialet.

(2) "Overensstemmelsestest" anvendes til at bestemme om testmaterialet er i overensstemmelse med en specifik referenceværdi. Testen fokuserer på kritiske betingelser og udvaskningsegenskaber, som er identificeret gennem en grundlæggende karakterisering.

(3) "On-site verifikation". Tests, der benyttes til en hurtig kontrol af hvorvidt materialet er det samme materiale, som det der er blevet underkastet en overensstemmelsestest.

Batchudvaskningstesten til organiske komponenter, som beskrives i denne protokol, bør ses i ovennævnte sammenhæng, og er en test på overensstemmelsesniveau (compliance test).

## Anvendelsesområde

Metoden anvendes til beskrivelse af udvaskningen af organiske komponenter fra jord.

Udvaskningstesten for organiske komponenter retter sig mod vurdering af genanvendelse af opgravet jord samt restprodukter

## Definitioner

*Udvaskningstest:* Test, hvor et testmateriale (her jord) bringes i kontakt med en væske under veldefinerede forhold.

*Udvaskningsmedium*: Væske, som anvendes i udvaskningstesten.

*Eluat:* Væske, som fås fra udvaskningstesten efter separation af væske- og faststof-fasen.

*Væske/faststof-forhold (forkortelse L/S efter Liquid/Solid):* Forhold mellem den totale mængde væske (udtrykt i liter), som under udvaskningen er i kontakt med jorden (udtrykt i kg tørstof).

*Tørstofindhold (forkortelse TS):* forhold udtrykt i procent mellem mængde af tørstof i jorden og den tilsvarende mængde rå jord.

*Laboratorieprøve:* Prøve eller delprøver, som modtages på laboratoriet.

*Testprøve:* Prøve af passende størrelse, som udtages repræsentativt fra laboratorieprøven.

*Testportion:* Prøve af passende størrelse, som udtages repræsentativt fra testprøven (i nogle tilfælde dog direkte fra laboratorieprøven) og som anvendes i udvaskningstesten.

## Udstyr og materialer

Alt materiale, som kommer i kontakt med jordprøverne, skal være udført i glas eller rustfrit stål. For de flygtige stoffer er det vigtigt, at det anvendte udstyr er lufttæt.

*Liste over udstyr og reagenser:*

(1) Glasbeholdere (specialfremstillet), glasflasker skal være glødet ved 550 °C i minimum 2 timer (med teflon coated septum (Red cap flaske), syrevasket og glødet ved 550 °C i minimum 2 timer).
(2) Roterapparat (end-over-end tumbler, 8 ± 2 rpm).
(3) Centrifuge (centrifugeringstid og -hastighed svarende til en partikelafskæringsdiameter på 0,45 µm).
(4) Udstyr til bestemmelse af elektrisk konduktivitet
(5) Udstyr til bestemmelse af pH
(6) Termometer til bestemmelse af rumtemperatur
(7) Vægt
(8) Riffelneddeler (til ikke-flygtige stoffer)
(9) Varmeskab til tørstofbestemmelse
(10) Eventuelt en glas- eller stålplade eller et betonunderlag til underlag for homogenisering af jorden
(11) Demineraliseret vand (5 < pH < 7,5) og ledningsevne < 0,5 mS/m
(12) 0,005M $CaCl_2$-opløsning i demineraliseret vand, som er gennemboblet med nitrogen i min. 12 timer
(13) Et ur

## Testprincipper

Testen udføres som en ét-trins batchudvaskningstest ved et L/S-forhold på 2 liter/kg tør prøve og ved stuetemperatur (20 ºC ± 5 ºC). Udvaskningstesten er designet således, at headspace i testbeholderen minimeres. Headspace må maksimalt udgøre 5 %, hvilket for en testbeholder på 650 ml svarer til et volumen på 32,5 ml.

## Forbehandling og håndtering af testmateriale og fremstilling af udvaskningsmedium

*Forbehandling af jordprøve*

For jordprøver, der er forurenet med ikke-flygtige komponenter, vil det af hensyn til testens repræsentativitet være mest hensigtsmæssigt at udtage en passende laboratorieprøve, dog minimum 2 kg, som sendes til laboratoriet til testning. Afhængigt af laboratorieprøvens størrelse udtages en testprøve (testprøven kan eventuelt udgøre hele laboratorieprøven) til videre forbehandling. Testprøven udtages repræsentativt ved ”coning and quartering” eller ved hjælp af en riffelneddeler. Testprøven vurderes visuelt og ved forekomst af klumper større end ca. 4 mm knuses klumperne forsigtigt manuelt med en genstand af metal på et passende underlag, som hverken afgiver eller sorberer stoffer, der indgår i undersøgelsen. Synlige sten og grene frasorteres manuelt. Det frasorterede materiale vejes. Testprøven homogeniseres, hvilket kan foregå ved hjælp af en blandemaskine (hvis prøven er våd) eller ved omskovling og blanding i en lukket beholder af stål eller glas (hvis prøven er tør). Efter homogenisering neddeles testprøven ved hjælp af ”coning and quartering” til en mængde svarende til ca. 500 g tørstof. Herfra udtages 3 testportioner á mindst 10 g repræsentativt med en ske til tørstofbestemmelse (se nedenfor). Efter homogenisering opbevares testprøven i en lukket beholder under forhold, som beskrevet i afsnittet ”opbevaring af prøven”.

## Forbehandling af et restprodukt

Der udtages en passende laboratorieprøve laboratorieprøve, dog minimum 2 kg, som sendes til laboratoriet til testning. Afhængigt af laboratorieprøvens størrelse udtages en testprøve (testprøven kan eventuelt udgøre hele laboratorieprøven) til videre forbehandling. Testprøven udtages repræsentativt ved ”coning and quartering” eller ved hjælp af en riffelneddeler. Testprøven sigtes gennem en 4 mm sigte og materiale større end 4 mm knuses i en kæbeknuser. Materiale, der ikke kan knuses sorteres fra og vægten på det frasorterede materiale registreres. Testprøven homogeniseres, hvilket kan foregå ved hjælp af en blandemaskine (hvis prøven er våd) eller ved omskovling og blanding i en lukket beholder af stål eller glas (hvis prøven er tør). Efter homogenisering neddeles testprøven ved hjælp af ”coning and quartering” til en mængde svarende til ca. 500 g tørstof. Herfra udtages 3 testportioner á mindst 10 g repræsentativt med en ske til tørstofbestemmelse (se nedenfor). Efter homogenisering opbevares testprøven i en lukket beholder under forhold, som beskrevet i afsnittet ”opbevaring af prøven”.

### Opbevaring af testmaterialer

Testmaterialer opbevares i beholdere af rustfrit stål eller andet metal, som kan lukkes tæt med en spænderem. Prøverne opbevares ved 4 °C. Det anbefales, at prøver ikke opbevares længere end 4 døgn før testningen af prøven gennemføres.

### Bestemmelse af tørstofindhold i testprøven

**Tørstofindholdet i hver af de 3 testportioner bestemmes ved 105 ºC ± 5 ºC i henhold til DS 204.**

Tørstofindholdet (TS i %) beregnes som:

$$TS = 100*M_D/M_w$$

hvor
$M_D$ er massen af prøven efter tørring ved 105 ºC (g)
$M_W$ er massen af prøven før tørring ved 105 ºC (g)

Vandindholdet i prøven (MC i %) kan beregnes som:

$$MC = 100*(M_W - M_D)/M_W$$

### Udtagning af testportion

Testportionens størrelse bestemmes, idet testbeholderens volumen er kendt og headspace i testbeholderen må maksimalt udgøre 5% af testbeholderens volumen. For testbeholdere med et volumen på 650 ml udtages der en testportion (M) svarende til 280 g +/- 10 g tørstof (MD). Den mængde prøve, M, som skal udtages, beregnes af formlen:

$$M = 100*MD/TS$$

Testportionen (M) udtages fra den neddelte testprøve.

