Remediation of Materials with Mixed Contaminants
Kristin Elgh-Dalgren

Remediation of Materials with Mixed Contaminants
Treatability, Technology and Final Disposal
ABSTRACT

Contaminated soils are a large issue worldwide and much effort has been made to find efficient remediation methods. At many contaminated sites, mixtures of different contaminants with different properties are present, which may lead to additional problems, and thus additional costs, during the remediation process. This thesis presents the results from soil remediation of two mixed contaminated soils, containing explosives and heavy metals and polycyclic aromatic hydrocarbons (PAH) and arsenic, respectively. The results demonstrate that bioremediation may be an efficient method for moderate explosives concentration, but that too high contaminant concentrations may prevent the biodegradation, measured by both chemical and ecotoxicological analyses. If the contaminant concentration is very high, soil washing with alkaline pH (~12, NaOH) may be a good alternative, which was observed to remove both explosives and heavy metals.

For a PAH and arsenic contaminated soil, little degradation of organics was observed during the bioremediation. However, the arsenic present was re-distributed in the soil, which could potentially lead to increased availability and thus increased risk for contaminant spreading. Soil washing at alkaline pH (~12-13; Ca(OH)$_2$) with a combination of a biodegradable non-ionic surfactant and a biodegradable chelating agent, executed at high temperature (50°C), reached treatment goals for both arsenic and PAH after 10 min treatment. Measurement of ecotoxicity using Microtox® demonstrated that remaining surfactant in the soil may lead to increased toxicity despite lower contaminant concentrations.

Soil is a basically non-renewable resource and thus re-cycling of remediated soil ought to be commonly occurring. Yet, the re-cycling of remediated masses has so far been limited in Sweden, mainly because of the risk of spreading of pollutant remains. However, a recent proposition from the Swedish EPA opens for re-cycling, even though the thresholds are very conservative. Risk assessment of the remediated soil includes the utilization of leaching tests to estimate the risk of spreading of remaining pollutants. A comparison of the leaching from four remediated soils using three different leaching solutions reveals that leaching of both heavy metals and PAH occurs. In addition, differences between different legislations were observed, which could imply that the same soil could be re-cycled in one country (the Netherlands) but not another (Sweden).

Keywords: Bioremediation, Microtox®, mixed contaminants, re-cycling, soil remediation, soil washing.
LIST OF PAPERS

This thesis is based on the following papers, which are referred to in the text by their roman numerals:


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1. BACKGROUND

Soil contamination is a large issue worldwide. Only in Sweden, more than 80,000 contaminated sites have been identified, of which approximately 1,400 are estimated to pose a very large risk to human health and the environment and needs to be remediated (S-EPA, 2009). All soil remediation require large financial resources and the presence of both organic and inorganic pollutants simultaneously may add to the costs considerably. Many industrial processes are known where mixtures of chemicals have been used, e.g. wood preservation (creosote and salts containing chromium, copper and arsenic, CCA), military activities (explosives and different heavy metals) and the chloralkali industry (dioxins and mercury). The U.S. Environmental protection agency (EPA) has reported that a mixture of both organic and inorganic contaminants is present at almost 50% of the superfund sites (US-EPA, 1997), which could be expected also in Sweden. Because of the different chemical and physical properties of organic and inorganic compounds, remediation of these sites may be difficult. Organic compounds are biodegradable, even though the susceptibility to biologic attack varies between different compounds. Many organic contaminants are lipophilic and their water solubilities are low, which implies that they are strongly adsorbed to soil particles and has a low bioavailability (Alexander, 1999). Inorganic contaminants, on the other hand, cannot be degraded, but their distribution and speciation are dependent on environmental factors such as pH and redox potential (McBride, 1994). Furthermore, the efficacy of a soil remediation activity is governed by different soil properties, such as soil texture (clay content), content of organic material, pH etc., which may play a large role in the adsorption of both organic and inorganic compounds (Nam et al., 1998; You et al., 1999). Most available soil remediation techniques, on the other hand, are adapted to single compound systems. If a mixture of different contaminants is present, more treatment steps may be required, implying increased costs (Khodadous et al., 2005; Maturi and Reddy, 2008).

1.1. Contaminants

Military sites

Mixtures of different explosives (e.g. 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX)) and heavy metals are often found simultaneously at old military sites. Explosives have been produced in large quantities since the beginning of the 20th century and are regularly found at sites where production and handling of these has taken place (Lewis et al., 2004). Due to their persistence and toxicity (Pennington and
Brannon, 2002; Rodgers and Bunce, 2001), explosives may remain in the environment and cause damage during long time. Selected properties of the explosives in this study are displayed in Table 1. The simultaneous presence of heavy metals at military sites may be a result of heavy metals containing casings, blasting caps and ammunition (Sunahara et al., 1999). Amongst others, lead (Pb), copper (Cu), zinc (Zn) and cadmium (Cd) are regularly found. Heavy metals are naturally occurring elements, but they have been enriched by anthropogenic activities such as mining and are spread in society by a large number of sources including agriculture and waste incineration and are now found both as global and local contaminants (S-EPA, 1993).

Table 1. Selected properties of the explosives in this study (Meyers, 2000).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight</th>
<th>Water solubility (mg/l)</th>
<th>Log K_{ow}</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explosives</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TNT</td>
<td>227</td>
<td>130</td>
<td>1.8</td>
<td>[Structure]</td>
</tr>
<tr>
<td>RDX</td>
<td>222</td>
<td>42</td>
<td>0.86</td>
<td>[Structure]</td>
</tr>
<tr>
<td>HMX</td>
<td>296</td>
<td>5</td>
<td>0.061</td>
<td>[Structure]</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>182</td>
<td>270</td>
<td>2.0</td>
<td>[Structure]</td>
</tr>
</tbody>
</table>

Wood preservation sites
In order to increase the longevity of outdoor constructions, wood preservation has been used in society for extended time. Creosote, which is produced from coal tar, has regularly been utilized to preserve timber, but restrictions have been introduced due to its toxicity (KIFS, 1998). The main cause is the content of different polycyclic aromatic hydrocarbons (PAH) which represent a vast group of organic contaminants consisting of carbon and oxygen arranged in cyclic or aromatic structures of two rings and more. Some of the PAH have been found to be both carcinogenic and mutagenic, especially some of the high molecular weight (HMW; 4-6 rings) congeners (Connell, 1997; Juhasz and Naidu, 2000). In general, 16 different PAH, which have been assigned priority pollutants by the U.S. EPA, are considered, and selected properties of these are displayed in Table 2.
Table 2. Selected properties of the 16 U.S. EPA priority PAH (ATSDR, 1995). The Swedish division into low (L), medium (M) and high (H) molecular weight PAH is also displayed.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight</th>
<th>Water solubility (mg/l)</th>
<th>Log K&lt;sub&gt;ow&lt;/sub&gt;</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PAH-L</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>128</td>
<td>31</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Acenaphtene</td>
<td>154</td>
<td>1.9</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>152</td>
<td>3.9</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td><strong>PAH-M</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorene</td>
<td>166</td>
<td>2.0</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>178</td>
<td>1.2</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>178</td>
<td>0.076</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>202</td>
<td>0.26</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>202</td>
<td>0.077</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td><strong>PAH-H</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>228</td>
<td>0.010</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td>228</td>
<td>0.0028</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>252</td>
<td>0.0012</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>252</td>
<td>0.00076</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>252</td>
<td>0.0023</td>
<td>6.06</td>
<td></td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>276</td>
<td>0.062</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>278</td>
<td>0.0005</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>278</td>
<td>0.00026</td>
<td>6.5</td>
<td></td>
</tr>
</tbody>
</table>

Another frequently utilized wood preservative is a mixture of different heavy metals salts, normally copper, chromium and arsenic (CCA). However, also this utilization has been restricted due to the toxicity of especially arsenic (KIFS, 1998). Arsenic has also been demonstrated to migrate from treated wood con-
structions, which may imply spreading of this to the surrounding environment (Townsend et al., 2003).

