Synergistic Effects of Organic and Metal Contaminants on Phytoremediation

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ABSTRACT: Numerous contaminated sites exist worldwide that contain a mixture of organic and heavy metal contaminants. Very few technologies are proven to be efficient to address the problem of such mixed contamination. Most of these technologies are energy-intensive and expensive and they can disturb the natural ecosystem. Phytoremediation has potential to be a green and sustainable approach to decontaminate and restore the contaminated sites, maintaining the biological activity and physical structure of the soils. However, its effectiveness for mixed contaminants is not well understood. This study presents series of laboratory experiments conducted to investigate the synergistic effects of organic and heavy metal contamination on phytoremediation. A silty clay (typical field soil) was spiked with: (1) naphthalene and phenanthrene (representative organic contaminants), (2) lead, cadmium, and chromium (representative heavy metals), or (3) combination of these organic and heavy metal contaminants. Different plant species, specifically Avena sativa (oat plant), Lolium perenne (perennial rye grass), Festuca arundinacea (tall fescue), and Helianthus annuus (sunflower), were grown in these contaminated soils as well as in uncontaminated soil for comparison purposes. Results showed that plants in the soil with organic contamination alone had growth characteristics similar to that in uncontaminated soil. However, the plants in the metal contaminated soil showed maximum distress. The plants in mixed contaminated soil performed better than those plants in soils with metal contaminants alone.

INTRODUCTION

Many sites worldwide are contaminated with a mixture of organic and heavy metal contaminants. Since many of remediation technologies aim to degrade or immobilize only a particular type of contaminant, remediation of sites co-contaminated with organic and heavy metal contaminants can be a difficult task. Many of the methods used for mixed contaminated soils are energy intensive or expensive. For large sites with shallow and moderate contamination, phytoremediation can be a practical option to remediate mixed contaminants. Phytoremediation is a low cost method, which has the potential to treat both organic and inorganic contaminants. Phytoremediation uses
various plants to degrade, extract, contain, or immobilize contaminants from soil and water (Sharma and Reddy 2004). This technology has been receiving attention lately as an innovative, cost-effective and sustainable alternative to more established treatment methods used at hazardous waste sites (USEPA 2000). The inherently aesthetic nature of planted sites makes phytoremediation an attractive option compared to other cleanup methods (ITRC 2009).

For phytoremediation of mixed contaminants, the properties and interactions of the different contaminants involved as well as their interactions with the plant and rhizosphere are important. The plants selected for the remediation of mixed contaminated sites should be able to perform in the presence of mixed contamination and also when the contaminants are present individually.

Many historically industrialized former wetland and grassland sites in Chicago have been found to be contaminated with a mixture of organic and heavy metals contaminants. Naphthalene, phenanthrene, lead (Pb), cadmium (Cd), and chromium (Cr) are observed to be the most common contaminants at many of the sites.

This paper presents a laboratory investigation to identify the effects of organic and heavy metal contaminants when they are present in the soil separately and in combination. The aim is to find the best and worst conditions of plants to grow and uptake or degrade the contaminants.

**EXPERIMENTAL METHODS**

**Soil Selected**

Gray silty clay, which represents typical Chicago glacial till, was selected for performing the pot experiments. The aim is to use the experimental results for phytoremediating some sites with mixed contamination in Chicago. Important physical properties of the soil used in the study are presented in Table 1.

**Soil Spiking Procedure**

Clean control soil was prepared by mixing the soil with 15% of water. For preparing the organic contaminated soil, naphthalene (50 mg/Kg soil) and phenanthrene (100 mg/Kg soil) were mixed with hexane. This hexane was mixed with the soil and dried in the fume hood until all the hexane was evaporated out. For preparing the heavy metal contaminated soil, Pb (500 mg/Kg soil), Cd (50 mg/Kg soil) and Cr (200 mg/Kg soil) were mixed with deionized water (15% water content), and this water was mixed in the clean dry soil. For preparing the mixed contaminated soil, the soil was mixed with the organic contaminants in hexane at first, and it was dried in the fume hood until all the hexane evaporated out. Then, this soil was mixed with heavy metal contaminants, dissolved in deionized water. Measured properties of the contaminated and uncontaminated (clean) soil at the time of seeding are presented in Table 2.
Table 1. Important Properties of Soil Used for the Experiments