### Fremstilling af udvaskningsmedie

Det volumen udvaskningsmedie ($L_2$ i ml), som skal tilsættes for at opnå L/S = 2 l/kg, beregnes ved hjælp af følgende formel:

$$L_2 = 2*MD - (M*MC)/100$$

hvor
M er mængden af testportion (g)
MD er mængden af testportion (g TS)

Der fremstilles en 0,005 M $CaCl_2$–opløsning i demineraliseret vand, som gennembobles med nitrogen i minimum 12 timer inden brug.

Det beregnede volumen udvaskningsmedie, som skal tilsættes, omregnes til en vægtbaseret mængde udvaskningsmedie ($M_2$) ved hjælp af følgende formel:

$$M_2 = L_2/k$$

hvor
k er en omsætningsfaktor mellem volumen og masse. I temperaturintervallet 17 – 23 °C sættes k = 1.00 ml/g (eller l/kg).

## *Testprocedure*

### Testbetingelser

Testen udføres ved stuetemperatur (20 ± 3 °C), som registreres løbende under testningen.

### Gennemførelse af testen

Afvej og tilsæt den beregnede mængde udvaskningsmedie til testbeholderen af glas med teflon coated septum. Herefter udtages testportionen (M) repræsentativt og overføres til testbeholderen og testbeholderen lukkes omgående.

Testbeholderen med testportionen og udvaskningsmediet rystes hurtigt et par gange i hånden for at sikre god opblanding. Herefter fastspændes testbeholderen opretstående i roter-apparatet, som er indrettet, så testbeholderen bringes til at rotere om sin tværakse ("end-over-end"). Roter-apparatet igangsættes og kører i 24 timer ± 0,5 timer med en hastighed på 8±2 omdrejninger/minut, hvorefter det standses. Testbeholderen med testportionen tages ud af apparatet og centrifugeres v. ca. 700 g i 10 minutter. Eluatet overføres forsigtigt til en stål centrifugebeholder med en glaspipette. Prøven centrifugeres ved 6200 g i 60 minutter. Efter centrifugering overføres eluatet med en glaspipette til et prøveglas. Prøveglasset fyldes helt op og sættes omgående på køl.

### Opbevaring af eluat

Prøverne opbevares ved 4 °C i højest 3 dage.

### Analysering af eluat

Eluaterne analyseres altid for pH, ledningsevne og turbiditet umiddelbart efter testningen. Analyse af øvrige forureningskomponenter i eluat fra batchudvaskningstesten er ikke omfattet af denne testprotokol.

## Beregning

Resultaterne af de kemiske analyser, som udføres på eluatet fra udvaskningstesten, angives som koncentrationer af de undersøgte komponenter i eluatet, udtrykt i mg/l. Resultatet kan endvidere udtrykkes som udvasket mængde af den enkelte komponent udtrykt relativt til den totale masse af testportionen, altså i mg/kg TS.

Mængden af en komponent udvasket fra testportionen kan beregnes ved hjælp af følgende formel:

$$A_2 = C_2 *(L_2 + M*MC/100*k) / MD$$

hvor

$A_2$ er den udvaskede mængde af en given komponent ved L/S = 2 l/kg (i mg/kg tørstof)
$C_2$ er koncentrationen af komponenten i eluatet (i mg/l)
$L_2$ er volumenet af udvaskningsmedie tilsat (i ml)
k er en omsætningsfaktor mellem volumen og masse. I temperaturintervallet 15 – 25 °C sættes k = 1,00 ml/g (eller l/kg)
M er mængden af testportion (g)
MD er mængden af testportion (g TS)

## Dokumentation og testrapport

Følgende informationer skal dokumenteres på en sådan måde, at de er tilgængelige. Informationer mærket med stjerne skal inkluderes i testrapporten.

Prøveforberedelse:

- Reference til metoden for udvaskningstesten*
- Reference til laboratorieprøven*
- Dato og tidspunkt for modtagelse af laboratorieprøven/testportioner i testbeholder*
- Adresse på laboratoriet og navne på ansvarlige personer*
- Vægten af laboratorieprøven*
- Dato for forberedelse af testportioner til bestemmelse af tørstofindhold
- Dato for forberedelse af testportion til udvaskningstest
- Opbevaringsforhold for perioden mellem de 3 ovenfor nævnte datoer
- Beskrivelse af hvordan testprøven er blevet forbehandlet (specielt mht. homogenisering, vægt og karakter af frasorteret materiale), og hvordan testportionen er blevet forberedt (neddelingsprocedure)
- Varighed og opbevaringsforhold mellem forberedelse af testportionen og udvaskning.

Produktion af eluat:

- Rå masse af testportion, M (g)*
- Tørstofindhold, TS (%)*
- Adresse på laboratoriet og navne på ansvarlige personer*
- Dato for udvaskningstest*
- Volumen af udvaskningsmedie, som er blevet tilsat ($L_2$)*
- Størrelse, udformning og materiale af testbeholderen
- Metode til agitation (indstilling)
- Varighed af udvaskningen (kontakttid)*
- Temperatur under hvilken testen er blevet udført
- Beskrivelse af metode til adskillelse af væske og faststof (dimensioner af centrifuge samt indstilling)

- Varighed af periode mellem endt agitation og begyndelse af centrifugering
- Varighed af centrifugering
- Resultater af målinger foretaget umiddelbart efter at der er udtaget prøve til kemiske analyser (pH, ledningsevne og eventuelt redox-forhold)*
- Mængde eluat opnået
- Konservering af eluat
- Opbevaring af eluat
- Dato for afsendelse af eluat til kemisk analyse

Analyse af eluat:
- Dato for analyse af eluat
- Opbevaring af eluat
- Anvendt analysemetode*
- Analysens detektionsgrænser*
- Navn og adresse på udførende laboratorium*
- Navn på ansvarlig person

Resultater af den gennemførte batchudvaskningstest*

## Bilag A (informativt)

Tabel A.1 angiver hvilke organiske komponenter, som hører ind under kategorien ikke-flygtige komponenter, samt hvilken type forureninger disse komponenter oftest forekommer i forbindelse med.

*Tabel A.1. Forureningstyper, som forskellige ikke-flygtige komponenter typisk forekommer i forbindelse med.*

| **Ikke-flygtige komponenter** | **Forekommer typisk i forbindelse med følgende typer forurening** |
|---|---|
| PAH | Tjære ved gasværker |
| Tungere olier ( > C10) | Spild på servicestationer og hvor der i øvrigt oparbejdes, håndteres og lagres olie |
| PCB | træimprægnering |

# *APPENDIX C*

## *Formulas for calculating the centrifugation force and time*

A particle moving in a circular track has an acceleration a against the centre given by:

$a = r*\omega^2$

where

a is the acceleration ($m/s^2$)
$\omega$ is the angular velocity ($s^{-1}$)
r is the radius from the centre (m)

Speed of centrifugation expressed in rounds per second is given by:

Speed of centrifugation = $\omega*2\pi$

The force of centrifugation is expressed in relation to the acceleration of gravity (g-value):

Force of centrifugation (g-value) = a / 9,81

From Stokes law it can be calculated how long time it will take for a given particle (diameter and density given) to reach the bottom of the centrifuge vessel.

$Vs = (Dp^2*a*(\rho_p - \rho))/(18*\eta)$

Where :

Dp : particle diameter (m)
a: acceleration ($s^{-2}$)
$\rho_p$: particle density (kg/m3)
$\rho$ : Liquid density (kg/m3)
$\eta$: Liquid viscosity (kg/(ms))

Reformulating Stokes law the time of centrifugation can be calculated by:

$dt =(18*\eta) / (Dp^2*a*(\rho_p - \rho))* dr$

$t = (18*\eta) / (Dp^2*a*(\rho_p - \rho))* \ln(r_2 /r_1)$

$t = (18*\eta) / (Dp^2*\omega^2*4*\pi^2*(\rho_p - \rho))* \ln(r_2 /r_1)$

where:

$r_2$ is the distance between the centre of the centrifuge and the bottom of the liquid
$r_1$ is the distance between the centre of the centrifuge and the top of the liquid

It is assumed that Reynolds number is between $10^{-5}$ and 2, which will be fulfilled in most cases that is relevant in this context.