1.2. Soil remediation techniques
Many different soil remediation techniques have been developed as a result of the increased awareness of soil pollution. Treatment of the soil in situ, where the soil is left in place while treating it, is desirable since the economic and environmental cost of the transportation may be avoided. However, in Sweden, the driving force behind much remediation is often a change in land-use. Historically, many industries were located near water in order to facilitate transport, and these sites are today increasingly exploited as residential areas as a part in large redevelopment schemes. Therefore, most remediation in Sweden is performed ex situ and off site, where the soil is dug up and treated elsewhere. Except for the removal capacity for the pollutants, it is important that the remediation technology is cost efficient and that new applications could be found for the soil after the treatment.

Bioremediation
Bioremediation utilizes microbes (bacteria, fungi etc.) which possess the ability to degrade organic compounds. Many different bioremediation techniques have been developed, but somewhat simplified two main concepts can be distinguished: biostimulation and bioaugmentation. For biostimulation, the inherent microbial population in the soil is utilized to degrade the pollutants. By changing different soil environmental factors, such as pH, water content, availability of nutrients or target contaminants, the activity of the native microorganisms is enhanced and thus the biodegradation made possible. Bioaugmentation, on the other hand, utilizes specially adapted bacteria or fungi, which are inoculated into the soil. The susceptibility of different contaminants to biological attack has been studied extensively in the literature. Both different explosives (Lewis et al., 2004; Spain et al., 2000) and PAH (Carriere and Mesana, 1996; Potter et al., 1999) have been shown to be degradable under certain conditions. For explosives, especially low oxygen availability (low redox potential) has been demonstrated to enhance the degradation (Bruns-Nagel et al., 1998). For PAH, on the other hand, aerobic remediation has shown the most promising results, even though the remediation of HMW PAH has been rarely recognized (Antizar-Ladislao et al., 2005). In addition to the degradation of organic compounds, bioremediation may affect the heavy metals and metalloids present in the soil. Microbial transformation of the less mobile arsenate (AsO$_4^{3-}$) to the more mobile arsenite (AsO$_3^{3-}$) has been suggested as a remediation method (bioleaching; Yamamura et al., 2005),
but without sufficient supervision, it could lead to spreading of arsenic into the surrounding environment and groundwater. Furthermore, elevated heavy metals concentration may imply toxicity to the soil living organisms, and thereby delay or prevent the degradation (Doelman and Haanstra, 1979; Roberts et al., 1998). The main advantage of bioremediation is the comparably low costs involved. Except for the labor necessary to construct the treatment piles, only comparably small amounts of additives are often necessary. Furthermore, the process does not imply large impact on the overall soil functions, which means that it can often be re-used. On the other hand, the bioremediation process may take long time, which can have consequences for future land-use at the treatment site if other projects are delayed. In addition, the biodegradation may result in unwanted degradation products, which at times are more toxic and recalcitrant than the mother compounds (Frische, 2002; Lundstedt et al., 2007; McConkey et al., 1997; Rodgers and Bunce, 2001; US-EPA, 1991a).

**Soil washing**

Soil washing is a soil remediation technique which in its simplest form is a physical separation of different soil particle sizes (Griffiths, 1995; US-EPA, 1991b). The larger relative surface area of the smaller soil particles compared to the larger ones implies that more contaminants can be adsorbed to the finest soil particles. Therefore, a separation of different soil particle sizes may in many cases be sufficient to get a clean over-sized fraction, and concentrate the contaminants in the fine fraction. However, this treatment is sometimes not enough, for example due to the presence of free non-aqueous phase liquids (NAPL), if the clay content is very high or in cases with very severe contamination (Sharma and Reddy, 2004). In such cases, addition of different amendments which facilitates the transport of contaminants into the soil washing solution may be necessary. Utilization of different amendments has been extensively evaluated in the literature, but to find a method which is applicable in real full scale operations, the amendment must also be environmentally friendly, cheap and it cannot be corrosive or possess a problem to the workers. Among amendments utilized are different complexing agents for heavy metals (e.g. ethylenediaminetetraacetic acid, EDTA; Heil et al., 1999; Lestan et al., 2008) and oxalic acid for arsenic (Bhattacharya et al., 2002). An EDTA-solution implies formation of soluble and mobile metal complexes, which are thus easily separated from the solid phase. EDTA has during the recent years, however, been questioned due to its low biodegradability, and more easily degradable chelating agents have been proposed, such as [S,S]-ethylenediaminedi-succinate (EDDS) and methylglycinediacetic acid (MGDA; Arwidsson et al.,...
2009; Tandy et al., 2004). The main mechanism behind arsenic-removal at oxalate-addition is through complexation of the iron in the soil, onto which the arsenic is strongly bound (Bhattacharya et al., 2002; Tao et al., 2006). For organic contaminants, surfactants have been widely evaluated for their ability to mobilize lipophilic compounds. This mobilization is achieved through the creation of micelles, which takes place at a concentration called the critical micelle concentration (CMC), unique for each surfactant (Paria, 2008). In addition, pH-adjustment may imply both heavy metal mobilization (McBride, 1994) and degradation of explosives (alkaline hydrolysis; Emmrich, 1999; Heilmann et al., 1996). Soil washing is a comparably fast treatment technology, and thus the costs for soil storage may be kept down. It also produces well characterized soil fractions which could be used in for example construction works. The main constraint against soil washing is that it may need additives if the soil or pollutant matrices are complex, or if the content of clay or organic matter is high, which may add to the costs considerably. In addition, remaining additives in the soil may affect the distribution and availability of residual contaminants in the soil after treatment.

1.3. Ecotoxicological analysis

In most risk assessment, only the total concentration of contaminants is considered (chemical analysis). Whilst giving knowledge of target compounds, these analyses lack information about other compounds, as well as information of contaminant availability. Therefore, the utilization of toxicity test has been increasingly implemented in soil remediation (Phillips et al., 2000a; Plaza et al., 2005). Toxicity tests do not indicate the effect of specific compounds, but rather the overall effect of the soil or a soil leachate on specific organisms. In soil remediation, a commonly utilized test is the Microtox®-test, where the bioluminescent bacterium *Vibrio fischeri* (ISO 11348:3) is used. By exposing the bacteria to a soil leachate, the survival rate of these can be measured as a result of luminescence changes, and an IC$_{50}$-value (where a 50% decrease in survival is observed) can be calculated. This information, in addition to the chemical analysis, gives a good picture of the overall soil health status and has also been utilized to evaluate the success of soil remediation of both organic and inorganic contaminants (Frische, 2003; Mendonça and Picardo, 2002; Phillips et al., 2000b).

1.4. Remediation goals and re-cycling

The future land use at the site is essential in Swedish risk assessment and different threshold values exist for different situations. In areas intended for residential areas, playgrounds etc, threshold values labeled KM (*känslig markanvändning;*
sensitive land use) are applied, whereas areas intended for offices, roads or industrial areas are designated MKM-values (mindre känslig markanvändning; less sensitive land use; S-EPA, 1999). In the present study, the MKM-values will serve as remediation goals for heavy metals and PAH. Due to a recent revision of the threshold values, As and PAH-values are adopted from the newer version whereas the heavy metals-values are derived from the older version (S-EPA, 1999; S-EPA, 2007a). For explosives, 2,4-DNT is the only compound with a Swedish MKM-value and for that reason, US-EPA Region III, risk based concentrations are utilized as remediation goals (US-EPA, 2007). All remediation goals utilized in the present study are listed in Table 3. It should however be clarified that in a real remediation situation, KM and MKM threshold values are rarely utilized as remediation goals. Instead, these thresholds have mainly been used for risk assessment of the contaminated soil and as guidelines during the excavation of the polluted site. When the soil has been removed, and is in the hands of the remediation company, the soil is often only treated sufficiently to reduce land filling costs (e.g. by minimizing contaminant leaching from the soil).

