13th Annual International Petroleum Environmental Conference
October 17-20, 2006
San Antonio, TX

MONDAY, OCTOBER 16, 2006

PRE-CONFERENCE WORKSHOPS	
Waste Minimization in Oil and Gas Exploration and Production	9:00 am - 4:30 pm
Instructed by: Bart Sims, Railroad Commission of Texas, Austin, TX *(Registration/Sign-in begins at 8:30 am)*	(Salon 3)
Oil & Gas Construction and the Changing Environmental Landscape: Working with the New/Revised Regulations	9:00 am - 12:00 pm
Instructed by: Peter McKone, Dunaway Associates, LP, Ft. Worth, TX; Becky J. Richards, Environmental Trainers, Inc., Ft. Worth, TX; and Allen Skinner, AR Consultants *(Registration/Sign-in begins at 8:30 am)*	(Salon 2)
Water Level and Water Quality Instrumentation – Selection and Uses in Pollution Investigation and Water Resource Management	1:00 pm - 4:30 pm
Instructed by: Jim Broderick and Michelle Haubrich, In-Situ, Inc., Ft. Collins, CO *(Registration/Sign-in begins at 12:30 pm)*	(Salon 2)
Recent Developments in LNAPL: If You Think You Already Understand LNAPL – You Probably Don't!	1:00 pm - 4:30 pm
Instructed by: Vic Kremesec, Atlantic Richfield, a BP Affiliated Company, Warrenville, IL and Mark Adamski, Atlantic Richfield, a BP Affiliated Company, Houston, TX *(Registration/Sign-in begins at 12:30 pm)*	(Salon 1)
IPEC Soil Remediation Workshop	6:30 pm - 9:30 pm
Instructed by: Phil Spurlin, BEACON Environmental Assistance Corp., Edmond, OK *(Registration/Sign-in begins at 6:00 pm)*	(Salon 1)
CONFERENCE REGISTRATION OPENS (Texas Ballroom Preconvene Area)	5:00 pm - 7:00 pm

TUESDAY, OCTOBER 17, 2006

CONFERENCE REGISTRATION (Texas Ballroom Preconvene Area)	7:00 am - 5:00 pm
I. OPENING BREAKFAST BUFFET (Exhibit Hall, Texas Ballroom A&B)	7:30 am - 8:30 am
II. EXHIBITS OPEN	7:30 am - 6:45 pm
III. OPENING PLENARY SESSION (Texas Ballroom C)	8:45 am - 11:30 am
WELCOME AND OPENING REMARKS	8:45 am - 9:00 am

Kerry L. Sublette, Conference Chair

PLENARY SPEAKERS:

John R. Duda , U.S. Department of Energy/NETL, Morgantown, WV 9:00 am - 9:30 am
"Framing the Critical Energy-Water Link "

Bruce Langhus , ALL Consulting, Tulsa, OK 9:30 am - 10:00 am
"Large-Volume Water Management Projects-CBNG in Powder River Basin "

John Veil, Argonne National Laboratory, Washington, DC 10:00 am - 10:30 am
"Disposal of Concentrate from Treatment of Water for Beneficial Reuse"

Paul Jehn, Ground Water Protection Council, Oklahoma City, OK 10:30 am - 11:00 am
"Source Water Protection and the Energy-Water Nexus"

David B. Burnett, Texas A&M University, College Station, TX and William Fox III, Texas Water Resources Institute, Texas A&M University, College Station, TX 11:00 am - 11:30 am
"Better Than an Inch of Rain in West Texas - Desalination of Oil Field Brine and Re-use for Beneficial Purposes"

IV. LUNCH BREAK (on your own) 11:30 am - 1:00 pm

V. CONCURRENT TECHNICAL SESSIONS 1:30 pm - 5:15 pm

- **Drilling Waste Management** (Salon 1)
- **Groundwater Remediation I** (Salon 2)
- **Produced Water & Wastewater Treatment; Vapor Intrusion & Fugitive Emissions** (Salon 3)
- **Environmental Management, Compliance & Auditing** (Salon 4)

VI. AFTERNOON REFRESHMENTS (Exhibit Hall, Texas Ballroom A&B) 3:10 pm - 3:35 pm

VII. **POSTER SESSION** (Exhibit Hall, Texas Ballroom A&B) 5:15 pm - 6:45 pm

VIII. EXHIBITOR RECEPTION (Exhibit Hall, Texas Ballroom A&B) 5:30 pm - 6:45 pm

IX. OPENING DINNER - Pirates of the Riverwalk (San Antonio Ballroom) 7:00 pm - 9:30 pm

WEDNESDAY, OCTOBER 18, 2006

CONFERENCE REGISTRATION (Texas Ballroom Preconvene Area) 7:30 am - 12:00 noon

I. CONTINENTAL BREAKFAST (Exhibit Hall, Texas Ballroom A&B) 7:30 am - 8:00 am

II. EXHIBITS OPEN 7:30 am - 12:00 noon

III. CONCURRENT TECHNICAL SESSIONS 8:00 am - 12:35 pm

- **Site Reclamation & Restoration I** (Salon 1)
- **Waste Management, Pollution Prevention & Safety** (Salon 2)
- **Toxic Metals in Produced Water; Site Assessment & Forensic Geochemistry** (Salon 4)

IV. MID-MORNING COFFEE BREAK (Exhibit Hall, Texas Ballroom A&B) 9:40 am - 10:05 am

V. LUNCH BREAK (on your own) 12:35 pm - 1:15 pm

VI. CONCURRENT WORKSHOPS *(Pre-registration Required)*

Effective Silt Fence for Pipeline and Construction Sites 1:30 pm - 5:00 pm

Instructed by: Bill Barfield, Sandeep Yeri, Ellen Stevens, and Khaled Gasem, Oklahoma State University, Stillwater, OK; Kevin Self, Charles Machine Works, Perry, OK (Salon 2)

A Practitioner's Guide to Using Molecular Biological Tools (MBTs): What Can These Analyses Tell Me? 1:30 pm - 5:00 pm

Instructed by: Greg Davis and Dora Ogles, Microbial Insights, Inc., Rockford, TN; Patrick W. McLoughlin, Microseeps, Inc., Pittsburgh, PA (Salon 4)

THURSDAY, OCTOBER 19, 2006

CONFERENCE REGISTRATION (Third Floor) 7:30 am - 5:30 pm

I. CONTINENTAL BREAKFAST 7:30 am - 8:00 am

II. CONCURRENT TECHNICAL SESSIONS 8:00 am - 11:45 pm

- **Remediation of Hydrocarbon Spills; Wave Tank Studies on Effectiveness of Chemical Dispersants** (Fiesta B)
- **Coalbed Natural Gas Produced Water** (Salon 4)
- **Brine Impacts at the Osage-Skiatook Petroleum Environmental Research Project Sites** (Fiesta A)

III. MID-MORNING COFFEE BREAK 9:40 am - 10:05 am

IV. LUNCH (San Antonio Ballroom) 12:15 pm - 1:30 pm

Guest Speaker: **Carole Fleming**, Chevron Energy Technology Company, Houston, TX

"*How I Came to be the Petroleum Magnolia*"

V. CONCURRENT TECHNICAL SESSIONS 1:30 pm - 5:15 pm

- **Groundwater Remediation II** (Salon 2)
- **Phytoremediation; Site Restoration & Reclamation II** (Salon 4)
- **Legal & Regulatory Issues** (Salon 5)

VI. AFTERNOON REFRESHMENTS 3:10 pm - 3:35 pm

VII. NETWORKING RECEPTION - Cash Bar (River Plaza) 5:30 pm - 6:30 pm

FRIDAY, OCTOBER 20, 2006

SYMPOSIUM REGISTRATION (Third Floor - Outside San Antonio Ballroom) 7:30 am - 8:00 am

I. **SPECIAL SYMPOSIUM** (San Antonio Ballroom) 8:00 am - 11:45 am

"Remediation and Restoration of Brine Impacted Sites"

Conference closes at 1:00 pm

Technical Sessions

TUESDAY, OCTOBER 17, 2006 - AFTERNOON

DRILLING WASTE MANAGEMENT (Salon 1)

Chair: John Candler, M-I SWACO, Houston, TX

• **Designing Environmental Performance into New Drilling Fluids and Waste Management Technology** John Candler and Jim Friedheim, M-I SWACO, Houston, TX	1:30 pm - 1:55 pm
• **New Innovative Process Allows Drilling Without Pits in New Mexico** William A. Piper, Piper Consulting, Stafford, TX; Dorsey Rogers, Cimarex, Hobbs, NM; and Gary Fout, M-I Swaco, Houston, TX	1:55 pm - 2:20 pm
• **New Reduce, Reuse, Recycle Drilling Waste Treatment Technologies and Programs** Manuel F. Gonzalez and Wayne Crawley, U.S. Liquids of Louisiana, L.P.; Dennis L. Patton, Western Consulting Services, Colorado City, TX	2:20 pm - 2:45 pm
• **Invert Fluid Flocculation - a Novel Technique for Drilling Fluid Recycling** Karen McCosh and Emma McLean, M-I SWACO, Aberdeen, Scotland, UK	2:45 pm - 3:10 pm
Break	3:10 pm - 3:35 pm
• **Calculation of Energy Requirements and Air Emissions for Drill Cuttings Management Options** Diana Garcia and Mukesh Kapila, M-I SWACO, Houston, TX	3:35 pm - 4:00 pm
• **Theoretical and Practical Models for Drilling Waste Volume Calculation with Field Case Studies** William A. Piper, Piper Consulting, Stafford, TX; Carole Fleming and Catalin Ivan, Chevron Corporation, Houston, TX	4:00 pm - 4:25 pm
• **Analysis of Drilling Fluid Based Oil Recovered from Drilling Waste by Thermal Desorption** Ron Morris and Simon Seaton, Halliburton, Houston, TX; Jack Blonquist and Barry Hogan, Duratherm, San Leon, TX	4:25 pm - 4:50 pm

GROUNDWATER REMEDIATION I (Salon 2)

Chair: Jennifer Busch-Harris, University of Tulsa, Tulsa, OK

- **Continued Success with Cool-OX™ Treatments of Petroleum and Commengled Halogenated Hydrocarbons at Petroleum Sites in Northwest Florida** — 1:30 pm - 1:55 pm

Thomas D. Douglas, Advanced Environmental Technologies (AET), LLC, Pensacola, FL; William Lundy, DeepEarth Technologes, Inc., Alsip, IL

- **Demonstrating Anaerobic Biodegradation of MTBE and TBA *In Situ* Using Bio-Sep® Bio-Traps and ^{13}C-Stable Isotope Probing** — 1:55 pm - 2:20 pm

J.L. Busch-Harris, K.L. Sublette, E. Jennings, and K.P. Roberts, The University of Tulsa, Tulsa, OK; G. Davis and D. Ogles, Microbial Insights, Inc., Rockford, TN; D.C. White and A. Peacock, University of Tennessee, Knoxville, TN; W. E. Holmes, University of Michigan, Ann Arbor, MI; X. Yang, Atlantic Richfield (a BP affiliated company), Warrenville, IL; A. Kolhatkar, Atlantic Richfield (a BP affiliated company), Houston, TX; D. Mackay and P. Kaiser, LAWR, University of California-Davis, Davis, CA

- **Stable Isotope Analysis in Remediation of Gasoline Oxygenates and Hydrocarbons** — 2:20 pm - 2:45 pm

Tomasz Kuder, Paul Philp, Jon Allen, and Evelyn Cortez, The University of Oklahoma, Norman, OK

- **Using Controlled *In-Situ* Chemical Oxidation to Predict the Outcome of Subsequent Enhanced Biodegradation of Petroleum Hydrocarbons** — 2:45 pm - 3:10 pm

William Lundy, DeepEarth Technologes, Inc., Alsip, IL; Thomas D. Douglas, Advanced Environmental Technologies (AET), LLC, Pensacola, FL; H. Eric Nuttall, University of New Mexico, Albuquerque, NM; Ian T. Osgerby, U.S. Army Corps of Engineers, Concord, MA; Wesley Wiley, DeepEarth Technologies, Inc., Pensacola, FL; Thomas A. Reed, DeepEarth Technologies, Inc., Denver, CO

Break — 3:10 pm - 3:35 pm

- **Three Domain Flow Systems and Risk-Based Corrective Action of Groundwater** — 3:35 pm - 4:00 pm

David B. Vance, ARCADIS G&M, Midland, TX

- **Stable Isotope Probing with ^{13}C-MTBE in Bio-Sep® Beads in MTBE-degrading Microcosms** — 4:00 pm - 4:25 pm

K.L. Sublette, E. Jennings, and J.L. Busch-Harris, The University of Tulsa, Tulsa, OK; Xiaomin Yang, Atlantic Richfield (a BP affiliate), Warrenville, IL; Ravi Kolhatkar and Arati Kolhatkar, Atlantic Richfield (a BP affiliate), Houston, TX; John T. Wilson and Cherri Adair, US EPA, Ada, OK; W.E. Holmes, University of Michigan, Ann Arbor, MI

- **Documentation of *In-Situ* Microbial Oxidation of ^{13}C-labeled Benzene Coupled to Denitrification-Based Bioremediation Using Bio-Trap™ Samplers** — 4:25 pm - 4:50 pm

Eric C. Hince, Geovation Consultants, Inc., Florida, NY; Greg Davis, Microbial Insights, Inc., Rockford, TN; Kerry Sublette, Jennifer Busch-Harris, and Eleanor Jennings, The University of Tulsa, Tulsa, OK

PRODUCED WATER AND WASTEWATER TREATMENT; VAPOR INTRUSION & FUGITIVE EMISSIONS (Salon 3)

Chair: Robert Babcock, University of Arkansas, Fayetteville, AR

PRODUCED WATER AND WASTEWATER TREATMENT

- **Upstream and In-Plant Water Reuse: A Systematic Approach** — 1:30 pm - 1:55 pm

Heyward Suber, Tom Sandy, and Guy Goettsch, CH2M HILL, Charlotte, NC; John Robertson, CH2M HILL, Calgary, AB, Canada; Jose Baeza, CH2M HILL, Houston, TX

- **Centrifugal Hyperfiltration: A Change in the Standard Reverse Osmosis Process** — 1:55 pm - 2:20 pm

Dirk Forman, Reverse Osmosis, LLC, Lafayette, LA

- **Organoclays Can Cut the Cost of Cleanup of Produced Water, Wastewater and Groundwater by 50%** — 2:20 pm - 2:45 pm

Tommy Wilkerson, Flo-Clean, LLC, Lafayette, LA; George Alther, Biomin, Inc., Femdale, MI

- **Treatment of High Sulfite Refinery Wastewater by Conventional Activated Sludge** — 2:45 pm - 3:10 pm

Reinaldo A. Gonzalez, Burns & McDonnell Engineering Company, Kansas City, KS; Enos L. Stover, The Stover Group, Stillwater, OK

Break — 3:10 pm - 3:35 pm

- **AltelaRain™ - State of the Art Produced Water Treatment Technology** — 3:35 pm - 4:00 pm

Ned A. Godshall, Altela, Inc., Albuquerque, NM

VAPOR INTRUSION & FUGITIVE EMISSIONS

- **Vapor Intrusion - Emerging Guidance, Investigative Methods, and Sampling Issues** — 4:00 pm - 4:25 pm

Loren Lund, Parsons, Shelley, ID

- **Assessing and Controlling Emissions of Greenhouse Gases: A Pragmatic Perspective for the Oil and Gas Industry**

Ronald L. Berglund, Terracon Consultants, Inc., Houston, TX; Susanne A. Cordery-Cotter, Terracon Consultants, Inc., Ft. Collins, CO; Roberto G. Morales, Terracon Consultants, Inc., Dallas, TX — 4:25 pm - 4:50 pm

- **The Problems of the Reduction of the Harmful Substances Which are Thrown Out in an Atmosphere from Furnaces of Heating Oilfields** — 4:50 pm - 5:15 pm

Ye.T. Zhanburshin, E.E. Oramalov, and E.A. Buketov, Karaganda State University, Aktau City, Kazakhstan

ENVIRONMENTAL MANAGEMENT, COMPLIANCE AND AUDITING (Salon 4)

Chair: Paul Jehn, Groundwater Protection Council, Oklahoma City, OK

- **Sediments: An Emerging Environmental Issue**

Lyle G. Bruce, BP-Atlantic Richfield, Warrenville, IL; Stacey Waterman, BP-Atlantic Richfield, Los Angeles, CA; Walt Hufford, BP-Atlantic Richfield, Towson, MD — 1:30 pm -1:55 pm

- **Increasing Access to Federal Lands in Western States Through Data Sharing**

Paul Jehn, Ground Water Protection Council, Oklahoma City, OK; Thom Kerr and Jim Milne, Colorado Oil & Gas Conservation Commission, Denver, CO; Bob Johnson, Premier Data Services, Inc, Denver, CO — 1:55 pm - 2:20 pm

- **Proactive Corporate Environmental Strategy and Liability Management**

Ralph Beck, WorleyParsons Komex, Westminster, CA; Sean Murphy, WorleyParsons Komex, Calgary, AB, Canada — 2:20 pm - 2:45 pm

- **Petroleum Industry, ISO 14001, EMS and Environmental Management Programs**

Susan Tybur Rost, Tybur Rost Management Strategies, Bakersfield, CA; Aston Hinds, Chempro International, Houston, TX — 2:45 pm - 3:10 pm

Break — 3:10 pm - 3:35 pm

- **An Interactive Integrated Information Data Management Process for Identification and Reduction of Liabilities** — 3:35 pm - 4:00 pm

Margaret Roy, Pilar Odland, and David Friday, URS Corporation, Austin, TX

- **Mitigating Environmental and Site Liability Through Electronic Data Management - A Case Study** — 4:00 pm - 4:25 pm

Dean Novak and James Hatcher, Peloton, Calgary, AB, Canada; Carol Howlett and Mark Tuturea, Trident Exploration, Calgary, AB, Canada

- **Environmental Drilling Fluids Selection Factors**

Susan Tybur Rost, Tybur Rost Management Strategies, Bakersfield, CA; Aston Hinds, Chempro International, Houston, TX — 4:25 pm - 4:50 pm

- **Regarding Methodology of Electromagnetic Investigation for Early Warning of Soil Pollution by Oil Products**

R.A. Tursunmetov, N.G. Mavlyanov, and Sh.H. Abdullaev, GIDROINGEO, Tashkent, Uzbekistan; M.F. Rahmatullaeva, Institute of Information and Computer Technologies, Tashkent, Uzbekistan — 4:50 pm - 5:15 pm

POSTER SESSION (Exhibit Hall, Texas Ballroom A&B)

Chair: Brandy Rutledge, Alchem Field Services, Ltd., Oklahoma City, OK

- **Treatability and Characterization of a Contaminated Soil from an Exploration Zone: Effect of the Particle Size Over the Washing Rate**
  Luis G. Torres, Jennifer Saquelares, Mariana Climent, Gustavo Sampayo, Guadalupe Urquiza and Rosario Iturbe, UNAM, Mexico DF, Mexico; Ercik R. Bandala, Instituto Mexicano de Tecnologia del Agua, Morelos, Mexico
- **Biodegradation of Oil Sludge by Amendment Addition and Landfarming**
  Donald Pope, Jennifer Smith, M.T. Balba, Sophia Dore, and Alan Weston, Conestoga Rovers and Associates, Niagara Falls, NY
- **Oil Oxidizing Microorganisms and Their Application in Bioremediation of Contaminated Soils**
  T.D. Mukasheva and M.Ch. Shigaeva, Al-Farabi Kazakh National University, Almaty, Kazakhstan
- **Bioremediation of Petro Polluted Soils of Kazakhstan Using Soil Microorganisms, Biohumus, and Specific Species of Plants**
  K.K. Boguspaev, E.T. Zamburshin, and A.B. Bigaliev, Al-Farabi Kazakh National University, Almaty, Kazakhstan
- **Biodegradation and Detoxification of Soil Contaminated with Heavily Weathered Hydrocarbons**
  Randy H. Adams, Ildefonso J. Díaz-Ramírez, and Francisco J. Guzman-Osorio, Juarez Autonomous University of Tabasco, Villahermosa, Tabasco, Mexico; Mariano Gutiérrez-Rojas, Universidad Autónoma Metropolitana-Iztapalapa, Mexico City, DF, Mexico
- **Biodegradation of Polycyclic Aromatics Hydrocarbons in Soil Polluted Using the Fungal Strain *Fusarium Santarosense***
  Enrique Terrazas-Siles, Lund University and Unibersidad Mayor de San Andres, La Paz, Bolivia; Bo Mattiasson, Lund University, Lund, Sweden; Alberto Giemenez, Unibersidad Mayor de San Andres, La Paz, Bolivia
- **Persistence of Oil Waste Lands in Osage County, Oklahoma**
  Melissa N. Barton, J. Berton Fisher, and J. Bryan Tapp, The University of Tulsa, Tulsa, OK

- **Biotreatment of Synthetic Drill-Cutting Waste**
  Laleh Rastegarzadeh and Yarrow Nelson, California Polytechnic State University, San Luis Obispo, CA; Todd Ririe, Unocal Corp., CA
- **Diluent Hydrocarbon Biodegradation in Laboratory Microcosms Using Anoxic Electron Acceptors**
  Laleh Rastegarzadeh, Meghann Chell, and Yarrow Nelson, California Polytechnic State University, San Luis Obispo, CA
- **Bio-Sep® Bio-Trap Stable Isotope Probing: A New Tool for Characterizing Biodegradation Potential and the Associated Microbial Ecology**
  J.L. Busch-Harris, K.L. Sublette, E. Jennings, and K.P. Roberts, The University of Tulsa, Tulsa, OK; G. Davis and D. Ogles, Microbial Insights, Inc., Rockford, TN; D.C. White and A. Peacock, University of Tennessee, Knoxville, TN; W.E. Holmes, University of Michigan, Ann Arbor, MI; X. Yang, Atlantic Richfield (a BP affiliated company), Warrenville, IL; A. Kolhatkar, Atlantic Richfield (a BP affiliated company), Houston, TX
- ***In-Situ* Remediation of Brine Impacted Soils and Groundwater Using Hydraulic Fracturing, Desalination, and Recharge Wells**
  Gordon H. Bures and Celeste Kaban, Frac Rite Environmental, Ltd., Calgary, AB, Canada; Craig Robertson and Ion Ratiu, Wiebe Environmental Services, Inc., Calgary, AB, Canada
- **Advancing Research Towards Preventing the Vertical Migration of Salt from Brine Exposure**
  Carla J. Landrum, J. Berton Fisher, Eleanor Jennings, Shoeb Munshi, Dan Weber, Kerry Sublette, and Bryan Tapp, The University of Tulsa, Tulsa, OK
- **The Image of Natural Gas Industry in Iran**
  Hedayat Omidvar, National Iranian Gas Company, Tehran, Iran

WEDNESDAY, OCTOBER 18, 2006 - MORNING

SITE RECLAMATION AND RESTORATION I (Salon 1)

Chair: Eleanor Jennings, University of Tulsa, Tulsa, OK

- **Exploratory Well Site Reclamation and Restoration in Albania**
  Rick Brower and Krish Ravishankar, Occidental Oil & Gas Corporation, Houston, TX — 8:00 am - 8:25 am

• **Lessons Learned in Remediation and Restoration in the Oklahoma Prairie** Kerry L. Sublette, Eleanor M. Jennings, J. Bryan Tapp, and J. Berton Fisher, The University of Tulsa, Tulsa, OK; Kathleen Duncan, The University of Oklahoma, Norman, OK; Greg Thoma, University of Arkansas, Fayetteville, AR; Josh Brokaw, Washington State University, Pullman, WA; Tim Todd, Kansas State University, Manhattan, KS	8:25 am - 8:50 am
• **Efficacy of Various Treatments on the Restoration of Nitrogen Cycling in Tallgrass Prairie Impacted by Oil and Brine Spills** Kathleen Duncan and Samer AbuBakr, The University of Oklahoma, Norman, OK; Kerry L. Sublette, Eleanor M. Jennings, and Nitya Alahari, The University of Tulsa, Tulsa, OK; Greg Thoma, Duane Wolf, and Jody Davis, University of Arkansas, Fayetteville, AR	8:50 am - 9:15 am
• **An Investigation into the Prevention of Vertical Capillary Transport of Brine Contamination** Carla J. Landrum, J. Berton Fisher, Eleanor Jennings, Shoeb Munshi, Kerry Sublette, Bryan Tapp, and Dan Weber, The University of Tulsa, Tulsa, OK	9:15 am - 9:40 am
Break	9:40 am - 10:05 am
• **Remediation and Restoration of an Historic Brine Scar - What Went Wrong?** Shoeb Munshi, Carla J. Landrum, Kerry Sublette, Eleanor Jennings, J. Berton Fisher, and Bryan Tapp, The University of Tulsa, Tulsa, OK	10:05 am - 10:30 am
• **Dose - Response Relationship of Organisms in Soil with Heavily Weathered Hydrocarbons and Changes in Fertility Parameters** Randy H. Adams, Ana Laura Ovando-Alvarez, and Erika Escalante-Espinosa, Juarez Autonomous University of Tabasco, Villahermosa, Tabasco, Mexico; Mariano Gutiérrez-Rojas, Universidad Autónoma Metropolitana-Iztapalapa, Mexico City, DF, Mexico	10:30 am - 10:55 am
• **The Potential for Boron Phytotoxicity in Produced Water Contaminated Tallgrass Prairie Soils** Dan Weber, E. Jennings, K.L. Sublette, Greg Lohrke, Kenneth Roberts, and Bryan Tapp, The University of Tulsa, Tulsa, OK	10:55 am - 11:20 am
• **Using Geographic Information Systems (GIS) to Enhance Remediation and Restoration Efforts** Carla J. Landrum, Jennifer Busch-Harris, Shoeb Munshi, Eleanor Jennings, Kerry Sublette, and Bryan Tapp, The University of Tulsa, Tulsa, OK	11:20 am - 11:45 pm

WASTE MANAGEMENT, POLLUTION PREVENTION AND SAFETY (Salon 2)

Chair: Gary Visscher, U.S. Chemical Safety Board, Washington, DC

• **Options and Costs for Offsite Management of Exploration and Production Waste** Markus G. Puder and John A. Veil, Argonne National Laboratory, Washington, DC	8:00 am - 8:25 am
• **Automated Spill Alarm for Clean Water Compliance & Discharge Prevention** Chris R. Chase, InterOcean Systems, Inc., San Diego, CA	8:25 am - 8:50 am
• **Maximizing Development Potential Through Environmental Impact Management** Nathan Walters, Katch Kan, Ltd, Edmonton, AB, Canada	8:50 am - 9:15 am
• **Investigating Causes of June, 2006 Fatal Oilfield Explosion and Fire** Gary Visscher, U.S. Chemical Safety Board, Washington, DC	9:15 am - 9:40 am
Break	9:40 am - 10:05 am
• **MEOR Case Studies at India's Oil and Natural Gas Corporation, Ltd.** Richard E. Woodward, Terracon Consultants, Inc., Houston, TX; Charles P. Siess, III, Glori Oil, Houston, TX	10:05 am - 10:30 am
• **Lessons Learned from Bioremediation and Their Implications for Microbial Enhanced Oil Recovery** Richard E. Woodward, Terracon Consultants, Inc., Houston, TX	10:30 am - 10:55 am
• **Establishing a Regulatory Framework for Recycling Exempt Oil & Gas Waste** David W. Cooney, Jr., Railroad Commission of Texas, Austin, TX	10:55 am - 11:20 am
• **Biodegradation of Highly Contaminated Crude Oil Soils Enhanced With Three Different Surfactants and Doses: Preliminary Results** Luis G. Torres and Rosario Iturbe, Universidad Nacional Autonoma de Mexico, Mexico DF, Mexico	11:20 am - 11:45 am
• **Petroleum Waste Management in Remote Access Locations** Tracy Barton and Roger Richter, Mobile Environmental Technologies, Portland, OR	11:45 am - 12:10 pm
• **From Pollution to Power - Using GTL Technology to Fuel America** Brandy Rutledge, Alchem Field Services, Inc., Oklahoma City, OK	12:10 pm - 12:35 pm

TOXIC METALS IN PRODUCED WATER; SITE ASSESSMENT AND FORENSIC

GEOCHEMISTRY (Salon 4)

Chair: Carl E. Hensman, Frontier GeoSciences, Inc., Seattle, WA

TOXIC METALS IN PRODUCED WATER

- **Risk Communication and Heavy Metals: How to Overcome the Industry's Bad Rap** — 8:00 am - 8:25 am
  Chuck Lambert, McDaniel Lambert, Inc., Venice, CA
- **Removal of Mercury and Arsenic from Produced Water** — 8:25 am - 8:50 am
  D.L. Gallup, Chevron Corporation, Houston, TX
- **Mercury: Real Problems . . .Not Greek Mythology** — 8:50 am - 9:15 am
  Michael L. Braden, Nalco Energy Services, Sugar Land, TX
- **Critique of Thermal Decomposition Analysis of Hydrocarbons for Hg Using a Commercially Available System** — 9:15 am - 9:40 am
  Carl E. Hensman, Frontier GeoSciences, Inc., Seattle, WA

Break — 9:40 am - 10:05 am

- **An Accurate, Precise and Cost Effective Method for Measuring Mercury in Production Gas Streams: Method 40 CFR Part 75 App K** — 10:05 am - 10:30 am
  Robert Brunette, Frontier GeoSciences, Inc., Seattle, WA

SITE ASSESSMENT AND FORENSIC GEOCHEMISTRY

- **Stable Isotopes - An Emerging Tool in Forensic Geochemistry** — 10:30 am - 10:55 am
  R. Paul Philp, Tomasz Kuder, and Jon Allen, The University of Oklahoma, Norman, OK
- **Helicopter Surveys for Locating Wells and Leaking Oilfield Infrastructure** — 10:55 am - 11:20 am
  Richard W. Hammack and Garret Veloski, U.S. Dept. of Energy-NETL, Pittsburg, PA; Greg Hodges, Fugro Airborne Surveys, Mississauga, ON, Canada

