

The Use of Nitrate for Hydrocarbon Remediation in Groundwater



RYAN DAVID
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Outline



- Reason for topic selection
- Overview of hydrocarbons
- Description of project conducted at Seal, Beach, CA
- My goals
- My results
- Conclusion

Topic Selection



- This topic was selected because of the use of Nitrate to treat/remediate water
- Nitrate is normally considered a contaminant not a treatment option
- Nitrate can cause birth defects and lead to Eutrophication in surface waters (Shrimali and Singh, 2001)

Negative affects of Nitrate



In Humans

- **Methemoglobinemia (form of Blue-Baby Syndrome)**
- **Contributes to the risk of Non-Hodgkin's Lymphoma, bladder cancer, and ovarian cancer**

(Camargo, 2006)

In the Environment

- **Nitrate and Nitrite have been linked to the acidification of freshwater ecosystems**
- **Increased Nitrate leads to Eutrophication which can then lead to dangerous algal growth**
- **Both of these can lead to large fish kills and severe damage to a freshwater ecosystem**

Hydrocarbons



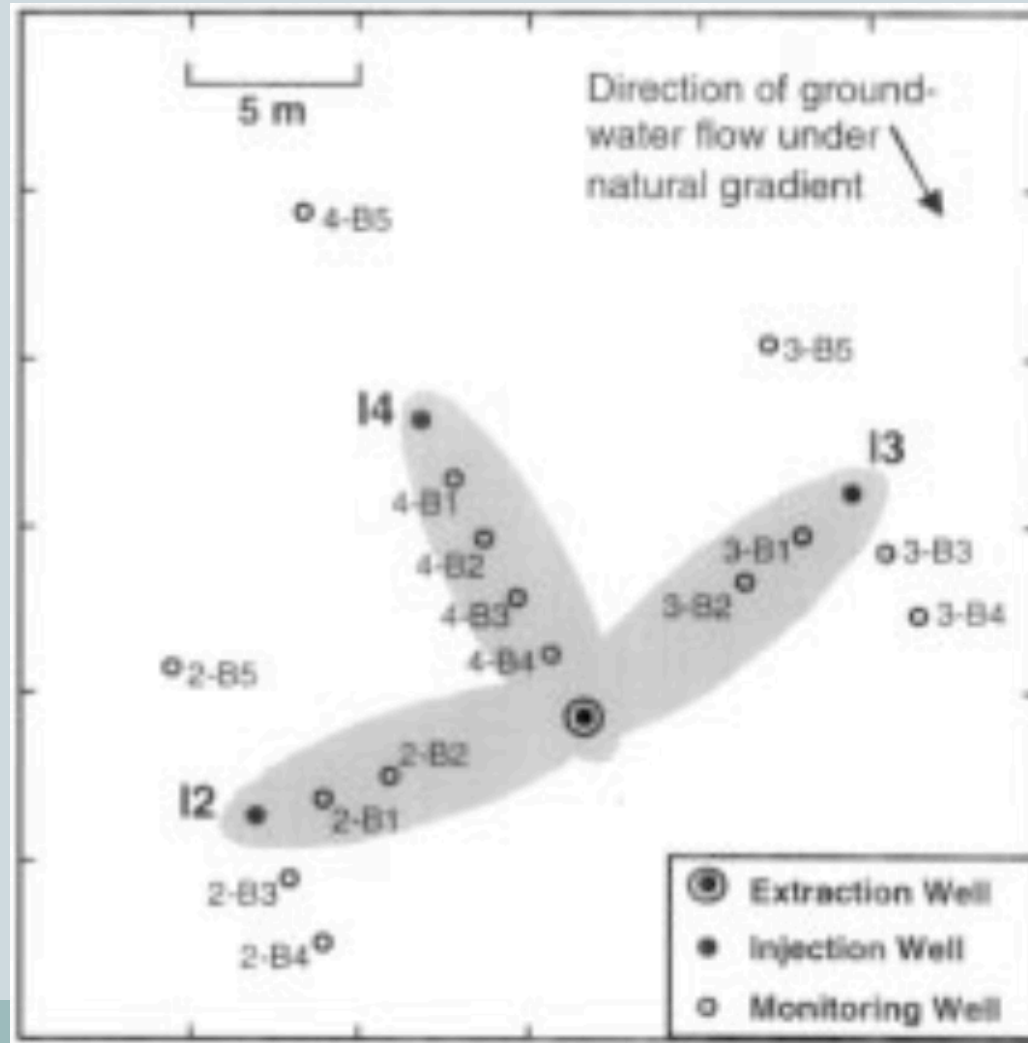
- Common Hydrocarbons
 - Gasoline
 - Diesel
 - BTEX
 - ✦ Benzene
 - ✦ Toluene
 - ✦ Ethylbenzene
 - ✦ Xylene
- There could be as many as 300,000 contaminated groundwater sites in the US alone. Most of these are caused by leaking underground hydrocarbon fuel tanks (Cunningham, 2000)