<table>
<thead>
<tr>
<th></th>
<th>Swedish MKM (mg/kg)</th>
<th>US-EPA Region III (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy metal(loid)s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>300</td>
<td>21</td>
</tr>
<tr>
<td>Cu</td>
<td>200</td>
<td>5.9</td>
</tr>
<tr>
<td>Zn</td>
<td>700</td>
<td>3900</td>
</tr>
<tr>
<td>Cd</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>As</td>
<td>25</td>
<td>160</td>
</tr>
<tr>
<td>Explosives</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TNT</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>RDX</td>
<td>-</td>
<td>5.9</td>
</tr>
<tr>
<td>HMX</td>
<td>-</td>
<td>3900</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>20</td>
<td>160</td>
</tr>
<tr>
<td>PAH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAH-L</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>PAH-M</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>PAH-H</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

The possible re-cycling of remediated soil has been debated frequently over the last years, mainly since large quantities of possibly treatable and re-usable soil is landfilled instead of re-cycled every year in Sweden (S-EPA, 2006). The main constraint against re-cycling is the possible spreading of pollutant remains from the
masses, but the good availability of comparably cheap, virgin construction material in Sweden has probably also had an influence. On the contrary, several countries, e.g. the Netherlands and Denmark, have developed tools to overcome these problems and thereby allow re-cycling of remediated masses as construction materials, fully or with restrictions. In many of these countries, leaching tests are utilized to assess the re-usability of the masses, in addition to total concentration measurements (Miljøministeriet, 2007; VROM, 1995). Utilization of leaching tests has also been suggested as an integrated part in the recent proposal by the Swedish EPA, which opens for the re-cycling of masses in Sweden (S-EPA, 2007b). One limitation of the new S-EPA proposal is, however, the lack of leaching criteria for organic contaminants. PAH and other organic contaminants have been shown to be mobilized during leaching procedures (Kim and Osako, 2003), however in both the Swedish proposal and in for example the Dutch legislation (VROM), the leaching of organic contaminants is not taken into account.

1.5. Objectives of this thesis
The overall objective of this thesis was to study the remediation of soils industrially contaminated by a mixture of both organic and inorganic contaminants. In addition, the future perspective of remediated soil, especially the possibility of re-cycling, was to be explored. These objectives will be achieved by:

- Studying and evaluating the possibility to degrade organic contaminants by commercially available bioremediation techniques, and the effect of or on the simultaneously present metal(loid)s.
- Utilizing soil washing to simultaneously remove both organic and inorganic contaminants from different industrially contaminated soils.
- Exploring re-cycling of remediated masses in Sweden, both in relation to current legislation and by utilization of leaching tests on real, remediated soils containing both organics and heavy metals.
2. MATERIALS AND METHODS

2.1. Soils
For the remediation experiments, two industrially contaminated soils with a mixture of organic and inorganic contaminants were utilized. The first soil (Paper I and II) was sampled at an old open burning/open destruction field at Bofors Test Center (BTC), Karlskoga, Sweden, and sampling was performed in two filling layers (the highly contaminated upper layer soil, UL, and the moderately contaminated bottom layer soil, BL). The second soil (Paper III and IV) was collected at an old wood preservation site in Elnaryd, Värnamo, Sweden. Both soils were sieved through a 2 mm mesh, thoroughly homogenized and stored in closed containers. In the study of the leaching behavior of already remediated soil, four different soils which had undergone large scale soil washing were utilized (Paper VI). Soil A-C were contaminated by heavy metals and soil D with PAH. These soils were sieved through a 4 mm mesh and homogenized before treatment. Selected chemical and physical characteristics of all soils are summarized in Table 4.

2.2. Bioremediation
To study the possibility to degrade the organic contaminants in the BTC and Elnaryd-soils, different commercially available bioremediation techniques were evaluated in laboratory scale. A summary of the experimental setup is displayed in Table 5. For the explosives and heavy metal-contaminated BTC-soil (Paper I), three different anaerobic treatment techniques were evaluated on each of the soil fractions (UL and BL). Treatments included commercial method Daramend\textsuperscript{®} amended with zero-valent iron (ZVI) to obtain anaerobicity (Daramend\textsuperscript{®}-systems), ZVI alone (ZVI-systems) or composting. To the treatments intended for Daramend\textsuperscript{®}, ZVI and control treatments (without amendments), deionized water (MQ) corresponding to 80\% of the water holding capacity (WHC) was added and the pH was sustained at 6.5-8. In the compost treatments, no pH-adjustment was made and anaerobic conditions were achieved through water logging. Initially, the soils were added 2\%\textsubscript{w/w} Daramend\textsuperscript{®}-granules and 0.5\%\textsubscript{w/w} ZVI-filings (Daramend\textsuperscript{®}-systems), 0.5\%\textsubscript{w/w} ZVI-filings (ZVI-systems), or 20\%\textsubscript{w/w} horse manure (compost-systems). No amendments were added to the control systems. During the experiments, additional Daramend\textsuperscript{®} and ZVI (as powder; Daramend\textsuperscript{®}-systems), ZVI (powdered; ZVI-systems) and glucose (compost-systems) were added. The jars were left for 20 weeks and samples for explosives analysis were withdrawn after 5, 10, 15 and 20 weeks.
<table>
<thead>
<tr>
<th></th>
<th>BTC</th>
<th>Elnaryd</th>
<th>Soil A</th>
<th>Soil B</th>
<th>Soil C</th>
<th>Soil D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
<td>5.0</td>
<td>6.5</td>
<td>6.6</td>
<td>7.5</td>
<td>7.1</td>
<td>7.1</td>
</tr>
<tr>
<td><strong>Moisture content (%)</strong></td>
<td>11</td>
<td>18</td>
<td>5</td>
<td>0.8</td>
<td>4.7</td>
<td>7.3</td>
</tr>
<tr>
<td><strong>LoI (%)</strong></td>
<td>20</td>
<td>12</td>
<td>1.1</td>
<td>1.4</td>
<td>0.5</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>WHC (%)</strong></td>
<td>75</td>
<td>88</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Particle size distribution (%)</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1 mm</td>
<td>2</td>
<td>12</td>
<td>17</td>
<td>21</td>
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<tr>
<td>500 µm</td>
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<tr>
<td>250 µm</td>
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<tr>
<td>125 µm</td>
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<tr>
<td>63 µm</td>
<td>7</td>
<td>8</td>
<td>3</td>
<td>1</td>
<td>8</td>
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<tr>
<td>&lt;63 µm</td>
<td>76</td>
<td>47</td>
<td>9</td>
<td>2</td>
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<tr>
<td><strong>Explosives (mg/kg)</strong></td>
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<tr>
<td>HMX</td>
<td>6,080±190</td>
<td>230±10</td>
<td>—</td>
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<tr>
<td>RDX</td>
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<td>1,340±80</td>
<td>—</td>
<td>—</td>
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<td>TNT</td>
<td>3,120±140</td>
<td>450±20</td>
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<tr>
<td>2,4-DNT</td>
<td>1,200±50</td>
<td>120±3</td>
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<td><strong>PAH (mg/kg)</strong></td>
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<td>PAH-L</td>
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<td>0.4±0.1</td>
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<td>PAH-M</td>
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<td>19±1.2</td>
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<td>PAH-H</td>
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<td>27±0.7</td>
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<td><strong>Heavy metals (mg/kg)</strong></td>
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<tr>
<td>Pb</td>
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<tr>
<td>Cu</td>
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<td>940±270</td>
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<tr>
<td>Zn</td>
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<td>140±15</td>
<td>96±10</td>
<td>1,780±80</td>
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<td>170±30</td>
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<tr>
<td>Cd</td>
<td>9±0.0</td>
<td>9±0.0</td>
<td>—</td>
<td>13±1</td>
<td>15±1</td>
<td>19±3</td>
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<tr>
<td>As</td>
<td>6±0.3</td>
<td>2±0.9</td>
<td>105±4</td>
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Table 5. Original experimental setup of the bioremediation experiments (Paper I and III).