THURSDAY, OCTOBER 19, 2006 - MORNING

REMEDIATION OF HYDROCARBON SPILLS; WAVE TANK STUDIES ON EFFECTIVENESS OF CHEMICAL DISPERSANTS (Fiesta B)

Chair: Albert Venosa, U.S. EPA, Cincinnati, OH

REMEDIATION OF HYDROCARBON SPILLS

• ***In-Situ* Destruction of Non-Aqueous Phase Liquids (NAPL) Using Activated Sodium Persulfate** Isaac M. Aboulafia, MECX, LLC, Houston, TX; Linda S. Osborne, FMC Active Oxidants, Philadelphia, PA	8:00 am - 8:25 am
• **The Use of ElectroChemical GeoOxidation for the Destruction of PAHs in Crude Oil** J. Kenneth Wittle, Electro Petroleum, Inc., Wayne, PA	8:25 am - 8:50 am
• **Combining Monitoring Well Gamma-Ray Logs and Boring Log Data to Define Petroleum Pollutant Source and Transport Zones** Leonard Billingsley and Frank Vernon, Oklahoma Corporation Commission, Oklahoma City, OK	8:50 am - 9:15 am
• **Experimental Evaluation of Various Commonly Used Oxidizers for Destruction of BTEX Compounds** Jesse Taylor, Remington Technologies, Loveland, CO	9:15 am - 9:40 am
Break	9:40 am - 10:05

WAVE TANK STUDIES ON EFFECTIVENESS OF CHEMICAL DISPERSANTS

• **Wave Tank Studies on Chemical Dispersant Effectiveness as a Function of Energy Dissipation Rate** Albert D. Venosa, US Environmental Protection Agency, Cincinnati, OH; Zhengkai Li, Kenneth Lee, and Paul Kepkay, Fisheries and Oceans Canada, Dartmouth, Nova Scota, Canada; Michel C. Boufadel, Temple University, Philadelphia, PA	10:05 am - 10:30 am
• **Hydrodynamic Characterization of a Wave Tank Facility for the Evaluation of Oil Dispersant Effectiveness** Michel C. Boufadel, Temple University, Philadelphia, PA; Zhengkai Li and Kenneth Lee, Fisheries and Oceans Canada, Dartmouth, Nova Scota, Canada; Albert D. Venosa, US Environmental Protection Agency, Cincinnati, OH	10:30 am - 10:55 am

- **Formation and Transport of Oil-Mineral-Aggregates in a Wave Tank**
  Kenneth Lee, Zhengkai Li, and Paul Kepkay, Fisheries and Oceans Canada, Dartmouth, Nova Scota, Canada; Michel C. Boufadel, Temple University, Philadelphia, PA; Albert D. Venosa, US Environmental Protection Agency, Cincinnati, OH — 10:55 am - 11:20 am

- **Wave Tank Studies on Dispersant Effectiveness as a Function of Oil Droplet Size Distribution**
  Zhengkai Li, Kenneth Lee, and Paul Kepkay, Fisheries and Oceans Canada, Dartmouth, Nova Scota, Canada; Michel C. Boufadel, Temple University, Philadelphia, PA; Albert D. Venosa, US Environmental Protection Agency, Cincinnati, OH — 11:20 am - 11:45 am

COALBED NATURAL GAS PRODUCED WATER (Salon 4)

Chairs: John and Deidre Boysen, BC Technologies Ltd., Laramie, WY

- **Developing a New Water Resource from Production Water**
  David R. Stewart, Stewart Environmental Consultants, Inc., Ft. Collins, CO — 8:00 am - 8:25 am

- **Equilibrium Adsorption of Carbon Dioxide, Methane, and Nitrogen Gases on Argonne Premium Coals and an Activated Carbon at Various Moisture Contents**
  Khaled A.M. Gasem, James E. Fitzgerald, and Robert L. Robinson, Jr., Oklahoma State University, Stillwater, OK — 8:25 am - 8:50 am

- **New Cleanup Agents for Membrane Filters used to Clean Up Oil Field Produced Water**
  David B. Burnett, Scott Beech, and Carl Vavra, Texas A&M University, College Station, TX; Albert Chan, SpacerTek Technology, Plano, TX — 8:50 am - 9:15 am

- **Integrated Electrodialysis Membrane Stability Results for Cost-Effective CBM Produced Water Demineralization**
  Paula Moon and Seth Snyder, Argonne National Laboratory, Argonne, IL; Thomas Hayes, Gas Technology Institute, Des Plaines, IL — 9:15 am - 9:40 am

Break — 9:40 am - 10:05 am

- **Electrodialysis Treatment of Coalbed Methane Produced Water: Engineering Issues and Cost Projections**
  Thomas Hayes, Gas Technology Institute, Des Plaines, IL; Sherif Gowelly, Paula Moon and Seth Snyder, Argonne National Laboratory, Argonne, IL — 10:05 am - 10:30 am

- **Pilot Scale Test of a Produced Water Treatment System for Organic Compounds**
  E.J. Sullivan, Los Alamos National Laboratory, Los Alamos, NM; Lynn Katz, Kerry Kinney, Soondong Kwon, Li-Jung Chen, and Elaine Darby, University of Texas-Austin, Austin, TX; Rob Bowman and Craig Altare, New Mexico Institute of Mining and Technology, Socorro, NM — 10:30 am - 10:55 am

- **Coalbed Methane - Produced Water Treatment Using Gas Clathrate Hydrates**
  Costas Tsouris, Phillip Szymcek, Scott McCallum, Patricia Taboada-Serrano, Megan Madden Elwood, and Tommy Phelps, Oak Ridge National Laboratory, Oak Ridge, TN — 10:55 am - 11:20 am

- **An Exciting New Produced Water Concentrator Technology for Tail and Brine Waters: AltelaRain™**
  Matthew Bruff, Altela, Inc., Englewood, CO; Ned Godhsall, Altela, Inc., Albuquerque, NM — 11:20 am - 11:45 pm

BRINE IMPACTS AT THE OSAGE-SKIATOOK PETROLEUM ENVIRONMENTAL RESEARCH PROJECT SITES (Fiesta A)

Chairs: James K. Otton, U.S. Geological Survey, Lakewood, CO and Yousif Kharaka, U.S. Geological Survey, Menlo Park, CA

- **Fate and Water Impacts of Produced Water Operations at OSPER Sites, Osage County, OK: Major Unresolved Issues**
  Yousif K. Kharaka, James J. Thordsen, Evangelos Kakouros, and William N. Herkelrath, U.S. Geological Survey, Menlo Park, CA; Marvin M. Abbott, U. S. Geological Survey, Oklahoma City, OK — 8:00 am - 8:25 am

- **Three Dimensional Visualization and Analysis of Geological, Geochemical, and Geophysical Data at the Osage Skiatook Petroleum Environmental Research "A" Site, Osage County, Oklahoma**
  Bruce D. Smith, James K. Otton, and Robert A. Zielinski, U.S. Geological Survey, Lakewood, CO; Marvin M. Abbott, U.S. Geological Survey, Oklahoma City, OK — 8:25 am - 8:50 am

- **Composition of Pore Water in Lake Sediments Near Research Site "B", Osage County, Oklahoma: Implications for Lake Water Quality and Ecosystem Health** — 8:50 am - 9:15 am
  Robert A. Zielinski and James K. Otton, U.S. Geological Survey, Lakewood, CO; William N. Herkelrath, U.S. Geological Survey, Menlo Park, CA

- **Modeling Subsurface Transport of Oil Field Brine at USGS OSPER "A", Osage County, Oklahoma** — 9:15 am - 9:40 am
  William N. Herkelrath and Yousif K. Kharaka, U.S. Geological Survey, Menlo Park, CA

Break — 9:40 am - 10:05 am

- **Induction Conductivity and Natural Gamma-Ray Logs at the Osage Skiatook Research Sites "A" and "B", Northeastern Oklahoma** — 10:05 am - 10:30 am
  Marvin M. Abbott, U.S. Geological Survey, Oklahoma City, OK; Bruce D. Smith, Robert A. Zielinski, and James K. Otton, U.S. Geological Survey, Lakewood, CO; James Thordsen, U.S. Geological Survey, Menlo Park, CA

- **Subsurface Distribution of Produced Water Salts at OSPER Site "B", Osage County, Oklahoma** — 10:30 am - 10:55 am
  James K. Otton and Robert A. Zielinski, U.S. Geological Survey, Lakewood, CO

- **Geospatial Estimates of Produced Water Contamination Near Skiatook Lake, Northeastern Oklahoma Using Dissolved Cl Concentrations in Tributary Streams** — 10:55 am - 11:20 am
  Cynthia Rice and Robert A. Zielinski, U.S. Geological Survey, Lakewood, CO; Marvin M. Abbott, U.S. Geological Survey, Oklahoma City, OK

- **Biotic Effects of Produced Water Intrusion in an Oklahoma Reservoir** — 11:20 am - 11:45 am
  Jonathan C. Fisher and Joseph R. Bidwell, Oklahoma State University, Stillwater, OK

THURSDAY, OCTOBER 19, 2006 - AFTERNOON

GROUNDWATER REMEDIATION II (Salon 2)

Chair: Eric Raes, Engineering & Land Planning Associates, Inc., Clinton, NJ

- **Determining Biodegradation Potential and *In Situ* Biodegradation Rate Constants for Benzene Using Bio-Sep®; Bio-Trap ^{13}C-Stable Isotope Probing**

J.L. Busch-Harris, K.L. Sublette, E. Jennings, and K.P. Roberts, The University of Tulsa, Tulsa, OK; G. Davis and D. Ogles, Microbial Insights, Inc., Rockford, TN; D.C. White and A. Peacock, University of Tennessee, Knoxville, TN; W.E. Holmes, University of Michigan, Ann Arbor, MI; E. Raes, Engineering & Land Planning Associates, Inc., Clinton, NJ; E. Hince, Geovation Consultants, Inc., Florida, NY — 1:30 pm - 1:55 pm

- **Innovative Design Build Solutions for the Environmental Remediation Program at JFK Airport** — 1:55 pm - 2:20 pm

August Arrigo, Shaw Environmental, Inc., Holbrook, NY

- **Improved Efficiency in Contaminated Groundwater Site Characterization: A Minimally Invasive Approach** — 2:20 pm - 2:45 pm

Paul Rollins, Willowstick Technologies, LLC, Draper, UT

- **Determining *In Situ* Degradation Rate Constants for Various Electron Acceptors via Bio-Trap Samples and Push Pull Tests, a Case Study at a Petroleum Distribution Facility**

Eric J. Raes and Amy V. Callaghan, Engineering & Land Planning Associates, Inc., Clinton, NJ; K.L. Sublette, J.L. Busch-Harris, and E. Jennings, The University of Tulsa, Tulsa, OK; Jack Istok, Oregon State University, Corvallis, OR; A. Peacock, University of Tennessee, Knoxville, TN; G. Davis, Microbial Insights, Inc., Rockford, TN — 2:45 pm - 3:10 pm

Break — 3:10 pm - 3:35 pm

- **Use of Fluorinated Analogs of PCE Adsorbed to Bio-Sep® Beads to Demonstrate the *In-Situ* Biodegradation Potential of Chlorinated Hydrocarbons**

K.L. Sublette, E. Jennings, and J.L. Busch-Harris, The University of Tulsa, Tulsa, OK; A. Peacock, University of Tennessee, Knoxville, TN; G. Davis and D. Ogles, Microbial Insights, Inc., Rockford, TN; Pat McLoughlin and Bob Pirkle, Microseeps, Inc., Pittsburgh, PA; Glenn White, Haley & Aldrich, Rochester, NY — 3:35 pm - 4:00 pm

- **Advances in *In-Situ* Bioremediation of Chlorinated Solvents**

Ryan A. Wymore and Kent S. Sorenson, CDM, Denver, CO; Tamzen W. Macbeth, North Wind, Inc., Idaho Falls, ID — 4:00 pm - 4:25 pm

- **Elucidation of Aerobic Cometabolism as an Important Intrinsic Degradation Mechanism for MNA of Chlorinated Ethene Hydrocarbons** — 4:25 pm - 4:50 pm
  Ryan A. Wymore and Kent S. Sorenson, CDM, Denver, CO; M Hope Lee, North Wind, Inc., Idaho Falls, ID

PHYTOREMEDIATION; SITE RESTORATION AND RECLAMATION II (Salon 4)

Chair: Greg Thoma, University of Arkansas, Fayetteville, AR

PHYTOREMEDIATION

- **Petroleum Degrader Microbial Populations in Rhizosphere and Non-Rhizosphere Crude Oil-Contaminated Soil** — 1:30 pm - 1:55 pm
  D.C. Wolf, W.D. Kirkpatrick, P.M. White, Jr., K.J. Davis, G.J. Thoma, University of Arkansas, Fayetteville, AR
- **Phytoremediation Approach for Contaminated Soil at Kalimantan, Indonesia** — 1:55 pm - 2:20 pm
  Tri Wisono, Chevron Indonesia Company, Balikpapan, Indonesia
- **Phytoremediation of a Weathered Flare-Pit Soil** — 2:20 pm - 2:45 pm
  Richard E. Farrell, Adam Gillespie, and James J. Germida, University of Saskatchewan, Saskatoon, SK, Canada
- **Influence of Sampling Variability in Assessing Phytoremediation Effectiveness of a Crude Oil-Contaminated Soil** — 2:45 pm - 3:10 pm
  K. Karim, G.J. Thoma, K.J. Davis, E.E. Gvur, and D.C. Wolf, University of Arkansas, Fayetteville, AR

Break — 3:10 pm - 3:35 pm

- **Phytoremediation of Flare-Pit Soil: The Impact of Mixed and Single Plant Treatments on Microbial Hydrocarbon Degradation Potential** — 3:35 pm - 4:00 pm
  Lori A. Phillips, Richard E. Farrell, and James J. Germida, University of Saskatchewan, Saskatoon, SK, Canada; Charles W. Greer, Biotechnology Research Institute, Montreal, QC, Canada
- **Effect of Nitrogen Addition on Rhizo-Degradation Rates of Pyrene** — 4:00 pm - 4:25 pm
  K. Karim, G.J. Thoma, Pei-Ting Hsu, Thang Ho, and D.C. Wolf, University of Arkansas, Fayetteville, AR

SITE RESTORATION AND RECLAMATION II

- **Of Earthworms and Nematodes in Restoration of E&P Sites**

Kerry Sublette, Nitya Alahari, and Eleanor Jennings, The University of Tulsa, Tulsa, OK; Kathleen Duncan, The University of Oklahoma, Norman, OK; Greg Thoma and Duane Wolf, University of Arkansas, Fayetteville, AR; Josh Brokaw, Washington State University, Pullman, WA; Mac A. Callaham, USDA Forest Service, Athens, GA — 4:25 pm - 4:50 pm

- **Things I Wonder About in the Restoration of Oil and Brine-impacted Sites**

Kerry Sublette, Eleanor Jennings, Dan Weber, Carla J. Landrum, Shoeb Munshi, Melissa Barton, and J. Berton Fisher, The University of Tulsa, Tulsa, OK; Kathleen Duncan, University of Oklahoma, Norman, OK; Greg Thoma, University of Arkansas, Fayetteville, AR; Tim Todd, Kansas State University, Manhattan, KS — 4:50 pm - 5:15 pm

LEGAL AND REGULATORY ISSUES (Salon 5)

Chair: Markus Puder, Argonne National Laboratory, Washington, DC

- **Modeled Impacts of Incremental Application for Permit to Drill (APD) Processing for Energy** — 1:30 pm - 1:55 pm

Jeffrey Eppink, Advanced Resources International, Inc., Arlington, VA

- **A Lawyer's View of the Barnett Shale: Legal and Environmental Issues** — 1:55 pm - 2:20 pm

Sarah K. Walls, Cantey & Hanger, LLP, Ft. Worth, TX

- **Why Are Produced Water Discharge Standards Different Throughout the World?** — 2:20 pm - 2:45 pm

John Veil, Argonne National Laboratory, Washington, DC

- **Improving Access to Oil & Gas Resources on Federal Lands** — 2:45 pm - 3:10 pm

J. Daniel Arthur, ALL Consulting, Tulsa, OK

Break — 3:10 pm - 3:35 pm

- **The Energy Policy and Conservation Act (EPCA) Cumulative Phase II Inventory: Implications for Development of Future Onshore National Oil & Gas Supply** — 3:35 pm - 4:00 pm
  Jeffrey Eppink, Advanced Resources International, Inc., Arlington, VA; Richard Watson, Bureau of Land Management, Washington DC; Robert Johnson, Premier Data Services, Denver, CO
- **Environmental Due Diligence in Oil & Gas Transactions** — 4:00 pm - 4:25 pm
  Seth Randle, Jenkens & Gilchrist, PC, Austin, TX
- **Developments in the Conduct and Regulation of Operations for Natural Gas from Coal in AB, Canada** — 4:25 pm - 4:50 pm
  J.D. Dilay, Alberta Energy and Utilities Board, Calgary, AB, Canada

SPECIAL SYMPOSIUM
FRIDAY, OCTOBER 20, 2006

REMEDIATION AND RESTORATION OF BRINE IMPACTED SITES (San Antonio Ballroom)

Chair: Kerry L. Sublette, University of Tulsa, Tulsa, OK

- **Environmental Impacts of Oil Production Operations at OSPER "A" Site, Osage County, Oklahoma: Implications for Site Remediation** — 8:00 am - 8:25 am
  Yousif K. Kharaka, James J. Thordsen, and William N. Herkelrath, U.S. Geological Survey, Menlo Park, CA; James K. Otton, U.S. Geological Survey, Lakewood, CO; Marvin M. Abbott, U.S. Geological Survey, Oklahoma City, OK
- **Practical Guidelines for Addressing Impacts of Produced Water Releases to Plants, Soil, and Groundwater (Click here for PowerPoint Presentation)** — 8:25 am - 8:50 am
  John A. Connor and Charles J. Newell, Groundwater Services, Inc., Houston, TX; Harley H. Hopkins, API, Washington, DC
- **The Oklahoma Corporation Commission's New Brine Spill Cleanup Guidance** — 8:50 am - 9:15 am
  Patricia Billingsley and Tim Baker, Oklahoma Corporation Commission, Oklahoma City, OK

- **Environmental Impacts of Produced-Water Salt Releases in the Conterminous U.S. - A Bibliography** — 9:15 am - 9:40 am
  James K. Otton, U.S. Geological Survey, Lakewood, CO

Break — 9:40 am - 10:05 am

- **Use of Risk-Based Criteria for Characterization of Environmental Liabilities in Upstream Oil & Gas Production Facilities** — 10:05 am - 10:30 am
  John A. Connor, Richard L. Bowers, and Silvia I. Maberti, Groundwater Services, Inc., Houston, TX; Juan Carlos Mejia, Occidental Andina, LLC, Bogotá, Colombia; Krish Ravishankar, Occidental Oil & Gas Corporation, Houston, TX; Sandra Yamile Alvarez, ECOPETROL, Bogotá, Colombia

- **Persistence of Oil Waste Lands in Osage County, Oklahoma** — 10:30 am - 10:55 am
  Melissa N. Barton, J. Berton Fisher, and J. Bryan Tapp, The University of Tulsa, Tulsa, OK

- **Southern Oklahoma Old Oilfield Stream Salinity Sampling Project** — 10:55 am - 11:20 am
  Patricia Billingsley, Oklahoma Corporation Commission, Oklahoma City, OK

- **The Use of Electro Kinetics for the Removal of Salt from Brine Impacted Soils** — 11:20 am - 11:45 am
  J. Kenneth Wittle, Electro Petroleum, Inc., Wayne, PA; Sibel Pamucku, Lehigh University, Bethleham, PA

Framing the Critical Energy-Water Link

13th IPEC Conference
San Antonio, TX

October 17-20, 2006

John R. Duda
U.S. Department of Energy

National Energy Technology Laboratory

Objectives

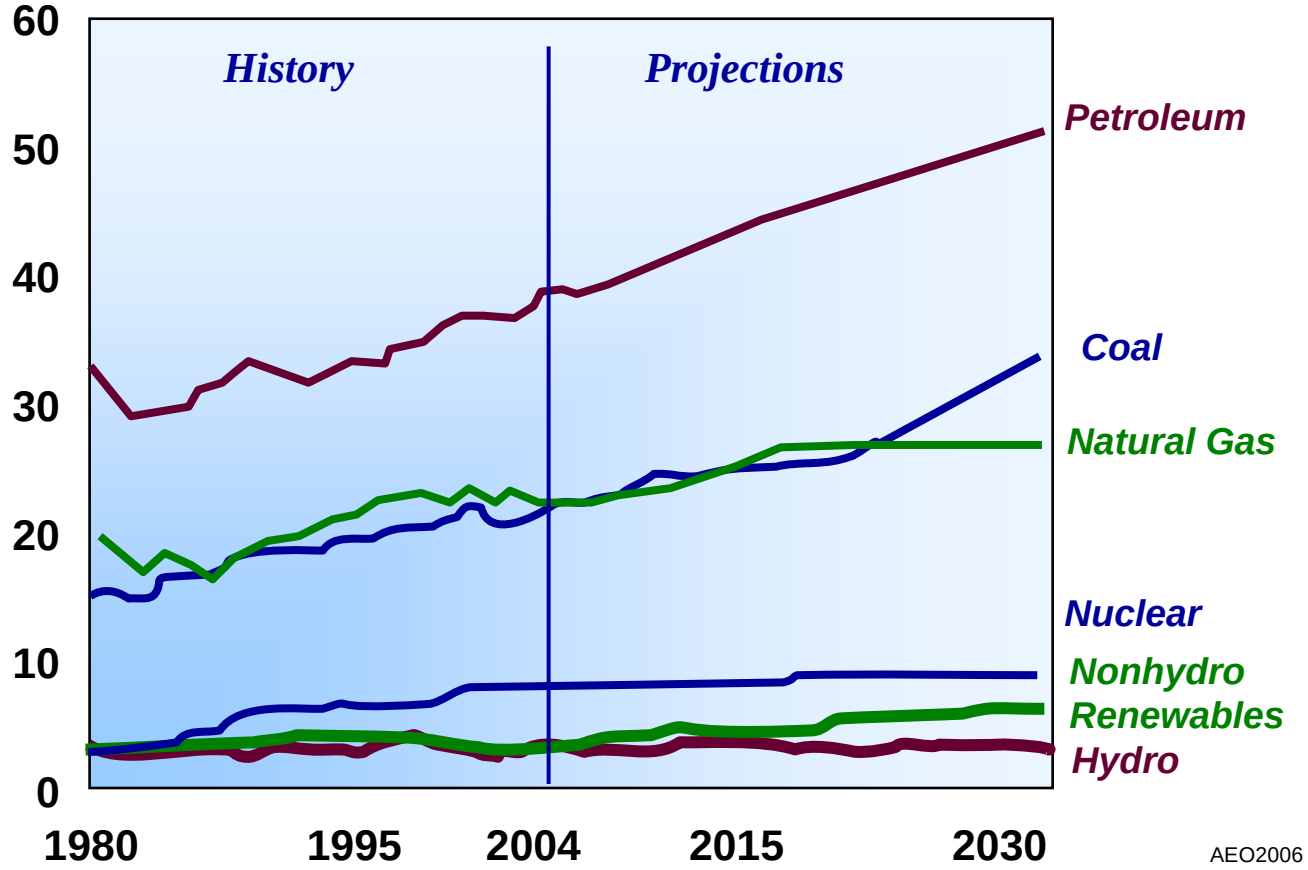
- **Provide a contemporary perspective on the energy-water relationship**
- **Enhance awareness**
- **Provide impetus for *new paradigm* when it comes to energy projects**

Outline

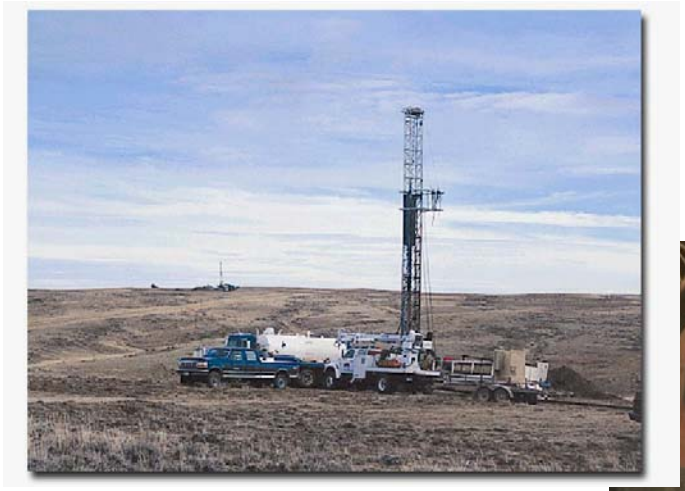
- **Energy forecasts**
- **[Energy]-water relationships**
  - Conventional
  - Emerging
  - *"On the peripheral"*
- **Time for a *new* paradigm?**

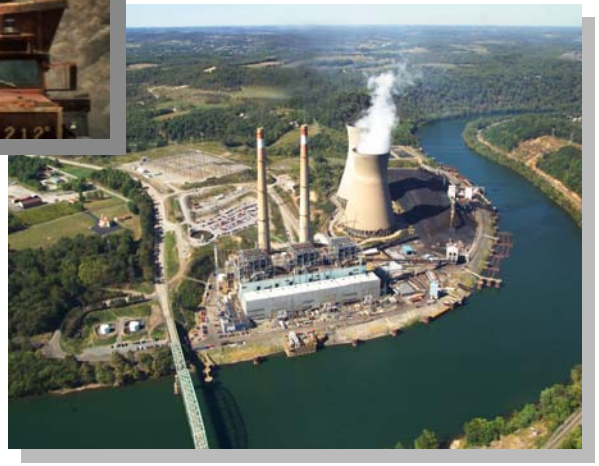
U.S. Energy Demand to Increase Water Requirements to *"Track Btu's"* ?

