Researches on the degradation of organic compounds in soils polluted with hydrocarbons and brine

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Abstract. The accidental pollution of soils with hydrocarbons due to leaks from oil pipes is an important environmental problem that needs to be tackled by applying adequate decontamination measures. However, in the case of historical pollution situations, it is important to know also how the pollution and the pollutants have evolved in the soil over time. The authors of this paper have analysed the site of an historical pollution in the area of the Neagra creek, Dambovita county, Romania, and have determined the state of decomposition and transformation of organic compounds in the affected soil over a total period of 17 years (1997-2014). The soil had a high natural content of salts, which significantly influenced the degradation processes. The analyses have revealed that the contents of pollutant organic matter has decreased, but in the area the vegetation could not recover adequately due to the destruction of the soil structure.

Key Words: contamination, oil-based compounds, brine, soil.

Introduction. Soil pollution is one of the most problematic types of pollution, because it has multiple negative effects and can persist over a long period of time (Chis 2003; White 2013; Pinedo et al 2013; Liu et al 2011).

Among the various types of soil pollution, the contamination with oil-derived products (hydrocarbons) is of increasing interest, because the presence of hydrocarbons in the soil tends to affect the normal biological circuits, blocking the development of plants (Kingston 2002; Onutu & Tanasescu 2004; Troeh & Thompson 2005).

This type of pollution can have several sources, among which can be mentioned (Avram et al 2006):
- accidental breaking of hydrocarbons pipelines;
- leakage from hydrocarbons storages or losses during their transportation;
- road and railway accidents which involve oil tanks;
- exploitation of research and exploitation wells;
- marine pollution due to the activity of oil rigs;
- pollution of water courses and their shores by intentional or accidental spilling.

The accidental pollution of soils with hydrocarbons due to leaks from oil pipelines is an important environmental problem that needs to be tackled by applying adequate decontamination measures.

Currently, there are numerous efforts worldwide to find solutions for an efficient depollution of the soils contaminated with hydrocarbons (Istrate et al 2010; Patrascu et al 2008; Stoica et al 2014).

In the case of historical pollutions, it might be more difficult to assess the best decontamination solution, on the one hand because one needs to take into account also the natural degradation of the pollutants in the soil, over time but also due to the possible presence in the contaminated area of supplemental problematic substances,
such as brine (Aleer et al 2011; Colin 2000; Rhykerd et al 1995; Toti et al 1998; Whittemore 2007).

In the current paper, the authors have therefore undertaken a study of the evolution in time of the chemical parameters of a polluted area that was detected in 1997, but where, for the very reason of allowing scientific studies on the rate of natural biodegradation of the pollutants, no decontamination measures were applied since then. There are presented and compared the results of two sets of analyses, one carried out in 2005 and one carried out in 2014.

The main aspects studied were the extent of the contamination with hydrocarbons in several locations and at various depths, but also the extent of salinisation and the interaction of the salts and brine in the soil with the hydrocarbons and the effect of the pollution on the vegetation.

**Material and Method.** The studied polluted area is located in the area of the Neagra river, a tributary of the Ialomita river, near the town of Moreni, Dambovita county (Figure 1).

The analyses carried out both in 2005 and in 2014 used the gas chromatography - mass spectrometry (GC-MS) method (Dumitrescu et al 2005) and included the determination of following elements:
- the contents of soluble salts in the soil:
  - contents of Na$^+$, Ca$^{2+}$, Mg$^{2+}$, K$^+$ cations,
- contents of chlorides (Cl⁻);
- contents of sulphates (SO₄²⁻);
- the sodium adsorption ratio (SAR);
- the electrical conductivity;
- the soil's pH;
- the saturation percentage;
- the theoretical gypsum requirement (TGR);
- the contents of mononuclear aromatic hydrocarbons (benzene, toluene, ethylbenzene xylene etc.);
- the contents of saturated hydrocarbons;
- the contents of C₁₁-C₄₀.

A first systematic analysis of the chemical parameters of the soil in the affected area was carried out in 2005. This analysis involved the extraction of 7 soil samples, 5 from the polluted area and 2 from a nonpolluted area next to an orchard and serving as reference samples. Figure 2 presents the situation of the polluted area near the Neagra river (from where two soil samples were extracted, 376136-5 and 376136-6).

The analyses on the polluted area were repeated in 2014. The analyses carried out and the targeted parameters were the same as in 2005. This time, there were collected 9 soil samples from various locations in the same general area. Two of the samples, coded P1 and P2, were collected from the same unpolluted location, near the orchard in the vicinity of the studied pollution (Figure 3.a), but from different depths (0-150 mm and 150-400 mm, respectively) and were used as reference samples (Figure 3.b).

