Impact of hydraulic fracturing on soil microbial functions & community

A Spill Scenario Study

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Spills of fluids can occur during CSG operations

Patterson et al. (2017) DOI: 10.1021/acs.est.6b05749

ACS Publications
High quality. High impact.
Study objectives

- To assess the potential impacts as a result of a spill of HF and produced water on soil microbial functions and community

1. degradation rate of selected chemicals in HF fluid and produced water, in soils;
2. sorption of selected chemicals in soils to assess their mobility through soils to shallow groundwater; and
3. potential impacts of HF fluid and produced water spills on soil microbial health.
Surat Basin

Five dominant soil types

1. Vertosol
2. Dermosol
3. Rudosol
4. Kandosol
5. Sodosol
A range of soil properties represented

<table>
<thead>
<tr>
<th>Soil</th>
<th>EC (1:5) dS/m</th>
<th>pH 0.01 M CaCl₂</th>
<th>Total Carbon %</th>
<th>Total Nitrogen %</th>
<th>Clay %</th>
<th>Silt %</th>
<th>CEC cmol(+)/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface soils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dermosol</td>
<td>0.07</td>
<td>5.0</td>
<td>0.89</td>
<td>0.09</td>
<td>17</td>
<td>28</td>
<td>7.9</td>
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<tr>
<td>Kandosol</td>
<td>0.02</td>
<td>4.8</td>
<td>0.61</td>
<td>0.07</td>
<td>10</td>
<td>16</td>
<td>4.2</td>
</tr>
<tr>
<td>Vertosol</td>
<td>0.08</td>
<td>5.0</td>
<td>1.30</td>
<td>0.11</td>
<td>37</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>Rudosol</td>
<td>0.01</td>
<td>5.1</td>
<td>0.29</td>
<td>0.04</td>
<td>3</td>
<td>5</td>
<td>1.8</td>
</tr>
<tr>
<td>Sodosol</td>
<td>0.13</td>
<td>5.2</td>
<td>1.2</td>
<td>0.11</td>
<td>25</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td><strong>Sub-surface soils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dermosol</td>
<td>0.42</td>
<td>5.7</td>
<td>0.64</td>
<td>0.08</td>
<td>32</td>
<td>21</td>
<td>13.0</td>
</tr>
<tr>
<td>Kandosol</td>
<td>0.05</td>
<td>5.6</td>
<td>0.39</td>
<td>0.05</td>
<td>16</td>
<td>16</td>
<td>5.6</td>
</tr>
<tr>
<td>Vertosol</td>
<td>0.24</td>
<td>6.4</td>
<td>1.10</td>
<td>0.09</td>
<td>33</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Rudosol</td>
<td>0.01</td>
<td>5.2</td>
<td>0.19</td>
<td>0.04</td>
<td>3</td>
<td>4</td>
<td>1.7</td>
</tr>
<tr>
<td>Sodosol</td>
<td>0.26</td>
<td>5.0</td>
<td>0.82</td>
<td>0.09</td>
<td>46</td>
<td>11</td>
<td>21</td>
</tr>
</tbody>
</table>
## Microbial assessment tests

<table>
<thead>
<tr>
<th>Microbial tests</th>
<th>Function</th>
<th>Tests involved</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Overall microbial activity</strong></td>
<td>Ecosystem services (carbon cycling, chemical breakdown)</td>
<td>Substrate-induced respiration (SIR) &amp; quantitative polymerase chain reaction (qPCR)</td>
<td>OECD protocol modified by Broos et al. (2007)</td>
</tr>
<tr>
<td><strong>Specialist function</strong></td>
<td>Nitrogen cycling (nitrification, nitrogen fixing)</td>
<td>Substrate induced nitrification (SIN) and quantitative polymerase chain reaction (qPCR)</td>
<td>OECD protocol modified by Broos et al. (2007)</td>
</tr>
<tr>
<td><strong>Microbial community structure</strong></td>
<td>Various ecosystem services</td>
<td>Next generation sequencing (NGS)</td>
<td>OECD (2015)</td>
</tr>
</tbody>
</table>
Preparation of hydraulic fracturing fluid