Using the formulas described above the centrifugation time can be calculated at varying g-values (force of centrifugation). This is exemplified in figure ZZ

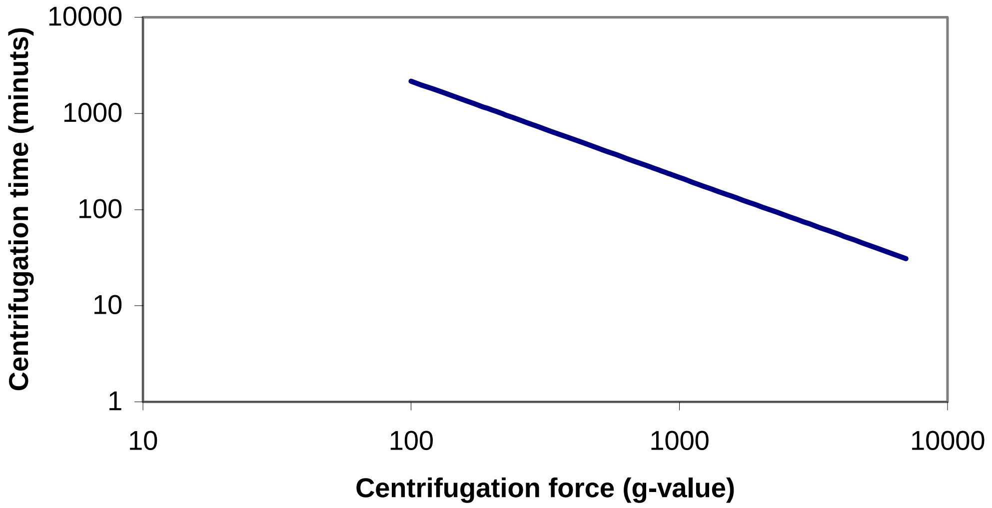


*Figure C1. Relation between centrifugation force and time assuming a density of 1100 k/m$^3$, a particle diameter of 0,45 μm and $r_2$ = 0,22 m, $r_1$=0,115 m.*

From Figure C1 it can be seen that theoretical it is possible to obtain identical centrifugation force by double the time of centrifugation if the acceleration is halved. On the other hand the centrifugation time must be four time doubled if the speed of centrifugation (rounds per second) is halved in order to obtain identical force of centrifugation.

# *APPENDIX D*

## *Detailed results of experimental work*

## Test information – Batch tests

*Detailed test conditions for batch leaching tests performed as replicates. After leaching the eluates was mixed and again splitted in 6 portions in order to eliminate influence of heterogeneity of the test materials on the test results.*

| **B&W soil (R-097-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** | **4. Replicate** | **5. Replicate** | **6. Replicate** |
|---|---|---|---|---|---|---|
| Dry matter content (g/kg) | 724 | 724 | 724 | 724 | 724 | 724 |
| Water content (g/kg) | 276 | 276 | 276 | 276 | 276 | 276 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 387 | 388 | 388 | 387 | 387 | 387 |
| Eluent (ml) | 438 | 438 | 440 | 448 | 448 | 440 |
| Contact time (hours) | 24 | 24 | 24 | 24 | 24 | 24 |
| L/S-ratio | 1,94 | 1,94 | 1,95 | 1,98 | 1,98 | 1,95 |
| Centrifugation ( force (g)/time (min)) | 27000 / 30 | 27000 / 30 | 27000 / 30 | 6200 / 60 | 6200 / 60 | 6200 / 60 |
| **Eluate** | | | | | | |
| pH | 7,8 | 7,8 | 7,8 | 7,6 | 7,6 | 7,7 |
| Turbidity (NTU) | 5,59 | 5,61 | 5,65 | | | |
| Conductivity (mS/m) | 399 | 401 | 404 | 407 | 407 | 401 |

| **Clay pigeon contaminated soil (R-132-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** | **4. Replicate** | **5. Replicate** | **6. Replicate** |
|---|---|---|---|---|---|---|
| Dry matter content (g/kg) | 834 | 834 | 834 | 834 | 834 | 834 |
| Water content (g/kg) | 166 | 166 | 166 | 166 | 166 | 166 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 320 | 320 | 320 | 320 | 320 | 320 |
| Eluent (ml) | 487 | 479 | 488 | 497 | 485 | 483 |
| Contact time (hours) | 24 | 24 | 24 | 24 | 24 | 24 |
| L/S-ratio | 2,02 | 1,99 | 2,03 | 2,06 | 2,02 | 2,01 |
| Centrifugation ( force (g)/time (min)) | 27000 / 30 | 27000 / 30 | 27000 / 30 | 6200 / 60 | 6200 / 60 | 6200 / 60 |
| **Eluate** | | | | | | |
| pH | 7,8 | 7,8 | 7,6 | 7,5 | 7,7 | 7,7 |
| Turbidity (NTU) | 3,77 | 3,33 | 6,4 | 3,52 | 2,98 | 2,97 |
| Conductivity (mS/m) | 134 | 133 | 135 | 134 | 134 | 134 |

| **Clay pigeon (R-107-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** | **4. Replicate** | **5. Replicate** | **6. Replicate** |
|---|---|---|---|---|---|---|
| Dry matter content (g/kg) | 999 | 999 | 999 | 999 | 999 | 999 |
| Water content (g/kg) | 1 | 1 | 1 | 1 | 1 | 1 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 237,1 | 237,5 | 240,6 | 239,5 | 244,7 | 247,5 |
| Eluent (ml) | 475,3 | 481,7 | 485,2 | 481,5 | 492,4 | 488,9 |
| Contact time (hours) | 24 | 24 | 24 | 24 | 24 | 24 |
| L/S-ratio | 2,01 | 2,03 | 2,02 | 2,01 | 2,02 | 1,98 |
| Centrifugation ( force (g)/time (min)) | 27000 / 30 | 27000 / 30 | 27000 / 30 | 6200 / 60 | 6200 / 60 | 6200 / 60 |
| **Eluate** | | | | | | |
| pH | 9,2 | 9,2 | 9,2 | 9,3 | 9,4 | 9,4 |
| Turbidity (NTU) | 0,4 | 0,29 | 0,47 | 2,62 | 2,61 | 2,37 |
| Conductivity (mS/m) | 16 | 16 | 16 | 16 | 16 | 16 |

| **Road sweepings (R-109-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** | **4. Replicate** | **5. Replicate** | **6. Replicate** |
|---|---|---|---|---|---|---|
| Dry matter content (g/kg) | 962 | 962 | 962 | 962 | 962 | 962 |
| Water content (g/kg) | 38 | 38 | 38 | 38 | 38 | 38 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 268,7 | 268,3 | 272,3 | 265,2 | 268,1 | 266 |
| Eluent (ml) | 522,1 | 521,9 | 534,2 | 520,2 | 522,4 | 523,3 |
| Contact time (hours) | 24 | 24 | 24 | 24 | 24 | 24 |
| L/S-ratio | 2,06 | 2,06 | 2,08 | 2,08 | 2,06 | 2,08 |
| Centrifugation ( force (g)/time (min)) | 27000 / 30 | 27000 / 30 | 27000 / 30 | 6200 / 60 | 6200 / 60 | 6200 / 60 |
| **Eluate** | | | | | | |
| pH | 8 | 8,1 | 8 | 7,6 | 7,6 | 7,7 |
| Turbidity (NTU) | 10,1 | 29,4 | 16,2 | 6,71 | 10,6 | 11,6 |
| Conductivity (mS/m) | 770 | 769 | 770 | 762 | 767 | 765 |