<table>
<thead>
<tr>
<th>Property</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Content</td>
<td>1.0%</td>
</tr>
<tr>
<td>Organic Content</td>
<td>2.5%</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.7</td>
</tr>
<tr>
<td>Liquid Limit</td>
<td>32.3%</td>
</tr>
<tr>
<td>Plastic Limit</td>
<td>19.2%</td>
</tr>
<tr>
<td>Plasticity Index</td>
<td>13.0%</td>
</tr>
<tr>
<td>Clay Fraction (&lt; 0.002mm)</td>
<td>40%</td>
</tr>
<tr>
<td>Silt Fraction (0.002 – 0.05mm)</td>
<td>44%</td>
</tr>
<tr>
<td>Sand Fraction (0.05 – 2 mm)</td>
<td>16%</td>
</tr>
<tr>
<td>USCS Classification</td>
<td>CL</td>
</tr>
<tr>
<td>USDA Classification</td>
<td>Silty clay</td>
</tr>
</tbody>
</table>

Table 2. Properties of Soil at the Time of Seeding

<table>
<thead>
<tr>
<th>Property</th>
<th>Soil Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clean Soil</td>
</tr>
<tr>
<td>pH</td>
<td>7.9</td>
</tr>
<tr>
<td>Oxidation Reduction Potential (mV)</td>
<td>66.2</td>
</tr>
<tr>
<td>Electrical Conductivity (mS/cm)</td>
<td>0.075</td>
</tr>
<tr>
<td>Water Content (%)</td>
<td>14.6</td>
</tr>
</tbody>
</table>

Prepared soil was filled in pots of 8cm diameter and 9 cm height for seeding the four plant species. Three sets of contaminated pots were prepared for each contaminant condition for each plant species. Plants seeded in uncontaminated pots were taken as control. One set of control pots was prepared for each plant species. The seeds were placed in the pots approximately a half inch below the soil surface. Each pot was kept on separate trays to ensure that the leachate does not get mixed up. The pots were placed under grow lights (metal halide lamps; average light intensity of 400 μmol/m²/s) hung ~ 12 inches above the plants to obtain the desired light intensity. A timer was set to provide 16 hours of light per day. The hanging height was adjusted as the plants started growing taller to reduce the heat stress caused by the hanging lamps to the plants. The temperature below the grow lights, at the height of the plants was measured as 25°C. Fans were used to control the temperatures of the grow lights.
Selected Plant Species

The plant species for the study were selected based on biomass and capability of survival based on some previous results. The plants selected were *Avena sativa* (oat plant), *Lolium perenne* (rye grass), *Festuca arundinacea* (tall fescue), and *Helianthus annuus* (sunflower). Number of seeds sown in each pot was ten for oat plant and sunflower and twenty for rye grass and tall fescue.

Pots Setup and Monitoring

The plants were grown for 61 days and the growth was monitored. Pots were watered every day. The locations of the pots were rotated periodically to ensure uniform light intensity to all the pots. Weekly monitoring was done by counting the number of plants in each pot and measuring the plant height. Photographs were also taken every week to record the plant growth and biomass production. Soil samples were taken at the beginning and end of the plant growth period to test for pH, electrical conductivity, oxidation reduction potential, and metals and organic contaminants concentrations.

At the end of the plant growth period, roots of the plants were separated out from shoots and washed in deionized water. The roots, shoots, and soil were dried in oven at 60°C for 6 days (until it attained constant weight). The dry weights of roots and shoots are recorded as root biomass and shoot biomass.

Analytical Testing

Testing of physical properties of the soil viz. water content (ASTM D2216), organic content (ASTM D2974), pH (ASTM D4972), and grain size analysis (ASTM D422) was done as per standards. Heavy metal and organic contaminant concentrations were determined based on the standard USEPA procedures.

RESULTS AND DISCUSSION

Germination percentages of the plants in contaminated and uncontaminated (control) soils are plotted in Figure 1. Here, germination is interpreted as the appearance of a green shoot/leaf above the soil. It was observed that for most of the plant species, the organic contaminated soil had similar germination and growth features compared to the control. The germination of all the plants was affected by the heavy metal contamination and mixed contamination, but the extent of reduction varied from species to species. Among the four plant species studied, oat plant had the highest germination rate in heavy metal contaminated and mixed contaminated soil compared to the other plant species. Germination rate of sunflower was considerably less in heavy metal contaminated soil and mixed contaminated soil compared to control and organic contaminated soil. In general, for all species, highest germination rate was in organic contaminated soil, followed by mixed contaminated soil, and then, by heavy metal contaminated soil.
Figure 2 shows the percentage survival of all the selected plants in clean soil and contaminated soils. Here, survival is expressed as the presence of green/live plant in the pot at the end of the test period. Percentage survival is the number of surviving plants as percentage of the number of seeds germinated. All the four plant species had survival rates similar to the control in organic contaminated soils. For oat plant, rye grass, and tall fescue, the plants had better survival rates in mixed contaminated soil than in heavy metal contaminated soil. For sunflower, mixed contaminated soil had lower survival rate than the heavy metal and organic contaminated soils. Rye grass was not survived in heavy metal contaminated soil.