1. The HF fluid was prepared in our laboratory by the **engineer of the company** involved in hydraulic fracturing in the field.
   - The **exact recipe and the composition** is proprietary information

2. The HF fluid was prepared **only an hour before its use**, using the same products and recipe being used in field.

3. The **produced water was collected from the field** and kept refrigerated before use in the experiment.
## Key organic chemicals

<table>
<thead>
<tr>
<th>Category</th>
<th>Source</th>
<th>Chemical ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biocides</td>
<td>HF fluid</td>
<td>MIT, CMIT, Used as a mixture</td>
</tr>
<tr>
<td>Breaker Aid</td>
<td>HF Fluid</td>
<td>TEA (triethanolamine)</td>
</tr>
<tr>
<td>Phenols</td>
<td>Produced water</td>
<td>Phenol + 10 chloro and nitrophenols</td>
</tr>
<tr>
<td>Cresols</td>
<td>Produced water</td>
<td><em>m</em>-cresol and <em>p</em>-cresol</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Produced water</td>
<td>PAHs, e.g. Naphthalene (16), BTEX (not detected)</td>
</tr>
</tbody>
</table>
Contamination of soils

• Soils were freshly collected from the field to ensure their microbial integrity.

• Aliquot of 500 g of air-dried soil was spiked with the required volume of fluid (80% of MWHC of soils).

• Homogenised and incubated in a temperature-controlled chamber (maintained at 25± 2°C); moisture maintained.

• The soils were subsampled at pre-determined period for chemical and microbial analysis.
Inherent microbial activities in the soils

- All soils were alive
- Nitrification varied more
- Subsurface low activity
Degradation of biocides – all gone in 3 days

MIT

Surface soil

Relative MIT Concentration

CMIT

Surface soil

Relative CMIT Concentration

Subsurface soil

Relative MIT Concentration

Subsurface soil

Relative CMIT Concentration
Degradation of phenol & cresols – all gone in 2 days

Phenol

Surface soils

Cresols

Surface soils

Relative Concentration

Time (days)
Breakdown of the breaker aid – TEA (frac fluid)

much slower – especially in sub soils
Breakdown of biocides – TEA (pure water)

In pure water – it disappeared more rapidly than in HF fluid

![Graph showing the breakdown of TEA in different soils](image)
Chemical degradation summary

1. The two biocides (MIT and CMIT) are readily degraded in all soils with >90% loss within a day of mixing into most soils.

2. Three geogenic chemicals (i.e. phenol, \(m\)-cresol, \(p\)-cresol) were completely degraded in soils within 2 days in surface soils.

3. Triethanolamine (TEA) degraded rapidly when introduced into soil with pure water (>90% within a week).

4. In the presence of HF fluid, its rate of degradation after 3 days became so slow that little further loss occurred in a month.
Overall microbial activity – carbon turnover

Small but significant effect and some recovery in two months

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Dermosol</th>
<th>Kandosol</th>
<th>Rudosol</th>
<th>Sodosol</th>
<th>Vertosol</th>
</tr>
</thead>
</table>

### During experiment

- **Pure Water**: AA, BB, CC, DD
- **Frac**: FF, GG
- **Fluid**: HH, II
- **Produced W**: JJ, KK

### After experiment

- **Pure Water**: AA, BB, CC, DD
- **Frac**: FF, GG
- **Fluid**: HH, II
- **Produced W**: JJ, KK

Relative response

**Surface**

- **Pure Water**: AA, BB, CC, DD
- **Frac**: FF, GG
- **Fluid**: HH, II
- **Produced W**: JJ, KK

**Subsurface**

- **Pure Water**: AA, BB, CC, DD
- **Frac**: FF, GG
- **Fluid**: HH, II
- **Produced W**: JJ, KK
Specialist functions - Nitrification

Major effect of HF fluid

Complete inhibition
No recovery

Produced water
Significant effect,
More in sub soils
Microbial functions – key findings

1. HF fluid had a marked effect on N cycling – complete inhibition; no recovery even after two months.

2. Produced water had a smaller effect – most soils recovered fully in two months in terms of C-turnover but not N-cycling.

