Graduate Studies in Hydrogeology: A Crash Course in Admission, Coursework, and Research

Charles Paradis
Student Alumni Career Forum
Earth and Planetary Science
UC Berkeley
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Introduction

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• 2007 BA Geology, UC Berkeley
• 2007-Current
  – Associate Geologist, Parsons, Walnut Creek
• 2010-Current
  – MS Candidate, UC Davis, Hydrology
Goal of UCB Alumni Student Careers Forum

• For students to become more aware of the career opportunities in the geosciences outside of the research university environment
  – Graduate school is not a career, but, it can be a stepping stone towards a better one
Preview

1. Why go to graduate school?
2. Why study hydrogeology?
3. How do I get into a graduate program?
4. What is the course work like?
5. What is the research like?
6. What can you do after you’re done?
7. Five tips for graduate school
Why go to graduate school?

• BA/BS is adequate for entry-level positions
• Most advanced geoscientists and hydrologists need a MS
  – Preferred educational requirement for technical positions in private industry, federal agencies, and state geological surveys
  – Ph.D. is necessary for most high-level research and college teaching positions
• Graduates with a master's degrees in geosciences or hydrology can expect excellent job opportunities
  – Ph.D.s may face competition for research and college teaching jobs
Where are they now?

- Paths of those before you (Boston, DC, Texas, SD, LA, Oakland, Walnut Creek)
  - 10 people I graduated with (as of Jan. 2011)
  - 5 Environmental Consulting (3 geologists, 1 geophysicist, 1 atmospheric)
  - 3 Graduate School (2 geologists PhD, 1 geologist MS)
  - 1 Research (geologist)
  - 1 Education (geologist)
Why study hydrogeology?

• Help address several important hydrologic problems
  – Efficient use and development of groundwater and surface water resources
  – Pollution of subsurface and surface waters from urban runoff, leaky underground storage tanks, and agricultural drainage
  – Water quality criteria for drinking water and for fish and aquatic life
  – Natural disasters such as flooding and landslides
  – Problems demand hydrologists with comprehensive, multi-disciplinary education

• Employment of hydrologists is expected to grow faster than average for all occupations
How do I get into a graduate program?

1. Undergraduate Degree
   - Environmental or physical sciences
   - Mathematics or Engineering

2. Prerequisites
   - Calculus I, II, III, Diff Eq., Linear algebra
   - Physics I, II with calculus
   - Chemistry I, II
   - Applied statistics
   - Computer programming
   - Geology

3. Graduate Record Examination (GRE) General

4. Most importantly: find a program that is a good fit for you
Finding the Right Graduate Program

• Must locate a professor or a group doing research that is both interesting to you and that you are qualified to do
  – Internet search
    • Read prof. bio’s, publications, current research
• Contact several professors directly (email)
  – Ask if they are taking on new grad students
  – Ask if the positions are funded
  – Ask what the scope of their grants are
• Begin applying
Graduate School Funding

• Most graduate programs in hydrology at research institutions are fully funded
  – Tuition and fees are paid for by your professor’s grant(s)
    • ≈$15,000/year at UC
  – Salary as a graduate student researcher (GSR)
    • ≈ 0.46*$40,000
    • ≈ $18,000

• Some programs don’t have a full time GSR option
  – You can subsidize your income via teaching assistant (TA), consulting, grants, loans, etc.

• Expectations
  – Complete a thesis in 2-3 years
  – Publish at least one research paper
  – Overall goal is to advance scientific understanding
What is the course work like?

• Fluid Dynamics
• Hydrology
  – Flow in porous media
  – Transport in porous media
• Hydrogeochemistry or Hydrobiology
  – Aqueous geochemistry (Inorganic & Organic)
• Hydrologic Policy
  – Water law
• Optional: geomorphology, stratigraphy, geostatistics, computer modeling, etc.
What is the research like?

• In my graduate group
  – Evaluation of tools used investigate the biodegradation of petroleum hydrocarbons in the sub-surface
    • Chevron, American Petroleum Institute
  – Impact of ethanol-blended biofuels on natural attenuation of petroleum hydrocarbons
    • Chevron, Superfund, American Petroleum Institute
  – 3D modeling of groundwater-surface water interactions in wetlands to better understand the potential response of predicted changes in climate
    • United States Forest Service
  – Spatial and temporal trends of nitrate concentrations in groundwater; Tulare Lake Basin and Salinas Valley, California
    • State Water Resource Control Board
  – Hydrogeology of the Yosemite Valley - groundwater and surface water interaction and numerical modeling
    • US National Park Service
• Great mix of field, lab, and office work (empirical and theoretical)
My Research