Energy Consumption by Fuel, 1980-2030 (quadrillion Btu)



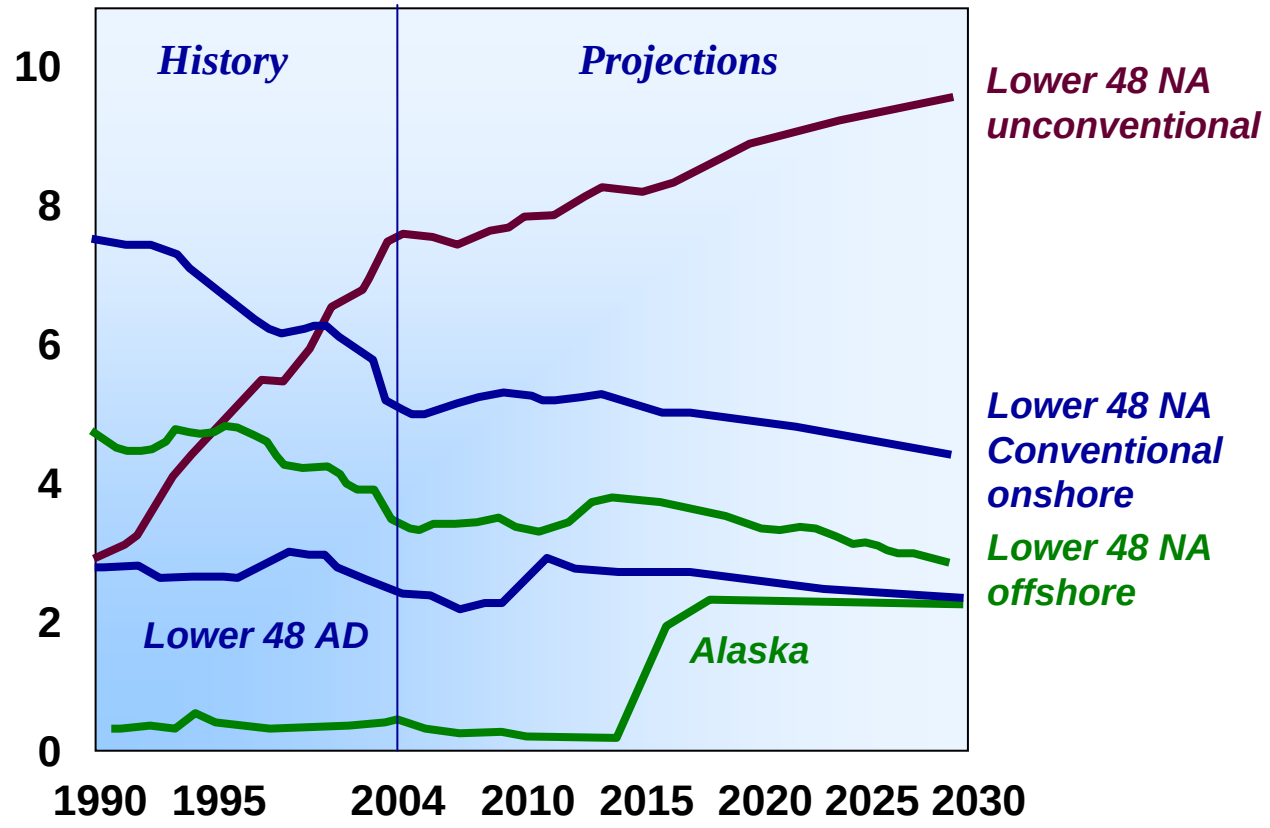
Energy and Water
A "*Cradle to Grave*" Relationship



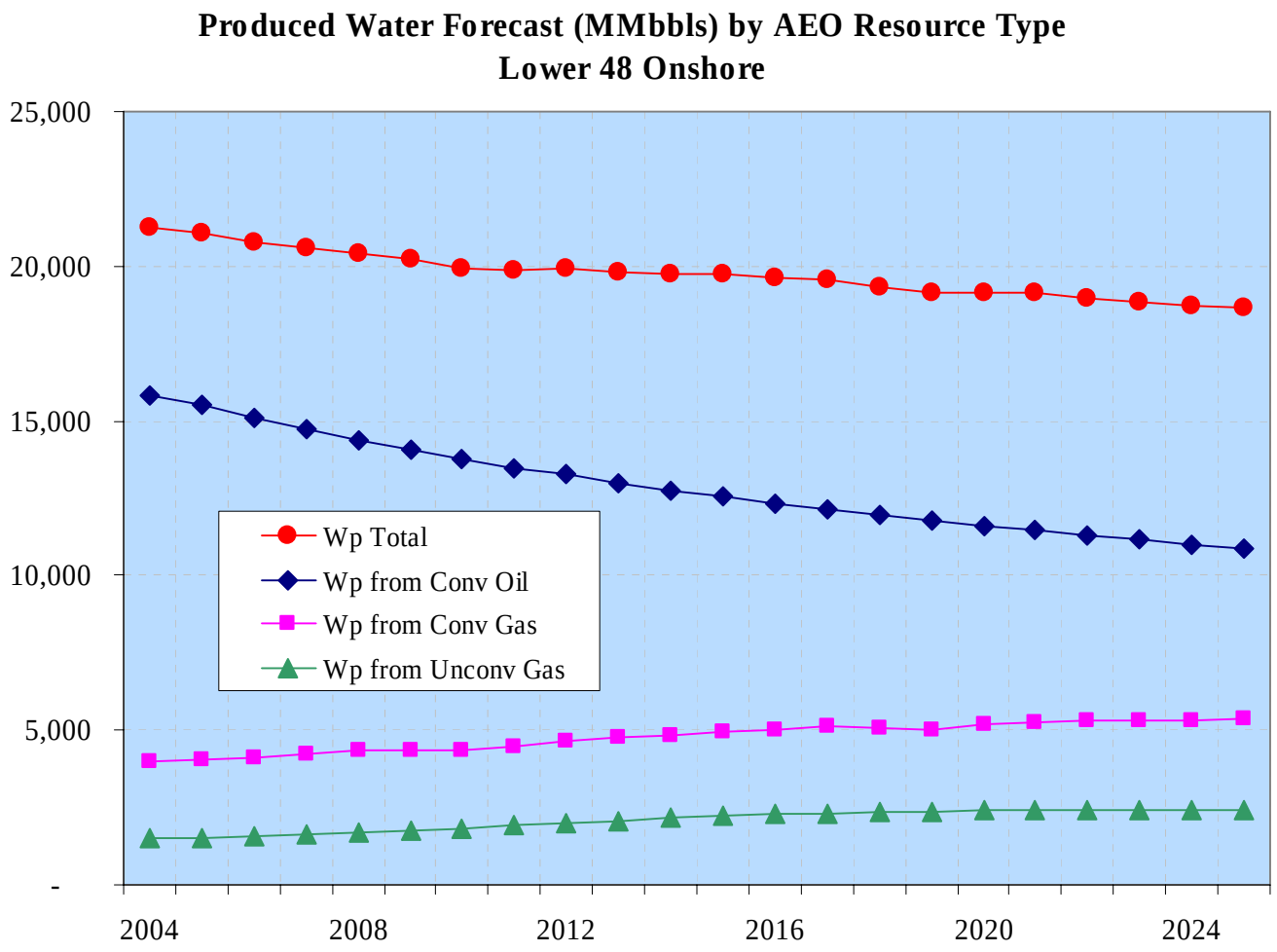


Domestic Supply Trends to Continue Increasing Reliance on UGR

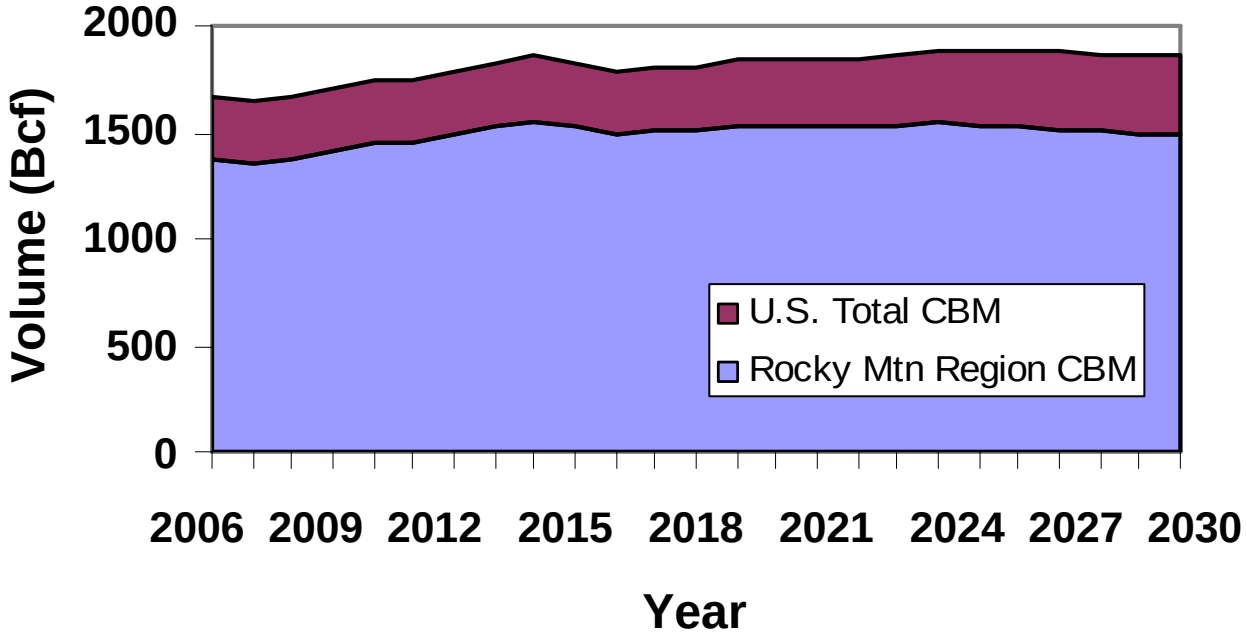
Natural gas production by source, 1980-2030 (trillion cubic feet)



$W_{p\ (total)}$ Volume Declines But Remains Significant

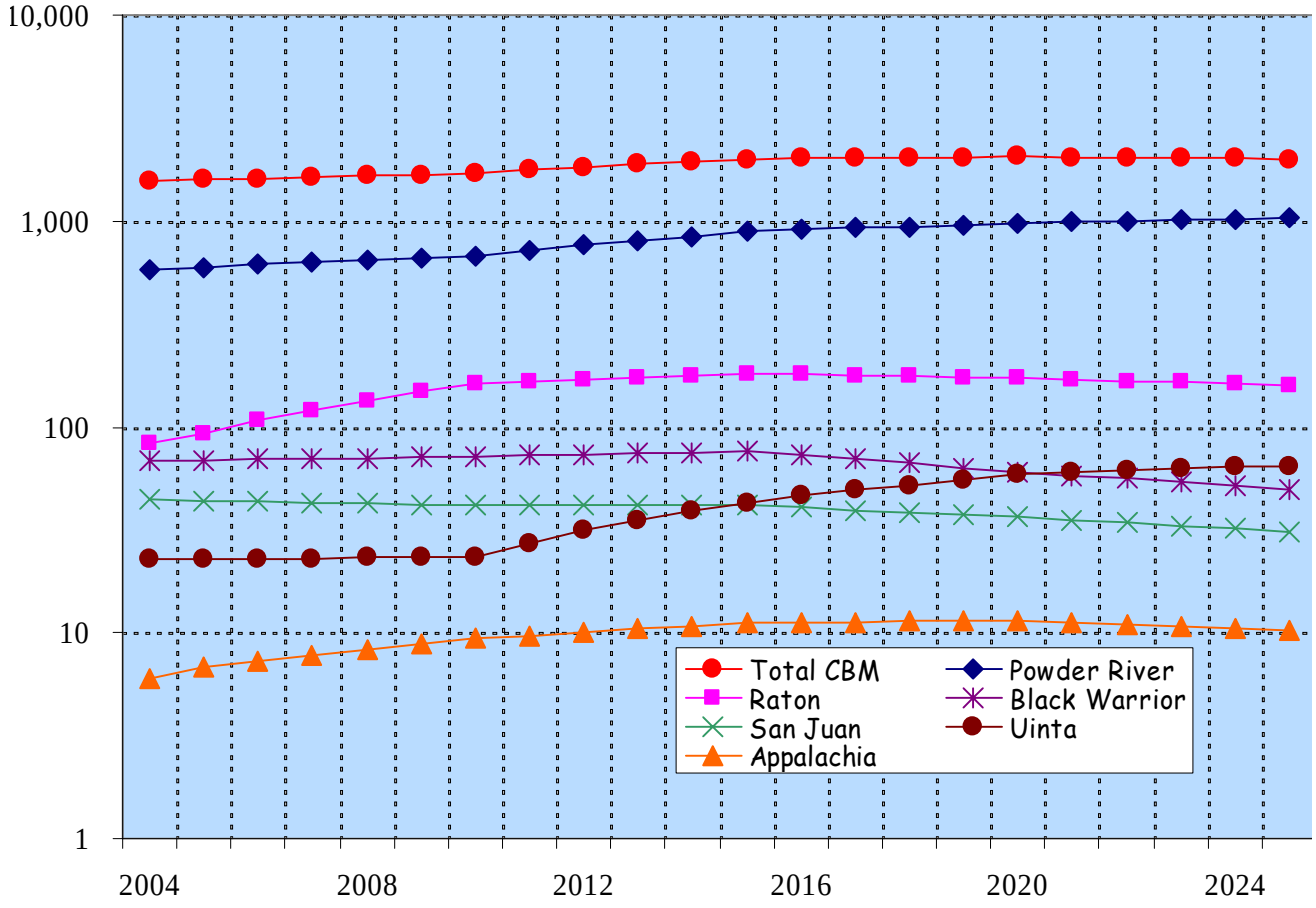


CBM Production Increases to Nearly 2 Tcf/yr
Rocky Mtn. Basins/Plays Remain Dominant



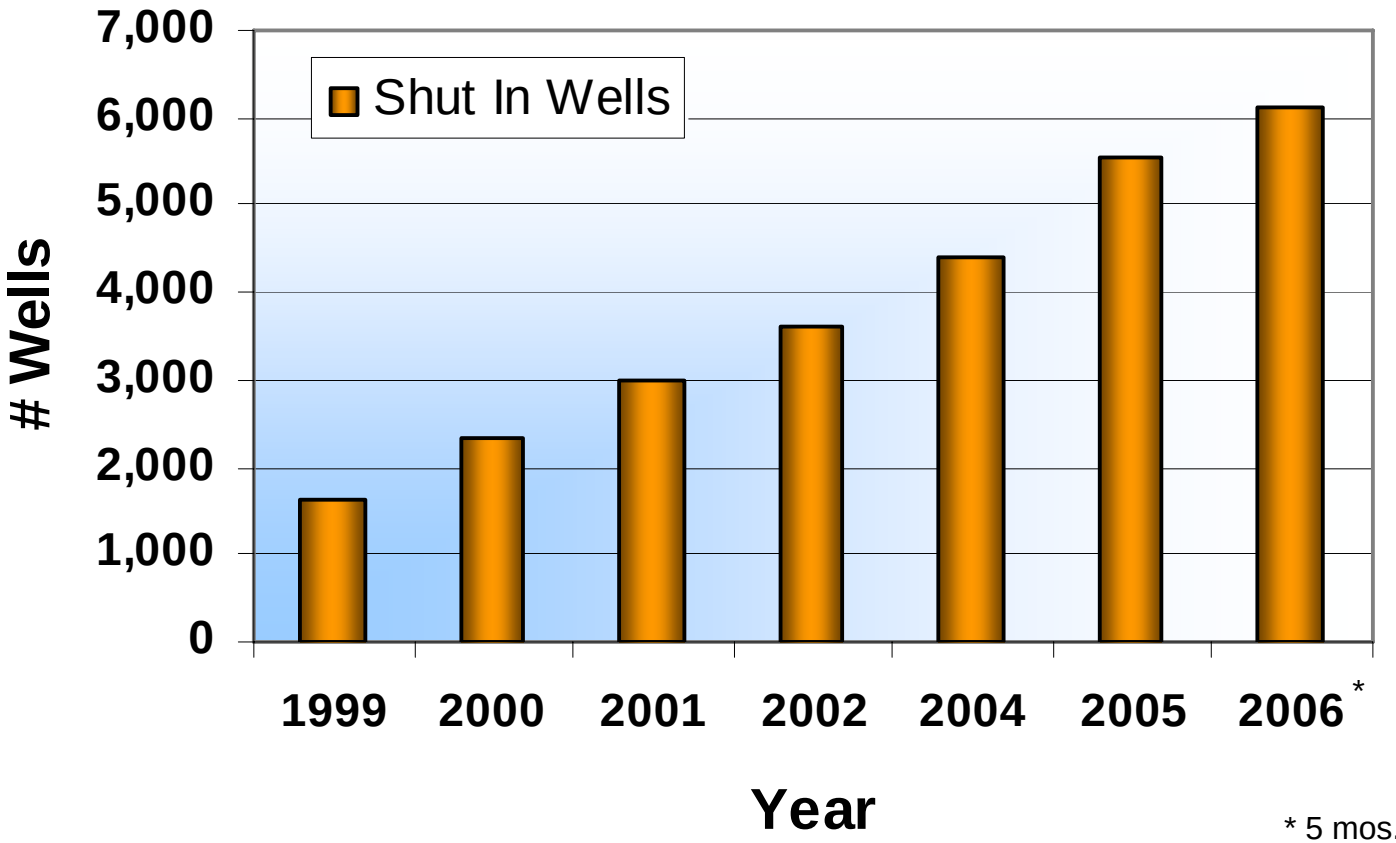
Expect a Commensurate Increase in W_p Volumes
Water Management *Key* for Rocky Mountain Region

Produced Water Forecast (MMbbls) by UnConv CBM Gas Play



W_p Management Issues ARE of Consequence! Powder River Basin CBM

Average number of shut-in coalbed methane wells



* 5 mos.

"W_p *Impacts*" on Energy are Far-Reaching "*Translation*"…

- **3000 wells**
- **60 Mcf/d**
- **365 day/yr**
- **$4/Mcf**
- **~ $263 <u>m</u>illion/yr (gross)**
  - Royalties
  - Taxes
  - Reinvestment capital
  - …etc.

…Far-Reaching – "Touching Consumers?"
An Implication?...You Be the Judge

Credits And Charges Since Your Last Bill

Balance from last bill

Payment on Aug 18, 2006 - Thank You

Balance

Current Charges

Residential Service Rate

Monthly Service Charge

Gas Usage Charge

XXXXXXXX $16.0080

Municipal Surcharge

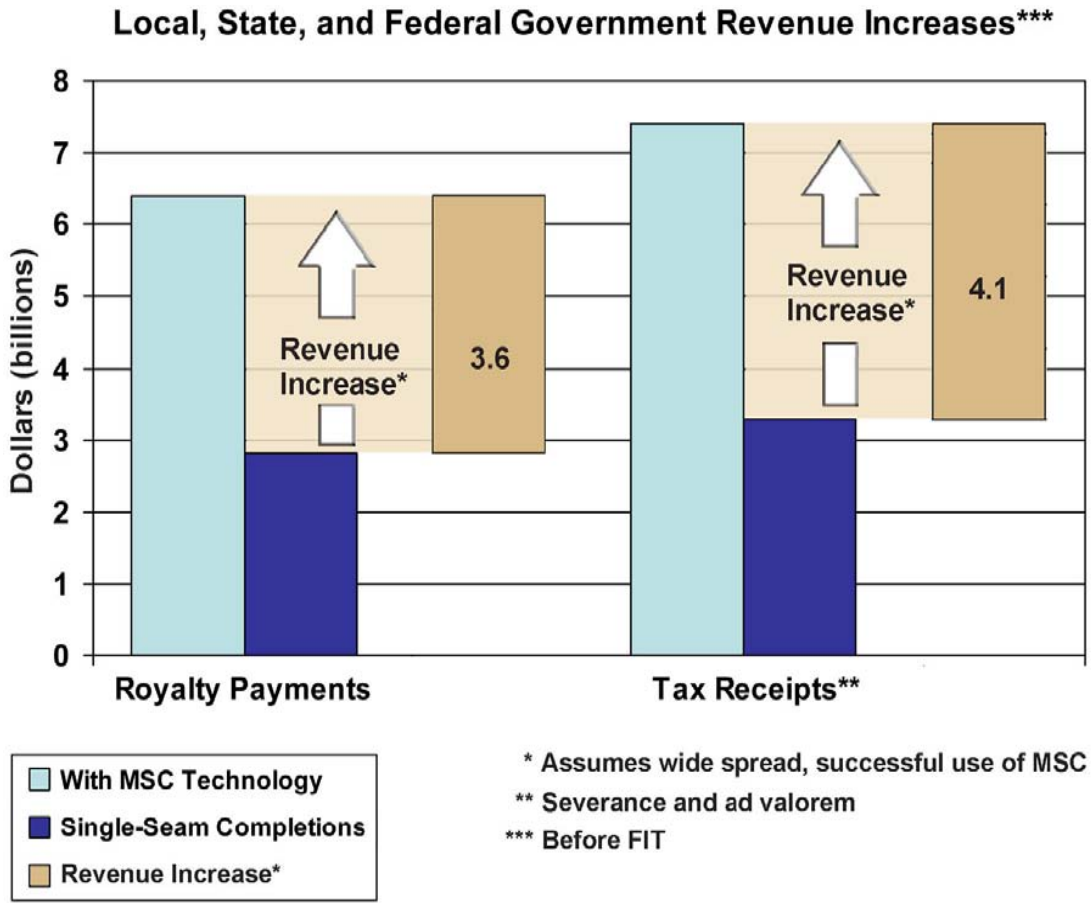
Excise Tax

Total Current Charges

Total Account Balance

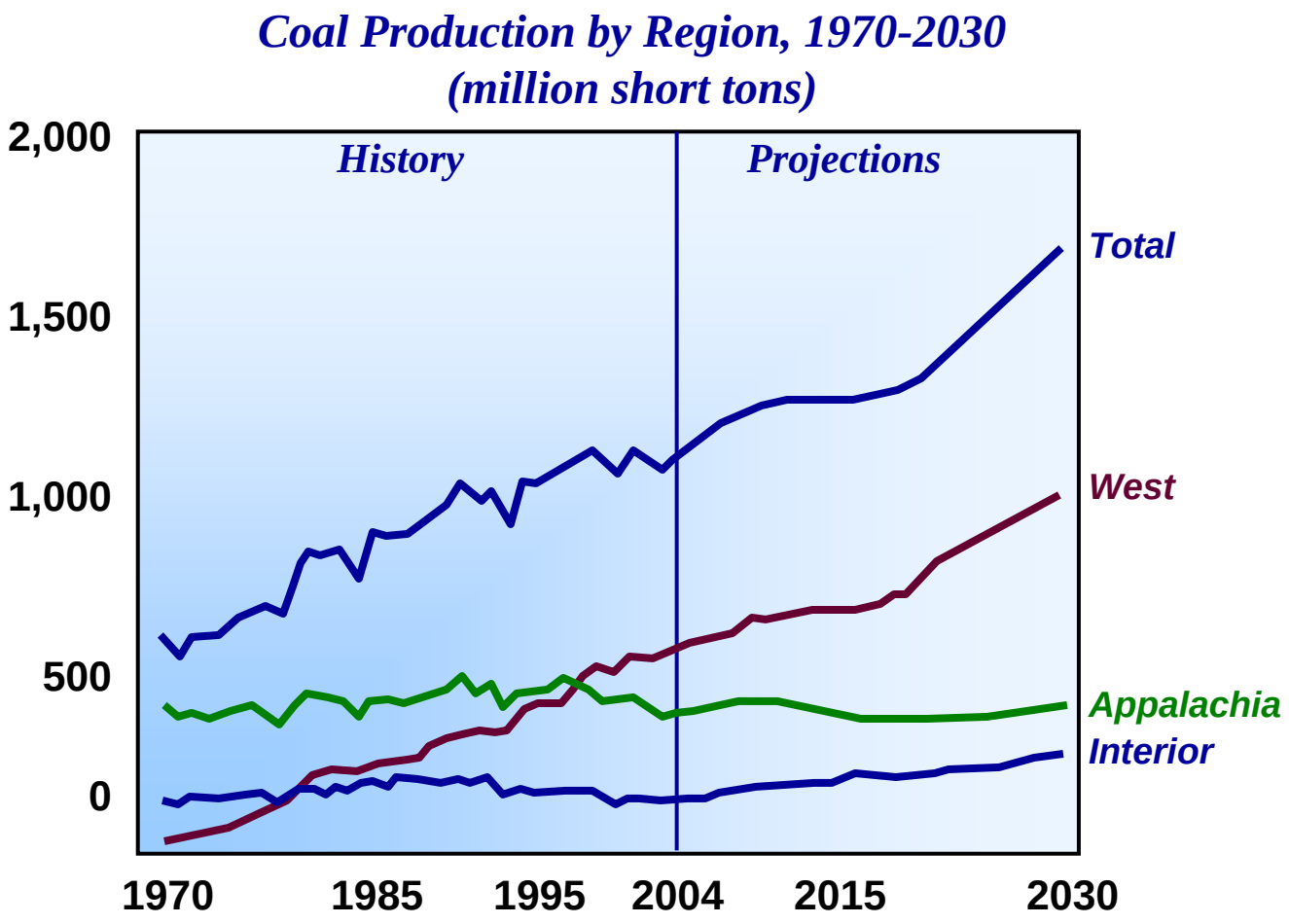
$16.0080

Technology Advances Can Yield Sign. Benefits
Water Management Requires ≥ Attention



Potential Economic Benefits Associated with MSC

Coal Continues to Fuel the Nation



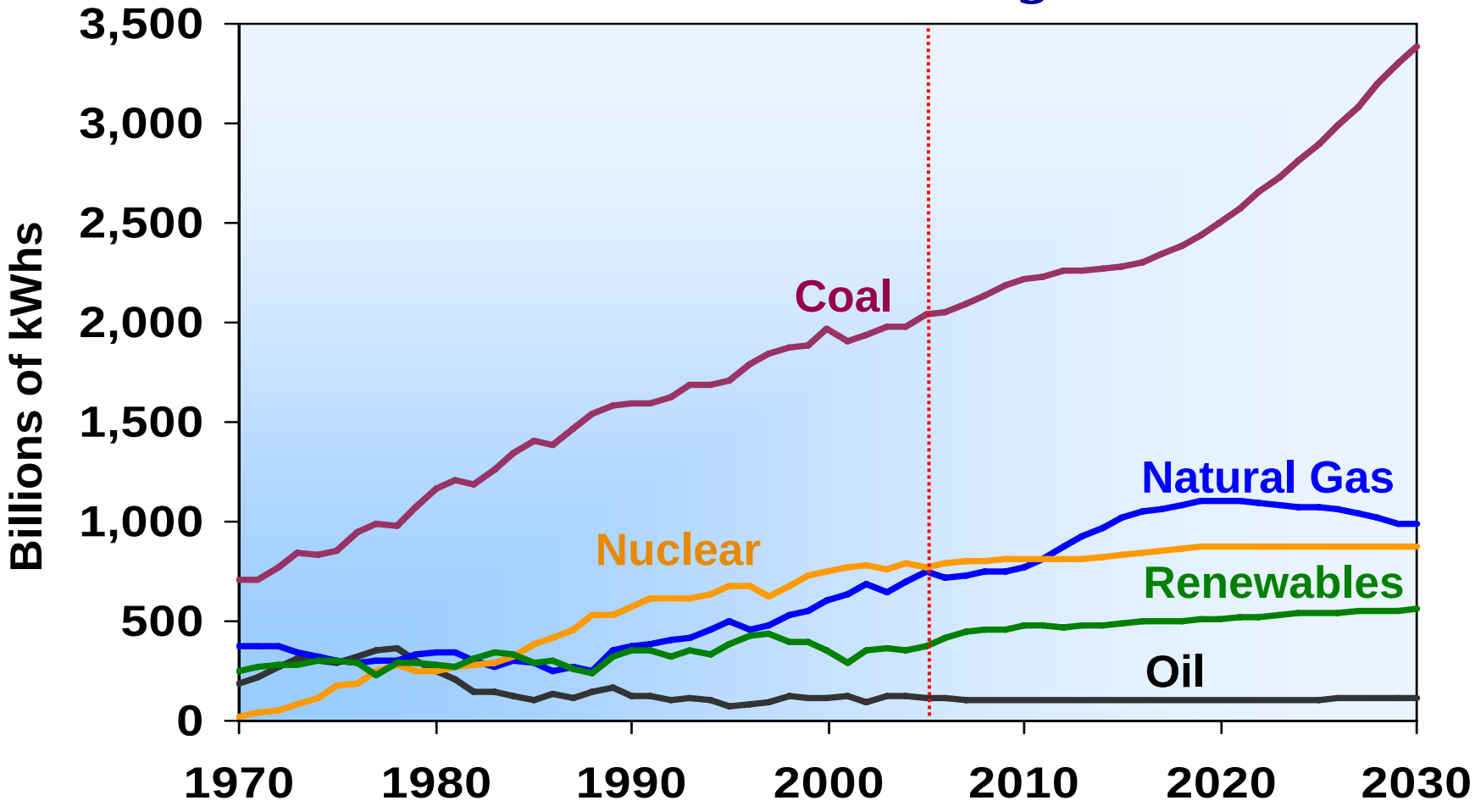
Coal Mining/Coal Prep

Underground Operations
Water Affects Working Conditions/Safety

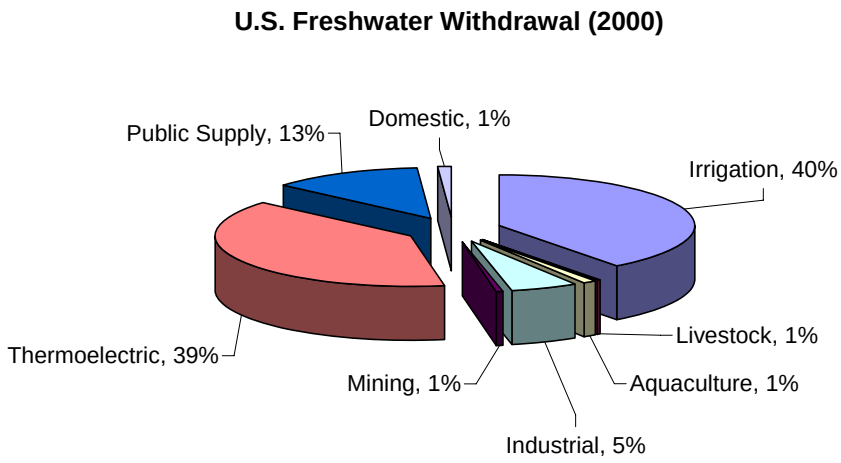
Legacy Operations Encumber Today's Industry

Current Practices are Environmentally *Aligned*

Electricity Demand Forecast to 2030
Coal Remains *King*

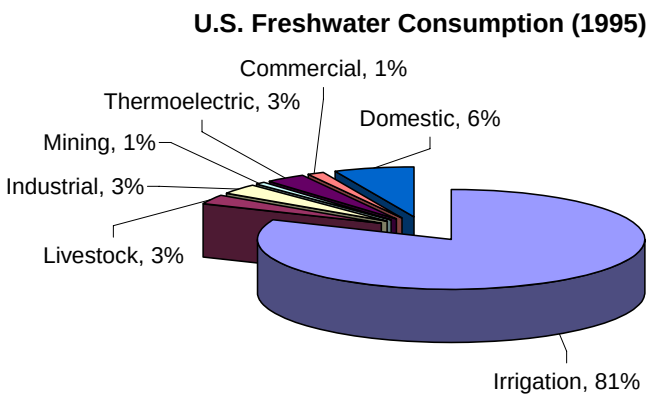


The Issues: Competing Water Uses



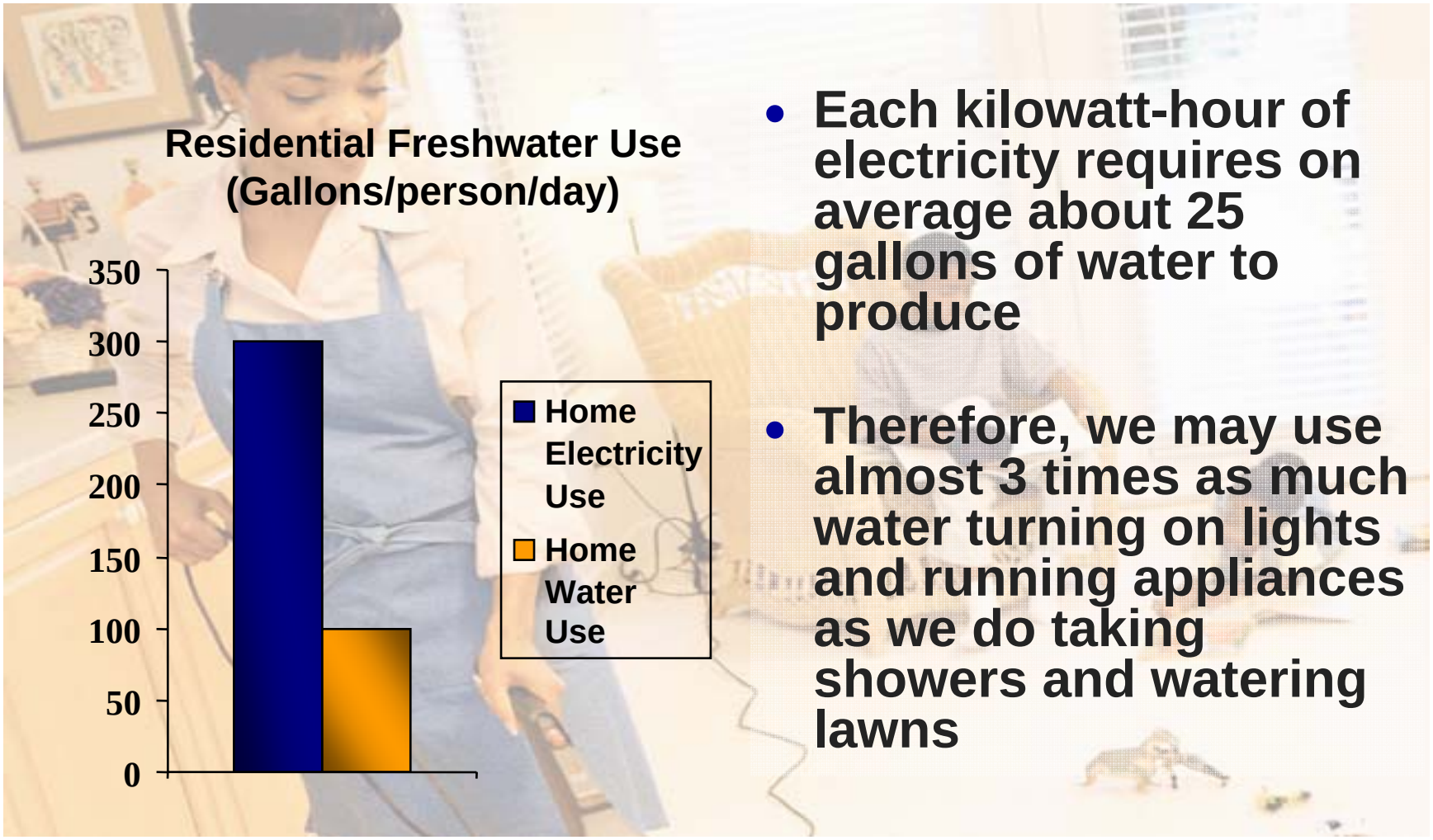
- **2000 thermoelectric water requirements:**
  - **Withdrawal: ~ 136 BGD**
  - **Consumption: ~ 3 BGD**