In the polluted area there were used 4 sample collection locations, some of them (P3, P6, P8) from the surface (0-150 mm of depth), one (P4) from a medium depth (150-400 mm) and the rest from a greater depth (400-600 mm). Samples 3-5 were collected from an area that presented a visible bituminous crust (Figure 4).

Figure 2. Situation of the polluted area near the Neagra river in 2005.
Results and Discussion. The results of the analyses carried out in 2005 are presented synthetically in Table 1.

When comparing the values resulting from these analyses with the interpretation limits for the various parameters, found in the speciality literature (Tang et al 2011; Chis 2003; Patrascu et al 2008; White 2013), it can be said that:

- the values for the two reference samples indicate a soil with neutral pH, nonsalinated from the point of view of Cl ions and weakly salinated from the point of view of Na ions and nonpolluted from the point of view of hydrocarbons contents;
- to the contrary, the samples 3, 4 and 6 from the polluted area show a weakly alkaline soil, strongly salinated and with a high amount of hydrocarbons;
- sample 5 indicates a soil with neutral pH, strongly salinated but with a much higher contents of hydrocarbons;
- sample 7 indicates a weakly salinated soil with neutral pH, but with a high hydrocarbons concentration, indicating that this pollution must have occurred around the time of the samples’ extraction or not long before this.

Table 1

Results of the analyses carried out in 2005

<table>
<thead>
<tr>
<th>Curr. no.</th>
<th>Analysed indicator</th>
<th>Measurement unit</th>
<th>376136-1</th>
<th>376136-2</th>
<th>376136-3</th>
<th>376136-4</th>
<th>376136-5</th>
<th>376136-6</th>
<th>376136-7</th>
<th>0-15 cm</th>
<th>30-60 cm</th>
<th>0-15 cm</th>
<th>30-60 cm</th>
<th>Near the Neagra river</th>
<th>Near the Neagra river</th>
<th>Surface with older oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>-</td>
<td>6.8</td>
<td>7.1</td>
<td>7.21</td>
<td>7.3</td>
<td>7.1</td>
<td>7.3</td>
<td>7.0</td>
<td>6.8</td>
<td>7.1</td>
<td>7.21</td>
<td>7.3</td>
<td>7.1</td>
<td>7.3</td>
<td>7.0</td>
</tr>
<tr>
<td>2</td>
<td>Electrical conductivity</td>
<td>dS/m at 25°C</td>
<td>0.21</td>
<td>0.32</td>
<td>16.0</td>
<td>11.4</td>
<td>4.45</td>
<td>2.08</td>
<td>0.44</td>
<td>0.21</td>
<td>0.32</td>
<td>16.0</td>
<td>11.4</td>
<td>4.45</td>
<td>2.08</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>SAR</td>
<td>%</td>
<td>0.5</td>
<td>0.9</td>
<td>36</td>
<td>37.5</td>
<td>7.9</td>
<td>30</td>
<td>1.3</td>
<td>0.5</td>
<td>0.9</td>
<td>36</td>
<td>37.5</td>
<td>7.9</td>
<td>30</td>
<td>1.3</td>
</tr>
<tr>
<td>4</td>
<td>Calcium (Ca²⁺)</td>
<td>mg kg⁻¹</td>
<td>18.5</td>
<td>19.7</td>
<td>523</td>
<td>165</td>
<td>610</td>
<td>10</td>
<td>4.5</td>
<td>18.5</td>
<td>19.7</td>
<td>523</td>
<td>165</td>
<td>610</td>
<td>10</td>
<td>4.5</td>
</tr>
<tr>
<td>5</td>
<td>Magnesium (Mg²⁺)</td>
<td>mg kg⁻¹</td>
<td>2.7</td>
<td>3.3</td>
<td>200</td>
<td>35</td>
<td>100</td>
<td>2</td>
<td>0.8</td>
<td>2.7</td>
<td>3.3</td>
<td>200</td>
<td>35</td>
<td>100</td>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>6</td>
<td>Sodium (Na⁺)</td>
<td>mg kg⁻¹</td>
<td>7</td>
<td>12</td>
<td>4030</td>
<td>1590</td>
<td>890</td>
<td>410</td>
<td>3</td>
<td>7</td>
<td>12</td>
<td>4030</td>
<td>1590</td>
<td>890</td>
<td>410</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>Potassium (K⁺)</td>
<td>mg kg⁻¹</td>
<td>1</td>
<td>&lt;0</td>
<td>20</td>
<td>9</td>
<td>20</td>
<td>&lt;9</td>
<td>1</td>
<td>1</td>
<td>&lt;0</td>
<td>20</td>
<td>9</td>
<td>20</td>
<td>&lt;9</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>Chlorides</td>
<td>mg kg⁻¹</td>
<td>3</td>
<td>8</td>
<td>7040</td>
<td>2500</td>
<td>497</td>
<td>526</td>
<td>2</td>
<td>3</td>
<td>8</td>
<td>7040</td>
<td>2500</td>
<td>497</td>
<td>526</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>Sulphates (SO₄⁻)</td>
<td>mg kg⁻¹</td>
<td>5</td>
<td>8.6</td>
<td>100</td>
<td>30</td>
<td>1000</td>
<td>30</td>
<td>2</td>
<td>5</td>
<td>8.6</td>
<td>100</td>
<td>30</td>
<td>1000</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Nitrites/nitrat es</td>
<td>mg kg⁻¹</td>
<td>2.2</td>
<td>2.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>1.0</td>
<td>&lt;0.04</td>
<td>2.2</td>
<td>2.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>1.0</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>11</td>
<td>TGR</td>
<td>T/ac</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&gt;20.0</td>
<td>&gt;20.0</td>
<td>0.5</td>
<td>0.7</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&gt;20.0</td>
<td>&gt;20.0</td>
<td>0.5</td>
<td>0.7</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>12</td>
<td>Saturation degree</td>
<td>%</td>
<td>58</td>
<td>53</td>
<td>113</td>
<td>61</td>
<td>122</td>
<td>93</td>
<td>8</td>
<td>58</td>
<td>53</td>
<td>113</td>
<td>61</td>
<td>122</td>
<td>93</td>
<td>8</td>
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</table>