• Hypothesis: Anaerobic biodegradation of recalcitrant petroleum hydrocarbon (PHC) groundwater plumes can be accelerated by mixing a portion of the plume with adjacent sulfate-rich groundwater

• Biodegradation of PHC is thought to be a simple redox reaction
  – \(2\text{CH}_2\text{O} + \text{SO}_4 + \text{H} = 2\text{CO}_2 + \text{HS} + 2\text{H}_2\text{O}\)

• Order of thermodynamics (high to low energy)
  – Oxygen to Carbon Dioxide
  – Nitrate to Nitrogen
  – Ferric Iron to Ferrous Iron
  – Sulfate to Sulfide
  – Carbon Dioxide to Methane
Idealized contaminant plume

Approximate Groundwater Flow Direction

TPH, BTEX plume

Source area
Redox zones in contaminant plumes

If electron acceptors are limited, biodegradation of contaminants will be too
Requirements for BTEX biodegradation

- Existence of microbes with required degradation potential
- Presence of specific degraders in contaminated zone
- Activity of specific degraders
- Availability of appropriate electron acceptors (oxygen, nitrate, etc.)
- Availability of nutrients (N, P, etc.)
- Adequate pH and buffering capacity
- Toxic or inhibitory substances absent or below inhibitory concentrations

Adapted from Alvarez and Illman, 2006
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Hypotheses for Site

1. Groundwater and sediments impacted by BTEX and TPH persist within a zone of electron acceptor depletion
2. Sulfate reduction has the potential to serve as the major mechanism in the biodegradation of BTEX
3. Sulfate reduction contributes to benzene biodegradation
4. Potential degraders are active in zones with favorable concentrations of BTEX/TPH and soluble electron acceptor (sulfate/nitrate)
Methods

• Analysis limited to groundwater samples
  – Geochemical parameters
  – Compound specific isotope analysis (CSIA)
  – Quantitative polymerase chain reaction (qPCR)

• Data Analysis
  – Correlations between analytes
  – Spatial distribution of analytes (cross sections)
  – CSIA
  – Expressed Assimilative Capacity (EAC)
Site Background

- Former Service Station
- Operated 1956 to 1981
- Site features:
  - One 5,000-gal and two 4,000-gal USTs
  - One 550-gal waste oil UST
- 1985 all USTs removed, 95-98 pump and treat, site vacant thereafter
- B, E, X, TPHg, TPHd exceed regulatory levels in groundwater
Site Geology and Hydrogeology

- Approximate Site Location
- Holocene alluvium (<10,000 yrs. old) deposited in standing flood waters (fresh)
- Qhaf: Poorly sorted fines, thin beds of sand and fine gravel (~15 ft thick)
- Upland bedrock: Franciscian complex, metamorphosed seawater sediments and volcanics, blueschists, serpentinite, Mg and Na-rich chain and sheet silicates (Alt & Hyndman 2000, Raymond 2002)
Muds 0-37 ft bgs. High K zone 37-42 ft bgs.
Site Aquifer Parameter Estimates

- Horizontal Hydraulic Gradient
  - 0.004 to 0.007 ft/ft North East
- Hydraulic Conductivity
  - 43 ft/day for gravelly sand (soil sample test)
  - K range for well-sorted sands 3-300 ft/day (Fetter 2001)
- Assume average porosity ~0.4
- Average ground water velocity estimate
  - 0.6 ft/day (Gravelly sand velocity)
- Assume mud K is 3 orders of magnitude less
  - 6E-2 ft/day (Mud velocity)
- Vertical hydraulic gradient very small, transient, within instrumental and human error
Benzene iso-concentration contours
San Jose GW, Deep (ppb)

- Sampled shallow and deep wells along plume center line
- Vertically discrete micro-purge groundwater samples in Apr 2011
UC Davis Sampling Cart

On site analyses for sulfate, sulfide, etc. Lab analyses for many other parameters, including microbial communities.

Stainless steel tubing lowered from reel into well.