- **Thermoelectric competes with other users, including in-stream use.**
- **Which is more important: drinking and personal use, growing food, or energy production?**



USGS, Estimated Use of Water in the United States in 2000, USGS Circular 1268, March 2004
USGS, Estimated Use of Water in the United States in 1995, USGS Circular 1200, 1998

Water and Electricity Are Inextricably Linked

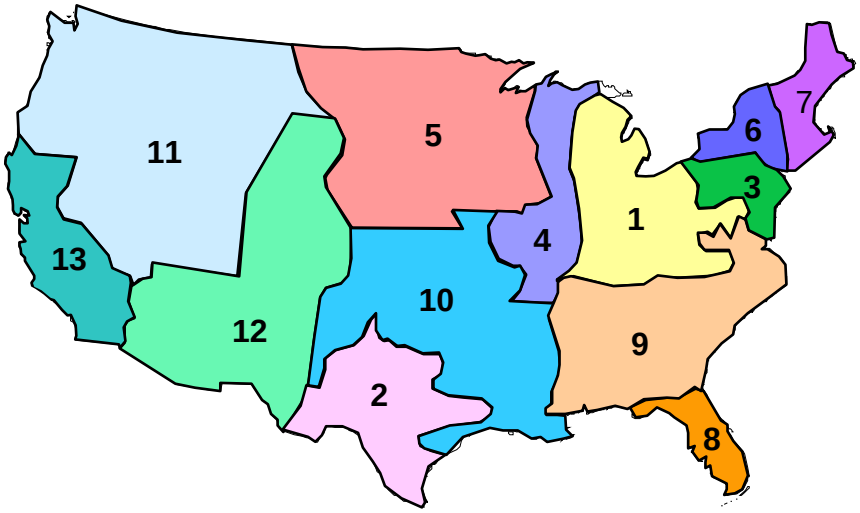


- Each kilowatt-hour of electricity requires on average about 25 gallons of water to produce
- Therefore, we may use almost 3 times as much water turning on lights and running appliances as we do taking showers and watering lawns

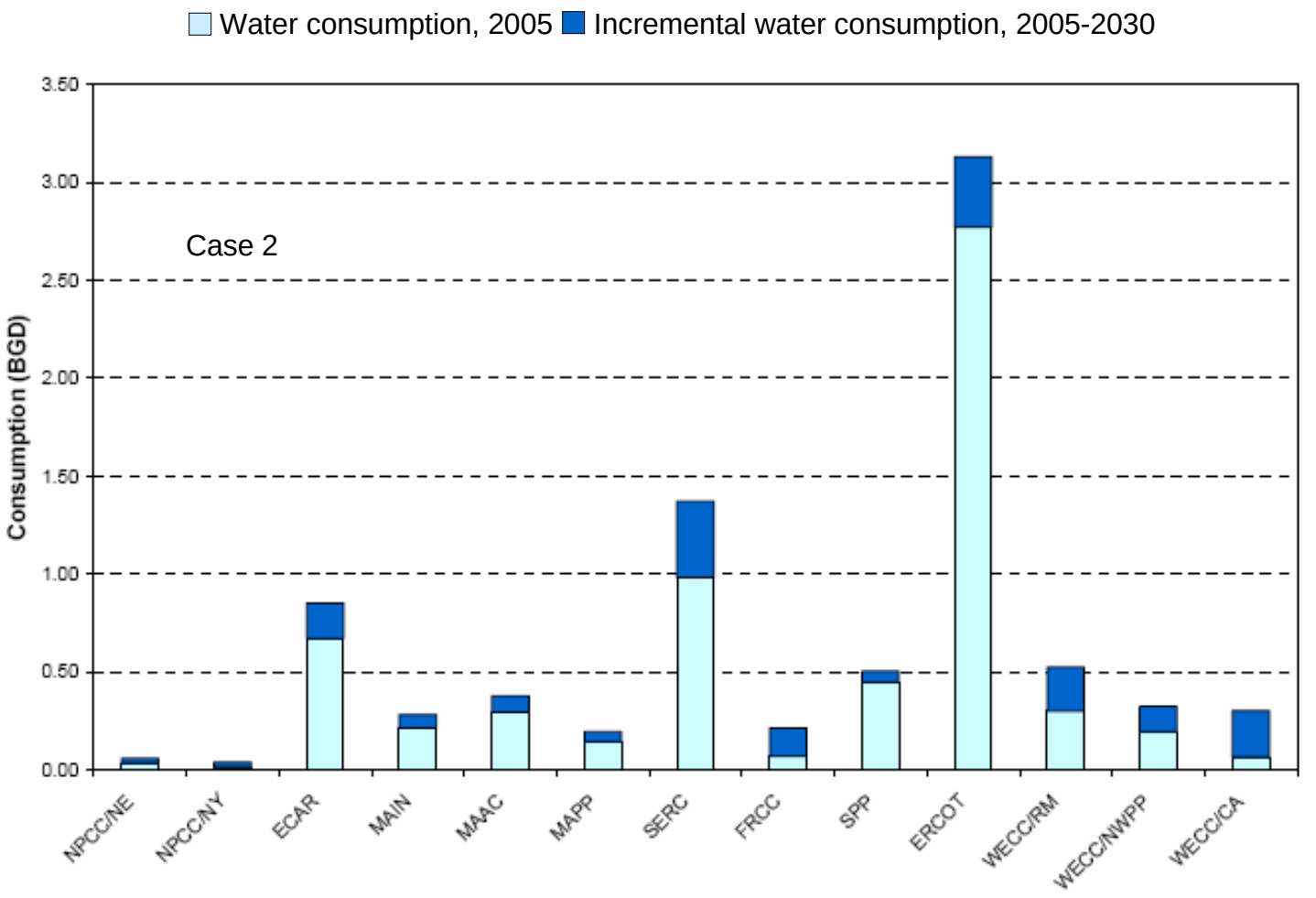
Ref. DOE/NETL Draft Final Report, "Water-Energy RD&D Scoping Report, September 2003"

Thermoelectric Power Plant Water Reqmnt's NERC Sub-Regions

Region Number	Abbreviation	Region
1	ECAR	East Central Area Reliability Coordination Agreement
2	ERCOT	Electric Reliability Council of Texas
3	MAAC	Mid-Atlantic Area Council
4	MAIN	Mid-America Interconnected Network
5	MAPP	Mid-Continent Area Power Pool
6	NPCC/NY	Northeast Power Coordinating Council / New York
7	NPCC/NE	Northeast Power Coordinating Council / New England
8	FRCC	Florida Reliability Coordinating Council
9	SERC	Southeastern Electric Reliability Council
10	SPP	Southwest Power Pool
11	WECC / NWCC	Western Electricity Coordinating Council/Northwest Power Pool
12	WECC/RM	Western Electricity Coordinating Council / Rocky Mountains, AZ, NM, southern NV
13	WECC/CA	Western Electricity Coordinating Council / California



Water Consumption Varies by Region But Increases in Every Region

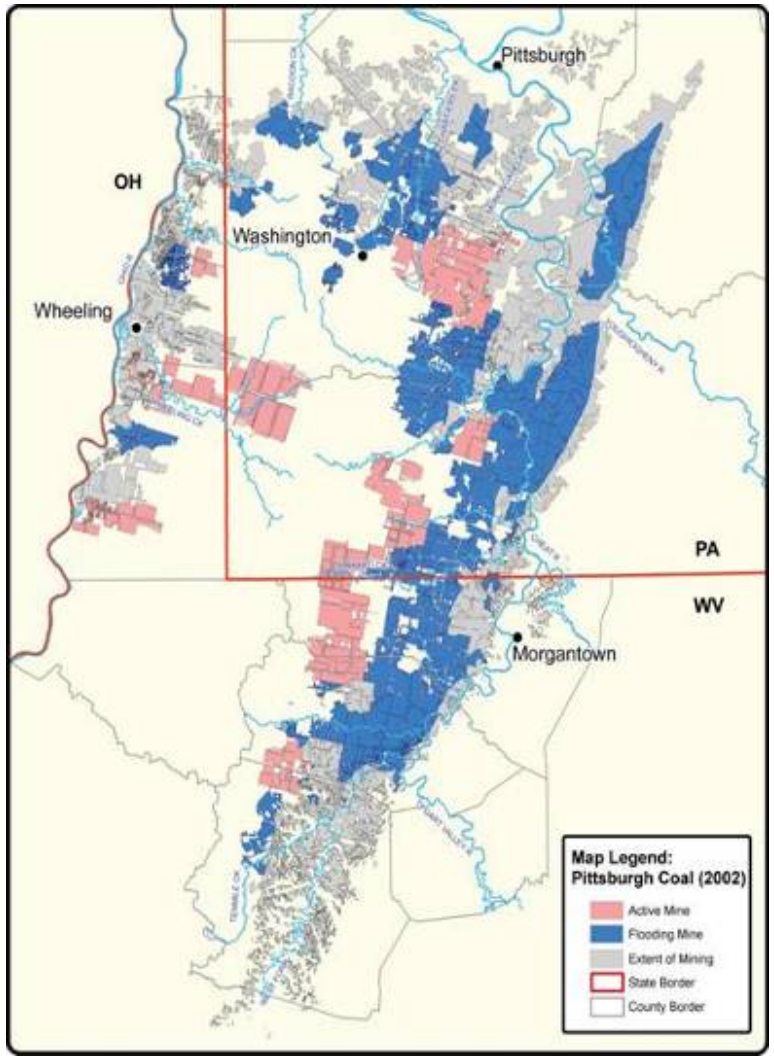


Recent Articles on Water-Related Impacts on Power Plant Siting and Operation

- **Idaho May Adopt Moratorium on Coal Power Due to Water Issues**
  - *Reuters, March 2006*
- **Sempra Energy Halts Gerlach Project Study**
  - *Associated Press, March 2006*
- **Desert Rock Water Agreement Passes Navajo National Committee**
  - *The Daily Times, February 2006*
- **California's Efforts to End Use of Sea Water to Cool Plants Could Jeopardize 24 GW**
  - *POWERnews*, March 2006
- **New Power Plants to Dry Up Water Supplies?**
  - *Transcript from Great Lakes Radio Consortium, August 2005*
- **Feds Order Susquehanna Power Plants and Others to Stop Killing Off Fish**
  - *Lancaster New Era, February 2005*

May 2006 Issue of Power Magazine

Alternative Sources of Cooling Water
Mine Pools



Pennsylvania Already Using Mine Pool Water for Cooling

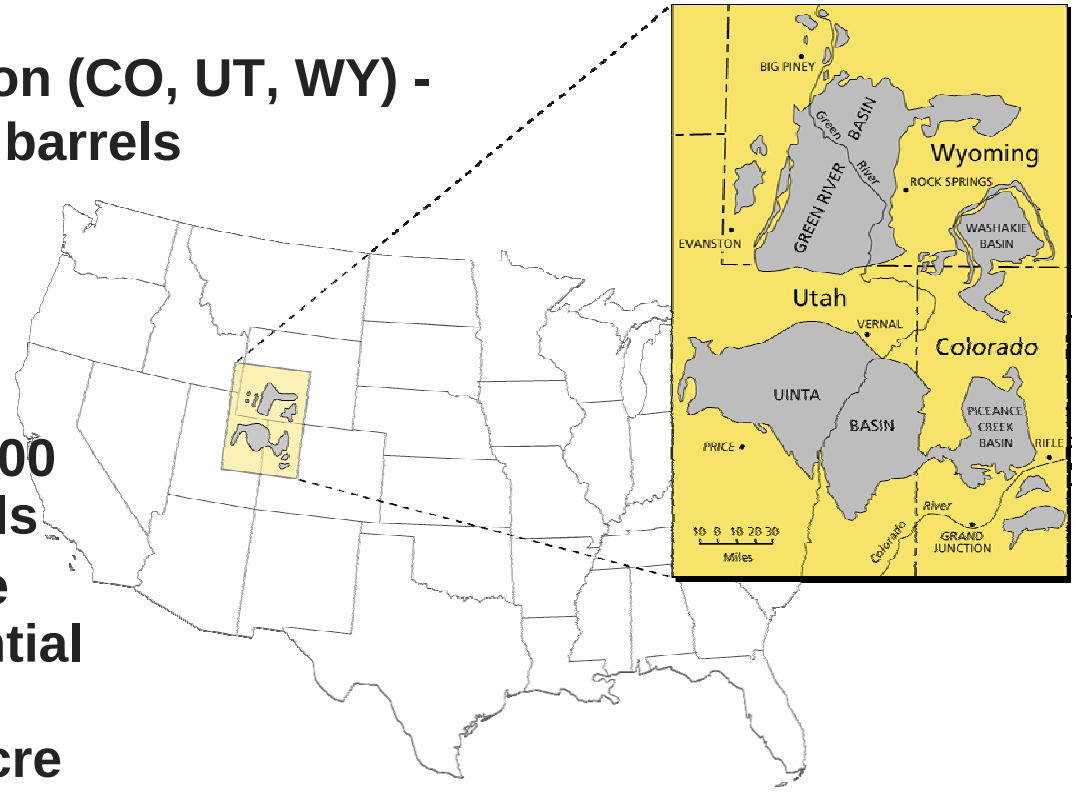
- **Exelon Corp.'s Limerick nuclear power plant reduced water withdrawal from Delaware River using water from Schuylkill County, PA coalmine during 4-5 month trial run in summer 2003**
- **A number of other small generators in the anthracite region of Pennsylvania are using mine water for cooling**

Limerick Nuclear Power Plant

Company Name	Plant Location	Generating Capacity (MW)	Cooling Water Source
Gilberton Power Co.	Frackville, PA	80	Unnamed mine pool
Northeastern Power Co.	McAdoo, PA	50	Siverbrook Mine
Panther Creek Generating Station	Nesquehoning, PA	83	Lausanne Mine
Schuylkill Energy Resources	Shenandoah, PA	80	Maple Hill Mine
WPS – Westwood Generation	Tremont, PA	31	Lyken Mine
Wheelabrator Frackville Energy Co.	Frackville, PA	42	Morea Mine

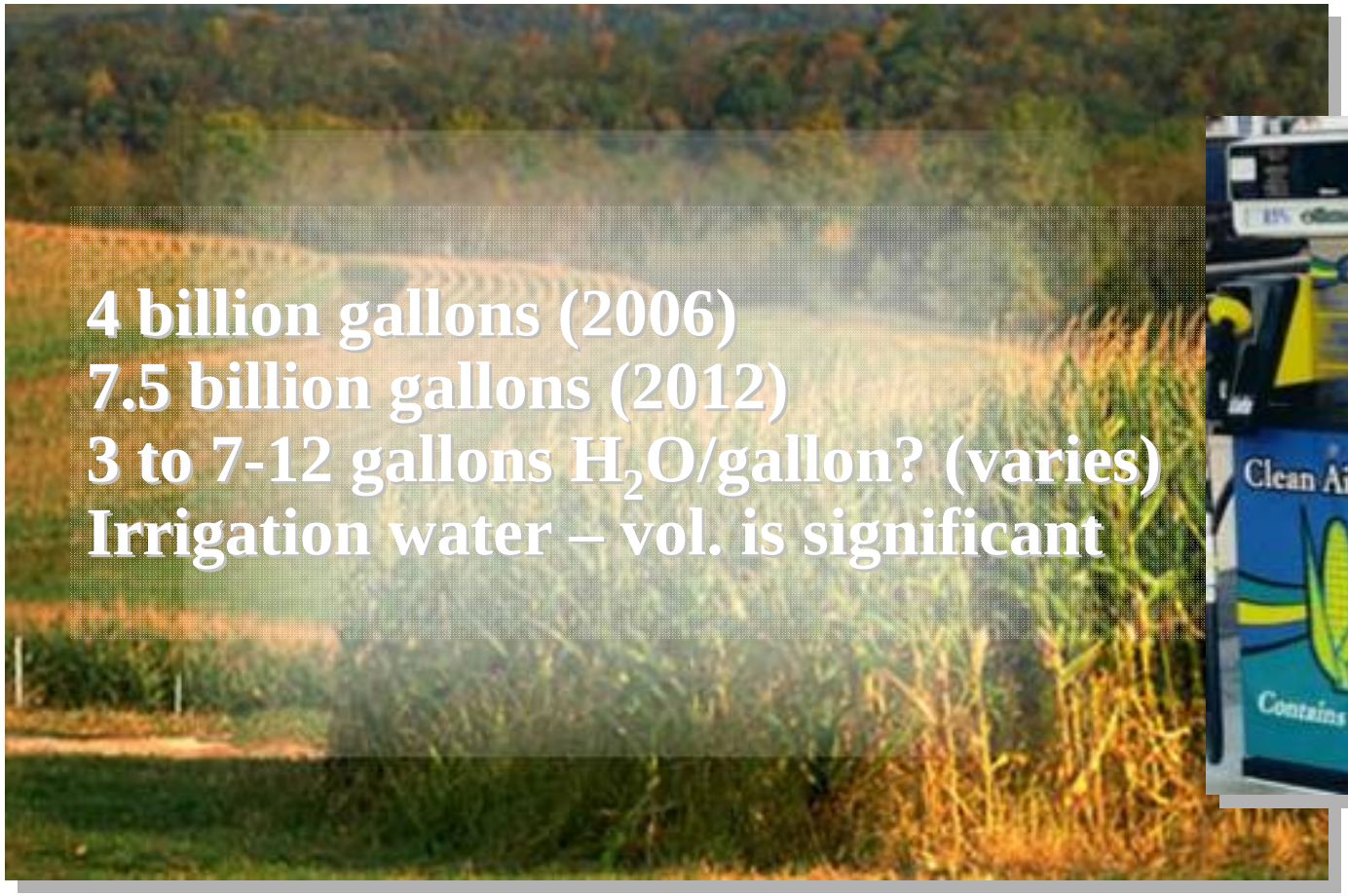
Western Oil Shale Resources
Water Requirements? – *Do the Algebra*

- **Green River Formation (CO, UT, WY) - estimated 1.5 trillion barrels**
- **Initial development - high-grade oil shale yielding 25 or more gallons per ton; estimated between 400 and 750 billion barrels**
- **Some portions of the basin have the potential of yielding over 2.5 million barrels per acre**
- **2 - 5 bbls H_20 per bbl product --- [contemporary data required!]**



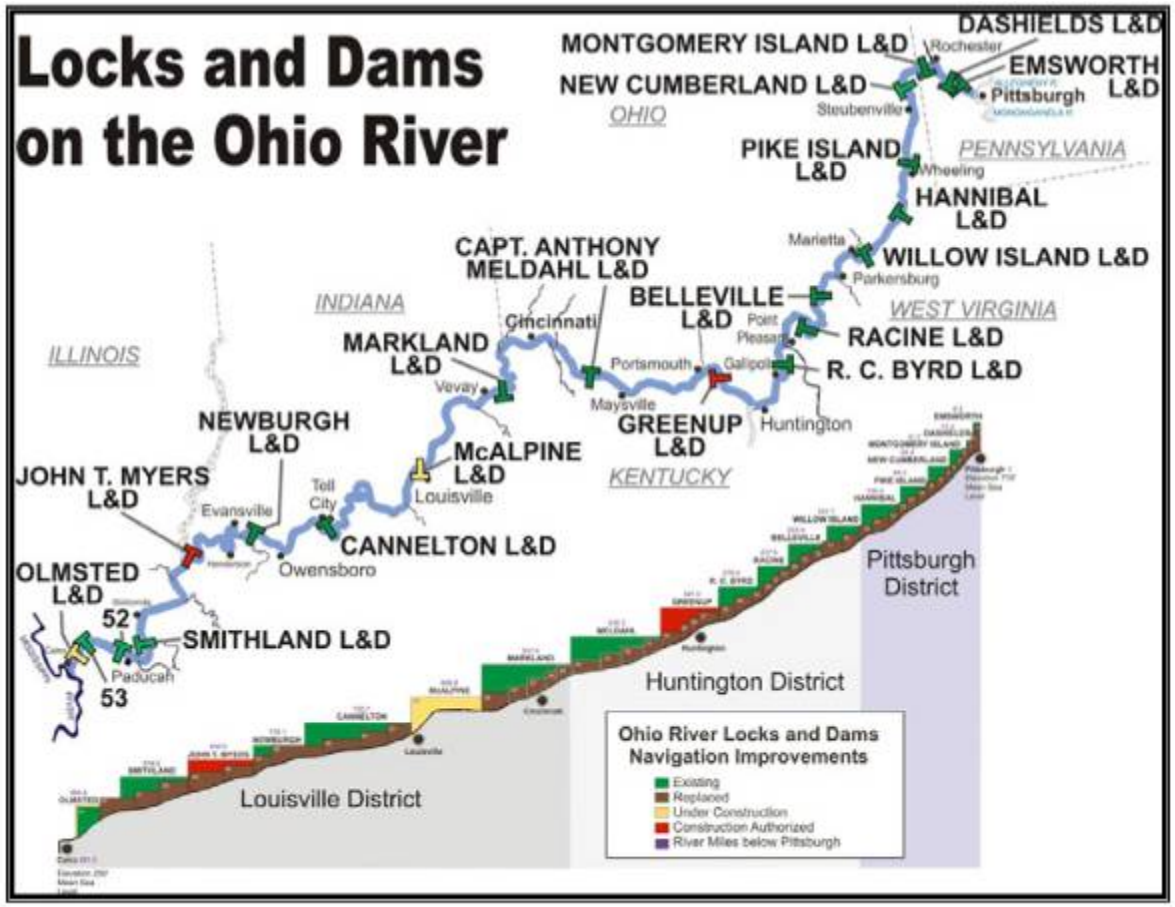
Even Energy Imports Impacted by H_2O *Concerns*
Open Rack Vaporizers

Bio-Fuels and Water
There's No Escaping the *Nexus!*



4 billion gallons (2006)
7.5 billion gallons (2012)
3 to 7-12 gallons H_2O/gallon? (varies)
Irrigation water – vol. is significant

Energy Infrastructures Are Tied to *Water*
Ohio River Mainstem Profile



Closing Remarks

- **Knowledge**
- **Awareness**
- ***Energ"y"*zed**
- **Aren't [energy] projects really water projects – with associated high-value *by-products* that keep the county [world] running?**
  - It's all about one's perspective….

SOURCE WATER PROTECTION AND THE ENERGY-WATER NEXUS

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Developing the data analysis tools to monitor water quality and to assess available supplies has become critical to resource management and to maintaining levels required to sustain energy production levels. In response, the GWPC is expanding its Risk Based Data Management System (RBDMS) into source water quality protection, laboratory information management, produced water management, and water quantity assessment. RBDMS for Water tracks water and waste stream parameters and makes site-specific monitoring data available in a GIS format. This paper discusses how RBDMS for Water is being customized to fit the very different goals of two regulatory agencies.

In Ohio, RBDMS for Water will be used to manage surface and ground water and waste stream (oil field brine and acid mine drainage) quality data associated with mining operations oversight. Oil and gas and mine owners and their laboratory consultants will be able to refer to the database through the Web to track compliance with water information reporting requirements.

In Nebraska, the GIS component of RBDMS for Water is being used to combine coverages of wellhead protection areas with oil, gas, and UIC well locations from its oil and gas database. The resulting maps allow NOGCC to manage its field inspection activities to target wells located in high-risk, environmentally sensitive areas for quarterly inspections.

The GWPC successfully deployed earlier versions of RBDMS for Water to agencies overseeing source water protection programs in Oklahoma, Nevada, Nebraska, and Mississippi.