Naval Weapons Station, Seal Beach, CA



- Shallow groundwater aquifer contaminated with BTEX
- Enhanced anaerobic biodegradation of BTEX was tested at this site
- Experiments started on the site in 1991
- The goal of this study was to show that Nitrate and sulfate are a feasible engineering solution to remediating this type of contaminated groundwater

Site layout and experiment overview



My Goals



- My First goal was to use PHREEQC to model how Nitrate degrades BTEX
- Unfortunately this goal was not possible, PHREEQC does not have any knowledge of the BTEX chemicals
- If I could have accomplished this goal I would have taken the Seal Beach experiment one step further by varying the temperature and pH to observe their affect on the biodegradation of BTEX with Nitrate
- My second was to use the MIX simulation of PHREEQC to analyze what could be expected during an accidental spill of the nitrate contaminated groundwater used for treating BTEX

MIX Simulator in PHREEQC



- Unfortunately I could not obtain groundwater data from the Seal Beach site. So I obtained a groundwater analysis from a study conducted on a gasoline contaminated aquifer.
- Cozzarelli et al., 1999

Constituent	Background perched water	Contaminated perched water
pH	4.73	6.01
D.O.	6.1	0
NO ₃ ⁻	39.7	0
SO ₄ ²⁻	23.7	4.73
HCO ₃ ⁻	2.4	158
Fe ²⁺	b.d. ^a	34.5
NH ₄ ⁺	b.d. ^a	2.88
H ₂ S	b.d. ^a	1.1
CH ₄	b.d. ^a	0.04

^ab.d. means below detection limit.

Mix Simulator



- Using the groundwater sample I created two spill scenarios
 1. Spill into a seawater source
 2. Spill that enters a groundwater source
- My Seawater solution came from the PHREEQC user manual Example 3 (Parkhurst and Appelo, 1998)

Mix Simulator



- First I had to define to Solutions in PHREEQC
- Second I had to define what percent of each of the two solutions I wanted PHREEQC to use for the MIX solution
 - I used a 10%, 25%, 50%, 75%, and 90% Nitrate contaminated groundwater solution mixed with the corresponding Seawater or non-contaminated groundwater solution
- Third I compared PHREEQC's output value for the Nitrate concentration of the mixed solution