Sampling cart for vertical profiling within existing wells, wheels, battery, peri-pump.
UC Davis Sampling Process

Lowering SS tubing into well with a parallel LDPE tube for faster acquisition of samples not affected by LDPE
Non-Parametric Statistics

• Analytical tool to identify strong geochemical correlations
• Make no assumptions on population distribution
• Spearman’s $\rho$ is a correlation coefficient computed on the ranks (not values) of the data
• If there is an exact linear relationship between two variables the correlation is 1 or –1

$$\rho = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2} \sqrt{\sum (y - \bar{y})^2}}$$

• Hypothesize that certain analytes will have strong correlations (benzene & sulfate, benzene & ferrous iron, sulfate & nitrate)
Spearman’s $\rho$

- Constrained $|\rho| \geq 0.6$
- Constrained $\text{Prob} > |\rho|$ to $\leq 0.05$
  - A value below 0.05 is interpreted as evidence that the parameter is significantly different from zero

| Analyte   | By Analyte        | Spearman’s Rho | Prob>|Rho| |
|-----------|-------------------|----------------|---------|
| Methane   | Benzene           | 0.748          | 0.0001  |
| Methane   | C6-C12-TPH-GRO    | 0.6749         | 0.0004  |
| Methane   | Xylene (Total)    | 0.6551         | 0.0007  |
| Methane   | Sulfate           | -0.8706        | 0.0001  |
| Sulfate   | Ethylbenzene      | -0.6078        | 0.0021  |
| Sulfate   | TEX               | -0.6274        | 0.0014  |
| Sulfate   | Xylene (Total)    | -0.6289        | 0.0013  |
| Sulfate   | C6-C12-TPH-GRO    | -0.6847        | 0.0003  |
| Sulfate   | Benzene           | -0.7372        | 0.0001  |

- No significant correlations of $|\rho| \geq 0.6$ for ferrous iron or nitrate
- Use this data to plot cross sections of analyte concentrations
- Cross section from A to A’ down plume center line
- No current data on up-gradient wells UR-2, U-2, U-7
Concentration is proportional to area of circle
2-4 vertically discrete micro-purge samples per well, note variability
Deep benzene plume “appears” to end abruptly, may have missed it
Plume appears to persist in and around gravelly sand
• Very strong correlation among all electron donors sampled for (BTEX, TPHg)
• Focus on benzene from this point on
Deep benzene plume depleted in sulfate and nitrate
Lack current up-gradient geochemistry (0-30’ A to A’)
• Open circles are historical (1999-2005) background averages in deep wells
• Data strongly suggest sulfate and nitrate are being utilized as electron acceptors in deep zone
- Deep benzene plume depleted of sulfate/nitrate and enriched in methane
- BTEX impacted plume persists within zone of sulfate and nitrate depletion
Quantification of Total Microbial Population

• Determine total bacterial population numbers using universal 16S rRNA genes

• Determine conserved functional gene numbers

• Normalize conserved functional genes to 16S rRNA numbers

• Compare functional gene prevalence to geochemical data
Implications of Microbial Analysis

• Benzene plume core depleted in sulfate, sulfate reducers present in sulfate depleted zone

• Contaminant degraders
  – low numbers and patchy distribution
  – conditions likely not suitable for degradation in plume (inhibition, toxicity?)
Expressed Assimilative Capacity (EAC)

• Screening calculation to estimate the capacity of the aquifer to degrade BTEX
• Calculate an EAC using the difference in concentration between a background well and a source well
  – Assumes instantaneous degradation of BTEX
  – Ignores organic compounds that exert an electron acceptor demand
  – Likely overestimates the mass of BTEX degraded
  – Relies on stoichiometric ratios of simple redox reactions
Expressed Assimilative Capacity (EAC)

<table>
<thead>
<tr>
<th></th>
<th>Nitrate</th>
<th>Ferrous Iron</th>
<th>Sulfate</th>
<th>Methane</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background Average</td>
<td>91</td>
<td>0.5</td>
<td>414</td>
<td>0.2</td>
<td>mg/L</td>
</tr>
<tr>
<td>Source Zone Average</td>
<td>1.3</td>
<td>1.0</td>
<td>15</td>
<td>4.4</td>
<td>mg/L</td>
</tr>
<tr>
<td>Utilization Factor</td>
<td>0.21</td>
<td>0.05</td>
<td>0.21</td>
<td>1.28</td>
<td>-</td>
</tr>
<tr>
<td>EAC</td>
<td>19</td>
<td>0.02</td>
<td>84</td>
<td>5</td>
<td>mg BTEX/L</td>
</tr>
</tbody>
</table>

- EAC suggest ~100 mg BTEX is degraded for every liter of groundwater that flows through the source zone
  - Support hypothesis #2
- Using conservative estimates of aquifer thickness, groundwater velocity, and total mass of dissolved BTEX plume, should degrade in 3 hours!
- Obviously something is inhibiting biodegradation
  - Slow reaction rates
  - Sinks for sulfate
  - Toxic byproducts
  - Toxicity of benzene
• Molecules containing lighter isotopes ($^{12}$C) tend to react more rapidly during biodegradation compared to heavy stable isotope ($^{13}$C)