*Detailed test conditions for batch leaching tests performed as triplicates.*

| **B&W soil (R-097-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** |
|---|---|---|---|
| Dry matter content (g/kg) | 724 | 724 | 724 |
| Water content (g/kg) | 276 | 276 | 276 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 368 | 367 | 367 |
| Eluent (ml) | 438 | 430 | 436 |
| Contact time (hours) | 24 | 24 | 24 |
| L/S-ratio | 2,03 | 2,00 | 2,02 |
| Centrifugation ( force (g) / time (min)) | 27000 / 30 | 27000 / 30 | 27000 / 30 |
| **Eluate** | | | |
| pH | 7,9 | 7,8 | 7,7 |
| Turbidity (NTU) | 3,41 | 3,5 | 3,6 |
| Conductivity (mS/m) | 403 | 402 | 402 |

| **Clay pigeons contaminated soil (R-132-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** |
|---|---|---|---|
| Dry matter content (g/kg) | 834 | 834 | 834 |
| Water content (g/kg) | 166 | 166 | 166 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 320 | 319 | 320 |
| Eluent (ml) | 482 | 484 | 478 |
| Contact time (hours) | 24 | 24 | 24 |
| L/S-ratio | 2,01 | 2,02 | 1,99 |
| Centrifugation ( force (g) / time (min)) | 27000 / 30 | 27000 / 30 | 27000 / 30 |
| **Eluate** | | | |
| pH | 7,7 | 7,7 | 7,8 |
| Turbidity (NTU) | 2,72 | 3,75 | 3,11 |
| Conductivity (mS/m) | 134 | 134 | 133 |

| **Clay pigeons (R-107-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** |
|---|---|---|---|
| Dry matter content (g/kg) | 999 | 999 | 999 |
| Water content (g/kg) | 1 | 1 | 1 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 237,3 | 237 | 239,7 |
| Eluent (ml) | 474,3 | 494 | 494,2 |
| Contact time (hours) | 24 | 24 | 24 |
| L/S-ratio | 2,00 | 2,09 | 2,06 |
| Centrifugation ( force (g) / time (min)) | 27000 / 30 | 27000 / 30 | 27000 / 30 |
| **Eluate** | | | |
| pH | 9,5 | 9,3 | 9,2 |
| Turbidity (NTU) | 0,37 | 0,51 | 0,41 |
| Conductivity (mS/m) | 14 | 13 | 12 |

| **Road sweepings (R-109-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** |
|---|---|---|---|
| Dry matter content (g/kg) | 962 | 962 | 962 |
| Water content (g/kg) | 38 | 38 | 38 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 265,2 | 271 | 273,1 |
| Eluent (ml) | 521,6 | 531,3 | 538,6 |
| Contact time (hours) | 24 | 24 | 24 |
| L/S-ratio | 2,08 | 2,08 | 2,09 |
| Centrifugation ( force (g) / time (min)) | 27000 / 30 | 27000 / 30 | 27000 / 30 |
| **Eluate** | | | |
| pH | 8 | 8,1 | 8,1 |
| Turbidity (NTU) | 27 | 10 | 14 |
| Conductivity (mS/m) | 784 | 763 | 737 |

# Test information – Column tests

*Detailed test conditions for column tests performed as replicates*

| **B&W soil (R-097-03)** | **Column 1** | **Column 2** | **Column 3** |
|---|---|---|---|
| Dry matter content (g/kg) | 724 | 724 | 724 |
| Water content (g/kg) | 276 | 276 | 276 |
| | | | |
| Filtersand - bottom of the column (g) | 30,92 | 29,84 | 30,12 |
| Filtersand - top of the column (g) | 50,65 | 51,25 | 50,63 |
| Contact time (days) | 7 | 7 | 7 |
| Test portion, wet mass (g) | 477,96 | 483,69 | 485,94 |
| Test portion, dry mass (g TS) | 346,0 | 350,2 | 351,8 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Concentration of NaN3 in the eluent (g/l) | 0,5 | 0,5 | 0,5 |
| Total amount of eluent (g) | 558,4 | 538,1 | 535,8 |
| Flow velocity (ml/h) | 20,7 | 20,5 | 19,57 |
| L/S-ratio | 1,6 | 1,5 | 1,5 |
| | | | |
| **Eluate** | | | |
| pH | 7,3 | 7,4 | 7,3 |
| Turbidity (NTU) | 3,45 | 2,85 | 3,25 |
| Conductivity (mS/cm) | 454 | 451 | 430 |

| **Clay pigeons contaminated soil (R-132-03)** | **Column 1** | **Column 2** | **Column 3** | **Column 4** |
|---|---|---|---|---|
| Dry matter content (g/kg) | 834 | 834 | 834 | 834 |
| Water content (g/kg) | 166 | 166 | 166 | 166 |
| | | | | |
| Filtersand - bottom of the column (g) | 42,1 | 42,3 | 43,3 | 43,7 |
| Filtersand - top of the column (g) | 78,2 | 76,5 | 59,8 | 61,8 |
| Contact time (days) | 7 | 7 | 7 | 7 |
| Test portion, wet mass (g) | 513,1 | 544,9 | 530,6 | 529,8 |
| Test portion, dry mass (g TS) | 427,9 | 454,4 | 442,6 | 441,8 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 | 0,005 |
| Concentration of NaN3 in the eluent (g/l) | 0,5 | 0,5 | 0,5 | 0,5 |
| Total amount of eluent (g) | 491,2 | 471,9 | 499,8 | 490,5 |
| Flow velocity (ml/h) | 22 | 20 | 20 | 20 |
| L/S-ratio | 1,1 | 1,0 | 1,1 | 1,1 |
| | | | | |
| **Eluate** | | | | |
| pH | | | | |
| Turbidity (NTU) | | | | |
| Conductivity (mS/cm) | | | | |

| **Clay pigeons (R-107-03)** | **Column 1** | **Column 2** | **Column 3** |
|---|---|---|---|
| Dry matter content (g/kg) | 999 | 999 | 999 |
| Water content (g/kg) | 1 | 1 | 1 |
| | | | |
| Filtersand - bottom of the column (g) | 75,0 | 75,0 | 75,1 |
| Filtersand - top of the column (g) | 75,1 | 68,9 | 74,0 |
| Contact time (days) | 7 | 7 | 7 |
| Test portion, wet mass (g) | 380,4 | 419,4 | 409,5 |
| Test portion, dry mass (g TS) | 380,0 | 419,0 | 409,1 |
| Concentration of CaCl2 in the eluent (M) | 0 | 0 | 0 |
| Concentration of NaN3 in the eluent (g/l) | 0,5 | 0,5 | 0,5 |
| Total amount of eluent (g) | 275,1 | 293,9 | 289,4 |
| Flow velocity (ml/h) | 20 | 20 | 20 |
| L/S-ratio | 0,7 | 0,7 | 0,7 |
| Eluate | | | |
| pH | 8,0 | 8,0 | 8,14 |
| Turbidity (NTU) | 2,18 | 4,2 | 2,05 |

| **Road sweepings (R-109-03)** | **Column 1** | **Column 2** | **Column 3** |
|---|---|---|---|
| Dry matter content (g/kg) | 971 | 971 | 971 |
| Water content (g/kg) | 29 | 29 | 29 |
| | | | |
| Filtersand - bottom of the column (g) | 75,2 | 75,3 | 75,4 |
| Filtersand - top of the column (g) | 75,1 | 75 | 75,9 |
| Contact time (days) | 7 | 7 | 7 |
| Test portion, wet mass (g) | 505,9 | 518,7 | 505,9 |
| Test portion, dry mass (g TS) | 491,2 | 503,7 | 491,2 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Concentration of NaN3 in the eluent (g/l) | 0,5 | 0,5 | 0,5 |
| Total amount of eluent (g) | 303,0 | 292,3 | 294,7 |
| Flow velocity (ml/h) | 20 | 20 | 20 |
| L/S-ratio | 0,6 | 0,6 | 0,6 |
| Eluate | | | |
| pH | 7,68 | 7,66 | 7,74 |
| Turbidity (NTU) | 4,87 | 3,1 | 1,33 |