<table>
<thead>
<tr>
<th>BTC-treatment (Paper I)</th>
<th>MQ</th>
<th>Daramend® 6390a</th>
<th>ZVib</th>
<th>Horse manurec</th>
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<tbody>
<tr>
<td>Daramend®</td>
<td>80% WHC</td>
<td>x</td>
<td>x</td>
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<tr>
<td>ZVI</td>
<td>80% WHC</td>
<td>x</td>
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<tr>
<td>Compost</td>
<td>Saturated</td>
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<td>x</td>
</tr>
<tr>
<td>Control</td>
<td>80% WHC</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Elinaryd-treatmentd (Paper III)</th>
<th>Daramend® 6386e</th>
<th>BioSan bacterial solutionf</th>
<th>MQg</th>
<th>Surfactanth</th>
<th>Nutrient solutioni</th>
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<tbody>
<tr>
<td>DaWa</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>DaWaNu</td>
<td>x</td>
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<tr>
<td>DaSuNu</td>
<td>x</td>
<td>x</td>
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<td>x</td>
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<td>BaSu</td>
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<td>Wa</td>
<td>x</td>
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<td>x</td>
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<tr>
<td>SuNu</td>
<td>x</td>
<td>x</td>
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</tr>
</tbody>
</table>

a 2%w/w  
b 0.5%w/w  
c 20%w/w  
d Abbreviations: Da=Daramend®, Wa=water, Nu=nutrient, Su=surfactant, Ba=BioSan bacterial solution.  
e 5%w/w  
f 1.5 ml of a solution prepared from 5,500 l water, 4 l diesel fuel, 3 kg of Nutrigranul powder (NP 26/6, including 26% N and 6% P), 2 kg yeast extract and 2.3 kg sodium bicarbonate and two “bio socks” of freeze dried bacteria (Sybron ABR Hydrocarbon).  
g Corresponding to 60% of WHC  
h Non-ionic surfactant added at a concentration corresponding to 3.2xCMC*.  
i 0.58 g Na2HPO4

For the PAH and As-contaminated Elinaryd soil (Paper III), aerobic bioremediation was evaluated. Two different commercially available techniques were evaluated: Daramend® and BioSan. The Daramend®-treatments were either performed only with water-addition (DaWa), with the addition of water and nutrients (DaWaNu) or with nutrients and a non-ionic surfactant (with active agent alkyl polyglucoside-C6; DaSuNu) to increase the bioavailability of the PAH (Paria, 2008; Yeom et al., 1995). BioSan-treatments were either performed with water-addition (BaWa) or with surfactant addition (BaSu). Control samples included water-content adjusted soil (Wa), soil with surfactant only (Su), nutrients and water-content adjustment (WaNu) and soil with surfactant and nutrients (SuNu). The water content was set to 60% of the WHC in treatments receiving water, whereas the surfactant was added in a concentration corresponding to 3.2xCMC* (measured by stalagmometer). Nutrient-amendment was performed by addition of 0.58 g Na2HPO4. Samples for PAH-analysis were withdrawn every 10th week, with at total treatment time of 30 weeks. Due to low CO2-evolution,
additional Daramend® was added to the corresponding treatments, whereas the BioSan-treatments were amended with diesel fuel (5,000 mg/kg) and NP 26/6-nutrients.

During both bioremediation experiments, measurements of redox, pH, CO₂-production and temperature were performed biweekly. Samples to monitor metalloid distribution (Pb and As for the BTC and Elnaryd-soils, respectively) and ecotoxicity (Microtox®) were taken at experiment closure. All samples were put in the freezer prior to analysis.

2.3. Soil washing
The possibility to simultaneously remove explosives and different heavy metals from the BTC-soil was evaluated by pH-adjustment (Paper II). For the experiments, 10 or 20 g of soil was put into plastic tubes and added MQ-water adjusted to pH 4 or 12 using HNO₃ or NaOH, respectively, at a liquid:solid-ratio (L:S) of 4:1. As control samples, non-pH-adjusted MQ was utilized. The soil slurries were thereafter end-over-end-tumbled for 30 min, 24 h or 10 days, with daily pH-adjustments. At withdrawal, the samples were left to settle for 15 min before the liquid phase was removed (centrifugation and filtration) and acidified for subsequent analysis of the leached amount of heavy metals. The soil was rinsed with pure MQ (to interrupt the pH-effect) and thereafter left in a vented hood to dry. The dried soil samples were extracted for remaining explosives, using the method described below.

For the simultaneous removal of PAH and arsenic (Paper IV), both laboratory and pilot scale experiments were performed. In the laboratory scale study, 300 g of soil was put in 1 l fluorinated HDPE jars and added 300 ml of soil washing solution (L:S 1:1). The additives in the soil washing solutions were selected based on their documented efficiency for As or PAH-removal. Consequently, different complexing agents (oxalate, EDDS and MGDA) were utilized for As-removal and two surfactants (non-ionic alkyl polyglucoside-C6, “AG”, and chelating surfactant, “amph”) were evaluated for PAH, in addition to pH-adjustment (pH 3 and 12) and tap water as control. First, all treatments were evaluated in single compound systems and thereafter mixtures of the best treatments for PAH and As, respectively, were evaluated. The best combinations were in addition evaluated utilizing heated (50°C) solutions. Three samples were withdrawn from each jar after 10, 20, 30 and 60 min, 24 h and 10 days during the first part of the laboratory survey (single compounds systems), whereas samples were only withdrawn...
after 10 min treatment when mixtures of additives were evaluated. The solid and liquid phases were separated by centrifugation and the liquid phase was subsequently acidified by HNO₃ and stored in the fridge to await heavy metals analysis. The solid phase was dried in a 40°C oven until completely dry and stored in the freezer before PAH-analysis.

The best treatments from the laboratory investigation were subsequently evaluated in pilot scale using the WTC-equipment (Water Treatment Construction, patented by Solventic AB; Fig. 1). The system is manufactured for continuous use, but was used in batch mode during these experiments. Approximately 5 kg of soil was put into the mixing chamber and held in place by a stainless steel net. Thereafter, the soil washing liquid was introduced into the soil from below using a high pressure pump (25 bars) and the liquid was evenly distributed on the soil surfaces using a set of dies. The soil particles, which fell down through the net under constant influence of the up-ward flow of the soil washing liquid, was collected in a tub below, together with the soil washing solution. Sampling was done in both the solid and liquid phases when all soil had fallen through the net (final L:S was approximately 2:1).
2.4. Leaching tests
Two different leaching tests, batch (EN 12457:3) and column (CEN/TS 14405), were utilized for the evaluation of the possibility of re-cycling of remediated soil (Paper VI). Three different leaching solutions were compared: deionized water (D.W.), a weak ionic solution (0.001 M CaCl₂; in agreement with a recently developed international standard, ISO 21268:2007) and artificially made soil water (ASW) to mimic environmental conditions. The composition of the ASW was adopted from van Hees et al. (2000) and consisted of a mixture of different salts and humic acids (extracted at pH>10 from peat).

**Batch leaching**
The batch leaching procedure followed the standard protocol EN 12457:3 (Two step batch leaching test). In brief, 0.175 g of soil was put into 500 ml HDPE (soils A-C) or fluorinated HDPE (soil D) containers and added solution at a ratio corresponding to an L:S of 2:1. After 6 h extraction at room temperature, separation of liquid and solution was performed by vacuum filtration (soil A-C) or centrifugation (soil D). Soil and filters were thereafter transferred to 2 l containers and added new leaching solution at an L:S of 8:1 and extracted for another 18 h before the same separation techniques were performed. Leached amount of heavy metals (soil A-C) or PAH (soil D) were measured in the liquid phase. All batch leachings were performed in triplicate.

**Column leaching**
Soils A-C were packed into plastic columns (5 cm i.d. x 30 cm length) according the standard protocol (CEN/TS 14405; Up-flow percolation test) and kept in place using coarse meshed plastic filters. The leaching solution was introduced from below using a peristaltic pump. When the soil was saturated, the column was left for 24 h to equilibrate before the leaching continued at a flow rate of 0.2 ml/min and the samples were collected in plastic sample bottles at the outflow. At time intervals corresponding to L:S ratios of 0.1, 0.2, 0.5, 1, 2, 5 and 10, the collection bottles were switched and sampling for heavy metals was performed.