3. It is not clear which constituent of HF fluid or produced water was responsible for toxic effects.
Number of taxa remaining in soils
(3 & 28 days after treatment)

<table>
<thead>
<tr>
<th>Soil types</th>
<th>HF fluid Day 3</th>
<th>HF fluid Day 28</th>
<th>Produced water Day 3</th>
<th>Produced water Day 28</th>
<th>Pure water Day 3</th>
<th>Pure water Day 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dermosol</td>
<td>7</td>
<td>2</td>
<td>8</td>
<td>5</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Kandosol</td>
<td>7</td>
<td>3</td>
<td>7</td>
<td>5</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Vertosol</td>
<td>5</td>
<td>3</td>
<td>6</td>
<td>4</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Rudosol</td>
<td>6</td>
<td>3</td>
<td>8</td>
<td>6</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Sodosol</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>
Population shift

Similar at the beginning but drifted apart by the end of experiment
Community structure

- HF fluid caused a significant alteration of microbial community composition with time.

- At the beginning, populations between treatments were found to be at least 90% similar.

- At Day 28, populations in soils treated with HF were 60% different to that in soils treated with pure water.

- Produced water had a lower impact on microbial community structure.
## Potential groundwater hazard

Data from this study and literature – mobility and degradation

<table>
<thead>
<tr>
<th>Chemical</th>
<th>$\text{DT}_{50}$ or Half-life (days)</th>
<th>Sorption ($K_{oc}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIT</td>
<td>&lt;2</td>
<td>4-450</td>
<td>This study</td>
</tr>
<tr>
<td>CMIT</td>
<td>&lt;2</td>
<td>35-695</td>
<td>This study</td>
</tr>
<tr>
<td>TEA</td>
<td>0.5 - &gt;30</td>
<td>71-733</td>
<td>This study; West and Gonsior (1996)</td>
</tr>
<tr>
<td>Phenol</td>
<td>1.7-10</td>
<td>7-710</td>
<td>This study; Boyd (1982); Southworth and Keller (1986)</td>
</tr>
<tr>
<td>m-Cresol and p-Cresol</td>
<td>1.8-13</td>
<td>18-3420</td>
<td>This study; Boyd (1982); Southworth and Keller (1986); Namkoong et al. (1988); Shibata et al. (2006)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>80</td>
<td>200-1470</td>
<td>Lewis et al. (2016)</td>
</tr>
</tbody>
</table>
Groundwater hazard – GUS Index

Generic hazard – risk depends on site conditions & specific events

Groundwater pollution hazard of chemicals

- MIT
- cresols
- Naphthalene
- CMIT
- Phenol
- Triethanolamine

Graph showing the relationship between Log (DT50) and Log Koc, with different chemicals classified as low, medium, and high hazard.
Groundwater hazard

1. Biocides (MIT, CMIT) phenol and cresols were highly mobile (low sorption) but low inherent groundwater contamination hazard
   - rapid breakdown in the aerobic soils.

2. Large volume spills, however, may result in rapid leaching of these, despite their observed short stability in soils.

3. Triethanolamine (TEA) and naphthalene – medium to high hazard
   - potentially longer persistence in soils.
Take home messages

1. HF fluid spill can seriously impair soil microbial functions, especially nitrification
2. Soil microbial community composition changed when exposed to HF fluid
3. Produced water had a lower but significant effect on microbial activity (nitrification)
4. All soils were able to rapidly breakdown two biocides and three geogenic chemicals tested
   - > 90% loss within 2 days; low groundwater hazard
5. TEA, a breaker aid in HF fluid, degraded slowly in soils
   - Medium to high groundwater hazard.
6. What constituents in HF fluid cause toxicity, need investigation.
Thank you

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