# Detailed test results – Batch test (mixed eluates)

| **Clay pigeon contaminated soil** | | **Centrifugation at 6200 g for 60 min** | | | **Centrifugation at 27000 in 30 min** | | |
|---|---|---|---|---|---|---|---|
| | | 1. replicate | 2.replicate | 3.replicate | 1. replicate | 2.replicate | 3.replicate |
| Naphthalene | µg/l | 0,97 | - | 0,35 | 3,8 | - | 0,64 |
| Acenaphthylene | µg/l | <0,010 | - | <0,010 | 0,02 | - | 0,012 |
| Acenaphthene | µg/l | 0,12 | - | 0,34 | 0,6 | - | 0,5 |
| Fluorene | µg/l | 0,15 | - | 0,26 | 0,44 | - | 0,38 |
| Phenanthrene | µg/l | 0,38 | 0,35 | 0,39 | 0,74 | 0,8 | 0,65 |
| Anthracene | µg/l | 0,052 | 0,057 | 0,055 | 0,087 | 0,25 | 0,13 |
| Fluoranthene | µg/l | 0,54 | 0,51 | 0,56 | 1 | 1,1 | 1,3 |
| Pyrene | µg/l | 0,31 | 0,29 | 0,31 | 0,7 | 0,73 | 0,91 |
| Benz(a)anthracene | µg/l | 0,1 | 0,1 | 0,1 | 0,32 | 0,34 | 0,59 |
| Chrysene/Triphenylene | µg/l | 0,16 | 0,16 | 0,15 | 0,45 | 0,47 | 0,78 |
| Benz(b+j+k)fluoranthene | µg/l | 0,16 | 0,15 | 0,16 | 0,65 | 0,62 | 1,3 |
| Benzo(a)pyrene | µg/l | 0,056 | 0,063 | 0,063 | 0,29 | 0,29 | 0,62 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,039 | 0,036 | 0,037 | 0,19 | 0,18 | 0,42 |
| Dibenz(a,h)anthracene | µg/l | 0,013 | 0,015 | 0,011 | 0,054 | 0,049 | 0,11 |
| Benzo(g,h,i)perylene | µg/l | 0,036 | 0,034 | 0,033 | 0,18 | 0,17 | 0,4 |
| Sum PAH (16 EPA) | µg/l | 1,8 | 2,8 | 2,8 | 9,6 | 4,9 | 8,7 |

| **Industrial soil** | | **Centrifugation at 6200 g for 60 min** | | | **Centrifugation at 27000 in 30 min** | | |
|---|---|---|---|---|---|---|---|
| B&W soil (R-097-04) | | 1. replicate | 2.replicate | 3.replicate | 1. replicate | 2.replicate | 3.replicate |
| Naphthalene | µg/l | 0,047 | 0,032 | 0,016 | 0,0035 | 0,013 | 0,019 |
| Acenaphthylene | µg/l | 0,11 | 0,088 | 0,1 | 0,084 | 0,072 | 0,097 |
| Acenaphthene | µg/l | 0,018 | 0,015 | 0,015 | 0,03 | 0,021 | 0,033 |
| Fluorene | µg/l | <0,01 | <0,01 | <0,1 | 0,023 | 0,014 | 0,02 |
| Phenanthrene | µg/l | 0,026 | 0,018 | <0,02 | 0,051 | 0,045 | 0,064 |
| Anthracene | µg/l | 0,094 | 0,082 | 0,1 | 0,084 | 0,077 | 0,086 |
| Fluoranthene | µg/l | 0,11 | 0,099 | 0,1 | 0,12 | 0,14 | 0,15 |
| Pyrene | µg/l | 0,12 | 0,12 | 0,13 | 0,16 | 0,17 | 0,2 |
| Benz(a)anthracene | µg/l | 0,037 | 0,027 | 0,03 | 0,032 | 0,037 | 0,043 |
| Chrysene/Triphenylene | µg/l | 0,066 | 0,062 | 0,075 | 0,054 | 0,072 | 0,068 |
| Benz(b+j+k)fluoranthene | µg/l | 0,21 | 0,19 | 0,3 | 0,12 | 0,16 | 0,15 |
| Benzo(a)pyrene | µg/l | 0,14 | 0,12 | 0,21 | 0,075 | 0,1 | 0,074 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,22 | 0,2 | 0,37 | 0,11 | 0,14 | 0,11 |
| Dibenz(a,h)anthracene | µg/l | 0,034 | 0,024 | 0,054 | 0,016 | 0,026 | 0,02 |
| Benzo(g,h,i)perylene | µg/l | 0,25 | 0,22 | 0,43 | 0,14 | 0,16 | 0,13 |
| Sum PAH (16 EPA) | µg/l | 1,5 | 1,3 | 2 | 1,1 | 1 | 1 |

| **Crushed clay pigeons** | | **Centrifugation at 6200 g for 60 min** | | | **Centrifugation at 27000 in 30 min** | | |
|---|---|---|---|---|---|---|---|
| (R-107-04) | | 1. replicate | 2.replicate | 3.replicate | 1. replicate | 2.replicate | 3.replicate |
| Naphthalene | µg/l | 9,2 | 9,3 | 11 | 9,3 | 10 | 9,4 |
| Acenaphthylene | µg/l | 0,076 | 0,061 | 0,079 | 0,078 | 0,085 | 0,077 |
| Acenaphthene | µg/l | 6,9 | 6,5 | 8 | 14 | 13 | 14 |
| Fluorene | µg/l | 3,3 | 3,2 | 4 | 8 | 8,2 | 8,1 |
| Phenanthrene | µg/l | 12 | 12 | 15 | 43 | 45 | 43 |
| Anthracene | µg/l | 3,8 | 3,8 | 4,7 | 10 | 10 | 10 |
| Fluoranthene | µg/l | 5,3 | 5 | 6,5 | 27 | 28 | 27 |
| Pyrene | µg/l | 4,1 | 3,8 | 5,1 | 22 | 22 | 22 |
| Benz(a)anthracene | µg/l | 1 | 0,96 | 1,3 | 4 | 5 | 4,7 |
| Chrysene/Triphenylene | µg/l | 1,3 | 1 | 1,4 | 4,4 | 4,7 | 4,4 |
| Benz(b+j+k)fluoranthene | µg/l | 1,3 | 0,76 | 1,2 | 1,6 | 2,2 | 2 |
| Benzo(a)pyrene | µg/l | 0,72 | 0,39 | 0,64 | 0,74 | 1,1 | 0,95 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,59 | 0,2 | 0,39 | 0,17 | 0,4 | 0,32 |
| Dibenz(a,h)anthracene | µg/l | 0,14 | 0,048 | 0,093 | 0,043 | 0,11 | 0,082 |
| Benzo(g,h,i)perylene | µg/l | 0,47 | 0,15 | 0,32 | 0,12 | 0,31 | 0,27 |
| Sum PAH (16 EPA) | µg/l | 50 | 47 | 60 | 140 | 150 | 150 |

| **Road sweepings** | | **Centrifugation at 6200 g for 60 min** | | | **Centrifugation at 27000 in 30 min** | | |
|---|---|---|---|---|---|---|---|
| (R-109-04) | | 1. replicate | 2.replicate | 3.replicate | 1. replicate | 2.replicate | 3.replicate |
| Naphthalene | µg/l | 0,053 | <0,05 | <0,05 | <0,05 | <0,05 | <0,05 |
| Acenaphthylene | µg/l | <0,010 | <0,010 | <0,010 | <0,010 | <0,010 | <0,010 |
| Acenaphthene | µg/l | 0,043 | 0,038 | 0,037 | 0,033 | 0,035 | 0,031 |
| Fluorene | µg/l | 0,031 | 0,018 | 0,021 | 0,021 | 0,018 | 0,013 |
| Phenanthrene | µg/l | 0,15 | 0,14 | 0,15 | 0,12 | 0,12 | 0,12 |
| Anthracene | µg/l | 0,029 | 0,029 | 0,024 | 0,031 | 0,024 | 0,018 |
| Fluoranthene | µg/l | 0,11 | 0,092 | 0,11 | 0,093 | 0,12 | 0,097 |
| Pyrene | µg/l | 0,098 | 0,087 | 0,095 | 0,087 | 0,12 | 0,09 |
| Benz(a)anthracene | µg/l | 0,019 | 0,012 | 0,016 | 0,015 | 0,034 | 0,013 |
| Chrysene/Triphenylene | µg/l | 0,028 | 0,02 | 0,026 | 0,024 | 0,057 | 0,025 |
| Benz(b+j+k)fluoranthene | µg/l | 0,03 | 0,019 | 0,029 | 0,018 | 0,071 | 0,022 |
| Benzo(a)pyrene | µg/l | 0,015 | <0,01 | 0,014 | <0,010 | 0,039 | <0,010 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,013 | 0,011 | 0,014 | <0,010 | 0,027 | <0,010 |
| Dibenz(a,h)anthracene | µg/l | <0,01 | <0,01 | <0,01 | <0,010 | <0,010 | <0,010 |
| Benzo(g,h,i)perylene | µg/l | <0,01 | <0,01 | 0,013 | <0,010 | 0,02 | <0,010 |
| Sum PAH (16 EPA) | µg/l | 0,62 | 0,46 | 0,54 | 0,44 | 0,69 | 0,43 |