Large-Scale Management of CBNG Produced Water

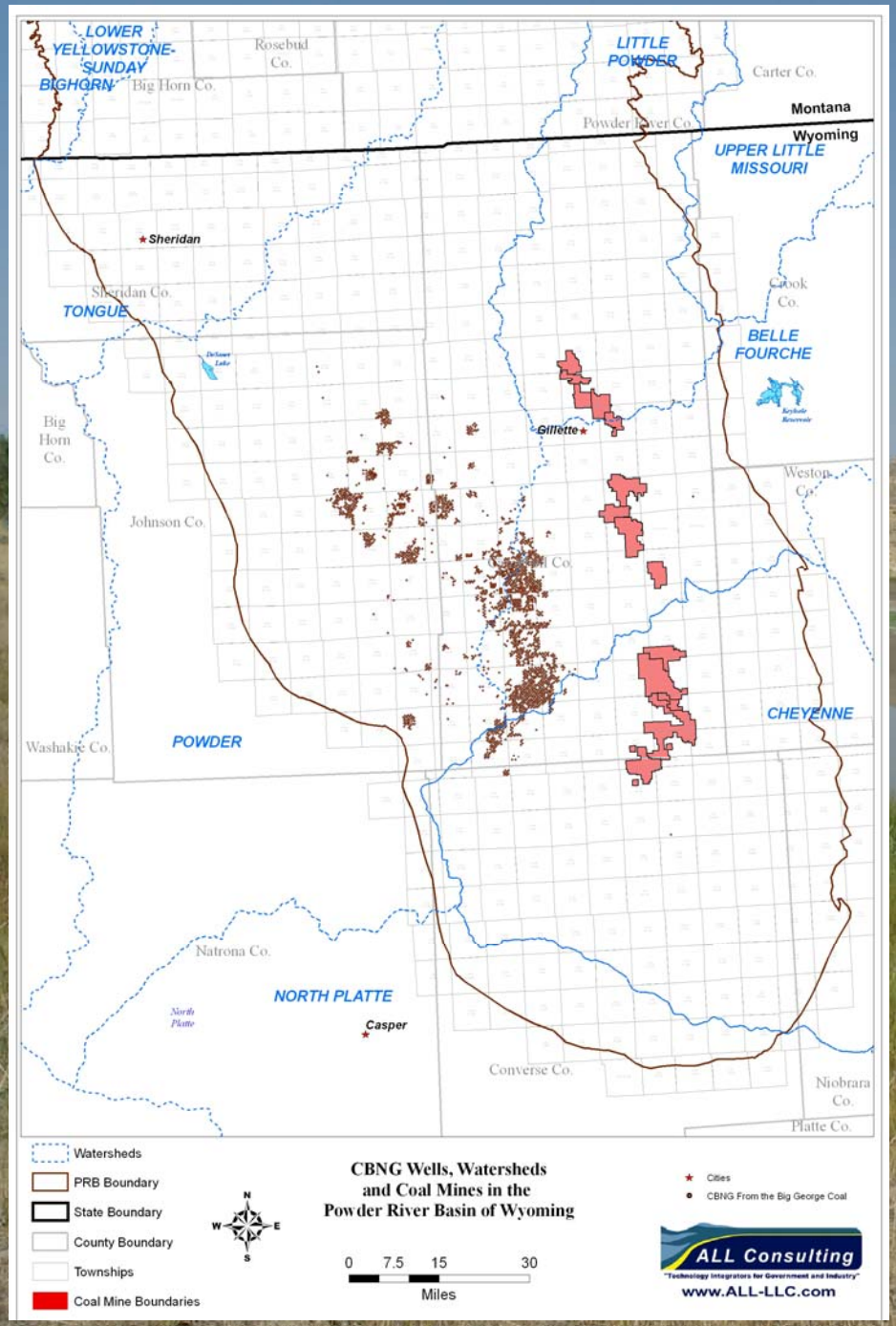
ALL Consulting

"Technology Integrators for Government and Industry"

www.ALL-LLC.com

NETL

Wyoming



Large-Scale Management of CBNG Produced Water

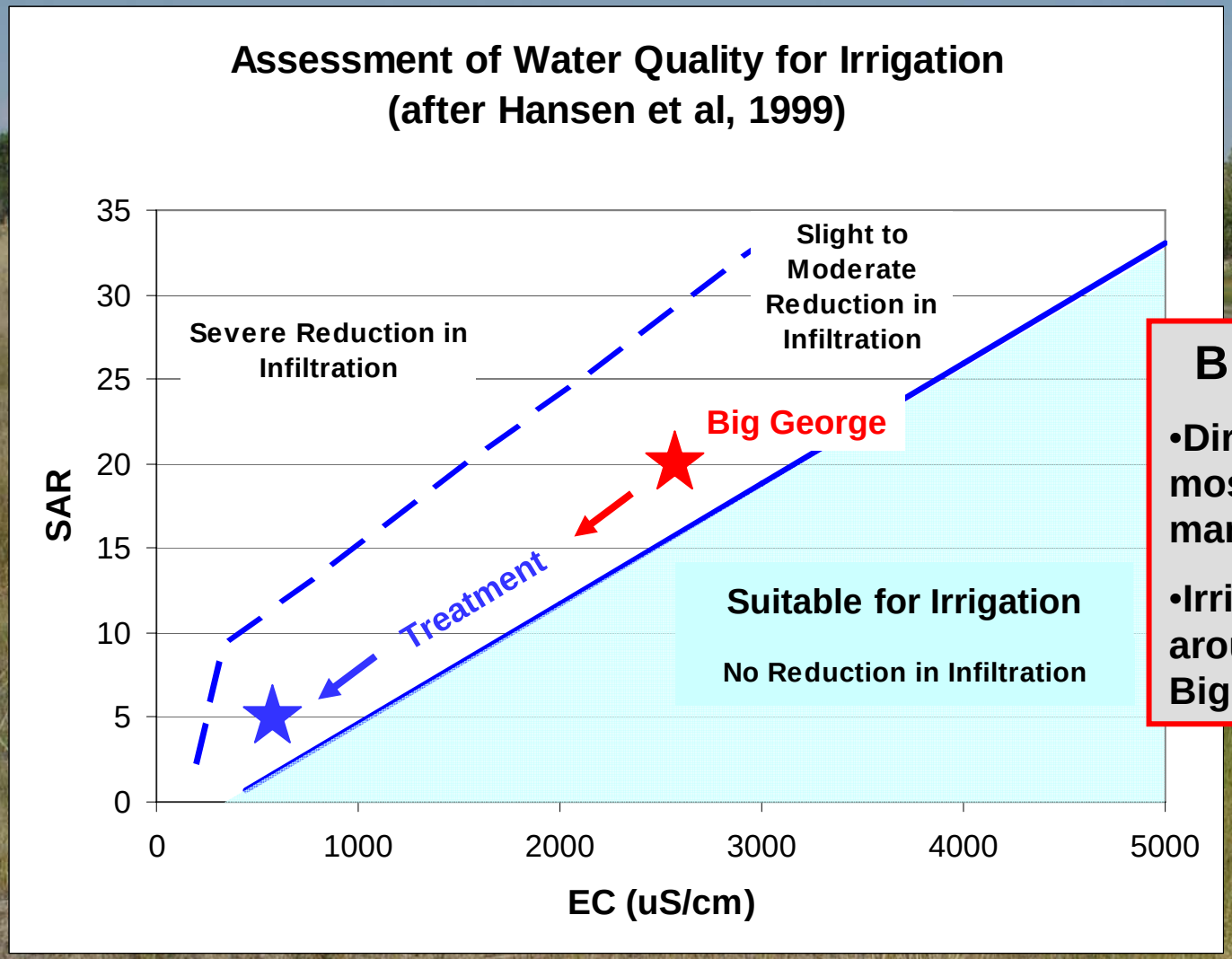
Big George CBNG

Approx. 500,000 bwpd in Powder River Basin

Water has uses but has limitations

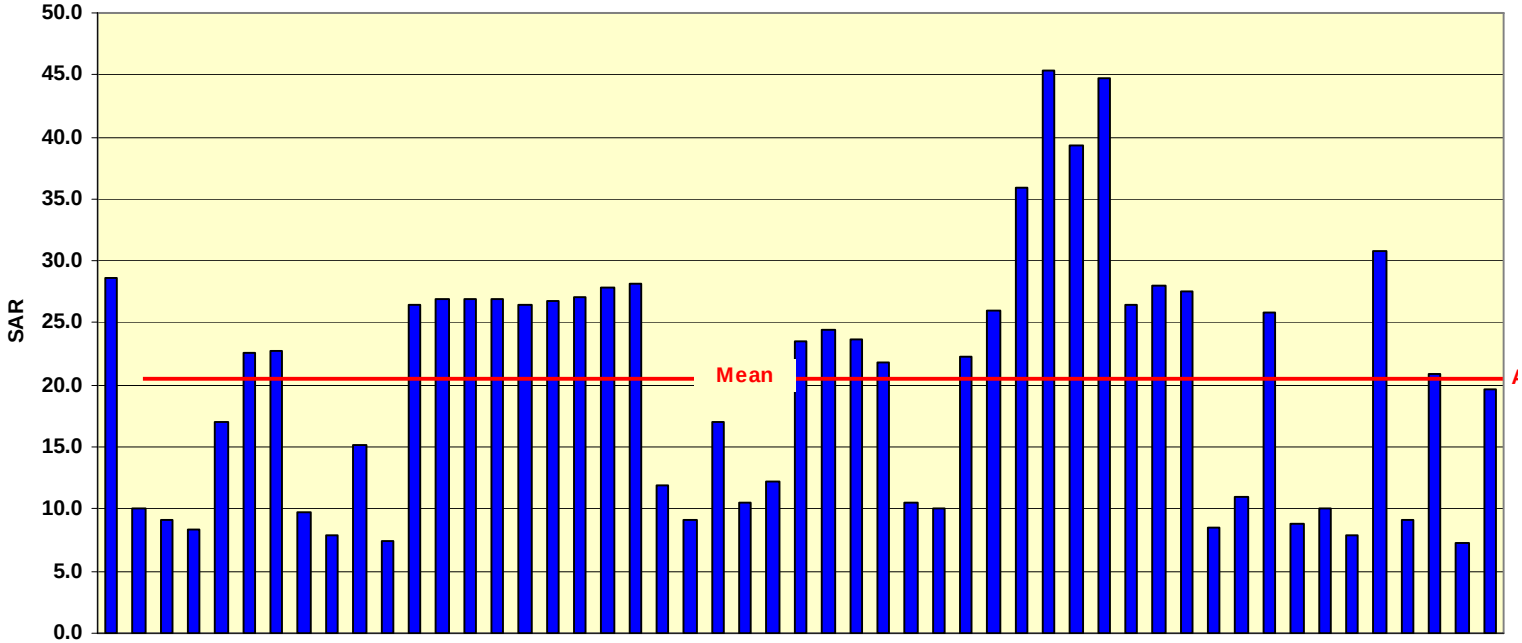
How to manage this water?

Large-Scale Management of CBNG Produced Water

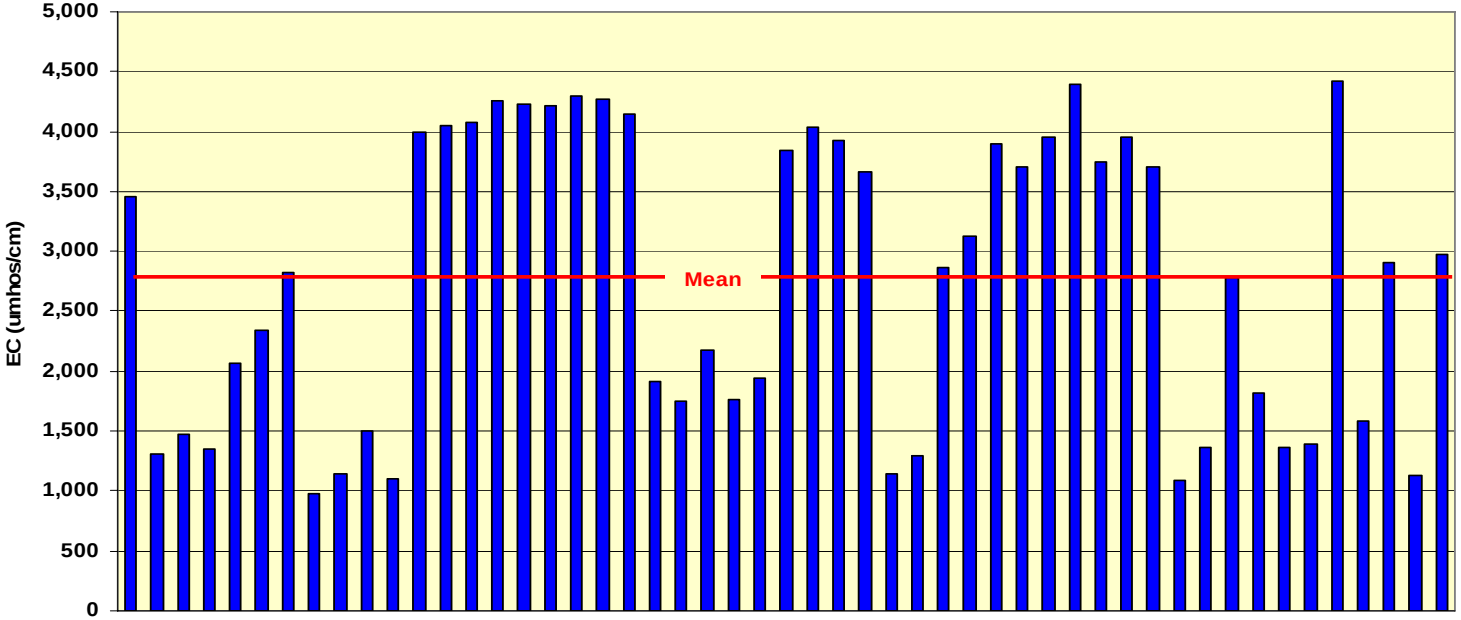


Big George CBNG

- Direct discharge is the most common management option
- Irrigation is common around the Basin but not Big George water

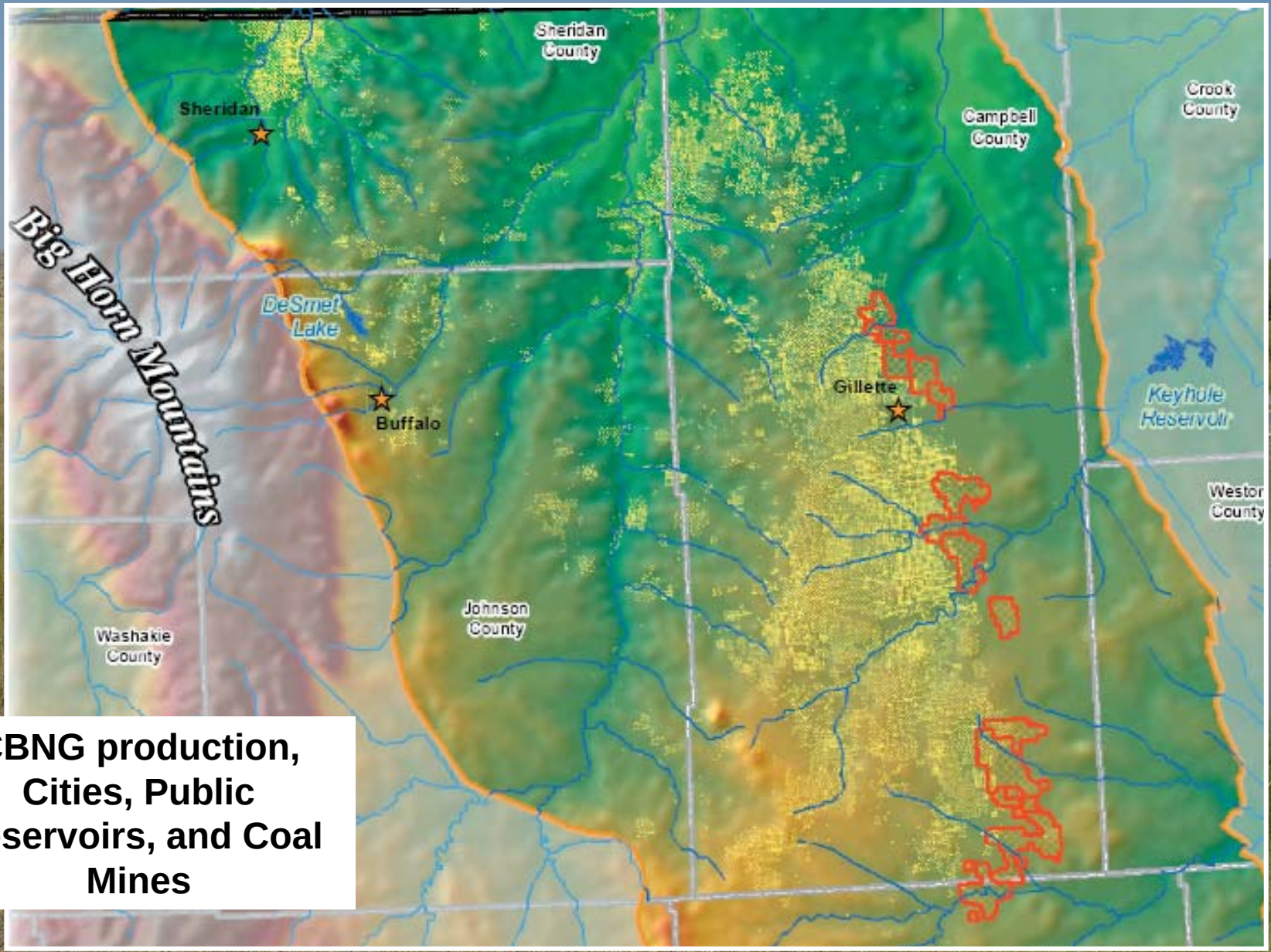


Big George Produced Water Quality



Large-Scale Management of CBNG Produced Water

Sources and End-Uses



CBNG production, Cities, Public Reservoirs, and Coal Mines

Large-Scale Management of CBNG Produced Water - Options

Class V Re-Injection into Coal Seams
Class V Injection into Shallow Sands
High-Pressure Class V Injection
Class IID Injection into Deep non-USDW Reservoirs
Class IIR Injection into Secondary Recovery Projects
Coal Slurry Pipeline
Subsurface Drip Irrigation
Cattle Feedlots
Treatment and Discharge
Dust Control and Other Process Water at Coal Mines
Cooling Tower Water at Power Plants
Public Water Supply
Discharge to Public Reservoirs

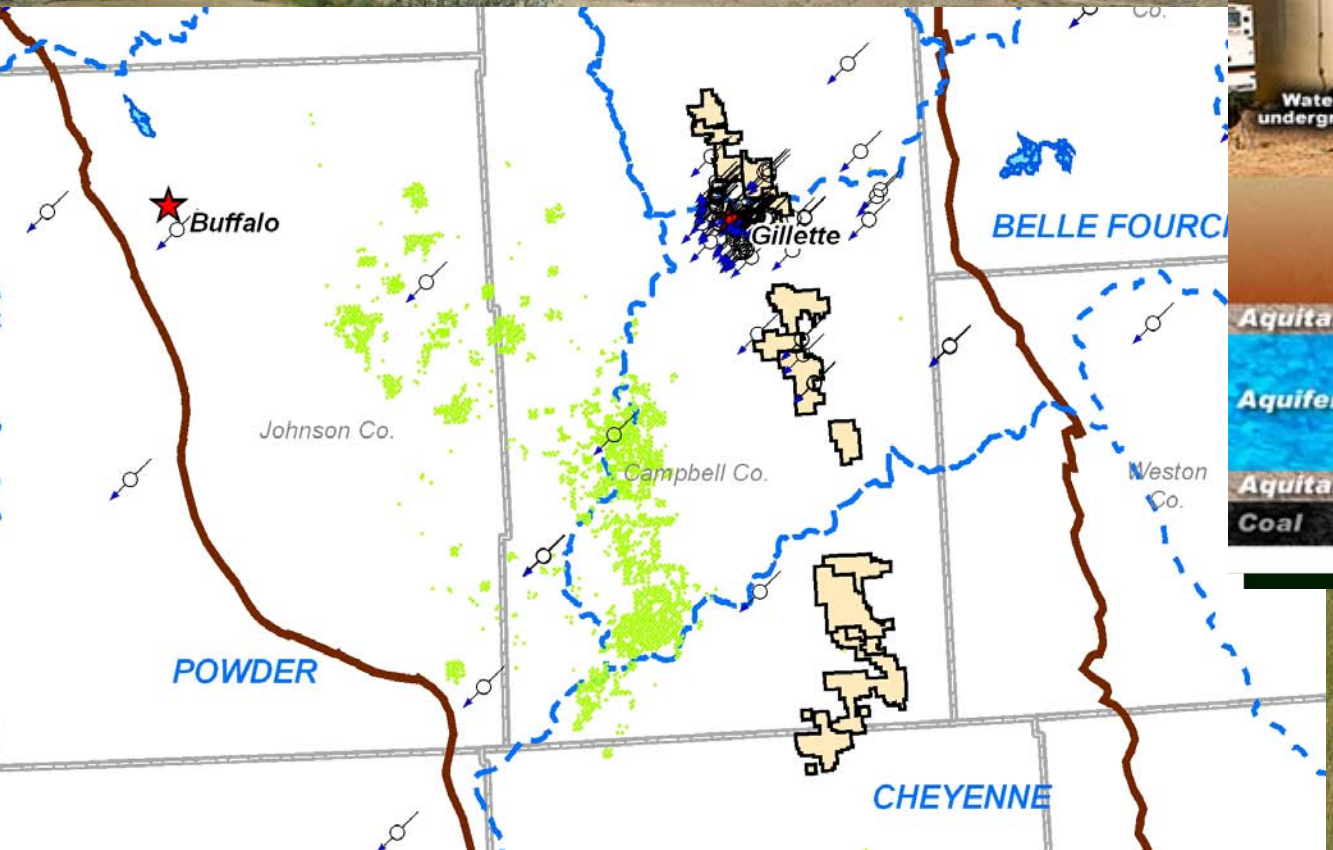
Large-Scale Management of CBNG Produced Water

Management Options

- Disposal (Class IID Injection)
- Treatment and Beneficial Use (Irrigation, Public Water Supply, Cooling, In-stream Flow, etc)
- Direct Use (Feedlot, Dust Control, Slurry Pipeline, etc)

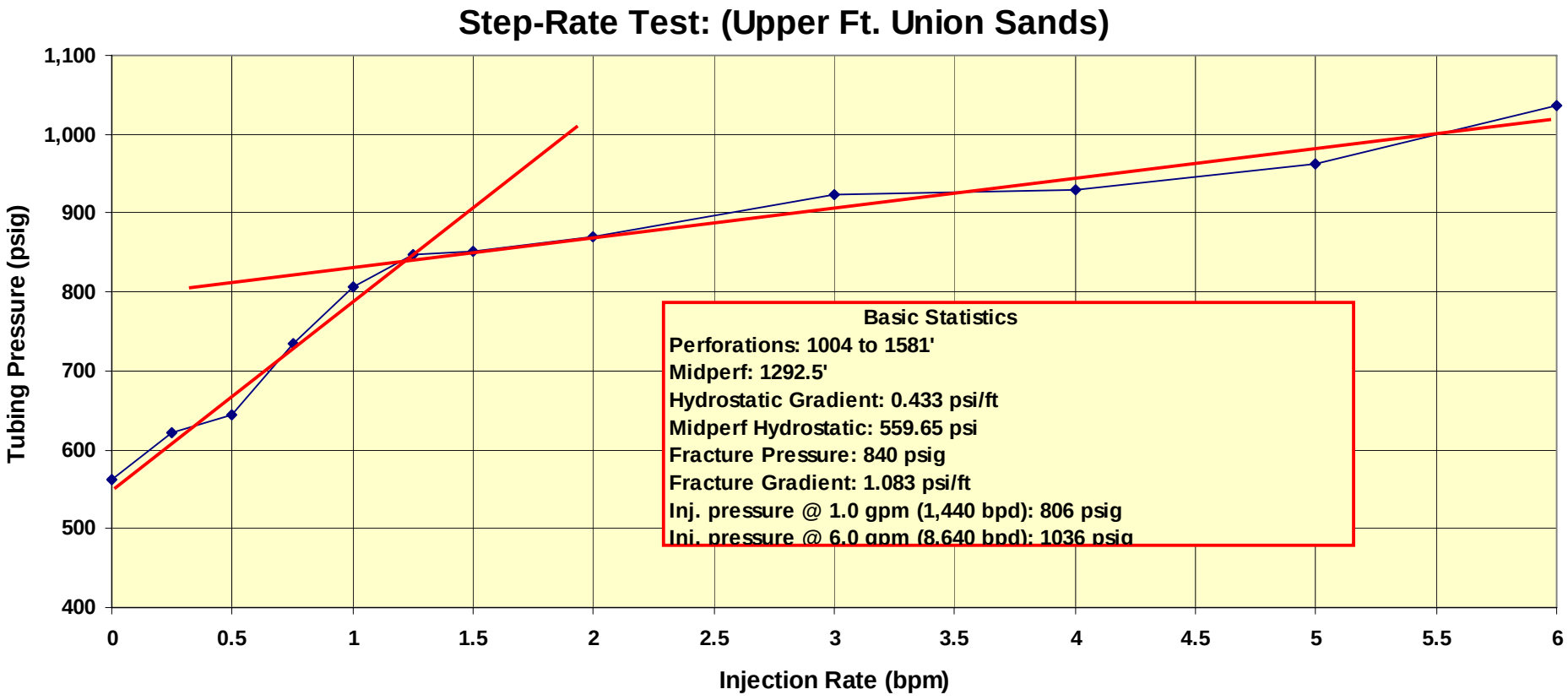
Large-Scale Management of CBNG Produced Water - Injection

Class V Injection Wells near Big George Production



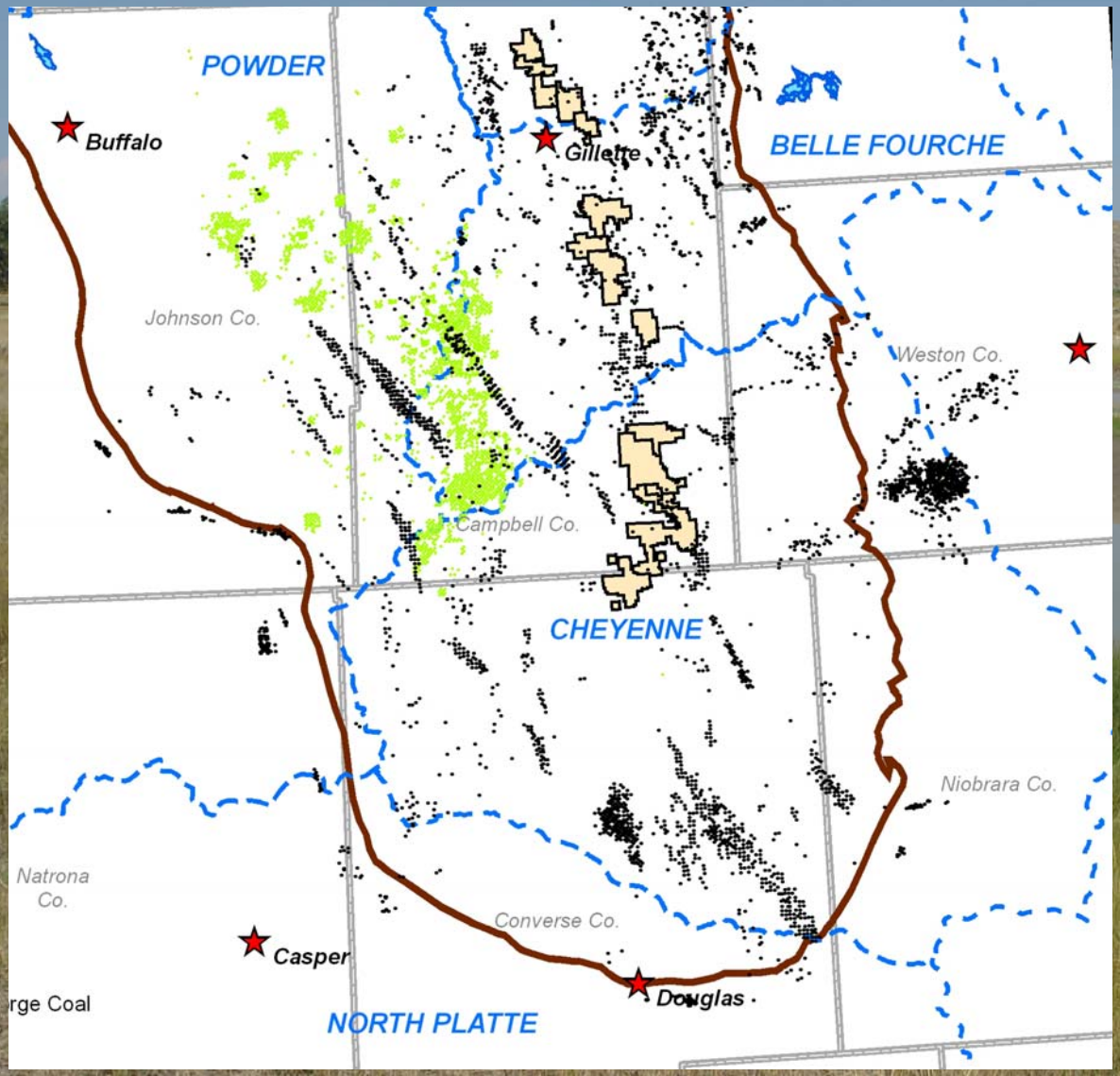
SOURCE: ALL Consulting

Large-Scale Management of CBNG Produced Water - Injection



Is Injection over Frac-Pressure Permittable?