For soil D, the soil column (4.8 cm i.d. x 30 cm length) as well as solution and collection bottles were made of glass and all tubings were made of FEP or FEP-lined polymer with low gas permeability. Before introduction, the leaching solution was sparged with nitrogen gas and the collection bottles were added 0.5 mg/l of NaN₃ in order to prevent biodegradation of target compounds. All equipment
was also covered in aluminum foil to prevent photodegradation. Sampling of the column leachates was made at the same time intervals as for soils A-C.

2.5. Analysis of explosives
The analysis of explosives was performed using a slight modification of the U.S. EPA standard method 8330. Ten grams of air-dried soil was put in a centrifuge tube and added 50 ml acetonitrile (L:S 5:1) and extracted at room-temperature for 18 h in the dark. After 15 min of sedimentation, 5 ml of the liquid phase was removed and added 5 ml of a 5 mg/l CaCl₂-solution, and the mixture was thoroughly shaken for 5 min. After another 15 min of settlement, the liquid phase was withdrawn and filtered (0.45 μm nylon filters) into a LC-vial after disposal of the first ml. The samples were then analyzed on a RP-HPLC-UV-system using methanol and MQ (1:1) as mobile phase in isocratic mode.

2.6. Analysis of PAH

Extraction of soil bound PAH
To two grams of dried soil, 100 μl of a 10 μg/ml internal standard (IS) mixture was added. The soil was extracted using 10 ml dichloromethane (DCM) and acetone (1:1), covered with aluminum foil for 24 h at room temperature. After centrifugation, and the liquid phase was transferred to amber glass vials, and the solvent was changed to n-hexane after evaporation under a gentle stream of nitrogen. The clean-up was performed on disposable glass Pasteur pipettes packed with glass wool, 10% deactivated silica (dried at 550°C for 3 h and added 10%w/w MQ) and on top dried Na₂SO₄ (150°C for 24h). The columns were pre-eluted with 3 ml n-hexane before sample addition, and the samples were thereafter eluted with 3 ml n-hexane followed by 3 ml of a 3:1 mixture of n-hexane:DCM. Eluates were evaporated under nitrogen and the solvent was changed to toluene before transferring the extracts to amber GC-vials. Before analysis, the samples were added 100 μl of a 10 μg/ml recovery standard (RS).

Extraction of dissolved PAH
Extraction of PAH from the aqueous solutions from the leaching tests was performed by liquid-liquid extraction in glass separation funnels. To the water samples, 100 μl of IS was added. Thereafter, n-hexane at a solvent:water-ratio of 1:5 was added and the mixtures were shaken manually for 5 min. The procedure was repeated three times, utilizing new hexane for each round. The combined samples were evaporated and the solvent changed to toluene before transferring to amber GC-vials. Before analysis, the samples were added 100 μl of RS.
**GC-MS Analysis**

The PAH were analyzed by GC-MS. The samples were injected in splitless mode and helium was utilized as carrier gas. The temperature program started at 75°C and was held for 1 min, 75-250°C (25°C/min), 250-310°C (3°C/min) and 310°C held for 7 min. A PAH-standard mixture with the US 16 priority PAHs was utilized together with IS and RS for peak identification and quantification. Software Masslynx V4.0 was utilized for quantification calculations.

### 2.7. Analysis of heavy metals

A slightly modified version of the sequential leaching procedure developed by Tessier et al. (1979) was used to study the distribution of heavy metals in the soils. Six fractions are obtained by sequentially leaching of one gram of soil:

(I) Water soluble metal
   20 ml of deionized water (15 min at room temperature),

(II) Cation exchangeable metal
   20 ml of 1.0 M NH₄Ac at pH 7 (1 h at room temperature),

(III) Carbonate bound metal
   20 ml of 1.0 M NH₄Ac at pH 5 (1 h at room temperature),

(IV) Metals bound to Fe- or Mn-(hydr)oxides
   20 ml of 0.043 M NH₂OH-HCl in 25% HAc (5 h in 80-90°C),

(V) Metal bound to organic matter and amorphous metal sulfides
   12 ml of 0.02 M HNO₃ and 30% H₂O₂ at pH 2 (3:5 v/v) at pH 2 (3 h at 80-90°C) and thereafter 7.5 ml of 3.2 M NH₄Ac in 20% HNO₃ and 10.5 ml deionized water (30 min at room temperature),

(VI) Residual (metal bound to consolidated organic matter and metal sulfides)
   Acid digestion in a microwave oven using either 14 M HNO₃ (Paper I, II and IV) or 7 M HNO₃ (Paper III and IV).

Between each leaching step, the sample was centrifuged, the supernatant decanted and the soil utilized in the next step. The supernatant from each step was acidified to <2 using HNO₃. The samples were thereafter analyzed on ICP-MS (Agilent 4500; Paper I, II and VI) or ICP-OES (Plasma 4000 DV, PerkinElmer; Paper III, IV and VI). To samples intended for ICP-MS, 100 μl of an internal standard (¹⁰³Rh) was added before analysis.
2.8. Ecotoxicological evaluation

In Paper I, III and IV, an ecotoxicological evaluation following ISO-standard 11348:3 was utilized to assess the efficiency of the remediation. In the test, the bioluminescent test bacterium *Vibrio fischeri* is utilized. Soil leachates were produced in accordance with the ISO/TS-standard 21268:2007, utilizing 0.001 M CaCl₂ as leaching solution. For the BTC-samples (Paper I), the L:S-ratio was set to 10:1 (2 g soil and 20 ml solution; ISO 21268:2) and for the Elnaryd soil (Paper III and IV), the L:S was 2:1 (5 g soil and 10 ml solution; ISO 21268:1). The samples were extracted for 24 h at room temperature. After 15 min of settlement, the BTC-samples were centrifuged at 16,500 rpm for 45 min, followed by filtration through 0.45 μm filter and the Elnaryd-samples were centrifuged at 4,000 rpm for 8 min without filtration. Thereafter, the luminescence change of *V. fischeri* was evaluated after 30 min exposure to the soil extracts at 15°C. The thirty-minute IC₅₀-values (the concentration where 50% reduction in bioluminescence is observed) with 95% confidence intervals were calculated based on mean values of duplicates performed at eight concentrations ranging from 6 to 80% of the original concentration using the software MicrotoxOmni™. Three control substances (K₂Cr₂O₇, ZnSO₄ and 2,4-dichlorophenol) with known toxicity were run at the beginning and at the end of the experiments to verify the toxic response of the test bacteria, corresponding to 50% light reduction. Correction for color was performed when necessary.
3. RESULTS

3.1. Remediation of explosives and heavy metals-contaminated soil

Percent remaining explosives after both the anaerobic bioremediation and soil washing experiments is displayed in Fig. 2 (Paper I and II). The results demonstrate that both bioremediation and soil washing were feasible for the removal of explosives from the moderately contaminated BL-soil (bottom layer; Fig. 2A). Among the bioremediation methods, Daramend® and ZVI achieved the highest removal of TNT, RDX and HMX, whereas both compost and control-treatment were generally much less efficient (Paper I). 2,4-DNT was also efficiently removed by the control-systems (water and pH-adjustment only), possibly due to the higher water solubility of this compound (see Table 1) and thus higher susceptibility to biological attack (Alexander, 1999). It was speculated that the high removal efficiency was a result of the low redox potential, due to the ZVI-addition, which was not added to the compost or control samples.

Lead was the only of the heavy metals in the soil exceeding regulatory guideline and was monitored by sequential extraction before and after the bioremediation. It was observed that the distribution of Pb was not affected by the bioremediation and consequently the risk of spreading under the current conditions should be low.