The final (after 61 days) plant height of oat plant, rye grass, tall fescue, and sunflower are presented in Figure 3. All the plants had lesser maximum plant heights in all contaminated soils than in control (clean) soil. In general, higher plant heights are observed in organic contaminated soil, followed by mixed contaminated soil and heavy metal contaminated soil. The final plant heights of heavy metal and mixed contaminated soils were considerably less compared to the control.

**FIG. 1. Germination of studied plants in clean soil vs contaminated soils.**
FIG. 2. Survival of studied plants in clean soil vs contaminated soils.

FIG. 3. Final maximum plant height for clean soil vs contaminated soils.
Average root and shoot biomass of plants in clean soil and contaminated soils are summarized in Table 3. Percent reduction of total biomass of the plants in contaminated soils, compared to the same plants in clean soil is presented in Figure 4.

Table 3: Average Root Biomass, Shoot Biomass, and Total Biomass of Plants in Clean and Contaminated Soils

<table>
<thead>
<tr>
<th>Plant</th>
<th>Clean Soil</th>
<th>Organic Contamination</th>
<th>Heavy Metal Contamination</th>
<th>Mixed Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root Biomass (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oat Plant</td>
<td>0.91</td>
<td>0.63</td>
<td>0.32</td>
<td>0.47</td>
</tr>
<tr>
<td>Rye Grass</td>
<td>0.49</td>
<td>0.32</td>
<td>0.00</td>
<td>0.19</td>
</tr>
<tr>
<td>Tall Fescue</td>
<td>0.28</td>
<td>0.15</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>Sunflower</td>
<td>1.29</td>
<td>1.24</td>
<td>0.38</td>
<td>0.73</td>
</tr>
<tr>
<td>Shoot Biomass (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oat Plant</td>
<td>1.41</td>
<td>0.78</td>
<td>0.18</td>
<td>0.87</td>
</tr>
<tr>
<td>Rye Grass</td>
<td>0.51</td>
<td>0.30</td>
<td>0.00</td>
<td>0.36</td>
</tr>
<tr>
<td>Tall Fescue</td>
<td>0.41</td>
<td>0.22</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Sunflower</td>
<td>4.19</td>
<td>4.25</td>
<td>0.59</td>
<td>1.57</td>
</tr>
<tr>
<td>Total Biomass (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oat Plant</td>
<td>2.31</td>
<td>1.41</td>
<td>0.50</td>
<td>1.33</td>
</tr>
<tr>
<td>Rye Grass</td>
<td>1.00</td>
<td>0.62</td>
<td>0.00</td>
<td>0.54</td>
</tr>
<tr>
<td>Tall Fescue</td>
<td>0.69</td>
<td>0.37</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>Sunflower</td>
<td>5.48</td>
<td>5.50</td>
<td>0.98</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Based on the growth characteristics, it can be observed that the germination, survival, plant height, and final biomass were greatly influenced by the contamination conditions. More phytotoxicity to the plants was observed under heavy metal contamination alone than under organic or combined contamination conditions. Phytotoxicity by different heavy metals has been studied by various researchers. Heavy-metal contaminants can be either essential or non-essential for plant growth. Essential micronutrients (i.e. Mn, Zn, Cu, Cr, B, Mo) are elements, which are required in small amounts for the normal functioning of plants and animals. But essential micronutrients also affect germination and survival at relatively high concentrations (Kranner and Colville, 2011). Cr is one of the micronutrient, which is required only in small amounts for plants. But higher concentrations of chromium are known to inhibit plant growth (Chandra and Kulshreshtha 2004). Pb and Cd are non-essential heavy metals, which are not known to have any metabolic function in plants, and are toxic to plants at high concentrations (Pahlsson 1989). In the case of organic contaminants, previous research studies also show that high molecular weight PAHs (3-5 rings) do not show phytotoxicity (Henner et al.1999).
FIG. 4. Reduction of total biomass in contaminated soils.

Better performance of plants in combined contaminated soil compared to the plants in metal contaminated soil may be due to the lower bioavailability of heavy metals in presence of organic contaminants. Research conducted by Galvez-Cloutier and Dube (2002) also indicated that the presence of organic contaminants can influence the metal mobility in soils. Difference in sorption of heavy metal contaminants in presence of organic contaminants (Poly and Sreedep 2011) may be the reason of lower bioavailability of heavy metals in combined contaminated soils.