Large-Scale Management of CBNG Produced Water – Secondary Recovery



Big George Water

&

Oil Production

Large-Scale Management of CBNG Produced Water – Dust Control

Dust on Roads

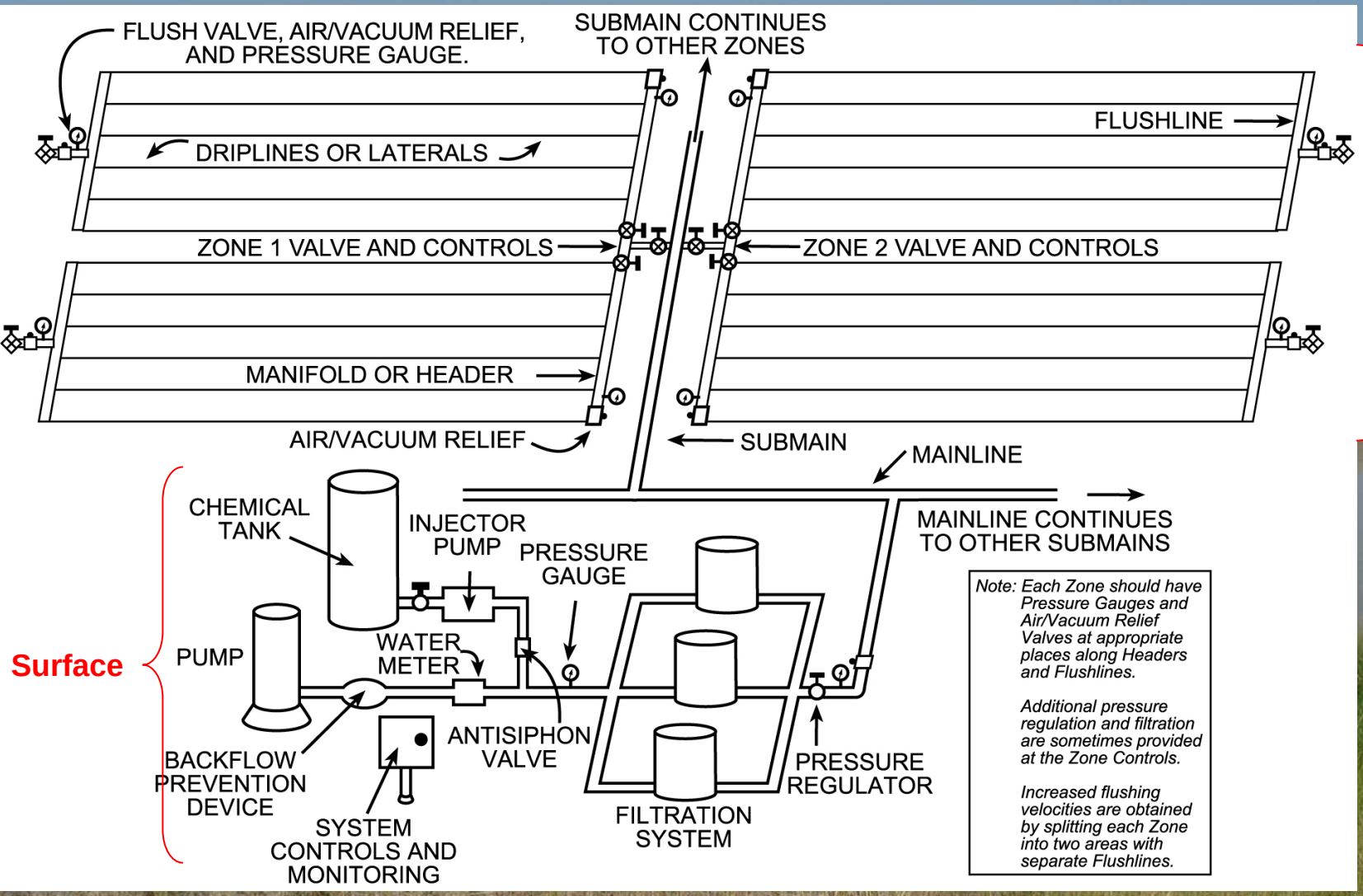
- **Increased coal production, local traffic, and drier climate add to dust**
- **Counties facing more dust complaints from public**
- **Coal mines facing violations**
- **Salt restrictions**

Large-Scale Management of CBNG Produced Water – Cooling Water

Wet-Cycle and Dry-Cycle Cooling

- **Massive water needs**
- **Varying water quality requirements**
- **What will plants do after CBNG goes away?**

Large-Scale Management of CBNG Produced Water – Subsurface Drip-Irrigation



Large-Scale Management of CBNG Produced Water

Management Option	In Use?	Capacity
Class IID Injection	Yes	1,000 bpd/well
Class IIR Injection	No	50,000 bpd/project
Subsurface Drip-Irr.	Yes	100 bpd per acre
Dust Control	Yes	100,000 bpd per mine
Cooling Water	Yes	400,000 bpd per mine
Public Reservoir	No	450,000 bpd

Comparison of Water Management Alternatives

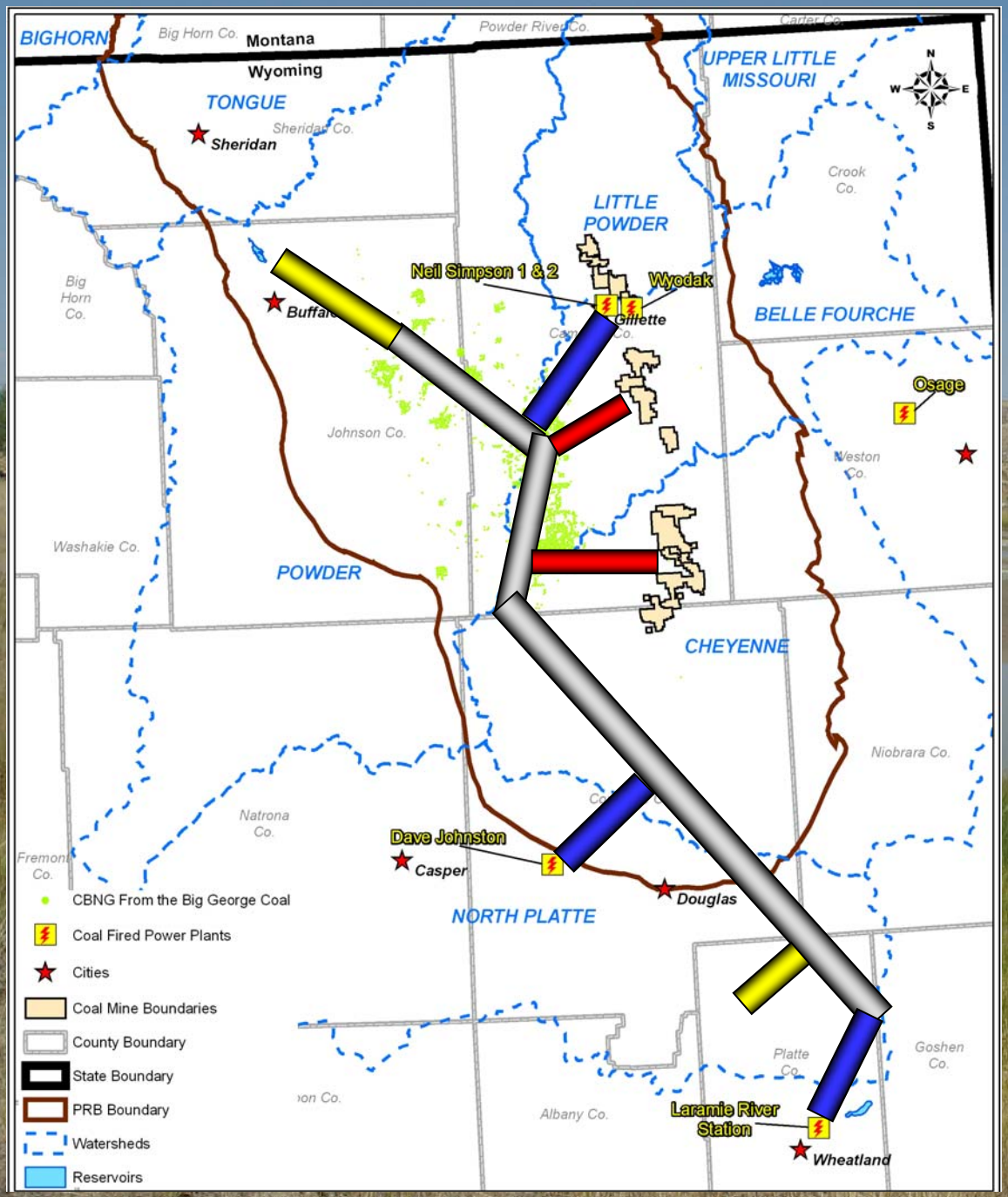
Management Option	Technical Feasibility	Non-Tech Feasibility	Potential Individual Capacity	Potential Overall Capacity	Capital Costs	Pipeline Costs	Operating Costs	Timing
Class v Injection Shallow Sands	Low	High	Low	Low	Low	Low	Med	< 6 mo
High Pressure Class V Injection	Unknown	Med	Unknown	Unknown	Low	Low	Med	< 1 yr
Class V Re-Injection into Coals	Unknown	High	Unknown	Unknown	Low	High	Med	> 1 yr
Class IID Injection	High	High	Med	Low	High	High	Med	> 1 yr
Class IIR Injection	High	High	Med	Low	Med	High	Med	> 1 yr
Treatment	Low	High	High	Low	High	Low-Med	High	< 1 yr
Dust Control	High	High	High	High	Low	High	Low	> 1 yr
Cooling Water	High	High	High	High	Low	High	Low	> 1 yr
Subsurface Drip-Irrigation	Med	Med	Low	Med	Med	Low	Med	< 1 yr
Feed Lots	Med	Med	Low	Low	Med	Unknown	Unknown	Unknown
Public Water Supply	Med	Low-Med	Med	Low	Med	High	Varies	> 3 yr
Public Reservoirs	High	Med	High	High	Med-High	High	Low	> 3 yr

Large-Scale Management of CBNG Produced Water

Questions:

- **Is CBNG water a waste or resource?**
- **Does a 200-mile, 30-inch pipeline make economic sense?**
- **How will pipeline be financed?**
- **Where will water treatment take place?**
- **What happens when CBNG production ceases? Where does end-user go for water?**

Large-Scale Management of CBNG Produced Water - Pipeline



Major pipeline

Cooling water

Dust control

Reservoir fill

Argonne NATIONAL LABORATORY

... for a brighter future

Disposal of Concentrate from Treatment of Water for Beneficial Reuse

John A. Veil – Argonne National Laboratory

David Burnett - Texas A&M University

Ben Grunewald - Ground Water Protection Council

13th IPEC

San Antonio, TX

October 17, 2006

U.S. Department of Energy

THE UNIVERSITY OF CHICAGO

A U.S. Department of Energy laboratory managed by The University of Chicago

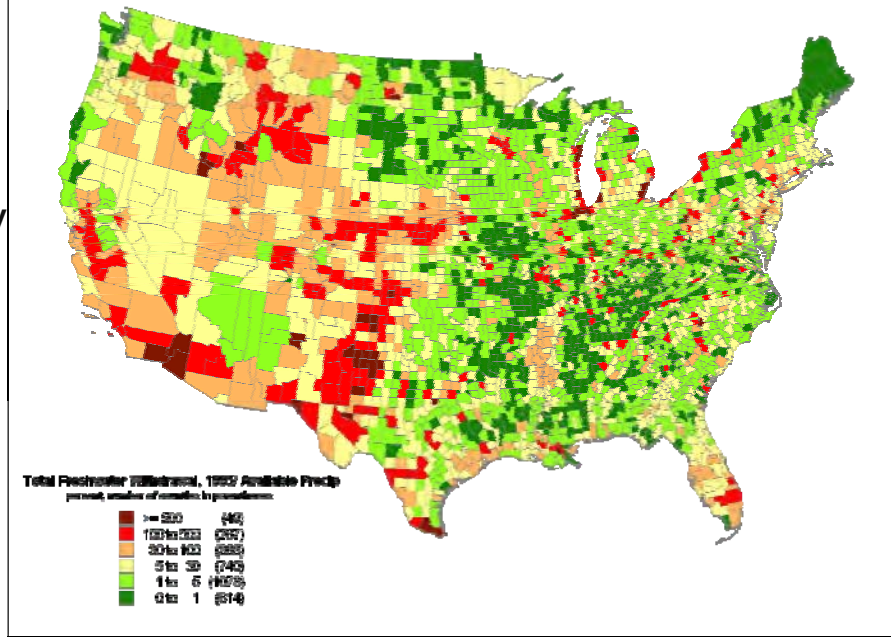
Contents of Presentation

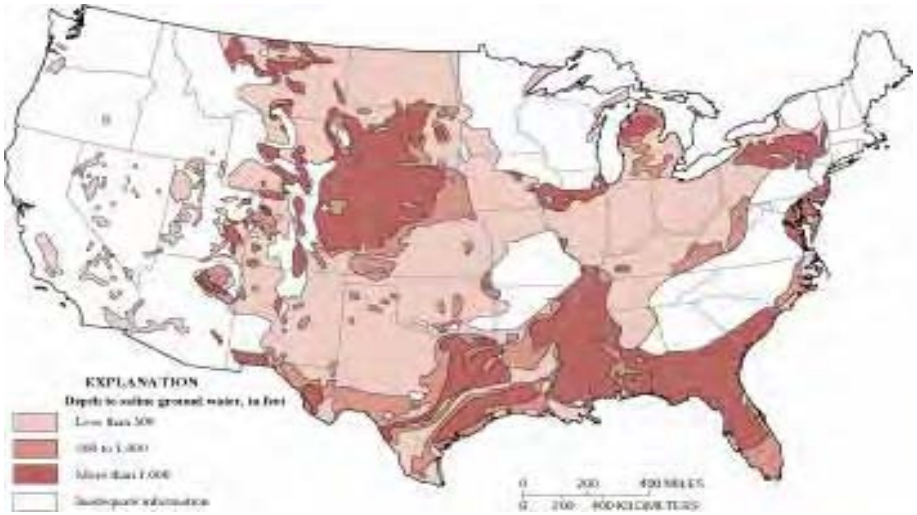
- Overview of water treatment processes
- SDWA drinking water standards
- CWA water quality criteria
- RCRA toxicity characteristic criteria
- Comparison
- What do the different regulatory programs and approaches mean?
- Some actual data

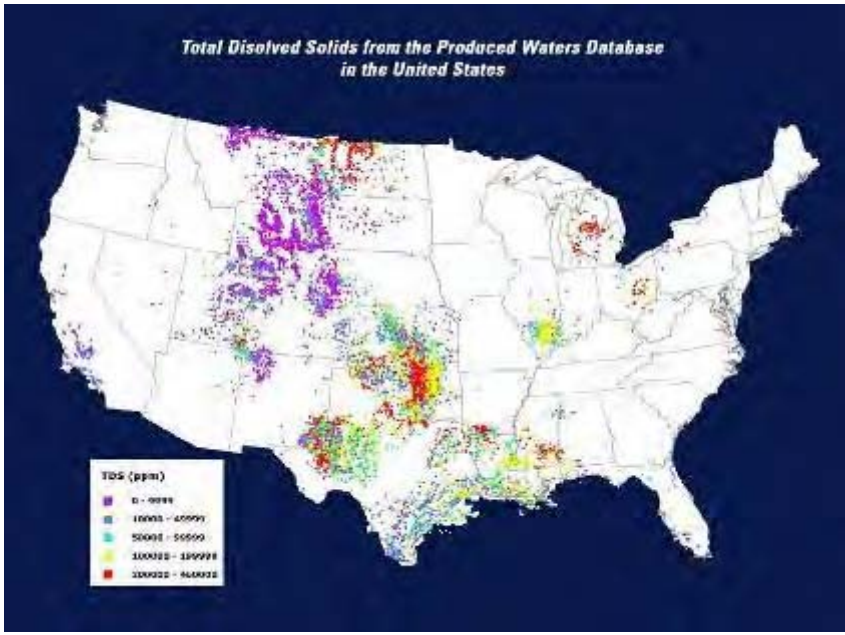
Fresh Water Availability

- Insufficient fresh water resources in many parts of U.S. (and world)

- Many of these areas have access to sources of saline water
  - Saline ground water
  - Produced water

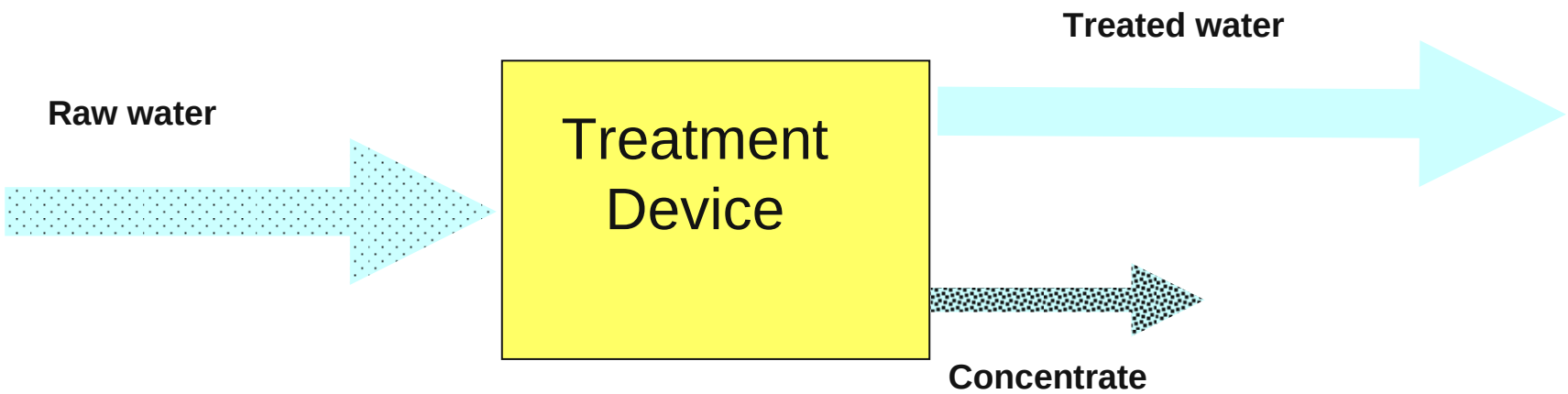






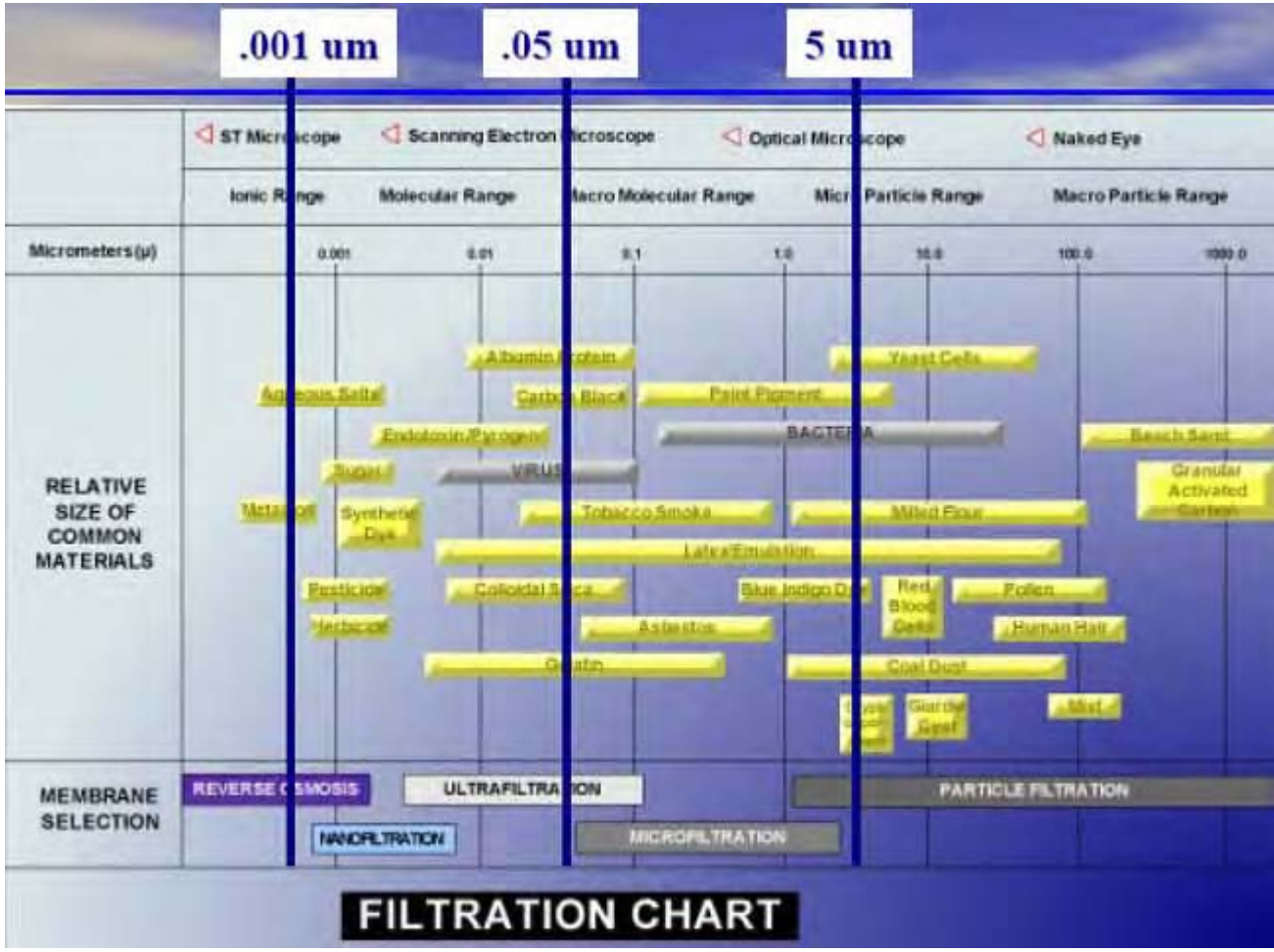
Several Technologies Exist to Remove Salinity

- Treatment results in two byproduct streams
  - Treated water
    - *In filtration systems this may be called permeate*
  - Concentrated solution containing removed constituents
    - *Called concentrate*



Processes Used to Treat Saline Water

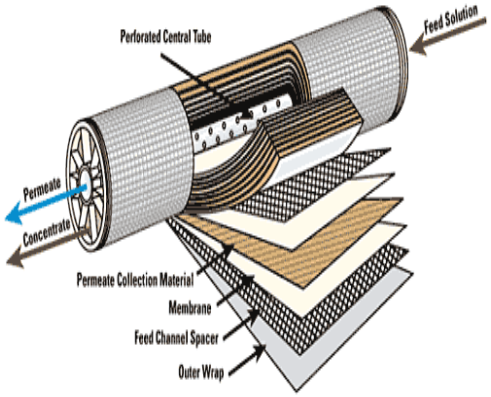
- Membrane processes
  - Microfiltration
  - Ultrafiltration
  - Nanofiltration
  - Reverse osmosis
- Electrodialysis
- Ion exchange
- Thermal distallation



Source: Ben Gould, Ashbrook Simon-Hartley

What membrane systems look like

- Cross flow
  - Flat sheet membrane
    - Spiral wound
    - Plate and frame
  - Tubular membrane
    - Fine fiber
    - Capillary fiber
    - Hollow tube
- Dead end
  - Cartridges
    - Pleated
  - Tubular membrane
    - Fine fiber
    - Capillary fiber



Source: Anders Hallsby, Nalco

Source: Roger Noack, HDR

Microfiltration System by US Filter

Source: Roger Noack, HDR

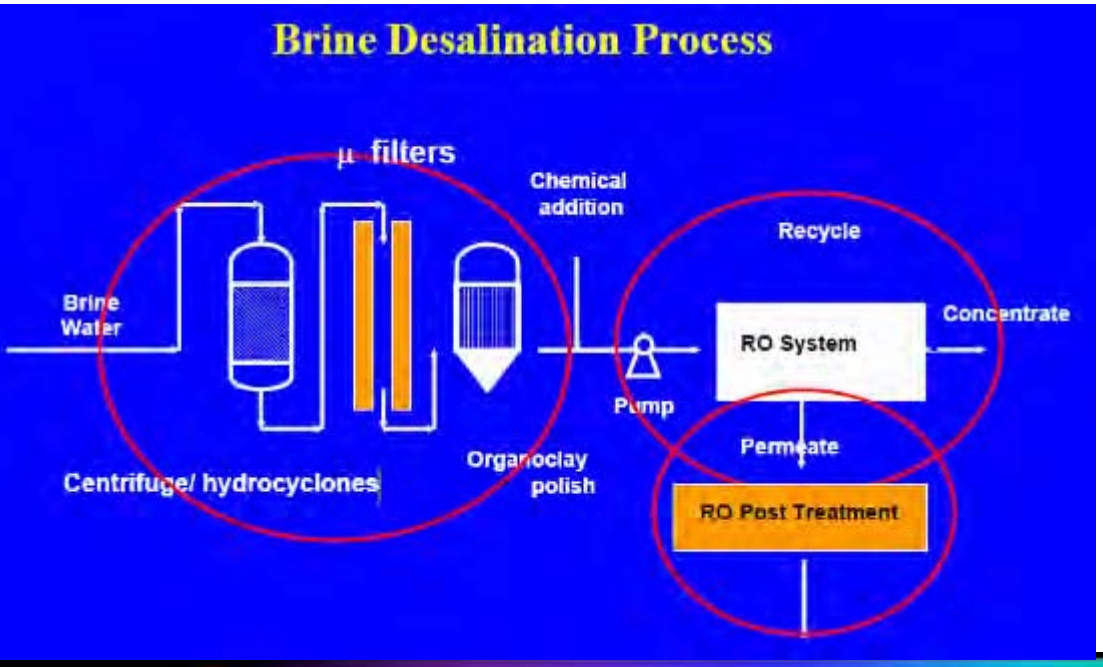
Reverse Osmosis

EDR System by GE/Ionics

Source: Roger Noack, HDR

Water Treatment System Must Remove a Variety of Constituents

- Different pretreatment steps are used to first remove:
  - Larger-sized materials (e.g., sand, microbes)
  - Constituents that would impair additional treatment (e.g., oil and grease)



Texas A&M Treatment Trailer

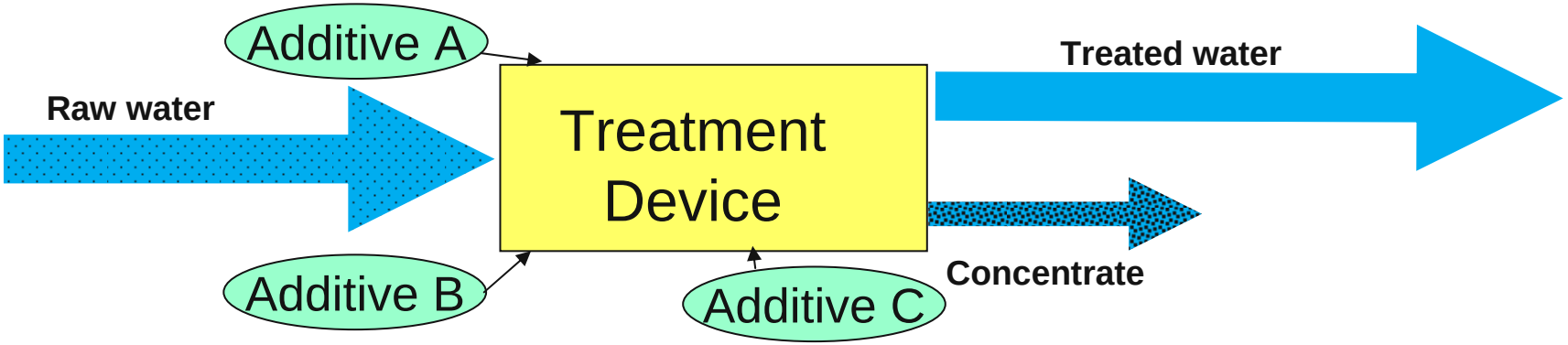
Four pillars of successful RO membrane operation …

Source: Anders Hallsby, Nalco

- Prevent Mineral scaling
  - Antiscalants
- Prevent Colloidal fouling
  - Particulate filtration
    - Improve efficacy with filter aid
- Prevent Microbial fouling
  - Control microbial activity in the feed
  - Minimize AOC (TOC)
  - Equipment design
    - Nowhere for bugs to hide
  - Equipment operation
    - Remove biofilm before it is "too late"
    - No inadvertent re-inoculation

- All of these steps add constituents to the water that may end up in the concentrate

How Is the Concentrate Disposed of/Managed?



- Volume and parameter concentration of concentrate stream are determined by operating parameters
  - Low volume means high energy input and high parameter concentrations
- Options:
  - Inject concentrate underground
    - *Disposal*
    - *Use for enhanced oil recovery*
  - Discharge to surface water body
  - Dispose of by land application
- Each of these practices is governed by different set of rules

Inject Concentrate Underground

- Safe Drinking Water Act (SDWA) establishes the Underground Injection Control (UIC) program
- Concentrate is injected for promoting additional oil and gas production (enhanced recovery):
  - Most states and EPA consider the injection well to be a Class II well
- Concentrate is injected solely for disposal:
  - States and EPA are not consistent of type of injection well
  - Raw water is produced water
    - *The resulting injection well is usually a Class II well*
  - Raw water is other than produced water (e.g., saline ground water)
    - *The resulting injection well could be Class I, II, or V*
    - *Depends on the situation and philosophy of agency*

Standards often Used for Injection

- SDWA directs EPA to develop two types of standards for drinking water quality:
  - Maximum Contaminant Levels (MCLs)
    - *Enforceable*
    - *Based on affordable treatment methods*
  - Maximum Contaminant Level Goals (MCLGs)
    - *Non-enforceable*
    - *Represents the public health goal*
- These are available for more than 75 contaminants
- http://www.epa.gov/safewater/consumer/pdf/mcl.pdf
- UIC permits other than Class II may require injectate to meet MCLs

Excerpt from EPA Drinking Water Standard Table

Contaminant	MCL or TT[1] (mg/L)[2]	Potential health effects from exposure above the MCL	Common sources of contaminant in drinking water	Public Health Goal
Chlordane	0.002	Liver or nervous system problems; increased risk of cancer	Residue of banned termiticide	zero
Chlorine (as Cl_2)	MRDL=4.0[1]	Eye/nose irritation; stomach discomfort	Water additive used to control microbes	MRDLG=4[1]
Chlorine dioxide (as ClO_2)	MRDL=0.8[1]	Anemia; infants & young children: nervous system effects	Water additive used to control microbes	MRDLG=0.8[1]
Chlorite	1.0	Anemia; infants & young children: nervous system effects	Byproduct of drinking water disinfection	0.8
Chlorobenzene	0.1	Liver or kidney problems	Discharge from chemical and agricultural chemical factories	0.1
Chromium (total)	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits	0.1
Copper	TT[7]; Action Level = 1.3	Short term exposure: Gastrointestinal distress. Long term exposure: Liver or kidney damage. People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	Corrosion of household plumbing systems; erosion of natural deposits	1.3
Cryptosporidium	TT[3]	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and fecal animal waste	zero
Cyanide (as free cyanide)	0.2	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories	0.2

Discharge of Concentrate and Relevant Standards

- Discharge of concentrate would require an NPDES permit
  - Permit includes limits that would ensure compliance with state water quality standards (WQS)
- Clean Water Act (CWA) directs each state to adopt enforceable WQS
- To help the states, EPA develops non-enforceable, technical recommendations called water quality criteria (WQC)
  - Aquatic life protection
    - *Fresh and salt water*
    - *Acute and chronic exposure*
  - Human health protection
    - *Eating fish/seafood from water*
    - *Drinking water and eating fish/seafood from water*
- These are available for about 150 substances

http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf

Excerpt from EPA WQ Criteria Table

NATIONAL RECOMMENDED WATER QUALITY CRITERIA FOR PRIORITY TOXIC POLLUTANTS

	Priority Pollutant	CAS Number	Freshwater CMC (µg/L)	Freshwater CCC (µg/L)	Saltwater CMC (µg/L)	Saltwater CCC (µg/L)	Human Health For Consumption of: Water + Organism (µg/L)	Human Health For Consumption of: Organism Only (µg/L)	FR Cite/ Source
1	Antimony	7440360					5.6 B	640 B	65FR66443
2	Arsenic	7440382	340 A,D,K	150 A,D,K	69 A,D,bb	36 A,D,bb	0.018 C,M,S	0.14 C,M,S	65FR31682 57FR60848
3	Beryllium	7440417					Z		65FR31682
4	Cadmium	7440439	2.0 D,E,K,bb	0.25 D,E,K,bb	40 D,bb	8.8 D,bb	Z		EPA-822-R-01-001 65FR31682
5a	Chromium (III)	16065831	570 D,E,K	74 D,E,K			Z Total		EPA820/B-96-001 65FR31682
5b	Chromium (VI)	18540299	16 D,K	11 D,K	1,100 D,bb	50 D,bb	Z Total		65FR31682
6	Copper	7440508	13 D,E,K,cc	9.0 D,E,K,cc	4.8 D,cc,ff	3.1 D,cc,ff	1,300 U		65FR31682
7	Lead	7439921	65 D,E,bb,gg	2.5 D,E,bb,gg	210 D,bb	8.1 D,bb			65FR31682
8a 8b	Mercury Methylmercury	7439976 22967926	1.4 D,K,hh	0.77 D,K,hh	1.8 D,cc,hh	0.94 D,cc,hh		0.3 mg/kg J	62FR42160 EPA823-R-01-001
9	Nickel	7440020	470 D,E,K	52 D,E,K	74 D,bb	8.2 D,bb	610 B	4,600 B	65FR31682
10	Selenium	7782492	L,R,T	5.0 T	290 D,bb,dd	71 D,bb,dd	170 Z	4200	62FR42160 65FR31682 65FR66443

Other Standards for Management of Concentrate

- Resource Conservation and Recovery Act (RCRA) includes various criteria for determining if a substance is subject to the hazardous waste program
- The toxicity characteristic is based on a leaching procedure
- Waste samples exceeding the regulatory limit meet EPA's definition of characteristic hazardous wastes
- Toxicity thresholds are often set at 100 times the MCL
- If concentrate constituents exceed hazardous waste thresholds
  - This could affect the class of UIC injection well used and could restrict other methods of managing the concentrate

Toxicity Characteristic Regulatory Thresholds (mg/L)

Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
Cresol	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor and its epoxide	0.008

Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane.	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentrachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

Comparison of Different Threshold Values (mg/L)

Type of Criterion	Benzene	Mercury
SDWA – MCL	0.005	0.002
SDWA - MCLG	0	0.002
CWA - Acute WQC – freshwater	No criterion	0.0014
CWA - Chronic WQC – fresh	No criterion	0.00077
CWA - Human Health WQC – fish	0.0022	0.3 mg/kg
CWA - Human Health WQC – water and fish	0.051	No criterion
RCRA toxicity	0.5	0.2

What Do These Different Standards Mean to the Regulators?