The removal of explosives from the BL-soil was also achieved by soil washing (Paper II), with pH 12 managing to remove more TNT and RDX than the other soil washing treatments (Fig. 2A). The removal of RDX may be a result of alkaline hydrolysis, which has been demonstrated before (Heilmann et al., 1996), but never in mixed systems. The observed removal of TNT by the pH 12-treatment did not exceed the reported water solubility of the compound, yet it cannot be ruled out that alkaline hydrolysis has also had an influence on the TNT-removal (Emmrich, 1999). In agreement with the results for TNT, the 2,4-DNT-removal was lower than the water solubility and the mobilization observed for MQ was equally efficient as pH 12. For HMX, no statistical difference was observable between the different treatments (pH 4, pH 12 and MQ), which may be a result of HMX binding to soil particles which are subsequently removed by the decantation, rather than dissolution or degradation by the washing solution.
In the highly contaminated UL-soil (upper layer-soil) bioremediation was not efficient (Fig. 2B), possibly due to the very high initial concentration rendering the soil too toxic to sustain a vital microbial population (Paper I). This was also supported by the low CO₂-evolution observed. In agreement with the BL-soil, no mobilization of lead occurred, as evaluated by sequential extraction. Soil washing was, on the other hand, shown to remove a substantial amount of all four explosives in the UL-soil (Paper II). For TNT and 2,4-DNT, pH 12 was the most efficient, whereas no larger difference between pH 12 and 4 was observed for RDX.
and HMX. In contrast to the BL-soil, the removal observed for TNT was above the water solubility limit, indicating a process which removes TNT from solution, i.e. alkaline hydrolysis (Emmrich, 1999). In total, 10 days of soil washing at pH 12 managed to completely remove all TNT in the UL-soil (C_{init} = 3,120 mg/kg) and the final 2,4-DNT concentration was 190 mg/kg and accordingly just slightly above the risk based concentration threshold level of 160 mg/kg.

In the soil washing experiments, the highest mobilization of the simultaneously occurring heavy metals from both the BL and UL-soils was obtained by pH 12-treatment (Paper II). This was somewhat surprising since cationic metals are generally mobilized at low pH (McBride, 1994). It was suggested that pH 4 was not low enough to obtain any sufficient metal mobilization and that the high removal-efficiency at pH 12 was a result of the formation of negative complexes (e.g. Pb(OH)\textsuperscript{2+} and Fe(OH)\textsubscript{4}\textsuperscript{2-}; Clevenger and Dave, 1998; Stumm and Morgan, 1996), which are repelled by the negative soil surfaces. In addition, organic matter is ionized at high pH (You et al., 1999), in combination with the dissolution of the Fe-(hydr)oxides (McBride, 1994), leading to mobilization of compounds adsorbed to these. Furthermore, it was noticed that lead and cadmium mobilization was more pronounced than the corresponding mobilization of copper and zinc. A comparison with natural background concentrations in the region (Allard, 1995) suggests that copper and zinc were present in natural concentrations, whereas lead and cadmium-concentrations were elevated and likely the result of contamination and thus possibly more available.

3.2. Remediation of PAH and As-contaminated soil

In Paper III, the possibility to utilize bioremediation to remove PAH from the Elnaryd-soil was evaluated. The results demonstrate that the PAH-degradation was generally low, even after 30 weeks of treatment. Too low bioavailability of the contaminants, possibly as a result of the ageing of the organic contaminants (Alexander, 1999), and too short treatment time may be plausible explanations. It was also speculated that the simultaneously present arsenic rendered problems to the remediation process, possibly through toxicity towards the PAH-degrading microorganisms. In addition, large re-distribution of arsenic was observed in all treatments which had undergone bioremediation, with more arsenic being present in the soluble fraction after treatment (Fig. 3). It has been shown that arsenic speciation can be changed as a result of microbial activity (Yamamura et al., 2005) and may be the result of a detoxification action (Páez-Espino et al., 2009). Since the re-distribution of arsenic was observed in all biotreatments, it is possible
that the combination of increased water content, addition of wood chips and storage under room temperature led to an increase in the number of arsenic-detoxification bacteria, already present in the soil. The bacteria suitable for PAH-degradation were, on the other hand, possibly disadvantaged by the increase in As-availability.

During the soil washing of the Elnaryd-soil (Paper IV) the L:S-ratio utilized was 1:1, in order to be more in line with the pilot scale soil washing equipment utilized in the experiments (Fig. 1). Oxalate buffer was the most efficient single compound system for arsenic and managed to reach treatment goal of 25 mg/kg ($C_{ini}=105$ mg/kg) within 24 h. Oxalate buffer acts through mobilizing the Fe onto which the arsenic is sorbed, and its efficiency has been demonstrated before (Bhattacharya et al., 2002). For PAH, both chelating agents (EDDS and MGDA) and the non-ionic surfactant (AG) managed to reach the treatment goal of 10 mg/kg PAH-H within 24 h. Furthermore, pH 12 (NaOH) implied quite high mobilization of both arsenic and PAH. Thus mixtures of both oxalate buffer, MGDA and AG at alkaline pH were evaluated in different mixtures as a second part in the evaluation. The results demonstrated that a mixture of MGDA and AG at high pH (12-13 using either NaOH or Ca(OH)$_2$) implied high removal of PAH and arsenic simultaneously (Fig. 4). The removal was further enhanced.
Figure 4. Remaining PAH-M, PAH-H and As in the Elnaryd-soil after soil washing treatment using different mixtures of additives. Samples were withdrawn after 10 min (laboratory scale) or immediately after mixing (WTC). The numbers into parenthesis represent the pH-value at sample withdrawal. The dashed line is the MKM-value for arsenic and the solid line the MKM for PAH-H. Values are mean±SE (n=3)
when the solution was heated before addition. It is likely that the surfactant micelles caused the mobilization of PAH (Paria, 2008) and that the alkaline pH lead to the arsenic removal (Lee et al., 2007). The role of the MGDA was to complex the Ca-ions from the Ca(OH)$_2$, which would otherwise have created solid complexes with arsenic (Dutré and Vandecasteele, 1998; Mahuli et al., 1997) and lead to arsenic precipitation. This was also supported by the low arsenic-mobilizing efficiency in treatment where the MGDA was left out (e.g. AG+Ca(OH)$_2$). In addition, utilization of high temperature facilitated the mobilization, possibly by speeding up the kinetically slow processes. Evaluation of the results using the WTC-equipment resulted in much less mobilization of both PAH and arsenic (see columns to the right in Fig. 4). It was speculated that the low efficiency of the WTC was due to the shorter contact time or a result of the lower ambient temperature during the pilot scale evaluation. Furthermore, a high pressure pump was utilized (25 bar) to introduce the soil washing solution into the soil, which could have had a negative impact on the micelles created (Baden et al., 2002; Kato et al., 1997).

3.3. Ecotoxicity testing of remediated masses

The results from the Microtox®-tests, performed on treated soil samples in Paper I, III and IV, are displayed in Fig. 5. IC$_{50}$-values (the concentration where 50% reduction in bioluminescence is observed) demonstrates that the bioremediation of the BTC BL-soil implied a decrease in toxicity (i.e. an increase in IC$_{50}$-values) compared to non-treated samples, whereas no difference before and after treatment was observed in the BTC UL-soil (Paper I). It has been observed in earlier studies that toxicity from explosives contaminated soils to $V. fischeri$ are almost entirely due to the toxicity of TNT (Frische, 2002; Frische, 2003; Sunahara et al., 1999). The main reason for this is the much higher water solubility of this compound compared to RDX and HMX, and the higher toxicity of TNT compared to 2,4-DNT. Furthermore, these results demonstrate that also other factors had an influence, since the highest toxicity-decrease was observed after the ZVI-treatments, despite Daramend® managing to reach lower target compounds concentrations. Toxicity of the co-existing lead could nevertheless likely be ruled out by comparison with earlier measurement of lead toxicity to $V. fischeri$ (Sillanpää and Oikari, 1996; Tsiridis et al., 2006).