The initial and final (after plant growth) soil samples from all the pots, were analyzed for pH, electrical conductivity, and oxidation-reduction potential. Table 4 shows the average values of pH, electrical conductivity, and oxidation-reduction potential for the soil samples after the plant growth period. According to this, pH, electrical conductivity, and oxidation-reduction potential are not significantly affected by contamination or by the presence of plants. This can be taken as a positive result for remediation, as microbial activities responsible for the rhizodegradation and rhizostabilization are dependent on the soil pH to a great extent (Atagana et al. 2003).
Table 4. Average pH, Oxidation Reduction Potential, and Electrical Conductivity Values for Clean Soil and Contaminated Soils

<table>
<thead>
<tr>
<th>Plant</th>
<th>Clean Soil pH</th>
<th>Organic Contamination pH</th>
<th>Heavy Metal Contamination pH</th>
<th>Mixed Contamination pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>7.9</td>
<td>7.7</td>
<td>7.7</td>
<td>7.6</td>
</tr>
<tr>
<td>Oat Plant</td>
<td>7.8</td>
<td>7.8</td>
<td>7.8</td>
<td>7.9</td>
</tr>
<tr>
<td>Rye Grass</td>
<td>7.9</td>
<td>7.8</td>
<td>7.8</td>
<td>7.9</td>
</tr>
<tr>
<td>Tall Fescue</td>
<td>8.0</td>
<td>7.8</td>
<td>7.9</td>
<td>7.9</td>
</tr>
<tr>
<td>Sunflower</td>
<td>7.7</td>
<td>7.7</td>
<td>8.0</td>
<td>7.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plant</th>
<th>ORP (mV)</th>
<th>ORP (mV)</th>
<th>ORP (mV)</th>
<th>ORP (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-66.2</td>
<td>-55.3</td>
<td>-54.5</td>
<td>-45.3</td>
</tr>
<tr>
<td>Oat Plant</td>
<td>-50.1</td>
<td>-46.1</td>
<td>-46.0</td>
<td>-50.9</td>
</tr>
<tr>
<td>Rye Grass</td>
<td>-52.9</td>
<td>-48.7</td>
<td>-45.3</td>
<td>-52.1</td>
</tr>
<tr>
<td>Tall Fescue</td>
<td>-57.2</td>
<td>-49.1</td>
<td>-56.2</td>
<td>-52.6</td>
</tr>
<tr>
<td>Sunflower</td>
<td>-41.7</td>
<td>-43.0</td>
<td>-56.8</td>
<td>-43.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plant</th>
<th>EC (mS/cm)</th>
<th>EC (mS/cm)</th>
<th>EC (mS/cm)</th>
<th>EC (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.08</td>
<td>0.12</td>
<td>0.12</td>
<td>0.17</td>
</tr>
<tr>
<td>Oat Plant</td>
<td>0.14</td>
<td>0.17</td>
<td>0.17</td>
<td>0.13</td>
</tr>
<tr>
<td>Rye Grass</td>
<td>0.13</td>
<td>0.15</td>
<td>0.17</td>
<td>0.13</td>
</tr>
<tr>
<td>Tall Fescue</td>
<td>0.11</td>
<td>0.15</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>Sunflower</td>
<td>0.19</td>
<td>0.19</td>
<td>0.11</td>
<td>0.19</td>
</tr>
</tbody>
</table>

CONCLUSIONS

In general, better germination and growth characteristics were observed in organic contamination soils compared to heavy metal contaminated soils and mixed contaminated soils. All plants showed delayed germination, reduced germination and survival rates in heavy metal contaminated soil and mixed contaminated soil compared to the control. Performance of plants in mixed contaminated soils was better compared to the plants in heavy metal contaminated soils. Phytotoxicity seems to be lesser when organic contaminants are present along with heavy metals compared to the situations when heavy metals are present alone. This indicates that a plant that is able to survive in the heavy metal contaminated soil may be able to perform better in heavy metal-PAH contaminated soils. Compared to the other plants studied, oat plant showed better germination in all contamination conditions. But, in heavy metal alone contaminated soil, survival rate of oat plant was very low. Even though rye grass had good germination and survival rates in organic and mixed contaminated soils, it had very low germination rate and no plants survived in heavy metal contaminated soil. Tall fescue also had lower germination rates and survival rates in heavy metal contamination and mixed contamination. Even though sunflower had reduced germination rates in heavy metal contaminated soil, its survival rates were better in all contaminations. Biomass of sunflower plants was considerably
higher than the biomass of all other plants in all contamination conditions. Since the contaminants may be present at a site individually or in combination, sunflower seems to be a good phytoremediation plant considering the growth characteristics in individual and combined contamination conditions. However, a detailed evaluation of contaminant fate and distribution in the soils and plants is being performed to better understand the uptake, stabilization and degradation of the contaminants by the plants.

REFERENCES


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