## Detailed test results – Column tests and Batch tests

| **Clay pigeon contaminated soil** | | **Column tests** | | | **Batch tests**<br>**Centrifugation at 27000 in 30 min** | | |
|---|---|---|---|---|---|---|---|
| (R-132-04) | | 1. replicate | 2.replicate | 3.replicate | 1. replicate | 2.replicate | 3.replicate |
| Naphthalene | µg/l | 11 | 12 | 12 | - | - | 0,88 |
| Acenaphthylene | µg/l | <0,02 | <0,03 | <0,03 | - | - | <0,010 |
| Acenaphthene | µg/l | 3,9 | 4,3 | 4,3 | - | - | 0,31 |
| Fluorene | µg/l | 3,3 | 3,7 | 3,7 | - | - | 0,25 |
| Phenanthrene | µg/l | 7,2 | 7,9 | 7,3 | 0,26 | 0,28 | 0,28 |
| Anthracene | µg/l | 1,2 | 1,4 | 1,3 | 0,07 | 0,056 | 0,065 |
| Fluoranthene | µg/l | 1,6 | 2,1 | 1,8 | 0,51 | 0,51 | 0,49 |
| Pyrene | µg/l | 1 | 1,5 | 1,3 | 0,28 | 0,28 | 0,28 |
| Benz(a)anthracene | µg/l | 0,14 | 0,23 | 0,16 | 0,10 | 0,081 | 0,08 |
| Chrysene/Triphenylene | µg/l | 0,18 | 0,3 | 0,21 | 0,16 | 0,14 | 0,13 |
| Benz(b+j+k)fluoranthene | µg/l | 0,078 | 0,18 | 0,11 | 0,13 | 0,11 | 0,091 |
| Benzo(a)pyrene | µg/l | 0,036 | 0,088 | 0,052 | 0,049 | 0,051 | 0,029 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,02 | 0,046 | 0,028 | 0,023 | 0,032 | 0,014 |
| Dibenz(a,h)anthracene | µg/l | <0,010 | 0,016 | <0,010 | 0,011 | 0,015 | <0,010 |
| Benzo(g,h,i)perylene | µg/l | 0,018 | 0,04 | 0,023 | 0,022 | 0,027 | 0,015 |
| Sum PAH (16 EPA) | µg/l | 30 | 33 | 32 | 1,6 | 1,6 | 2,9 |

| **Industrial soil** | | **Column tests** | | | **Batch tests**<br>**Centrifugation at 27000 in 30 min** | | |
|---|---|---|---|---|---|---|---|
| B&W soil (R-097-04) | | 1. replicate | 2.replicate | 3.replicate | 1. replicate | 2.replicate | 3.replicate |
| Naphthalene | µg/l | 0,13 | 0,11 | 0,1 | 0,013 | 0,013 | 0,017 |
| Acenaphthylene | µg/l | 0,19 | 0,062 | 0,11 | 0,057 | 0,045 | 0,081 |
| Acenaphthene | µg/l | 0,062 | 0,036 | 0,04 | <0,01 | <0,01 | 0,018 |
| Fluorene | µg/l | 0,049 | 0,027 | 0,031 | <0,01 | <0,01 | <0,01 |
| Phenanthrene | µg/l | 0,075 | 0,061 | 0,071 | 0,023 | 0,017 | 0,02 |
| Anthracene | µg/l | 0,21 | 0,067 | 0,098 | 0,057 | 0,05 | 0,055 |
| Fluoranthene | µg/l | 0,073 | 0,067 | 0,089 | 0,066 | 0,073 | 0,079 |
| Pyrene | µg/l | 0,099 | 0,095 | 0,12 | 0,11 | 0,1 | 0,13 |
| Benz(a)anthracene | µg/l | 0,02 | 0,011 | 0,02 | <0,01 | 0,016 | 0,016 |
| Chrysene/Triphenylene | µg/l | 0,035 | 0,023 | 0,034 | 0,026 | 0,026 | 0,041 |
| Benz(b+j+k)fluoranthene | µg/l | 0,05 | 0,023 | 0,062 | 0,031 | 0,032 | 0,1 |
| Benzo(a)pyrene | µg/l | 0,025 | 0,016 | 0,029 | 0,017 | 0,024 | 0,058 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,025 | 0,017 | 0,047 | 0,031 | 0,03 | 0,12 |
| Dibenz(a,h)anthracene | µg/l | <0,010 | <0,010 | <0,010 | <0,01 | <0,01 | 0,014 |
| Benzo(g,h,i)perylene | µg/l | 0,025 | 0,019 | 0,054 | 0,032 | 0,026 | 0,13 |
| Sum PAH (16 EPA) | µg/l | 1,1 | 0,63 | 0,9 | 0,47 | 0,45 | 0,87 |

| **Crushed clay pigeons** | | **Column tests** | | | **Batch tests** | | |
|---|---|---|---|---|---|---|---|
| | | | | | **Centrifugation at 27000 in 30 min** | | |
| (R-107-04) | | 1. replicate | 2.replicate | 3.replicate | 1. replicate | 2.replicate | 3.replicate |
| Naphthalene | µg/l | 9,6 | 10 | 11 | 12 | 5,9 | 9,8 |
| Acenaphthylene | µg/l | 0,086 | 0,099 | 0,074 | 0,082 | 0,036 | 0,064 |
| Acenaphthene | µg/l | 7,2 | 7,5 | 8 | 13 | 7 | 9,4 |
| Fluorene | µg/l | 3,2 | 3,4 | 3,7 | 7,3 | 3,9 | 5 |
| Phenanthrene | µg/l | 10 | 10 | 12 | 37 | 20 | 28 |
| Anthracene | µg/l | 4,2 | 4,2 | 4,4 | 9,3 | 4,8 | 7,2 |
| Fluoranthene | µg/l | 6,7 | 4,7 | 6 | 22 | 12 | 19 |
| Pyrene | µg/l | 5,4 | 3,9 | 4,9 | 18 | 9,9 | 15 |
| Benz(a)anthracene | µg/l | 2,5 | 1,2 | 1,6 | 3,6 | 1,8 | 2,8 |
| Chrysene/Triphenylene | µg/l | 2,4 | 1 | 1,5 | 3,3 | 1,6 | 2,7 |
| Benz(b+j+k)fluoranthene | µg/l | 3,9 | 0,76 | 2,1 | 1,4 | 0,67 | 1,4 |
| Benzo(a)pyrene | µg/l | 1,8 | 0,37 | 0,95 | 0,69 | 0,31 | 0,73 |
| Indeno(1,2,3-cd)pyrene | µg/l | 1,4 | 0,16 | 0,67 | 0,24 | 0,086 | 0,34 |
| Dibenz(a,h)anthracene | µg/l | 0,26 | 0,034 | 0,14 | 0,067 | 0,021 | 0,081 |
| Benzo(g,h,i)perylene | µg/l | 1,2 | 0,11 | 0,55 | 0,21 | 0,06 | 0,27 |
| Sum PAH (16 EPA) | µg/l | 60 | 48 | 58 | 130 | 69 | 100 |