Table 1 continued

- Mononuclear aromatic hydrocarbons

<table>
<thead>
<tr>
<th>Curr. no.</th>
<th>Analysed indicator</th>
<th>Measurement unit</th>
<th>376136-1</th>
<th>376136-2</th>
<th>376136-3</th>
<th>376136-4</th>
<th>376136-5</th>
<th>376136-6</th>
<th>376136-7</th>
<th>0-15 cm</th>
<th>30-60 cm</th>
<th>0-15 cm</th>
<th>30-60 cm</th>
<th>Near the Neagra river</th>
<th>Near the Neagra river</th>
<th>Surface with older oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>Benzene</td>
<td>mg kg⁻¹</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>14</td>
<td>Toluene</td>
<td>mg kg⁻¹</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.07</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.07</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>15</td>
<td>Ethylbenzene</td>
<td>mg kg⁻¹</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.06</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.06</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>16</td>
<td>Total xilene</td>
<td>mg kg⁻¹</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.29</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.29</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>17</td>
<td>Total C₆-C₁₀</td>
<td>mg kg⁻¹</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>18</td>
<td>Total C₁₁-C₄₀</td>
<td>mg kg⁻¹</td>
<td>530</td>
<td>90</td>
<td>56900</td>
<td>35700</td>
<td>279000</td>
<td>10900</td>
<td>257000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the case of the samples taken near the Neagra river, at the surface (0-150 mm), the SAR value is within reasonable limits, but at depths of 300-600 mm, the value reaches 30, indicating a lack of calcium ions. Also, while at the surface the pollution with hydrocarbons is high, 28%, in depth (300-600 mm) the hydrocarbons concentration is very low, 0.1%, which means the pollution has not advanced in depth, there existing a still active hydrocarbons pollution source feeding the area, but the pollutant had no time to infiltrate in depth.

The results of the laboratory analyses of the samples collected in 2014 are presented in Table 2.

Concerning the samples collected in 2014, it can be concluded that:
- the values for the two reference samples indicate a soil with weakly acid pH, nonsalinated from the point of view of Cl ions and weakly salinated from the point of view of Na ions and nonpolluted from the point of view of hydrocarbons contents;
- some of the samples indicate soil not polluted with hydrocarbons (P6, P7), while others (P3, P4, P5, P8, P9) are still polluted with hydrocarbons (alkanes, isoalkanes and cyclic alkanes), but at much lower levels than in 2005.
Table 2