Input File Example



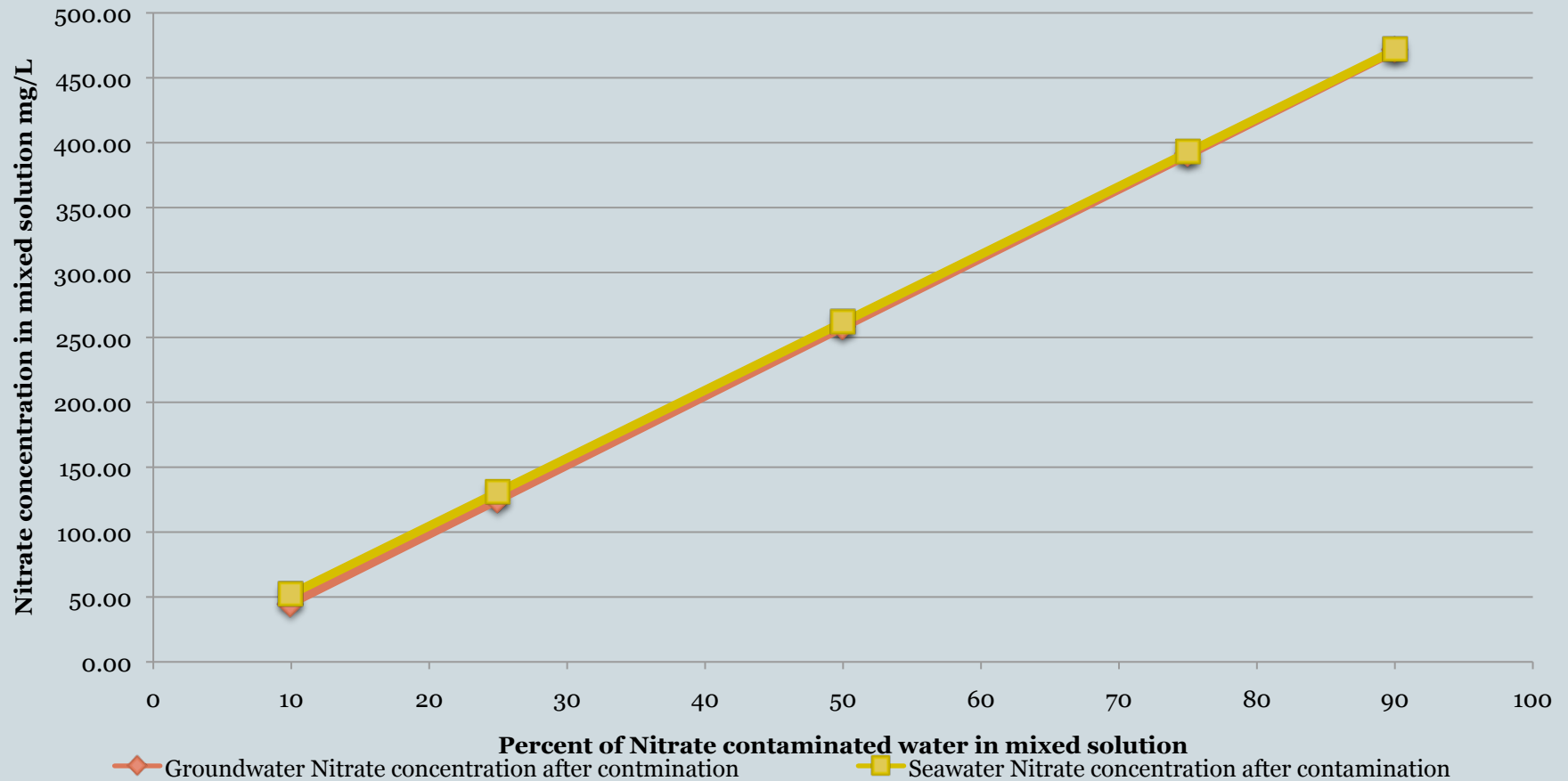
```
• TITLE Mixing Nitrate groundwater with freshwater or sea water
• SOLUTION 1 Groundwater from VW10
•   units mg/l
•   temp  25.0
•       S(6)          20
•       C(4)          158
•       FE(2)         34.5
•       C(-4)         0.04
•       N(5)          120
• END
• Title Definition of Seawater
• SOLUTION 2 Seawater
•   units ppm
•   pH    8.22
•   pe    8.451
•   density 1.023
•   temp  25.0
•   Ca    412.3
•   Mg    1291.8
•   Na    10768.0
•   K     399.1
•   Si    4.28
•   Cl    19353.0
•   Alkalinity 141.682 as HCO3
•   S(6)    2712.0
• END
• Title Mix 25% groundwater, 75% Seawater
• MIX 1
•     1          0.9
•     2          0.1
• END
```

Output File Example



			Log	Log	Log	mole V	
	Species	Molality	Activity	Molality	Activity	Gamma	cm≥/mol
•	N(o)	1.276e-04					
•	N2	6.379e-05	6.387e-05	-4.195	-4.195	0.001	29.29
•	N(3)	4.415e-13					
•	NO2-	4.415e-13	4.079e-13	-12.355	-12.389	-0.034	25.01
•	N(5)	7.586e-03					
•	NO3-	7.586e-03	7.009e-03	-2.120	-2.154	-0.034	29.53

Comparison of Results



Conclusions



- PHREEQC is a very large program that I did not have enough time to master
- My simple tests using the MIX simulator could have been helpful to the researchers at Seal Beach in the case of a spill
- The speed of PHREEQC and its ability solve very complex problems could have been used to estimate the nitrate concentration immediately following an accidental spill allowing ease of reporting and cleanup of the spill
- PHREEQC's mix simulator could be an inexpensive tool that could accurately estimate the concentration of Nitrate in a contaminated source of water
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Thank You!



- Questions?

Refernces



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- Cunningham, Jeffery A., Gary D. Hopkins, Carmen A. Lebron, and Martin Reinhard. "Enhanced Anaerobic Bioremediation of Groundwater Contaminated by Fuel Hydrocarbons at Seal Beach, California." *Biodegradation* 11 (2000): 159-70. *Elsevier*. Web. 2 Dec. 2014.
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