| **Road sweepings** | | **Column tests** | | | **Batch tests** | | |
|---|---|---|---|---|---|---|---|
| | | | | | **Centrifugation at 27000 in 30 min** | | |
| (R-109-04) | | 1. replicate | 2.replicate | 3.replicate | 1. replicate | 2.replicate | 3.replicate |
| Naphthalene | µg/l | 0,11 | 0,082 | 0,078 | 0,2 | 0,087 | 0,089 |
| Acenaphthylene | µg/l | 0,013 | 0,028 | 0,012 | <0,010 | <0,010 | <0,010 |
| Acenaphthene | µg/l | 0,038 | 0,053 | 0,04 | 0,24 | 0,043 | 0,031 |
| Fluorene | µg/l | 0,038 | 0,045 | 0,029 | 0,18 | 0,033 | 0,021 |
| Phenanthrene | µg/l | 0,13 | 0,18 | 0,14 | 0,82 | 0,14 | 0,095 |
| Anthracene | µg/l | 0,03 | 0,045 | 0,043 | 0,13 | 0,032 | 0,029 |
| Fluoranthene | µg/l | 0,07 | 0,14 | 0,099 | 0,24 | 0,1 | 0,069 |
| Pyrene | µg/l | 0,066 | 0,12 | 0,09 | 0,19 | 0,092 | 0,064 |
| Benz(a)anthracene | µg/l | <0,010 | 0,037 | 0,017 | 0,018 | 0,015 | 0,013 |
| Chrysene/Triphenylene | µg/l | 0,011 | 0,038 | 0,028 | 0,032 | 0,026 | 0,021 |
| Benz(b+j+k)fluoranthene | µg/l | <0,010 | 0,066 | 0,028 | 0,025 | 0,028 | 0,025 |
| Benzo(a)pyrene | µg/l | <0,010 | 0,033 | 0,012 | 0,012 | 0,011 | 0,011 |
| Indeno(1,2,3-cd)pyrene | µg/l | <0,010 | 0,028 | 0,013 | <0,010 | 0,011 | 0,01 |
| Dibenz(a,h)anthracene | µg/l | <0,010 | <0,010 | <0,010 | <0,010 | <0,010 | <0,010 |
| Benzo(g,h,i)perylene | µg/l | <0,010 | 0,019 | <0,010 | <0,010 | <0,010 | <0,010 |
| Sum PAH (16 EPA) | µg/l | 0,51 | 0,91 | 0,63 | 2,1 | 0,62 | 0,48 |

# APPENDIX E

## Detailed results from testing column and batch methods at Nordic laboratories

## *Test informations:*

## Column tests and batch tests performed at DHI

*Detailed test conditions for column tests performed as replicates*

| **Clay pigeon contaminated soil (R-132-03)** | **Column 1** | **Column 2** | **Column 3** |
|---|---|---|---|
| Dry matter content (g/kg) | 724 | 724 | 724 |
| Water content (g/kg) | 276 | 276 | 276 |
| | | | |
| Filtersand – bottom of the column (g) | 32,44 | 31,17 | 30,23 |
| Filtersand - top of the column (g) | 70,58 | 59,73 | 57,06 |
| Contact time (days) | 7 | 7 | 7 |
| Test portion, wet mass (g) | 543,53 | 543,71 | 550,03 |
| Test portion, dry mass (g TS) | 454,2 | 454,4 | 459,6 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Concentration of NaN3 in the eluent (g/l) | 0,5 | 0,5 | 0,5 |
| Total amount of eluent (g) | 489,3 | 516,2 | 528,8 |
| Flow velocity (ml/h) | 20,7 | 20,5 | 19,57 |
| L/S-ratio | 1,1 | 1,1 | 1,2 |
| | | | |
| **Eluate** | | | |
| pH | 7,8 | 7,7 | 7,7 |
| Turbidity (NTU) | 1,77 | 3,52 | 3,14 |
| Conductivity (mS/cm) | 130 | 130 | 130 |

*Detailed test conditions for batch tests performed as replicates*

| **Clay pigeon contaminated soil (R-132-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** |
|---|---|---|---|
| Dry matter content (g/kg) | 724 | 724 | 724 |
| Water content (g/kg) | 276 | 276 | 276 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 308 | 304 | 307 |
| Eluent (ml) | 494 | 489 | 506 |
| Contact time (hours) | 24 | 24 | 24 |
| L/S-ratio | 2 | 2 | 2 |
| Centrifugation ( force (g)/time (min)) | 6200 / 60 | 6200 / 60 | 6200 / 60 |
| **Eluate** | | | |
| pH | 7,8 | 7,7 | 7,7 |
| Turbidity (NTU) | 1,77 | 3,5 | 3,1 |
| Conductivity (mS/m) | 130 | 130 | 130 |

## Column tests performed at VTT

*Detailed test conditions for column tests performed as replicates*

| | **Column 1** | **Column 2** | **Column 3** |
|---|---|---|---|
| Start of test (date) | 11.5.2004 | 25.5.2004 | 2.6.2004 |
| L/S ratio | 1,0 | 1,0 | 1,0 |
| pH (eluate) | 7,48 | 7,47 | 7,60 |
| Turbidity | 1,68 | - | 2,48 |
| conductivity (eluate), mS/m (25 $^{o}$C) | 184,6 | 162,08 | 170,3 |
| redox (eluate), mV | 353 | 422 | 382 |
| Remark | Air bubbles appeared in beginning of test | Cracks in the lid of column. The lid was replaced during test (on second testing day). Soil material appeared above glass pearls after change of lid. Note! Only small loss of eluate during change of lid. | Air bubbles appeared during the whole test |
| Remarks | Flow rate not constant | Flow rate not constant | Flow rate not constant |

## Batch tests performed at NGI

*Detailed test conditions for batch tests performed as replicates*

| **B&W soil (R-097-03)** | **1. Replicate** | **2. Replicate** | **3. Replicate** |
|---|---|---|---|
| Dry matter content (g/kg) | 724 | 724 | 724 |
| Water content (g/kg) | 276 | 276 | 276 |
| Concentration of CaCl2 in the eluent (M) | 0,005 | 0,005 | 0,005 |
| Test portion (g) | 560 | 560 | 560 |
| Eluent (ml) | 841,7 | 841,3 | 841,8 |
| Contact time (hours) | 24 | 24 | 24 |
| L/S-ratio | 2,00 | 2,00 | 2,00 |
| Centrifugation ( force (g)/time (min)) | 2807/144 | 2807/144 | 2807/144 |
| **Eluate** | | | |
| pH | 7,3 | 7,3 | 7,3 |
| Turbidity (NTU) | 5,02 | 5,16 | 4,88 |
| Conductivity (mS/m) | 129,9 | 128,0 | 130,0 |

## *Results for tests:*

Column tests and batch tests performed at DHI:

**Column tests**

| | | 1. Replicate | 2. Replicate | 3. Replicate | Average | STD | Rel. std (%) |
|---|---|---|---|---|---|---|---|
| Naphthalene | µg/l | 6,3 | 5,7 | 7 | 6 | 0,65 | 10 |
| Acenaphthylene | µg/l | <0,02 | <0,02 | <0,02 | <0,02 | - | - |
| Acenaphthene | µg/l | 2,6 | 2,3 | 2,8 | 2,6 | 0,25 | 10 |
| Fluorene | µg/l | 2,2 | 1,9 | 2,3 | 2,1 | 0,21 | 10 |
| Phenanthrene | µg/l | 4,5 | 3,9 | 4,6 | 4,3 | 0,38 | 9 |
| Anthracene | µg/l | 0,9 | 0,86 | 0,93 | 0,9 | 0,035 | 4 |
| Fluoranthene | µg/l | 1,2 | 1,3 | 1,3 | 1,3 | 0,058 | 5 |
| Pyrene | µg/l | 0,75 | 0,84 | 0,81 | 0,8 | 0,046 | 6 |
| Benz(a)anthracene | µg/l | 0,16 | 0,19 | 0,16 | 0,17 | 0,017 | 10 |
| Chrysene/Triphenylene | µg/l | 0,2 | 0,22 | 0,2 | 0,21 | 0,012 | 6 |
| Benz(b+j+k)fluoranthene | µg/l | 0,11 | 0,14 | 0,11 | 0,12 | 0,017 | 14 |
| Benzo(a)pyrene | µg/l | 0,051 | 0,064 | 0,052 | 0,056 | 0,0072 | 13 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,02 | 0,03 | 0,023 | 0,024 | 0,0051 | 21 |
| Dibenz(a,h)anthracene | µg/l | <0,01 | <0,01 | <0,01 | <0,010 | - | - |
| Benzo(g,h,i)perylene | µg/l | 0,017 | 0,028 | 0,015 | 0,020 | 0,007 | 35 |
| Sum PAH (16 EPA) | µg/l | 19 | 17 | 20 | 19 | 1,5 | 8 |
| | | | | | | | |
| NVOC | mg/l | 55 | 43 | 41 | 46,33 | 7,6 | 16 |
| Fe | µg/l | 74 | 46 | 36 | 52 | 20 | 38 |

**Batch test** **6200 g for 60 min**

| | | 1. Replicate | 2. Replicate | 3. Replicate | Average | STD | Rel. std (%) |
|---|---|---|---|---|---|---|---|
| Naphthalene | µg/l | 1,3 | 1,1 | 1,1 | 1,166667 | 0,12 | 10 |
| Acenaphthylene | µg/l | <0,02 | <0,02 | <0,02 | 0,02 | - | - |
| Acenaphthene | µg/l | 0,6 | 0,58 | 0,48 | 0,55 | 0,064 | 12 |
| Fluorene | µg/l | 0,49 | 0,48 | 0,37 | 0,45 | 0,067 | 15 |
| Phenanthrene | µg/l | 0,69 | 0,5 | 0,41 | 0,53 | 0,14 | 27 |
| Anthracene | µg/l | 0,12 | 0,15 | 0,12 | 0,130 | 0,017 | 13 |
| Fluoranthene | µg/l | 0,32 | 0,27 | 0,25 | 0,28 | 0,036 | 13 |
| Pyrene | µg/l | 0,22 | 0,16 | 0,15 | 0,18 | 0,038 | 21 |
| Benz(a)anthracene | µg/l | 0,14 | 0,14 | 0,12 | 0,13 | 0,012 | 9 |
| Chrysene/Triphenylene | µg/l | 0,2 | 0,21 | 0,17 | 0,19 | 0,021 | 11 |
| Benz(b+j+k)fluoranthene | µg/l | 0,25 | 0,27 | 0,22 | 0,25 | 0,025 | 10 |
| Benzo(a)pyrene | µg/l | 0,12 | 0,13 | 0,11 | 0,120 | 0,01 | 8 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,084 | 0,093 | 0,077 | 0,085 | 0,0080 | 9 |
| Dibenz(a,h)anthracene | µg/l | <0,02 | 0,022 | 0,021 | 0,022 | 0,00071 | 3 |
| Benzo(g,h,i)perylene | µg/l | 0,064 | 0,071 | 0,061 | 0,065 | 0,0051 | 8 |
| Sum PAH (16 EPA) | µg/l | 4,6 | 4,2 | 3,7 | 4,17 | 0,45 | 11 |
| | | | | | | | |
| NVOC | mg/l | 6,4 | 7 | 6,9 | 6,77 | 0,32 | 5 |
| Fe | µg/l | 300 | 160 | 170 | 210 | 78 | 37 |

## Column tests performed at VTT:

| | | 1. replicate | 2. replicate | 3. replicate | Average | STD | Rel. std (%) |
|---|---|---|---|---|---|---|---|
| Naphthalene | µg/l | 4,3 | | 2,1 | 3 | 1,6 | 49 |
| Acenaphthylene | µg/l | <0,02 | | <0,05 | 0,02 | - | - |
| Acenaphthene | µg/l | 1,9 | | 1,1 | 1,5 | 0,57 | 38 |
| Fluorene | µg/l | 1,7 | | 0,82 | 1,3 | 0,62 | 49 |
| Phenanthrene | µg/l | 3,4 | | 1,6 | 2,5 | 1,3 | 51 |
| Anthracene | µg/l | 0,61 | | 0,33 | 0,5 | 0,20 | 42 |
| Fluoranthene | µg/l | 1,4 | | 0,62 | 1,0 | 0,55 | 55 |
| Pyrene | µg/l | 0,94 | | 0,41 | 0,7 | 0,37 | 56 |
| Benz(a)anthracene | µg/l | 0,19 | | 0,086 | 0,14 | 0,074 | 53 |
| Chrysene/Triphenylene | µg/l | 0,25 | | 0,11 | 0,18 | 0,099 | 55 |
| Benz(b+j+k)fluoranthene | µg/l | 0,22 | | 0,081 | 0,15 | 0,098 | 65 |
| Benzo(a)pyrene | µg/l | 0,097 | | 0,032 | 0,065 | 0,046 | 71 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,053 | | 0,02 | 0,037 | 0,023 | 64 |
| Dibenz(a,h)anthracene | µg/l | <0,02 | | <0,01 | 0,020 | - | - |
| Benzo(g,h,i)perylene | µg/l | 0,053 | | 0,014 | 0,034 | 0,028 | 82 |
| Sum PAH (16 EPA) | µg/l | 15 | | 7,3 | 11 | 5,4 | 49 |
| NVOC | mg/l | 41 | | 27 | | | |

**Replicate no. 2. was lost shipping the eluates from VTT to DHI.**

## Batch tests performed at NGI:

Batch tests

| | | 1. replicate | 2. replicate | 3. replicate | Average | STD | Rel. std (%) |
|---|---|---|---|---|---|---|---|
| Naphthalene | µg/l | <0,01 | <0,01 | <0,01 | <0,01 | - | - |
| Acenaphthylene | µg/l | <0,01 | <0,01 | <0,01 | <0,01 | - | - |
| Acenaphthene | µg/l | <0,01 | <0,01 | <0,01 | <0,01 | - | - |
| Fluorene | µg/l | <0,01 | <0,01 | <0,01 | <0,01 | - | - |
| Phenanthrene | µg/l | 0,033 | 0,045 | 0,038 | 0,04 | 0,0060 | 16 |
| Anthracene | µg/l | <0,01 | 0,012 | 0,01 | 0,011 | 0,0014 | 13 |
| Fluoranthene | µg/l | 0,12 | 0,17 | 0,15 | 0,15 | 0,025 | 17 |
| Pyrene | µg/l | 0,11 | 0,17 | 0,14 | 0,14 | 0,030 | 21 |
| Benz(a)anthracene | µg/l | 0,12 | 0,16 | 0,14 | 0,14 | 0,020 | 14 |
| Chrysene/Triphenylene | µg/l | 0,19 | 0,24 | 0,2 | 0,21 | 0,026 | 13 |
| Benz(b+j+k)fluoranthene | µg/l | 0,46 | 0,55 | 0,47 | 0,49 | 0,049 | 10 |
| Benzo(a)pyrene | µg/l | 0,22 | 0,27 | 0,23 | 0,240 | 0,026 | 11 |
| Indeno(1,2,3-cd)pyrene | µg/l | 0,19 | 0,21 | 0,18 | 0,193 | 0,015 | 8 |
| Dibenz(a,h)anthracene | µg/l | 0,036 | 0,046 | 0,04 | 0,041 | 0,0050 | 12 |
| Benzo(g,h,i)perylene | µg/l | 0,14 | 0,18 | 0,15 | 0,157 | 0,021 | 13 |
| Sum PAH (16 EPA) | µg/l | 1,6 | 2,1 | 1,7 | 1,80 | 0,26 | 15 |
| NVOC | mg/l | 6,1 | 7 | 6,5 | 6,5 | 0,45 | 6,9 |

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