Biochemical Characterization of the Influences of Pump-and-Treat Remediation on Aquifer Conditions on the Central Plateau of the Hanford Site

September 2019

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Richland, Washington 99354
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ABSTRACT

The aim of this research was to quantify and characterize the organic carbon present in the subsurface on the Hanford site, specifically where groundwater pump-and-treat (P&T) operations are currently taking place. The primary purpose of P&T is to remediate groundwater contaminants, however water treatment can alter subsurface conditions by introducing a low, but consistent supply of organic carbon to the subsurface. These inputs have not been characterized and the consequences therein have not been considered prior. Approximately 40 L of groundwater from the P&T facility was processed by stepwise ultra-filtration for carbon characterization. Groundwater was first filtered to remove particulate organic carbon (POC) and colloids (operationally defined as > 0.2 µm) and subsequently, two size fractions of dissolved organic carbon (DOC, operationally defined as <0.2 µm), the > 10 kDa fraction and the >5 kDa fraction. POC was analyzed via X-Ray powder Diffraction (XRD) for structural and phase characterization of groundwater particulates. Dissolved organic carbon (10 kDa fraction) was quantified using a total carbon analyzer (NPOC, non-particulate organic carbon) and the chemical character of this carbon further defined by specific UV absorption and Fourier-Transform Ion Cyclotron Resonance - Mass Spectrometry (FTICR-MS). This detailed analysis of groundwater carbon reveals how P&T operations are affecting subsurface nutrient dynamics, which in turn could have a positive feedback on natural attenuation pathways in the 200W contaminant plume at the Hanford Site.
I. INTRODUCTION

As part of the Department of Energy’s Environmental Management (DOE-EM) mission, subsurface sediments and groundwater impacted by past nuclear production and processing operations at the Hanford Site are being actively remediated. A major effort to clean up contaminated groundwater includes pump-and-treat (P&T) facilities where contaminated groundwater is pumped from the subsurface contaminant plume, treated for the removal of priority contaminants, and cleaned groundwater is then injected back into the subsurface for plume containment (1). The chemistry of treated groundwater is affected by this treatment process and could potentially affect aquifer biogeochemistry. In the past the P&T was introducing a steady supply of organic carbon and nutrients into the Hanford subsurface which is naturally poor in carbon and nutrients (3). These inputs could potentially impact subsurface microbial populations in affected regions by stimulating growth or activity due to the increased availability of biological nutrients. Moreover, if P&T operations are providing a low but consistent supply of organic carbon to the subsurface, there could be unanticipated effects on aquifer development and plume behavior over time; however these potential impacts have not been evaluated.

II. METHODS

A. Filtration

Treated water was collected from the P&T Facility in the 200 West area of the Hanford site. Approximately 40 L of water was first filtered through a 0.2 \( \mu \text{m} \) pore size filter to remove particulate organic carbon (POC), bacterial cells, and colloids. 12 L of the filtered water was then pumped through a 10 kDa filter using an Amicon stirred cell (Figure 2) to capture dissolved organic carbon (DOC). Material collected on the 10 kDa filter was recovered in 50 mL of deionized H\(_2\)O.
and stored at 4°C for analysis. 2 L of this processed water was then pumped through a 5 kDa filter to extract DOC < 10 kDa but > 5 kDa.

![Filter Setup Diagram](image.png)

**FIG. 1 Filter setup** Groundwater was added to Amicon Reservoir Cell, then pumped into Amicon Stirred cell and stirred as it passed through a 5 or 10 kDa filter. Dissolved organic carbon retained by the filter was analyzed. (image from Sigma Aldrich)

**B. Analyses**

POC material collected on the 0.2 µm filter was dried to a constant weight in a 30 °C oven. The dried material was mixed with 15% TiO₂ and ground to a fine powder using a mortar and pestle. The TiO₂ serves as an internal calibration and quantitation standard during analysis of the sample. The prepared sample was analyzed by X-ray Powder Diffraction (XRD) to examine its structural properties. The spectra were interpreted by Mark Bowden at the Environmental Molecular Sciences Laboratory (EMSL).

DOC material collected on the 10 kDa filter was quantified using a total carbon analyzer. To infer some information about the complexity and reactivity of this DOC fraction, the sample was measured at 254 nm on a UV/VIS spectrophotometer. 254 nm is a wavelength that is readily
absorbed by organic matter and thus serves as a good parameter for measuring aromaticity and polymeric complexity of organic carbon captured from the groundwater (4). As reference standards, the absorbance at 254 nm of glucose, yeast extract, lignin and humic acid at varying concentrations were also measured. Stock solutions (1g/L) of yeast extract, glucose, lignin and humic acid were diluted to 1000, 500, 100, 75, 50, 25, 10, 5, and 1 mg/L solutions. An absorbance at 254 nm vs. concentration plot for all four solutions was generated in Excel.