A different pattern was observed regarding the toxicity changes after the remediation activities in the Elnaryd soil (Paper III and IV). Irrespective of treatment selection, a toxicity increase was observed in all treated (both bioremediation and
Figure 5. Microtox®-measurements before and after different treatments in the BTC and Elnaryd soils. Values are IC₅₀-values (the concentration where 50% reduction in bioluminescence is observed; mg soil/ml CaCl₂-solution). Errorbars represent SE, please note the logarithmic scale.
soil washing) soil samples (i.e. decrease in IC$_{50}$-values). The low initial toxicity of the Elnaryd-samples may be a result of the low water solubility of PAH (see Table 2; Eom et al., 2007). In addition, V. fischeri has been demonstrated to have quite low sensitivity to arsenic at the concentrations present in the available fraction (Fig. 3; Fulladosa et al., 2005). In fact, not even the increase in available arsenic in the biological treatment (Paper III) would most likely result in any toxicological response in the Microtox®. However, the bioremediation may have led to the creation of degradation products, such as oxygenated PAH (Lundstedt et al., 2007), of which some have been demonstrated to imply higher toxicity towards V. fischeri than the mother compounds (McConkey et al., 1997). A comparison between all Microtox®-results from the Elnardy-soil (Paper III and IV), however, demonstrate that one factor is common between all treatments implying the largest toxicity increase: the addition of surfactant. The AG-surfactant was selected based on its comparably high biodegradability, but yet its amendment to the soil increased the overall soil toxicity to the test bacteria. It is possible that the low surface tension resulting from the surfactant amendment had a negative impact on the test bacteria (Mazidji et al., 1992; Sherrard et al., 1996). These observations are interesting, since surfactants are increasingly been suggested as amendment to improve the soil remediation of hydrophobic organic compounds (Paria, 2008).

3.4. Re-cycling of remediated soil

Contaminated soil and waste

Soil is increasingly being considered to be a non-renewable resource, in agreement with the proposed European soil framework directive (not yet approved). As a result, the remediation of contaminated masses is generally considered to be a way to re-vitalize a resource that has been damaged and thus find new applications for it. The desire to find new application is even more pronounced in the light of the large economic costs involved in most soil remediation projects. However, the possibility to re-cycle remediated masses in Sweden is limited by a number of factors, which are discussed in Paper V.

According to an inventory performed by the Swedish EPA on accomplished remediation projects, almost 90% of these were performed ex situ/off site, which implies excavation and transport to another location before treatment (S-EPA, 2006). In total approximately 600 000 tons of contaminated soil is estimated to be excavated on a yearly basis. Time constrains (e.g. due to redevelopment schemes) and in order to calm the neighboring public are two plausible reasons
for the comparably rare in situ or on site-treatments. When excavating the soil, it is automatically considered to be waste and should thus be treated as such in agreement with the European waste directive, which in practice often imply landflling rather than re-cycling. One large constraint has so far been the lack of declassification tools in the waste legislation, so called end of waste (EOW) criteria. In the revised waste directive, which was approved in the late 2008 (EC, 2008), such EOW are however included under certain conditions. These conditions include (a) when the substance is commonly used for specific purposes; (b) if a market demand exist; (c) the substance fulfills the technical requirements for the specific purposes; and (d) the use of the substance will not lead to overall adverse environmental or human health impacts. Furthermore, by-products (such as non-contaminated soil excavated together with the contaminated masses) should be able to re-use at the site. Most of the content of the new directive should be enforced into the national legislations by December 2010.

In addition to the inclusion of EOW, among the fundamentals in the revised waste directive is the so called waste hierarchy (Fig. 6). It promotes the reduction of the production of waste (implying the most resource conservation) whereas disposal is considered the least favorable. Reduction of the contaminated soil is not applicable, since the waste has already been produced and re-use (without pre-treatment) is often neither possible nor desirable. Re-cycling (after treatment) is however a desirable scenario. The inclusion of the waste hierarchy into the European waste legislation could thus lead to more widespread re-cycling of remediated masses by providing environmental incentives for re-cycling rather than disposal.

**Re-cycling of remediated soil**

So far, re-cycling of remediated masses has been restricted in Sweden. Several different aspects underlie this fact: the risk of spreading of pollutant remains from the masses, the exclusion of contaminated soil from the land filling tax (implying that it is less expensive to landfill these masses than normal waste) and the comparably good supply of virgin land. However, in line with the changes in the Waste Directive, a recent S-EPA proposition (not yet decided) suggests that recycling of remediated masses should be allowed under certain conditions (S-EPA,
The proposal includes threshold values for total concentration and leachability of contaminants, and two classes of re-cycling are proposed: general re-cycling (roads, construction etc.) and as landfill coverage. The threshold limits for general use are low, normally in the same range as the Swedish KM-values, especially for compounds which should be phased-out (Hg, Cd and Pb), where the natural background concentrations underlies the decision. Whilst the Swedish proposition is not yet decided upon, some countries already have legislations where re-cycling is possible, with the Dutch building materials decree (VROM, 1995) likely being one of the most extensive schemes. The high population density of the Netherland (and thus the comparably low access to virgin material) is likely a large contributor to the need for re-cycling of masses. The Netherlands also has a ban on landfilling of treatable soil and consequently only approximately 20% of all contaminated soil is land filled (Honders et al., 2003), the same number in Sweden is estimated to be around 70% (RVF, 2005; S-EPA, 2006).

**Leaching tests**

Before re-cycling of a mass is allowed, a thorough risk assessment is necessary, often including different leaching test. These tests are simplified tools to predict the possible spreading of pollutants from the soil (van der Sloot et al., 1997). Differences in leaching test setup, evaluation of the results and legislative threshold values (i.e. maximum total or leached concentrations) between different countries and legislations exist (e.g. the Dutch BMD: column leaching at pH 4; the EC waste acceptance criteria (WAC): column and batch leaching using deionized water; and the ISO 21268:2007-standard: column and batch leaching using CaCl₂). This could imply that a soil may be allowed to re-cycle in one country but not in another. In addition, most re-cycling legislation only take inorganic compounds into account during the leaching tests. This is mainly due to the lack of standardized leaching procedures for organic compounds, despite much research on the leaching of these (Bjuggren et al., 1999; Enell et al., 2004; Reemtsma and Mehrtens, 1997). The main constraints to find a common solution are the properties of these compounds, including sorption to the test equipment and their susceptibility to degradation etc. (Hansen et al., 2004).

In **Paper VI**, two standardized leaching tests (two step batch leaching EN 12457:3 and up-flow percolation test CEN/TS 14405) were evaluated for their leachability of both heavy metals and PAH. Three different leaching solutions were evaluated to study whether composition of the leaching media might imply different results.
Table 6. Categorization of the heavy metals contaminated soil A-C in relation to EC, S-EPA and BMD-legislations (A). The green categories are the least restricted, the yellow are restricted and the red are highly restricted, but the thresholds differ between the legislations. Part (B) categorizes the leaching of PAH from soil D, and whether the threshold values from US-EPA, EC and S-EPA are exceeded: yes or no.

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<td>General</td>
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<td>BMD®</td>
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<td>---</td>
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<th>Column (CEN/TS 14405)</th>
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**B**

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</tbody>
</table>

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*Deionized water
*0.001 M CaCl₂ solution
*Artificial soil water (filtered before analysis)
*Artificial soil water (not filtered before analysis)
*WAC – waste acceptance criteria (EC, 2003), divided into inert, non-hazardous or hazardous.
*Swedish thresholds from (S-EPA, 2007b), divided into general re-cycling or no re-cycling.
*Dutch thresholds from (VROM, 1995), divided into category 1, category 2 or no re-cycling.
and thus different characterization of the soils. The results were compared with three legislations: the S-EPA, the Dutch VROM and WAC. A summary of the classification of soils, as a result of the leaching of heavy metals (soil A-C) and PAH (soil D) from full scale remediated soils (soil washing), are displayed in Table 6. All three evaluated heavy metals contaminated soils contained remaining heavy metals concentrations higher than the guidelines, which would imply that none of the soil would be allowed to re-cycle. In large, the results from the leaching tests indicate that utilization of CaCl₂ may underestimate the leached amount of heavy metals possibly due to the low mobilization of organic matter (Comans, 2001; van Herwijnen et al., 2007). In addition, utilization of ASW may not result in high heavy metal mobilization, despite the high metal sorbing capacity of dissolved organic matter (Berselli et al., 2004; Wong et al., 2007), due to the removal of heavy metals from the solution by filtration of the samples before analysis. A comparison between filtered and non-filtered ASW confirmed this and the results demonstrate that filtered ASW could be re-cycled without restriction, whereas the non-filtered samples would imply restricted re-cycling (soil A) or prevented re-cycling (soil B and C) in the cumulative L:S 10 column leaching. The leaching obtained by D.W. would in some cases fully prevent re-cycling in Sweden, but allow re-cycling without restrictions in the Netherlands. Furthermore, the batch leaching implied higher heavy metal mobilization than the column leaching, and consequently the threshold limits would be exceeded more often by batch than by column leaching. The rough treatment of the soils during the batch leaching is known to cause an increased mobilization of soil fines (Bergendahl and Grasso, 1998).