- For most drinking water concentrate in arid areas, surface water discharge is not a viable option
  - Therefore, CWA WQC are not applicable
- For concentrate injection, regulators will want to know if the concentrations are:
  - < MCL
  - > MCL but < RCRA toxicity threshold
  - > MCL and RCRA toxicity threshold
- This information will allow them to decide what class of well can be used for injection
  - At this time, there is not a uniform approach to determining the classification of concentrate disposal wells

Examples of Data from Treatment of Produced Water

- The Texas A&M desalination trailer has been operated on several produced water samples
- Various analytical results of the raw water, treated water (permeate), and concentrate are shown in the following slides

Production Well - Brazos County TX, August 4th, 2006
Water Treated by Texas A&M Trailer

Constituent	Raw Water	Reject*	Permeate
TDS	13,320	14,021	323
Sodium	4,490	4,726	127
Chlorides	7,494	7,888	184
Potassium	76	80	1.2

*Estimated at 95% reject volume

Units are mg/L

Comparison of Desalinated Produced Water with Municipal Water from College Station. TX

		College Station Municipal Water (1)	Desalinated Produced Water (2)	Desalinated Produced Water (3)
	Substance	Amount	Amount	Amount
Agronomic Properties				
	pH	7.8	7.1	6.2
Physical Properties				
	Conductivity	882	2270	17
	TDS	523	1290	17
	SAR		23	0.1
Major Ions				
	Alkalinity (CaCo3)		34	5
	Bicarbonate (HCO3)	450	41	6
	Chloride	54	706	1
	Sulfate	9	3	ND
	Ca, Mg, K, Na, B	203	94 ppm	1.3
Metals, Dissolved				
	Barium, etc	2 ug/L	0.9 mg/L	ND
Volatile Organics				
	Chloroform, +	14 ug/L	3.4 ug/L	85 ug/L

(1) College Station municipal treatment plant

(2) Neuman gas well – treated by A&M trailer

(3) Fife #3 oil well – treated by A&M trailer

Detailed Data from Fife #3 Oil Well

- The A&M Desalination Unit was towed to the Fife Well site in Washington Co, TX
- Produced water from the Buda Lime was treated and desalted with a single stage one-pass RO configuration
  - Concentrate stream = 76% of volume

Units are mg/L

Analyte	Raw Feed	microfilter pass-through	microfilter reject	RO filter pass-through	Reduction
Alkalinity, Total as CaCO3	188	187	235	34	82%
Bicarbonate as HCO3	230	229	287	41	81%
Carbonate as CO3	< 1.2	1	1	1	n/d
Hydroxide as OH	< 1	1	1	1	n/d
Conductivity	33000	36500	46000	2270	93%
Magnesium	73	72	93	1	99%
Silicon	78	77	85	2	97%
Calcium	1055	1039	1363	23	98%
Potassium	124	126	172	5	96%
Sodium	11570	12480	16240	416	96%
Boron	87	87	105	34	61%
Silica	1664	162	181	4	99%
pH	6.1	6	7	7	
Solids, Total Dissolved TDS @ 180 C	38300	37700	49740	1291	97%

Preliminary Results - Darst Field Pilot Plant Test

&Analyte	Raw Feed	Concentrate	RO Perm.	RO Perm	RO Perm
Phosphorus, Dissolved Orthophosphate as P	< 2.25			1.156	< 0.15
Fluoride	8.82	9.07	0.456	0.311	0.448
Chloride	14588	16504	624	530	790
Sulfate	1118	1276	10	10	13
Bromide	88.4	100	5.19	4.74	7.04
Potassium	272	310	26.2	22.2	31.3
Magnesium	547	610	2.66	2.26	2.89
Silicon	12.5	12.5	0.258	0.255	0.328
Calcium	1692	1876	8.096	5.75	8.67
Sodium	6850	7490	402.4	341.6	488.8
Boron	16.8	16.8	11.1	10.6	11.4
Silica	26.6	26.8	0.552	0.545	0.701
Solids, Total Dissolved TDS @ 180 C	28780	31720	1215	1051	1458
Solids, Total Suspended TSS @ 105 C	2	< 4	< 4	<4	<4
Total Petroleum Hydrocarbons	5.24	0.311	< 1.1	< 1.1	<1.1
Nitrogen, Nitrate as N		34.2	3.28	6.48	16.1
SAR	52.4			43.2	
			No filter	Old C filter	New C filter

Detailed Data from Neuman Gas Well

Parameter	Units	Raw Water	Microfiltr-ation Permeate	RO Permeate	RO Concentrate	
pH	SU	7.1	7.2	6.8	8.3	
Conductivity	umhos/cm	536	478	23	3,130	
Solids, Total Dissolved	mg/L	149	135	ND	924	
Sodium Adsorption Ratio	unitless	5	5	0.9	13	
Solids, Total Suspended	mg/l	9	4	ND	ND	
Alkalinity	mg/L	126	110	9	677	
Bicarbonate	mg/l	154	134	11	826	
Carbonate	mg/l	ND	ND	ND	ND	
Chloride	mg/L	65	58	ND	404	
Sulfate	mg/L	1	1	ND	9	
Calcium	mg/L	14	12	ND	87	
Magnesium	mg/L	ND	ND	ND	4	

Detailed Data from Neuman Gas Well - continued

Parameter	Units	Raw Water	Microfiltration Permeate	RO Permeate	RO Concentrate
Potassium	mg/L	ND	ND	ND	6
Sodium	mg/L	70	64	1	471
Boron	mg/L	7.67	6.8	1.47	28.2
Silicon	mg/L	1.36	1.48	ND	11.2
Silica	mg/L	2.9	3.2	ND	24
Anions	meq/l	4.4	3.8	0.21	25
Cations	meq/l	3.8	3.4	0.049	25
Benzene	ug/l	498	290	8.3	30
Ethylbenzene	ug/l	9.3	4.6	ND	ND
Toluene	ug/l	290	149	0.5	17
Total Xylenes	ug/l	44	14	ND	4
Total Petroleum Hydrocarbon	mg/l	8.15	1.38	ND	4.85

Questions?

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Designing Environmental Performance into New Drilling Fluids and Waste Management Technology

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ABSTRACT

The design of new products for the petroleum industry requires a delicate balance of economic issues, drilling performance and HSE considerations. Increasing demands placed on drilling fluid technology to meet difficult operating conditions have continued to push the limits of the technology forward. Further, greater awareness and tighter regulatory controls have combined to advance fluids and drilling waste management technology. In addition to technical challenges, the industry requires cost-effective performance from selected technology. This paper provides the framework and examples of how these forces continue to shape the forward progress of technology with specific examples of new water and synthetic-based fluids and drilling waste management technology introduced into the global exploration and production industry.

INTRODUCTION

Typically, drilling fluids and the resulting cuttings constitute the largest volume of waste generated from a drilling operation. Consequently, it comes as no surprise that these two waste streams have long received significant attention from regulators, industry, and the public.

Since drilling fluid technology pre-dates the rise of environmental regulatory structures in the US and other areas of the world, the first round of investigations focused on evaluating existing technology to determine potential environmental impacts from drilling fluids and cuttings. These early investigations found no significant environmental hazards from drilling fluids, but rather found areas for improvement. Accordingly, the regulatory process in the US and elsewhere began to develop regulations designed to lowering potential impacts from discharges of drill cuttings and drilling fluids. In the drilling fluids sector, the initial reaction to these regulations was to simply remove the excluded products through regulatory controls and continue to sell the remaining product lines. As time progressed, environmental regulatory controls have become a significant aspect of designing new products.

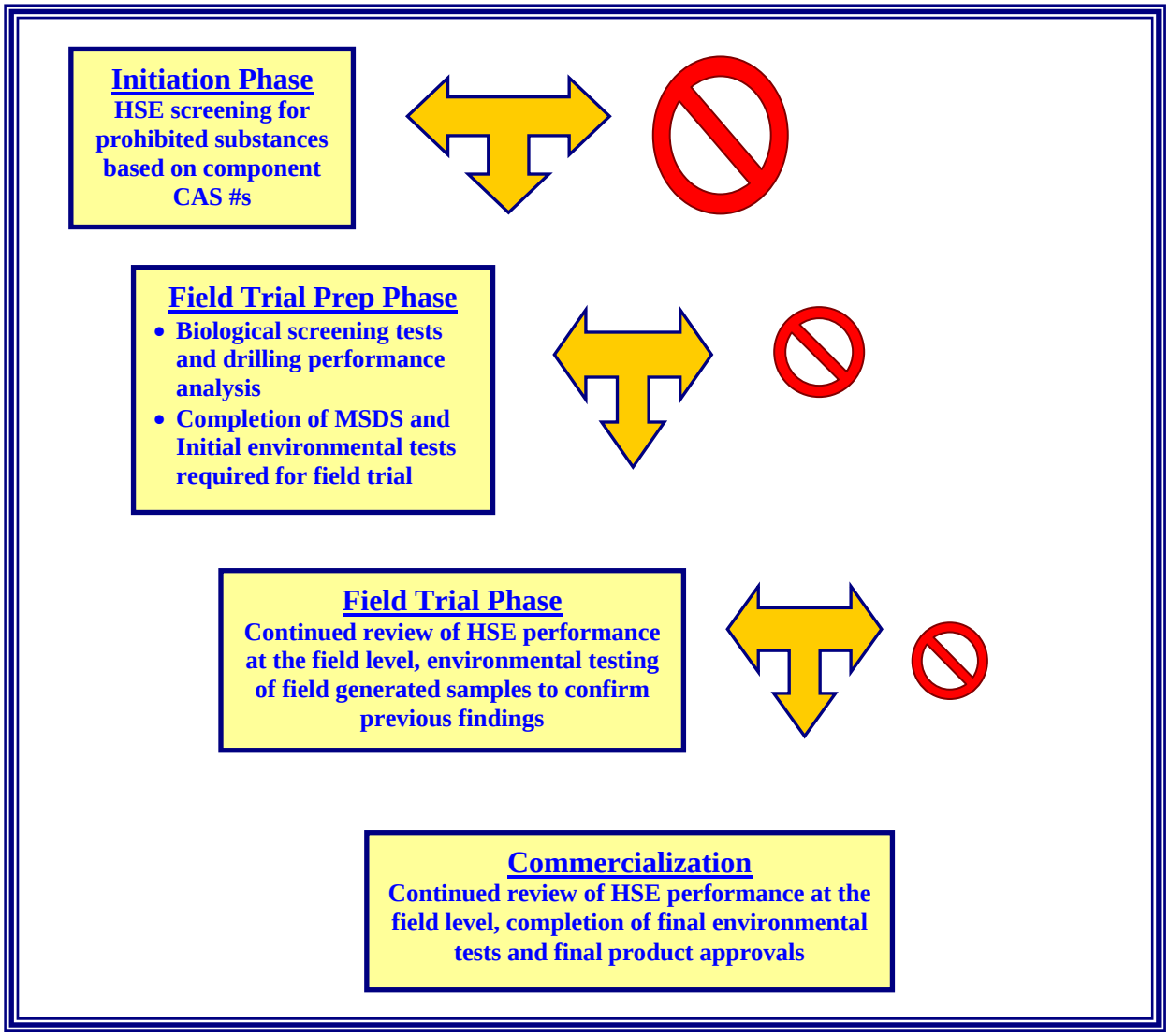
In current product development cycles, HSE concerns have equal weight to economic and drilling performance considerations. Consequently, product development and environmental scientists work closely together to identify products that meet the needs of customers. In addition to having a product development focus, these teams have an environmental science focus that drives them to work with industry and government to promote regulations and testing procedures that will continue to minimize environmental impacts from drilling fluids and cuttings. Continued efforts by industry and regulators to minimize potential risks associated drilling fluids requires close cooperation and good science to advance the process.

Product Development and Deployment Processes

In a model approach, the development and deployment of new drilling fluids products includes three key elements. Proposed products are conceived in the R& D process that is managed and directed by the product development group. This first element begins at the initiation phase of a new product and continues to the pre-field trial phase where other groups become increasingly involved. The second element is a product approval process where the development group continues to support the product and makes adjustments as needed to resolve issues. The third element is the interaction between the product development group and other groups such as marketing, legal, purchasing, and technical services in a committee format.

In response to the regulatory limitation and tests, the product approval element has evolved into a structured approach where not only environmental limitations, but a host of other HSE and non-HSE issues are addressed. In a model program depicted in the following diagram, the product moves through various stages of screening and evaluation during the product approval process before it reaches a field trial. During the field trial and through commercialization, the product continues to be evaluated. After commercialization and throughout the product's life cycle the evaluations continue as it is exposed to continued stress of field conditions. At any point in the developmental and deployment process, a product can be rejected due to environmental or regulatory issues. This process is generally iterated on a regional basis wherein the regulations and testing protocols change. Thus the market for products need to be identified relatively early in the process or this process is iterated when new markets are considered. As a product moves through this process with HSE reviews conducted regularly, the liability and chances of rejection decrease as environmental performance data is generated and reviewed prior to proceeding to the next step.

Experimental Product & Deployment Schematic



Regulatory Process and Development

Onshore and offshore regulatory development has followed different pathways over the years. Offshore, two of the major regulatory development approaches have been in the North Sea which is driven by Oslo and Paris Commissions (OSPARCOM) and in the Gulf of Mexico, which is driven by the US Environmental Protection Agency (EPA). A discussion of current product approval requirements from these two areas follows in order to compare and contrast their current requirements. Onshore, regulatory approaches have focused on constituents of the discharges and design of containment systems. Louisiana regulations are provided as an example to this approach.

In most cases, new products are developed and introduced in order to meet existing regulatory limits and definitions. In a few cases, new regulations are written to address new

technologies that become available on the market. Typically, new products that are introduced under existing regulations provide incremental improvements. New regulations based on new technology tend to make major changes in environmental and drilling performance. New products approved under existing regulations typically takes weeks and months while developing new regulations can take years.

When new regulations are written for a technology, they serve the purpose of authorizing and defining the new technology, as well as protecting the technology from being misused and potentially damaging the environment. Consequently, the regulatory system acts to both authorize and limit the technology at the same time. Through the regulatory development process there is a constant tension between making more restrictive limits to insure the new technology is used property and making less restrictive limits so that the new technology is more available.

New products are typically globally available. Regulations are regional in nature which results in multiple approvals for a new product. The introduction of new regulatory tests or limits in one region tends to have a ripple effect on new regulations as each region reviews what is happening on a global basis. Both new products and new regulations impact each other and because of the global nature of new technology and the regional nature of drilling operations, the process of developing new products and new regulations has to be considered both on a global and regional basis.

Product Approval – North Sea, United Kingdom (UK) sector

While several countries follow the OSPAR approach, this review focuses on the UK sector of the North Sea. The UK offshore petroleum industry manages chemical use and discharge with The Offshore Chemical Notification Scheme (OCNS). The Department of Trade and Industry (DTI) regulates this process using scientific and environmental advice from Cefas and the Fisheries Research Services (FRS).

All of the countries in the North Sea area follow the OSPAR harmonized mandatory control scheme (HMCS). As with many regulations, there are various acronyms and details in the regulation. The main focus of the current review is to identify the key drivers in the product development process. The HMCS was developed through the OSPAR Decision 2002/2. This system ranks chemical products according to Hazard Quotient (HQ), calculated using the CHARM (Chemical and Risk Management) model. The focus of this approach is to identify and exclude components that can damage the marine environment. By excluding them from use they are barred from discharge. Using this approach, the suppliers bear most of the regulatory burden and it allows operators to simply focus on use of approved chemicals.

The HMCS requires testing of all substances and preparations used offshore to adhere to the requirements of the Harmonised Offshore Chemical Notification Format. The HCMS also requires testing on a substance-by-substance basis of all offshore chemicals to OSPAR Recommendation 2000/4 on a Harmonised Pre-screening Scheme for Offshore Chemicals. In addition, the HCMS ranks chemicals according using the Chemical Hazard Assessment and Risk Management (CHARM) ‘hazard assessment’ module. Finally the HCMS results in management decisions based on assessment of the process with the following outcomes:

- Permission

- Substitution
- Temporary Permission
- Refusal of Permission

Operators can only use offshore chemicals that have been assessed by CEFAS and are published on the current version of the List of Notified Chemicals (www.cefas.co.uk/ocns).

The HOCF has tests for toxicity, biodegradation and bioaccumulation. Table 1 summarizes the required testing elements and their associated testing protocols. In addition to the performance in the required tests, experiences with test parameters entered into the CHARM model also drive the design of new products and product components.

In response to the implementation of OSPAR testing requirements, the research efforts to find new product components is highly influenced by the knowledge of their likelihood to perform well in the required tests and the CHARM model. For example, if the CHARM model favors products with low P_{ow} instead of low toxicity, the new products will have low log P_{ow} and potentially higher toxicity.

The introduction of the HOCF and CHARM is leading to the exclusion of some existing products and provides a driver for new substitution products and increased product offerings. However, the complexity and expense of testing and registration of new products serves as a barrier and acts as a driver to slow down the introduction of new chemicals and limit the number of products vendors are willing to support.

Product-focused systems such as the HMCS and CHARM model are designed to reduce the hazardous nature of products approved for use offshore. However, such product focused systems sometimes result in unintended consequences which can lead to greater overall discharge volumes and more days on location. If a critical lubricant or shale inhibition product is terminated from use or discharge it could easily lead to stuck-pipe incidents requiring many more days on location to re-drill hole sections and adopt alternative drilling practices that result in more days on location and higher discharges of associated waste streams.

For the five mandatory tests, the process of contracting and conducting the required tests can be a time-consuming process. Additional steps of data validation and administration can further delay completion of required elements. Consequently, scheduling and tracking the progress of new products is a significant responsibility shared by both environmental and product development groups.

Product Approval – US Gulf of Mexico:

Discharges in the US Gulf of Mexico are regulated by the General Permit GMG 290000 in the Western Gulf of Mexico. The Gulf of Mexico permit contains limitations for both products and discharges with a strong emphasis on end-of-pipe testing. Table 2 summarizes these test requirements and procedures. Prior to being accepted for discharge, two major product categories (barite and base fluids) have to pass acceptance criteria. The significant driver for product development is the use of end-of-pipe limitations for toxicity. The additive effects of toxicity and combined with potential downhole contamination and toxicity test variability commonly drive

operators to act conservatively regulatory limits consequently, the environmental compliance issues continue well after the initial product introduction. The focus on end-of-pipe test also results in a routine requirement for bioassay testing and a high focus on consistent test results from bioassay labs. Use of the end-of-pipe testing regulatory limits allows rapid introduction of new products and places significant regulatory burden on the operators who must pay fines if the new products cause non-compliance with end-of-pipe limitations.

Product Approval – Onshore Louisiana

Onshore discharges regulations tend to focus on the contents of the waste pit and control of the pit design. Consequently, the focus of product development is to make sure the pit content is below regulatory limits. For most onshore discharge regulations, chemical testing has dominated disposal limits with a focus on heavy metals, salt contamination, and hydrocarbon contamination. The limits in Louisiana for pit closure of soil waste mixtures are listed in Table 4.

Development of New Tests for Onshore and Offshore Disposal Criteria

The evaluation of fluid components using environmental testing provides a pathway to controlled discharges. Controlled discharge of drilling fluids and cuttings has been shown in other areas of the world to represent a pollution prevention technology and is accepted as a defensible environmental practice. Two of the key advantages of advanced products and technology are lowering current disposal costs and minimizing long-term liability. The objective of research into new test procedures is to develop viable environmental tests for the purposes of discriminating advanced technology from traditional products known to have environmental concerns. By using drilling fluid products that have been tested previously and have established environmental performance records, the focus can be on evaluating test procedures and adjusting testing parameters in order to obtain viable test procedures that meet the stated objectives. The design criteria for the test protocols should include the following elements:

a) The tests should have ecological relevance to the discharge environment.
b) The tests should be practical to conduct at commercial labs.
c) The tests should be repeatable.
d) The tests should be able to consistently discriminate between traditional products and advanced products.
e) The tests should be acceptable to regulators for use as regulatory tools to control discharges.

While established protocols are a suitable place to start, they frequently have to be modified to address the issues specific to drilling fluid products. Once viable protocols have been established, appropriate round robin testing using local labs is required to validate the testing procedures and prepare them for use regulatory tools.

Examples of Environmentally Responsive Product Development & Deployment

As discussed above, products developed under the model system involve elements of human health and safety evaluations as well as specific and general impact assessments on the receiving environmental where the potential drilling fluid system or additive will be utilized. These R&D projects take on two primary forms: typical technology development in which these HS&E matters are considered within the process and those projects that target specific achievable environmental performance along with an acceptable technical level. The following examples are mixtures of these two types of R&D efforts in which the environmental performance of a product plays a significant role in the developmental story.

Water-Based Drilling Fluid

One of the 2005 drilling fluids R&D projects was to develop a relatively inexpensive inhibitive water-based (WBM) drilling fluid. Inhibition is necessary to prevent or retard the reactivity of shales to swelling or dispersion. This technology can be approached in several ways, including using salts, silicates, aluminates, amine containing compounds or other organic or inorganic chemistries. The objective here is using chemistries that will be reactive enough to interact with the surface or interstitial layers of the shale, thus decreasing the reactivity of the shales while showing little to no effect if discharged on a drilled cutting.

The standard environmental screening in the R&D process for developing water-based drilling fluids and additives is to conduct a ***mysid shrimp*** LC_{50} (as per EPA end-of-pipe protocol). A pass for discharge into the Gulf of Mexico from an LC_{50} perspective is 30,000 ppm. Typically, because test variability concerns, there is an acceptable value of >100,000 ppm for any new WBM additives. During this process, the research scientists are responsible for submitting samples and reporting results to R&D management on particular candidates for use.

In this instance, the research scientist had developed a shale inhibitor based on amine chemistry. It was a waxy compound and one material selected to aid in making this waxy compound easier to handle was tallow nitrile. This product was chosen because of its solvency, cost and expected easy of degradation, but initial LC_{50} screening showed this blend of products to be extremely toxic. The primary contributor was determined to be the tallow nitrile material. After reformulations, the amine-based composition was retested and then submitted for LC_{50} screening tests. The scientist obtained an acceptable result (> 500,000 ppm) in a generic mud formulation and briefed management on both the technical and environmental results. The process moved forward to finalize this product and obtain a field trial prior to commercialization. At this point, the product was submitted to a model product approval process, which bridges the development and deployment processes by taking experimental products from the laboratory and shepherding them through to commercialization. The product approval process flows through various departments required to ensure that all the proper documentation and data required for legal and responsible product introduction to be accomplished (i.e. MSDS, PDMs, and product specifications).

Environmental approval is required prior to both field trail and final commercialization. In the meantime, since the amine compound was a naturally waxy material, attempts were made to adjust a final formulation by using a mild acid and water. Subsequent testing by environmental

in a field mud formulation prior to the field trial gave much lower LC_{50} values (less than 50,000 ppm). The original material was also retested with similar results in the field mud formulation, with the apparent explanation for the anomaly with the first result being the differences in the base mud formulations. Weeks prior to scaling-up the product and a subsequent field trial application, the product was pulled from consideration and major redesign was undertaken to address the toxicity issue.

In this case, even though there was some conflicting environmental test data, the decision was made to err on the side of caution and not proceed with the formulation. Several months worth of R&D time had been spent on the development side, external and health and safety testing had been completed and a field trial well had been scheduled, but the choice was made to withdraw back to the laboratory to maintain the environmental profile of the product. In most cases, environmental failures that result in non-compliance are not tolerated. Consequently, performance risks are usually taken before environmental risks.

Invert Drilling Fluid – Synthetic-Based and Ultra Low-Toxic Mineral Oil-Based Muds

Invert drilling fluids are invert emulsions (water-in-oil (invert) and comprise non-aqueous and brine phase, along with a weight material (i.e. barite, hematite), emulsifiers, wetting agents, viscosifiers and filtration control agents. The non-aqueous phase can range from diesel, mineral oil, paraffinic compounds, olefins and esters to mention a few. Some of these base fluids are considered "synthetics" such as olefins and esters and thus fall into special considerations for discharges in the Western Gulf of Mexico under the General Permit GMG 290000. Among these considerations, the whole "mud" (as opposed to the base fluids) must pass a four-day sediment toxicity test.

This 4-day test is based on protocol developed for sediment toxicity testing of the species during the 2000 – 2002 efforts by the SBM Toxicity Workgroup. The test is designed to evaluate synthetic-based mud as opposed to just the base fluid itself. Although toxicity effects of the base fluid tend to dominate its outcome, other additives and potential field contaminations also play a major role in the toxicity of the whole mud. Therefore any changes in additives (emulsifier, wetting agent, viscosifier or filtration control agent) must be thoroughly tested using this test protocol prior to introductions.

Due to regulatory changes on specific chemistries in Canada and their subsequent appearance on the Canadian Environmental Protection Agency (CEPA) Environmental Registry Toxic Substance List, a new product was requested with a small component change (less than 13%) of the primary emulsifier package of its synthetic-based mud system. This component was not the active ingredient but instead a pour-point depressant required to make the emulsifier flowable under reasonable temperatures (≥–15°C). The new material was not a regulatory concern for any of the markets in which this emulsifier was available.

A sample was prepared containing the replacement pour-point depressant chemical. These samples along with the original emulsifier were used to make synthetic-based muds (SBMs) and these SBMs were tested in-house for 4-day sediment toxicity test. After numerous tests, statistical analysis showed both materials performed similarly. To insure that a replacement such as this would not jeopardize the environmental status of the SBM, it was decide to introduce only a trial batch of the reformulated product into the field and monitor actual field toxicity

results. This proved successful and validated the environmental safeguard in the current product development and deployment process. Because of biological variability subtle changes in environmental performance are difficult to determine leading to a requirement for many tests to be conducted and evaluated statistically. This can be a time consuming, expensive, and frustrating process.

An example in which a research project was focused primarily on environmental goals was recently carried out in the Norwegian sector of the North Sea. Like the UK, Norway uses the HMCS. However, there continue to be differences in regulatory requirements and implementation of HMCS. For drilling operations in the entire North Sea, there is no discharge of anything related to the drilling fluid when low toxic mineral oil-based muds are used. This includes whole mud, drilling fluids and cuttings. Even though these materials or associated cuttings associated are not permitted to be discharged, the Norwegian Pollution Control Authority (Statens Forurensningstilsyn or SFT) wanted all operators and their suppliers to improve the classification of the drilling fluids and drilling fluid additives.

Currently there are four classifications for offshore usage of chemicals in the Norwegian sector of the North Sea (Table 5). These classifications are based on several factors that in addition to marine toxicity (2 types) and biodegradation include hormone disrupters, mutagenic potential, fish taint and effects on reproductive ability. Once these factors are determined, the substances are categorized by severity proceeding from best to worst as Green, Yellow, Red and then Black. The Black chemistries are either banned from use or highly discouraged, while the ones listed as Red are intended for those materials that the SFT expects the operators to "retool" or find substitutions that will be able to obtain the Yellow or Green classification. Many components of invert emulsion drilling fluids reside in the Red classification primarily because of their extremely low biodegradability (<20%).

A few years ago, a new ultra-low toxicity base oil obtained a Yellow classifications prompting a review of the other components of the drilling fluid formulation to find that only a few needed either data or chemical modification and retesting to also obtain a Yellow classification. Therefore, a research project was initiated to develop Yellow alternatives for those few products that were still listed under the Red classification. In addition to the environmental goals of acceptable toxicity and biodegradation (>20%), performance criteria also had to be addressed and satisfied. After analysis of components of the products in questions, modification to those chemistries that were known or suspected culprits, and performance screening of alternatives, final environmental testing was accomplished in external laboratories with results acceptable to obtain the desired Yellow classification.

Drilling Waste Management Technology

From an industry and company perspective the ultimate goal is to technically and commercially unite the process and selection of drilling with the final environmental solution for remediation, disposal or management of the waste produced. One project which emulated these aspects of product and system design was that which focused on an invert emulsion drilling fluid for land use and remediation. This project utilized a variety of remediation methods to deal with the cuttings generated from drilling with the fluid and these methods were fundamental in the development of the new technology designed to result in beneficial use of cuttings and other byproducts traditionally treated as waste.

As describe above an invert emulsion drilling fluid is composed of a base fluid (non-aqueous), internal phase (brine), viscosifiers, emulsifiers, wetting agents, fluid loss additives and weight material. One of the key elements of this system is the base fluid. Typically, the base fluid makes up anywhere from 40 – 90% of the fluid composition with the brine comprising 10 – 30%, weight material 5 – 50% and the remainder of the components 5 – 8% by a volume percent basis. On land applications, aerobic degradability and toxicity is the critical factor for the base fluid. Table 6 shows comparisons between various base fluids and their aerobic degradability. Based solely on degradability testing, there are several candidates for a base fluid selection – linear paraffin (LP), ester and liner alpha olefin (LAO). After various toxicity testing (microtox, animal and plant), only the LP and LAO options remain (Table 7).