• **CSIA can help determine if biodegradation is occurring (Rayleigh Fit) and estimate predominant redox conditions (2D CSIA)**
 Compound Specific Isotope Analysis (CSIA) Review

- As biodegradation proceeds the ratio of $^{13}\text{C}/^{12}\text{C}$ increases, expressed as $\delta^{13}\text{C}$ (‰)
- Dashed line is total analytical error (1‰ for $\delta^{13}\text{C}$ in $\text{C}_6\text{H}_6$)
- Red arrow is threshold to show biodegradation (1‰ analytical plus 1‰ non-degradative: volatilization, dissolution and sorption)
Compound Specific Isotope Analysis (CSIA)

• More lines of evidence for biodegradation
  – If biodegradation is occurring (Rayleigh Fit)
    • $^{13}$C and $^2$H in $C_6H_6$
  – For predominant redox conditions (2D CSIA)
    • $^{34}$S and $^{18}$O in $SO_4$
Rayleigh Fit $^{13}\text{C}$ in $\text{C}_6\text{H}_6$

- Error bars ±0.5‰ analytical error
- Red arrow is biodegradation threshold (2x total analytical error, 2‰) (EPA 2008)
- Results not conclusive
Rayleigh Fit $^2\text{H}$ in C$_6$H$_6$

$R^2 = 0.8804$

- Error bars are ±10‰ analytical error for non-fitted data
- Error bars are ±5‰ analytical error for fitted data
- **Red arrow** is biodegradation threshold (20 ‰)
- Results are not conclusive
Plot change (Δ) in δ²H vs change (Δ) in δ¹³C, with respect to most negative δ value.

Slope suggests biodegradation dominated by nitrate reduction (Fischer et al. 2009), but correlation is weak; expected slopes:

- Nitrate reducing 8 to 19
- Sulfate reducing 24 to 28
- Methanogenic 28 to 39
\[ y = -0.10x + 0.74 \]
\[ R^2 = 0.20 \]

- Red arrow is biodegradation threshold (2.4 ‰)
- Extent of fractionation is large but data scattered
- \( \delta^{34}\text{S-SO}_4^{2-} \) is sensitive to environmental conditions (disp., dilution, mixing, mineral ppt)
• Deep gravelly sand layer has much lower del values than in shallow muds
• It is possible that fresh sulfate in high K zone is masking the true extent of isotopic fractionation
Rayleigh Fit $^{18}$O in SO$_4$

- Deep gravelly sand layer has much lower del values than in shallow muds
- It is possible that fresh sulfate in high K zone is masking the true extent of isotopic fractionation
A linear relationship between δ³⁴S and δ¹⁸O in SO₄ can be interpreted as evidence for biodegradation at redox conditions.
CSIA Summary

• Weak evidence of biodegradation of benzene
• Strong evidence of sulfate reduction
• Can not reject evidence of nitrate reduction
• Did not examine methanogenesis or other redox conditions by CSIA
• Data support hypothesis #3
  – Sulfate reduction is a mechanism contributing to benzene biodegradation
Site Summary

- Groundwater and sediments impacted by BTEX and TPH persist within a zone of sulfate depletion.
- Sulfate reduction is a mechanism in the biodegradation of benzene.
- Some evidence of inhibition and/or toxicity.
- Downsides for continued UCD field research:
  - Only one well with significant contamination.
  - Possibly no well immediately down gradient.
- Upsides for continued UCD field research:
  - A conductive contaminated layer.
Site Plans

• Discussed in more detail later, but options:
  – Application of new In Situ Pilot Test (ISPT)
  – Push-pull test
  – Two-well recirculation test

• Both could examine impact on in situ degradation of adding
  – Sulfate
  – Other species with or without sulfate if promising to overcome inhibiting factors
What can you do after you’re done?

- Environmental consulting in the private sector (in house or as a contractor)
- Hydrogeologist in the public sector (DWR, USGS, SWRCB)
- Research in academia (UC Davis has lots of these)
- Teach K-12 earth science
- Teach community college geology
- Move on to a Ph.D program
Five Tips for Graduate School

1. Safety First: our work is inherently dangerous, mitigate those risks
2. Find a professor who is a good fit: 2-3 year commitment, 4-6 for Ph.D
3. Make sure your program has solid funding: don’t be afraid to ask about details
4. Practice writing and public speaking: communicating your research is important
5. Make sure you publish: very important for your resume
What does environmental consulting look like?
• Former MGP
• Coal Tar?
• Sulfur?
• Ammonia?
• Site Characterization
• 2 months
• Night work
• China Town
• No traffic
• Light pole incident and good notes
Contacts & Questions

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