Finally, the 10kDa DOC sample diluted to 1.5 mg C / L and dried to constant weight. DOC was suspended in analytical grade methanol for analysis by FTICR-MS at EMSL. The data were processed using the FTMS R Exploratory Data Analysis (FREDA) tool available in the EMSL toolbox.

III. RESULTS

A. X-ray diffraction

FIG. 2. POC analysis. The X-ray diffractogram suggests that the POC captured from treated groundwater is non-crystalline, amorphous material.
### Specific absorbance at UV 254 nm (SUVA)

<table>
<thead>
<tr>
<th>mg/L</th>
<th>Glucose</th>
<th>YE</th>
<th>Lignin</th>
<th>Humic Acid</th>
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<tr>
<td>1000</td>
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<td>3.974</td>
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<td>0</td>
<td>0</td>
<td>0.008</td>
</tr>
</tbody>
</table>

**Table 1.** UV254 absorbance for glucose, yeast extract, lignin and humic acid at a range of concentrations.
FIG. 3. Carbon structural complexity. Plotted correlation between specific UV absorbance and concentration for different carbon sources. The specific absorbance of groundwater DOC aligned most closely with lignin, suggesting this fraction possess a significant aromatic signature.
B. FTICR-MS

FIG. 4. Van Krevelen diagram of DOC chemical complexity as measured by FTICR-MS. Microbial lipids and macromolecules (proteins) were more prevalent in treated groundwater than highly refractory, photosynthetically derived DOC.

FIG. 5. Van Krevelen diagram from FTICR-MS of untreated Hanford groundwater and saturated sediments shown for comparison (2). These preparations revealed noticeably more lignin, tannin and unsaturated hydrocarbon compounds than the P&T water. The specific contributions from groundwater and sediment need to be resolved.
IV. DISCUSSION

Analysis of POC in the groundwater showed non-crystalline, amorphous chemical composition. This result is consistent with previous analysis of this material which is presumed to be precipitated or flocculated Mn and possibly Ca. This analysis is consistent with the fact that the subsurface environment is complex and heterogeneous and particulate material found in groundwater is likely to be impure.

For SUVA, the absorbance for carbon in the groundwater was plotted alongside the absorbance of four reference solutions: glucose, yeast extract, lignin and humic acid (FIG. 3). Glucose and yeast extract are simple carbon sources while lignin and humic acid are more complex carbon sources. The groundwater sample likely contains both simple and complex forms of carbon so comparing its absorbance to known simple and complex carbon sources can indicate which type of carbon likely predominates in the water. Specific UV absorption results showed that the specific absorbance of groundwater aligned most closely with that of lignin, suggesting that structurally complex carbon molecules may predominate in the groundwater. The FTICR-MS results, however, show that lignin only makes up a small portion of the organic material in the groundwater. Lipid compounds, probably derived from microbial cell wall material, were more prevalent than more complex material such as lignin. The combination of results from specific UV absorbance at 254 nm (SUVA) and FTICR-MS further suggest that treated groundwater contains a variety of organic carbon compounds, some of which can serve as a viable energy source for subsurface microorganisms at or near groundwater re-injection sites.

Comparison of Van Krevelen plots from FTICR of treated and untreated Hanford groundwater further show the difference in chemical character of treated vs. untreated water. FTICR-MS gives the exact molecular mass of different molecules in the sample. Molecular formulas can be derived
from the exact mass and used to derive information about the type and abundance of different carbon compounds in the Hanford groundwater. Treated Hanford water has more lipid compounds than untreated, and fewer lignin, tannins, and unsaturated hydrocarbon compounds. If more bioavailable carbon sources are present in treated water, it could potentially help to sustain natural attenuation pathways in the subsurface which would benefit remediation efforts at the site.

V. CONCLUSIONS

Current P&T operations do alter the characteristics of Hanford groundwater. Not only are contaminants removed, but the input of new carbon could impact the biogeochemistry of subsurface sediments. The availability of organic carbon could have a positive effect on contaminant degradation pathways in the 200 West contaminant plume. Even though the concentration of organic carbon in P&T water is low; at an average injection rate of 200 L/min per injection well, significant carbon is being introduced into the aquifer. Detailed characterization of this carbon suggests that it is a viable energy source for subsurface microorganisms. Natural microbial activity in the subsurface could benefit P&T operations by helping to reduce contaminant levels in aquifer.

VI. ACKNOWLEDGEMENTS

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VII. REFERENCES

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