The initial concentration of PAH in soil D was very low, and re-cycling of the soil would thus be allowed. A substantial leaching of PAH was despite this observed and drinking water, tap water and groundwater criteria were exceeded by all three leaching solutions (Table 6B). Quite high L:S or long contact time was required to imply thresholds to be exceeded, but in a real situation, the soil would be in contact with the pore water for extended time periods, thus the results are worrying despite the high L:S requirements. Consequently, this pinpoints the necessity to implement the leaching of PAH (and other organic contaminants) in the risk assessment of remediated soils.
4. CONCLUDING REMARKS

4.1. General conclusions

- Anaerobic bioremediation (using Daramend®-amended with ZVI or ZVI alone) is feasible for moderate explosives concentrations, whereas very high initial concentrations may prevent the biodegradation. Lead distribution is not affected by the anaerobic treatment.

- Irrespective of treatment selection (biostimulation, bioaugmentation or control treatments), the PAH-degradation may be limited if the contaminant availability is low. Very long treatment times (>30 weeks) may be required.

- Arsenic present in a PAH-contaminated soil undergoing aerobic bioremediation may be affected by the microbial activity, leading to increased mobility and possibly toxicity.

- Soil washing may be a suitable remediation technique for the simultaneous removal of organics and heavy metals from soil. Alkaline conditions (pH 12, NaOH) can simultaneously remove explosives (especially TNT) and heavy metals in both moderately and highly contaminated soil.

- PAH and arsenic could efficiently be removed by the utilization of alkaline pH (using 1% Ca(OH)₂) in combination with a non-ionic surfactant and chelating agent (MGDA) and at elevated temperature (50°C). Treatment goals were met within 10 min of treatment in laboratory scale, whereas implementation of the best treatments in a WTC-equipment led to less mobilization, possibly as a result of shorter contact time.

- Anaerobic bioremediation of the explosives and lead contaminated soil led to a decrease in ecotoxicity (Microtox®) in the moderately contaminated soil which was not always in concordance with the chemical analysis.

- Remaining surfactant in treated soil may increase the overall toxicity since too low surface tension implies toxicity to the test bacterium.

- Re-cycling of remediated soil is increasingly being discussed due to the environmental gains of re-cycling of a non-renewable resource and to find new applications for a soil which has undergone a costly process. However, the re-cycling must follow a thorough risk assessment.

- Differences in leaching test design and leaching medium may result in divergent results from the risk assessment in different countries. Filtration of the samples may underestimate the heavy metal mobilization and CaCl₂ implies lower heavy metal mobilization than deionized water. In addition, it is necessary and urgent to implement the leaching of organic compounds in the risk assessment.
4.2. Future perspectives

The results of the thesis demonstrate that remediation of mixed contaminated soils is feasible, but that both redistribution of co-contaminants and remains of amendments may lead to unforeseen problems during the remediation process. Some considerations for future research and application could thus be suggested:

- If different contaminants are present in the soil simultaneously, this thesis demonstrates the necessity to monitor all of them during a remediation process, even though the treatment is focusing on one compound.
- Soil washing was demonstrated to be an efficient remediation technique for mixed contaminated soil, but it leads to production of contaminated waste water which has not been considered in this thesis. It is however important to find cost efficient and environmentally safe ways to handle this waste water and other waste produced during the remediation process.
- Utilization of amendments for efficient contaminant removal implies extra costs to the remediation process. Future research should investigate the possibility to re-cycle the washing solutions or to find ways to regenerate for example the complexing agents and/or surfactants in order to decrease the treatment costs.
- Ecotoxicological tests should be included in all risk assessment since (vulnerable) critical information on the overall soil health status may be obtained. This information may concern remaining contaminants and amendments in the soil, which may have consequences for the subsequent application of the remediated soil.
- Re-cycling should be considered the natural application of remediated soil, in order to sustain the environmental gain of the remediation process. The re-cycling must however undergo a thorough risk assessment (e.g. by leaching tests) and the application must be strictly regulated. In addition, harmonization of European legislations is desirable.
5. POPULÄRVETENSKAPLIG SAMMANFATTNING


Två vanligt förekommande saneringsmetoder är biosanering, där olika organismer (bakterier, svampar m.m.) som kan bryta ner organiska föroreningar används, och jordtvätt, där jorden bearbetas genom tillsats av en tvättvätska. Endast organiska föroreningar kan brytas ner, men också oorganiska föroreningar kan påverka biosaneringsprocessen genom att deras giftighet minskar mikrobernas tillväxt. Jordtvätt har potential att sanera olika föroreningar samtidigt, men större kunskap krävs eftersom tvättvätskans sammansättning måste anpassas till föroreningarna.

På gamla militärfält finns ofta en blandning av sprängämnen och olika tungmetaller. En biosanering i laboratorieskala med jord från Bofors, Karlskoga, visade att explosivämneshalten sjönk i de måttligt förorenade jordarna, samtidigt som saneringseffektiviteten var låg i högförorenade jordar, vilket också kunde visas med toxicitetstester. Testet visade också att biobehandlingen inte hade någon påverkan på det bly som också fanns i marken. Jordtvättsförsök med samma jord visade att användandet av högt pH (ca pH 12) gav relativt stor nedbrytning av explosivämnen samtidigt som både bly och andra tungmetaller mobiliserades. Denna tendens kunde ses i både den mattna och den högförorenade jorden. slutsatsen blir att biologisk sanering av explosivämnen är användbart ifall halten för orenningar inte är för hög, i det senare fallet kan istället jordtvätt vara ett bra alternativ.

Även jord från gamla träimpregneringsindustrier kan innehålla en blandning av olika föroreningar, såsom polycykliska kolväten (PAH) och arsenik. För att mikrobiellt bryta ner PAH användes två olika kommersiella metoder, med eller
utan tillsats av tensid. Resultaten visade att PAH-nedbrytningen var mycket liten, men däremot förändrades kemiskt hos arseniken i marken. Mikroorganismer har utvecklat olika försvarssystem för att skydda sig mot arsenik och det är möjligt att de relativt höga arsenikhaltarna i marken gjorde att dessa system aktiverades, vilket mobiliserade arsenik. Jordtvättsförsök med samma jord visade att en blandning av en substans som gör metall underlägsen (s.k. komplexbildare; MGDA) och tensid vid högt pH (ca 12-13) gav mycket god mobilisering av både PAH och arsenik, framför allt ifall temperaturen höjdes till ca 50°C. I denna studie utvärderades också en pilotskaleanläggning (WTC), men effekten av denna var måttlig, troligvis eftersom kontakttiden mellan lakvätskan och jorden var kortare än i labbförsöken, samt att temperaturen var låg. Toxtester gjorda efter båda saneringsförsök visade att rester av tensid i marken ökade toxiciteten efter behandling.


Utlakningen av kvarvarande föroreningar från fyra färdigsanerade massor, tre med tungmetaller och en med PAH studerades med hjälp av två standardiserade laktester som används inom riskklassificering. En jämförelse med tillåtna lakmängder i olika länder visade att olika lagstiftningar skiljer sig mycket åt, vilket gör att en jord som skulle vara förbjuden att återanvända i ett land (Sverige) skulle kunna användas helt utan restriktioner i ett annat (Holland). Vidare diskuterades viken av att använda laktester även för jordar med organiska föroreningar, något som inte görs idag.
6. ACKNOWLEDGEMENTS - TACK

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7. REFERENCES


Publications in the series
Örebro Studies in Environmental Science