Results of the laboratory analyses carried out in 2014 for the targeted area

<table>
<thead>
<tr>
<th>Curr. no.</th>
<th>Samples</th>
<th>pH</th>
<th>Electrical conductivity [µS cm⁻¹]</th>
<th>Chlorides [mg kg⁻¹]</th>
<th>Sulphates [mg kg⁻¹]</th>
<th>Na [mg kg⁻¹]</th>
<th>Ca [mg kg⁻¹]</th>
<th>Mg [mg kg⁻¹]</th>
<th>SAR [%]</th>
<th>Hydrocarbons [mg/g soil]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P₁ - reference sample (0-150 mm)</td>
<td>6.35</td>
<td>101</td>
<td>10</td>
<td>25</td>
<td>15</td>
<td>62</td>
<td>9.5</td>
<td>0.22</td>
<td>0.228</td>
</tr>
<tr>
<td>2</td>
<td>P₂ - reference sample (150-400 mm)</td>
<td>6.3</td>
<td>64</td>
<td>7</td>
<td>30</td>
<td>13</td>
<td>59</td>
<td>9</td>
<td>0.17</td>
<td>0.148</td>
</tr>
<tr>
<td>3</td>
<td>P₃ - area with solidified hydrocarb. (0-150 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>417.2</td>
</tr>
<tr>
<td>4</td>
<td>P₄ - area with solidified hydrocarb. (150-400 mm)</td>
<td>6.56</td>
<td>429</td>
<td>120</td>
<td>225</td>
<td>153</td>
<td>258</td>
<td>30</td>
<td>5.76</td>
<td>121.1</td>
</tr>
<tr>
<td>5</td>
<td>P₅ - area with solidified hydrocarb. (400-600 mm)</td>
<td>6.8</td>
<td>251</td>
<td>90</td>
<td>130</td>
<td>160</td>
<td>95</td>
<td>11</td>
<td>17.11</td>
<td>12.64</td>
</tr>
<tr>
<td>6</td>
<td>P₆ - area near the Neagra river (0-150 mm)</td>
<td>6.55</td>
<td>326</td>
<td>35</td>
<td>35</td>
<td>145</td>
<td>182</td>
<td>36</td>
<td>6.59</td>
<td>0.2</td>
</tr>
<tr>
<td>7</td>
<td>P₇ - area near the Neagra river (150-400 mm)</td>
<td>6.88</td>
<td>182</td>
<td>25</td>
<td>30</td>
<td>190</td>
<td>121</td>
<td>17</td>
<td>18.32</td>
<td>0.148</td>
</tr>
<tr>
<td>8</td>
<td>P₈ - area with brine on surface (0-150 mm)</td>
<td>7.2</td>
<td>2580</td>
<td>3250</td>
<td>200</td>
<td>2500</td>
<td>200</td>
<td>36</td>
<td>1822.9</td>
<td>23.2</td>
</tr>
<tr>
<td>9</td>
<td>P₉ - area with brine on surface (400-600 mm)</td>
<td>7.19</td>
<td>2062</td>
<td>2650</td>
<td>100</td>
<td>1938</td>
<td>200</td>
<td>28</td>
<td>1154.1</td>
<td>70</td>
</tr>
</tbody>
</table>

Even if the contents in organic pollutants has been reduced by biodegradation over time, the degree of coverage with vegetation is still reduced or even non-existing in the area, due to the destruction of the soil’s structure.

The analysis and interpretation of the results from 2005 and 2014 reveals that the analysed surface is polluted with brine and hydrocarbons, but also that the hydrocarbons have degraded over time through combined processed of salinisation, alkalinisation and bituminisation that are unfolding in the soil, with varied intensities. There are strong interconditioning processes function of the concentration and compositions of the existing soluble salts.

The soil, based on its properties as disperse, heterogeneous body, acts like a chromatographic column within which the hydrocarbons are redistributed in layers. As the hydrocarbons move along the soil’s profile, the upper layers of the soil retain mainly tars and asphaltenes, which also gives the soil a specific bituminous aspect, while at a depth of 60 cm, there is a much lower concentration of hydrocarbons. This profile is valid both for the 2005 and for the 2014 determinations, even if the contents is lower for the more recent data.

There have been noticed high contents of cations and anions - the salinisation with sodium ions is severe up to a depth of 150 mm, becoming more moderate on the interval between 300-600 mm, which means that the soluble salts too have not migrated in depth.

The high concentrations of sodium and potassium (as monovalent ions) have dispersed the clay particles, thus preventing the water’s penetration in the soil (reducing the soil’s permeability), with visible effects on the soil’s structure and on the development of vegetation. The osmotic pressures in the soil increase and lead to a water stress; the plants are unable to extract water and nutrients from the soil, so cannot develop properly. This thus results in the creation of an adverse environment for plants, whose effects can last for a long time, as the analyses from 2014 show.
Conclusions. In this paper, the authors have analysed the site of a historical pollution in the area of the Neagra creek, Dambovita county, Romania, and have determined the state of decomposition and transformation of organic compounds in the affected soil in 2005 (8 years after the pollution was discovered) and in 2014.

The high natural contents of the soil in salts significantly influenced the degradation processes. The analyses have revealed that the contents of pollutant organic matter has decreased naturally over the years due to natural biodegradation processes, but in the area the vegetation could not recover adequately due to the initial destruction of the soil structure.

Most heavy hydrocarbons remained at or near the surface. These compounds cannot be decomposed completely, but if adequate conditions (aerobic conditions) are provided, the decomposition can be relatively fast.

At the same time, it was noticed that the soluble salts too have remained mostly in the surface layer and have not migrated in depth.

The authors intend to continue monitoring the targeted area and also to unfold further analyses, in order to better understand the processes that occur there.

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