Traditionally, the brine phase of an invert is a chloride-based salt ($CaCl_2$ or NaCl). Two of the options to changing away from a chloride type salt were: a nitrate or acetate internal phase. The weight material for higher densities (when weight material becomes an important factor) is chosen to be hematite, illmenite or calcium carbonate in lieu of the traditional barite. The final formulation incorporating biodegradable emulsifiers and wetting agents is screened using a variety of toxicity testes (Table 8).

The remediation techniques can range from bioremediation via bioreactors, biocells, composting, land farming or vermiculture. The system has been successfully employed in New Zealand using the latter technique on over half-a-dozen wells. The vermiculture technique utilizes worms to process a blend of fluid covered cuttings and organic material to generate a vermicast fertilizer. Thus a potential drilling waste is converted to a viable and useful by-product. While a technical and environmental success, introducing this new technology has been difficult in areas where existing OBM regulatory structures are designed for waste disposal and not for beneficial reuse.

CONCLUSIONS

Drilling fluid formulations have continued to develop to meet the technical demands of deepwater, high temperature, high pressure, directional, extended reach and depleted zone drilling. Environmental impacts are designed into new products as performance criteria. As mechanical and chemical treatment options continue to work towards the goal of keeping the pollutants in the operation system, it can be expected that new lines of research will evolve that focus on matching drilling fluid formulations with physical and chemical treatments that result in waste minimization. Because of the consumable nature of drilling fluid products, they are often the fastest and most flexible way to introduce and achieve environmental performance goals. Therefore, research and development opportunities for advances in drilling fluids technology continue at the forefront of environmental protection efforts. Cooperation and coordination between environmental scientists and product development scientist is a key element for the continue progress toward waste minimization goals.

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Table 1

HCNOF Section	Test function	Applicability of test	Recommended protocols
2.1.1	***Log P_{ow}***	***(Mandatory) except not applicable for surface active substances and inorganic substances***	OECD 107 or OECD 117
2.1.2	***Bioconcentration/ bioaccumulation***	***(Conditional)*** These data are only required in the following circumstances: +where a log P_{ow} has been estimated as being greater than 3 but where the substance is thought not to be bioaccumulating. +the substance is a synthetic organic phase base fluid (OPF).	*Mytilus edulis* in a modified OECD 305 or ASTM E1022 study.
2.2.1	***Aerobic biodegradability***	***(Mandatory for all organic substances)***	Preferred: OECD 306 (Marine Ready Biodegradation) Acceptable: +The Marine CO2 Headspace Biodegradation Test (modified ISO method N182). +The Marine CO2 Evolution Test (modified Sturm test) +BOD Test for Insoluble Substances (Marine BODIS-test).
2.2.2	***Aerobic inherent biodegradability***	***(Optional)***	Any substance that exceeds 20% 'ready' biodegradation in 28 days will be assumed to be ‘inherently’ biodegradable An optional inherent biodegradation test to OECD aerobic inherent biodegradation protocol, 302 A-C may more be appropriate for polymers, which can fare badly in the ready test.
2.2.3	***Anaerobic biodegradability***	***(Optional)***	ECETOC Technical reports No. 28 (1988) and No. 54 (1993) or the ISO protocol for the "Evaluation of the "Ultimate" Anaerobic Biodegradability of Organic Compounds in Digestive Sludge", ISO/TC 147/SC5, N103, 1992

Table 1 (Continued)

2.3	**Tainting**	***(Required)***)	Review of OSPAR List of Substances/Compounds Liable to Cause Taint.
2.4.1	***Algae test***	***(Mandatory)***	*Skeletonema costatum* ISO/DIS 10253.
2.4.2	***Crustacean test***	***(Mandatory)***	The OSPAR recommended species for the crustacean test are: *Acartia tonsa*, ISO TC 147/SC5/WG2 if *Acartia tonsa*, is unavailable *Tisbe battagliai* *Mysidopsis bahia*
2.4.3	***Fish test***	***(Mandatory)***	*Scophthalmus maximus*, PARCOM Protocol 1995 Pt B. or if unavailable *Cyprinodon variegatus*
2.4.4	***Sediment reworker test***	***(Conditional)*** Sediment reworker data are required for those **preparations** that fulfil at least one of the following Conditions: • are sinkers • have a K_{oc} >1000	*Corophium volutator* PARCOM Protocol 1995 Pt A.
2.4.5	**Long-term toxicity data**	**(Optional)**	This data is not utilised by CHARM and therefore does not form part of the hazard ranking system
2.5	**Adsorbability**	**(Conditional)**	. The Netherlands have been charged with finding a suitable protocol for presentation to OIC 2000

Table 2

Requirement Categories	**Frequency**	**Permit Discharge Limit**	**Method Reference**
Free Oil	Once per week when discharging	No free oil (*i. e*. no static sheen)	Static Sheen Testing and Requirements 40 CFR 435 Subpart A, Appendix A
Mercury/ Cadmium Content of Stock Barite	Once prior to drilling a well	1.0 mg/kg mercury max.; 3.0 mg/kg cadmium max.	Mercury/ Cadmium Certification Requirements
SPP Aquatic Toxicity Test with *Mysidopsis bahia*	Monthly and EOW	96-hour $LC_{50} \geq$ 30,000 ppm	Mud SPP Toxicity Testing and Requirements 40 CFR 435, Subpart A, Appendix 2
Sediment Toxicity Test with *Leptocheirus plumulosus* **SBM ONLY**	Internal Olefins: Monthly and EOW with NAFs. Ester: Once/well at EOW with NAFs.	Ratio of 96- hour $LC_{50} \leq$ 1.00	Mud Sediment Toxicity Testing and Requirements 40 CFR 435 Subpart A, Appendix A
Formation Oil **SBM Only**	Once prior to drilling a well	No Discharge	GC/MS Testing 40 CFR 435 Subpart A, Appendix 5
	Weekly	No Discharge	RPE 40 CFR 435 Subpart A, Appendix 6
Base Fluids Retained on Cuttings (ROC) **SBM Only**	Once per day, every 500 ft if interval drilled with synthetic base mud. Maximum 3 per day. BMP Exemptions	≤ 6.9% IO ≤ 9.4% ester or default value: 25% 10 bbls for displaced interfaces 75 bbls for pit cleanout	Retort Test Method 40 CFR 435 Subpart A, Appendix 7

Table 3

Monitoring/ Sampling Requirement	**Frequency**	**Permit Discharge Limit**	**Method Reference**
Polynuclear Aromatic Hydrocarbon (PAH) as phenanthrene	Once/year on each base fluid or base fluid blend formulation	<0.00001 gm PAH per gram of base stock fluid (10 ppm PAH)	PAH Testing and Requirements: PAH Content of Oil by HPLC/UV Method 1654A 40 CFR 435.11(u); EPA-821-R-92-008
Sediment Toxicity with *Leptocheirus plumulosus*	Once/year on each base fluid or base fluid blend formulation	Ratio of 10-day $LC_{50} \leq 1.00$	Sediment Toxicity: Modified ASTM Method E1367-99
Biodegradation Rate	Once/year on each base fluid or base fluid blend formulation	Biodegradation rate ratio ≤ 1.00	Closed Bottle Test: Modified ISO 11734:1995 40 CFR 435 Subpart A, Appendix 4

Table 4

Parameter		Limitation
pH		range of 6 – 9
Total Metals Content	Arsenic	10 ppm
	Barium • Submerged Wetland Area • Elevated Wetland Area • Upland Area	 20,000 ppm 20,000 ppm 40,000 ppm
	Cadmium	10 ppm
	Chromium	500 ppm
	Lead	500 ppm
	Mercury	10 ppm
	Selenium	10 ppm
	Silver	200 ppm
	Zinc	500 ppm
Oil and grease	content of the waste/soil mixture after closure is	<1% (dry weight)
In elevated, freshwater wetland areas where the disposal site is not normally inundated	a. electrical conductivity (EC-solution phase):	<8 mmhos/cm
	b. sodium adsorption ratio (SAR-solution phase):	<14
	c. exchangeable sodium percentage (ESP-solid phase)	25%
Additional parameters for land treatment of NOW in upland areas:	a. electrical conductivity (EC-solution phase):	<4 mmhos/cm
	b. sodium adsorption ratio (SAR-solution phase)	<12
	c. exchangeable sodium percentage (ESP-solid phase):	<15%

TABLE 5
SFT Classifications for Chemicals for Use on Offshore Installations

Category	Environmental properties	Classification
1	Hormone disruptors, mutagenic and substances affecting reproduction ability	No discharge
2	Priority list from White paper no. 25 (2002-2003)	No discharge
3	Biodegradation <20% and Log $P_{ow} \geq 5$	No discharge
4	Biodegradation <20% and marine toxicity EC_{50} or $LC_{50} \leq 10$ mg/l	No discharge
5	OSPAR Strategy regarding Hazardous Substances, Annex 2	No discharge
6	Chemicals listed on OSPARS tainting list	Substitution
7	Two out of three categories: Biodegradation < 60%, Log $P_{ow} \geq 3$, EC_{50} or $LC_{50} \leq 10$ mg/L	Substitution
8	Inorganic chemicals with LC_{50} or $EC_{50} \leq 1$ mg/L	Substitution
9	Biodegradation <20 %	Substitution
	Other chemicals	Acceptable
	Water	OK
	PLONOR chemicals	OK

Table 6
Aerobic Biodegradability Comparison for a Variety of Base Fluids

Biodegradability of Various Base Fluids		
Treatment	**% Reduction of Hydrocarbons**	**Biodegradability Rank**
C11-14 LP	**97**	**1**
C12-13 LP	**94**	**2**
Ester	**91**	**3**
C14 Linear Alpha olefin (LAO)	**90**	**4**
Isomerized Tetradecene C14 (IO)	**83**	**5**
Diesel	**61**	**6**
Branched Paraffin	**43**	**7**

Table 7
Toxicity of Various Base Fluids *

Treatment	Water Toxicity	*Animal Toxicity*	Alfalfa Phytotoxicity*		Toxicity Rank
	Microtox IC50	% Earthworm Survival	% Seed Emergence	% Root Elongation	
Branched Paraffin	106	100	95	107	1
C11-14 LP	98.5	100	96	134	2
C12-13 LP	65.9	100	95	120	3
C14 Linear Alpha olefin (LAO)	62.3	100	97	115	4
Isomerized Tetradecene C14 (IO)	61.7	100	101	144	5
Diesel	10.3	0	7	2	6
Ester	5.9	0	0	0	7

*** Seed Emergence and Root Elongation test results are normalized to Control test values of 100.** (Ref 8)

Table 8

Biodegradability , Toxicity & Electrical Conductivity of Formulations and Treated Cuttings 6% w/w Loading on Topsoil from Southern Alberta Grassland							
	Biodegradability (65 days)	Animal Toxicity		Alfalfa Phytotoxicity*			Relative Electrical Conductivity (after 65 days)
System	% Loss of Extractable Hydrocarbons	% Springtail Survival	% Earthworm Survival	% Seed Emergence	% Root Elongation	% Shoot Mass	
Formulation A	98	80	100	100	149	97	1.0
Formulation N	98	87	93	4	11	47	4.0
Std. Diesel / CaCl2 / Barite	68	0	0	3	8	25	4.9
Formulation A with Barite	99	90	100	100	108	105	0.8
Treated Cuttings, Form. NA	-	93	100	109	134	129	-
Treated Cuttings, Form. N	-	73	100	113	116	121	3.9

***Animal Toxicity and Phytotoxicity test results are normalized to Control test values of 100**.. (Ref 8)

New Innovative Process Allows Drilling Without Pits in New Mexico

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ABSTRACT

Several factors have led to the use of reserve pits in New Mexico. Primarily, poor solids control efficiency dictated a "dump and dilute" strategy where a large reserve of dilution fluid was required to maintain a low concentration of detrimental drilled solids. The "horseshoe" designed pit allowed a single pit to double as a collection point for drilled cuttings and associated fluid waste.

Recent improvements in solids control equipment coupled with new developments in chemical flocculants and coagulants have allowed high solids control efficiencies to be achieved without dilution. Further, the solid waste generated contains very little associated fluid.

This paper discusses the new, innovative process and the impact it has on waste generation and character, disposal options, cost, and liability issues.

DISCUSSION

Solids Control and the Role of Earthen Pits

Earthen reserve pits have a number of functions in the drilling operation. Two are more prominent than the others and are relevant to the topic this paper. The first function of the reserve pit is to hold an abundance of "reserve" fluid for use as drilling fluid. The second function is to contain the waste generated by drilling a hole in the ground. This waste is generally called cuttings, but in this paper will be called discard or waste for reasons that will be described.

The role of the earthen reserve pit in the circulating system should be understood. In the circulating system, drilling fluid is pumped down the inside of the drill pipe and through nozzles in the bit where it sweeps cuttings chips or shavings away from the cutting face. These cuttings are carried in the fluid stream back to the surface on the outside of the drill pipe. The cuttings at this point are suspended particles in a fluid stream. At the surface, the returning fluid laden with drilled cuttings is directed to the shale shakers, which are the first components of a solids control system.

Shale shakers are equipped with vibrating screens that bounce the particles off the end of the shakers and allow fluid to flow through the small openings in the screen. The size of the particle removed depends on the opening size of the screen. The opening size that can be used on the shakers depends on the amount of fluid being pumped that must be processed. The "discard" is the portion of the particles along with associated drilling fluid that <u>does not</u> go through the screen openings. Not all of the particles are rejected from the fluid stream at the shale shakers.

The fluid stream that passes through the shale shakers (along with fine particles not removed) enters a series of steel tanks and may be processed by additional pieces of solids control devices. Each device has a similar characteristic to the shale shakers in that the device removes some portion of solid particles along with some associated drilling fluid and fails to remove some portion. Each solids control system is defined by its available pieces of equipment.

The efficiency of the solids control system is defined as the amount of particles removed divided by the amount of solid particles generated by the bit. A solids control system with low solids removal efficiency will leave large amounts of cuttings particles in the drilling fluid. These particles are detrimental to the drilling process in a number of areas. If the concentration of particles (called low gravity solids or LGS) exceeds 3% to 5%, then studies have shown a significant reduction in penetration rate. Also some of the fluid properties, like fluid loss or viscosity, are adversely affected by high concentrations of low gravity solids. The solids control system efficiency could be improved by supplying additional solids control equipment, but this is sometimes an expensive solution. With low efficiency systems, a strategy called "dump and dilute" has been adopted to meet the fluid needs without the expense associated with supplying additional solids control equipment.

The dump and dilute strategy can be described in the following terms. As the concentration of low gravity solids increases to some unacceptable level, dump some amount of drilling fluid containing the high concentration of LGS to the reserve pit. Replace the dumped volume with a like volume of fresh fluid without low gravity solids. This process is repeated over and over, as needed. If the cost of maintaining the drilling fluid properties is low, then this can be a low cost, effective strategy.

The total waste is the sum of the discard volume from all of the components of the solids control system and the total volume of dumped fluid. The affect of dumped fluid on waste volume can be seen in Figure 1. This table is a simple theoretical calculation where mud is dumped at 7% LGS. The table shows the effect of increasing solids control efficiency while drilling the same amount of hole volume. As the efficiency increases, the amount of discard increases linearly, but the amount of dumped volume decreases at a larger rate. The result is that the waste volume decreases with increasing solids control efficiency.

A second term is introduced in Figure 1. The term is the ratio of waste to hole volume. Since the hole volume drilled varies from well type to well type, a comparison between well types must be made on an equal basis. This is accomplished by creating the ratio of waste to hole volume (R). The ratio decreases with increasing efficiency. A ratio of 3 to 5 indicates very high efficiency. A ratio of 8 to 12 indicates low efficiency. A ratio higher than 12 indicates very low efficiencies and indicates poor solids control practices.

Sometimes the earthen reserve pit is incorporated into the solids control system. This technique is called "circulating the pit" and is commonly used in the Permian Basin and other areas. In this system, an initial load of "reserve" water is brought to the pit. Conventional mechanical solids control equipment is not used (is by-passed). Instead, returning fluid laden with drilled cuttings particles is discharged directly to the earthen reserve pit. The pit is designed to allow the low gravity solids to settle in the first part of the pit. Fluid continues to flow to the "deep" end, allowing solids to settle along the way. Fluid is recovered at the deep end and re-used in the drilling process. The waste volume created by this technique is very high. The ratio of waste to hole volume is frequently about 20.

In the Permian Basin a "horseshoe" pit has been developed and is in common use. Figure 2 shows a picture of a typical dual, lined horseshoe pit built above ground. The inside compartment of the pit generally holds fresh water for drilling surface hole and, later, brine for dilution of drilled solids in the active mud system. The outside portion of the pit is used in the "circulating the pit" technique. The solids side of the pit slopes gently away from the discharge point getting deeper with distance. At the far end of the pit there may be a shallow earthen wall that acts as a weir, over which fluid flows after a certain fluid depth has been reached. A floating suction is installed on the fluid side to complete the loop through the pit.

Eliminating the Pit

The reserve pit serves a useful function in the drilling operation. However, it is viewed by some as a liability with the potential for causing contamination. It also poses a potential for future clean-up. In the wrong site, with poor management, or if not closed properly it certainly could create unwanted liability.

For those wanting to eliminate the pit, certain technical and financial issues must be addressed. The solids control system must be highly efficient and capable of removing almost all of the drilled solids generated. With a highly efficient solids control system very little fluid would need to be dumped and discarded. The discard stream from the solids control system should be relatively dry, too. A system to handle and store the collected discard stream must be available. An alternate disposal plan, other than burial, must be developed; otherwise much of the logic for eliminating the pit is lost. And, finally, the net affect on drilling cost must be minor or the plan will not be implemented.

A system has been developed and used by Cimarex in New Mexico that can process water-based drilling fluid at the rig site with very high efficiencies and with relatively low fluid retention with the removed cuttings. The system consists of shale shakers sized to run fine screens at the required flow rate. Two shakers are generally required for the hole size and flow

rate involved. Both can be fitted with 175 mesh to 200 mesh screens. There is also a mud cleaner to process the fluid. The mud cleaner consists of desilting hydrocyclones over a shale shaker.

The system is also equipped with a water-based mud de-watering system consisting of a chemically enhanced centrifuge package. The centrifuge is a high gravity separation device that can remove fine particles not removed by conventional shale shakers or hydrocyclones. Chemical flocculants or coagulants are injected into the suction line along with the drilling fluid to be processed. The chemicals cause the fine drilled solids particles to form "clumps" increasing their size. In addition to removing fine particles, the removed mass is relatively dry.

Figure 3 shows one view of the solids control equipment layout. The two shale shakers are on the left side of the picture. The hydrocyclones can be seen above the third shaker to the left of an operator. The enhanced centrifuge operation is on the right being tended by another operator.

As drilled solids are removed from the system, the waste is collected in a modified steel tank. In Figure 3 the steel tanks can be seen under the solids control equipment in the foreground. Dirt and gravel has been pushed in front of the tanks to prevent any liquid from escaping. Excess liquid can be recovered with a diaphragm pump.

As loader quantities are generated, a front-end loader removes the waste and begins stacking it on a specially prepared pad. The pad is constructed of compacted clay dirt (approximately six inches) over a plastic liner to prevent infiltration of any draining liquid. The perimeter of the pad is lined with ditches to prevent any run-off. The stacked cuttings are piled, mixed and turned to expose the small amount of liquid to the air for evaporation. Occasionally, a small amount of dirt or lime is added to aid in drying. The cuttings pile soon becomes dry enough to resemble a large mound of dirt. The cutting pile is shown being stacked on the pad in figure 4. The pad and ditch can be seen in the foreground with the rig and solids control system in the background.

The burial disposal option remains viable, but without a pit, a burial cell would have to be constructed. Burial is not desired in this case, though, since the object was to eliminate a pit. Another option is to remove the stacked cuttings to a commercial disposal site, which in New Mexico primarily means landfill burial or, occasionally, land farming. A third option would be to use a minimal treatment to convert the cuttings to usable fill material for future pad construction. The third option has not been tried yet and is still being considered.

Affect on Waste Generation

The increased attention to solids control has an impact on the quality and quantity of drilling waste produced. At the time of this paper three wells have been drilled using this new procedure. The approximate wellbore configuration of the wells is shown in figure 5. The hole volume representing the approximate amount of dirt removed from the wellbore is about 177 cubic meters. Waste generation will be a multiple of this volume.

For land locations with pits drilling waste is usually estimated by two techniques: pit volume estimation and the water delivery technique. In the case of this project in New Mexico, previous wells were drilled with pits. Subsequently, several of these pits have undergone remediation. The contents of the pits were removed and taken for commercial disposal. This means that the transportation volumes can be added to obtain the waste volume.

Records indicate that an average of 5,000 cubic yards (24,044 barrels or 3,823 cubic meters) of waste material was removed from each pit. Since the hole volume for each well was 177 cubic meters, this represents a ratio of 21.6 times the hole volume. This figure compares reasonably well with other information collected during other jobs where pits are used. Figure 6 shows waste generation figures from jobs in other areas. The data was collected from two

different well types using pits in West Texas. The first well type (designated "A") is a relatively deep well. The second well type (designated "B") is a moderate depth well. The ratios on these well vary from a low of 20:1. The higher numbers of 30 and above may be due to completion activities using the same pit with drilling activities adding waste volume to the pit.

With the new process the waste volume can be estimated by estimating the volume of the cuttings pile created. No significant amount of fluid, other than contaminated mud/cement returns, has been removed for disposal. Figure 7 shows one pile quantity estimation diagram for the new system. The volume of cuttings estimated in the pile is 819 cubic meters. This represents a ratio of 4.6 times the gauge hole volume. This is dramatically lower than the 21.6 ratio to hole volume for cuttings and fluid left in the pit for disposal under the previous operating mode.

Affect on Drilling Cost

Any time a change is made to the drilling process, there is a ripple affect which changes many other aspects of the operation. The same principle applies to solids control and waste management modifications. Not only are equipment costs added, but other drilling process costs are affected too. In order to determine the net impact on overall drilling cost, all of the associated changes must be addressed.

When using an earthen reserve pit, the pit is constructed and possibly lined. Water deliveries to the location will be high, since the amount of fluid used will be high. If mud is needed, mud costs may be high (relative to mud costs with reduced fluid usage). Solids control equipment is not used extensively, so rental equipment costs are minimal or non-existent. After drilling, fluid is removed from the pit and disposed. Solids may be removed or buried in place. The pit is closed and surface remediation is addressed.

When the pit is eliminated, the costs associated with the pit are eliminated, but other costs must be considered. Equipment rental costs are increased, including surface handling of the removed discard. Mud costs and water usage costs are decreased, since fluid usage volume is reduced. A staging pad must be constructed to store and dry the discard prior to ultimate disposal. In addition, maintaining low levels of low gravity solids can decrease drilling time and reduce non-productive time (NPT) associated with stuck pipe and loss of circulation. This last affect is the most difficult to quantify.

Figure 8 shows the cost of operations associated with having an earthen pit. All of these costs may be changed by eliminating the pit, thus they must be considered as part of the overall cost associated with that decision. Figure 9 shows the cost associated with operations where the pit is not used.

The results of this analysis indicate that eliminating the pit in New Mexico is cost effective and does not add significant cost to the overall operation. When solids can not be buried on-site and must be hauled to commercial disposal, eliminating the pit actually saves money.

FIGURES

Efficiency	Hole Volume (bbls)	Discard Volume (bbls)	Dumped Volume (bbls)	Waste Volume (bbls)	Ratio - Waste:HV
10%	2,000	400	25,352	25,752	12.9
30%	2,000	1,200	19,718	20,918	10.5
50%	2,000	2,000	14,085	16,085	8.0
70%	2,000	2,800	8,451	11,251	5.6
90%	2,000	3,600	2,817	6,417	3.2

Figure 1. Theoretical waste volume with respect to solids control efficiency

Figure 2. Dual lined horseshoe pit in the Permian Basin

Figure 3. Solids control system being used to eliminate the pit

Figure 4. Discard pile being stacked on the drying pad

Hole Volume Calculation			Cimarex - New Mexico Wells		
Hole Size	**Depth**	**Length**	**Cu. Ft.**	**Bbls**	**Cu. M.**
17.500	300	300	501	89	14.2
12.250	1,900	1,600	1,310	233	37.1
8.750	12,500	10,600	4,426	788	125.3
		12,500	6,237	1,111	176.6

Figure 5. Wellbore configuration showing hole volume calculation

Well	Hole Volume (bbls)	Fluid to Location (bbls)	Fluid from Location (bbls)	Waste Generation Ratio - R	Ratio of Waste Left in Pit to HV
A1	1,100	33,850	15,260	31.8	16.9
A2	1,100	50,110	9,835	46.6	36.6
A3	1,100	22,980	8,480	21.9	13.2
A4	1,100	24,220	13,550	23.0	9.7
A5	1,100	38,090	6,830	35.6	28.4
B1	700	12,930	4,390	19.5	12.2
B2	700	13,180	3,140	19.8	14.3

Figure 6. Waste generation as a ratio to hole volume

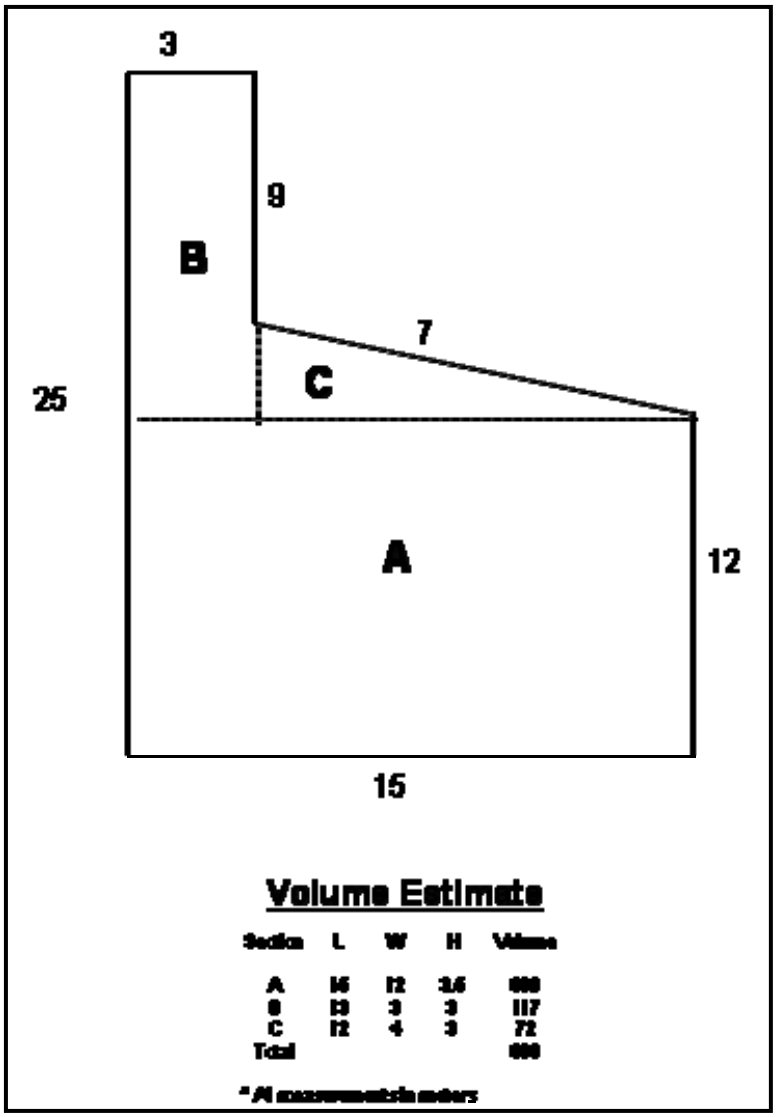

Figure 7. Waste volume estimate for one cuttings pile

Cost comparison items	Low	High
Reserve pit construction, liner	$31,000	$54,000
Water delivery, transport and cost	$13,500	$18,000
Water haul off, disposal	$42,000	$47,000
Mud costs	$74,000	$74,000
Pit closure activities	$50,000	$104,000
Extra rig time, NPT		$150,000
Total Cost	$210,500	$447,000

Figure 8. Cost of portions of operation affected by using a pit

Cost comparison items	Low	High
Pad construction, liner	$5,000	$12,000
Water delivery, cost	$5,000	$5,000
Trucking recycled fluid	$4,000	$4,000
Solids control equipment rental	$100,000	$127,000
Surface handling equipment rental	$18,000	$26,000
Mud costs	$40,000	$40,000
Re-use solids costs	$14,000	
Haul and dispose solids		$50,000
Pad closure, restoration	$3,000	$3,000
Total Cost	$189,000	$267,000

Figure 9. Cost of portions of operation affected by eliminating the pit

NEW REDUCE, REUSE, RECYCLE DRILLING WASTE TREATMENT TECHNOLOGIES AND PROGRAMS

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ABSTRACT

New waste treatment and disposal practices are being used in Texas and Louisiana to reduce, reuse and recycle (R3) drilling waste. In these areas, R3^{SM} technologies and programs can convert drill cuttings to beneficial and environmentally friendly road base and levee fill reuse material to help minimize exploration and production (E&P) operator liability.

Land treatment has been used for years to segregate water, cuttings and oil so that soluble salt content is decreased, oil concentration is reduced by recovery or degradation, and clean cuttings or reuse materials can be separated and stored in secure onsite stockpiles and landfills. What's new about the R3 Process is that converting the reuse material to road base and levee fill can safely transform an otherwise waste material to a reusable product.

Lab tests of the new road base recyclable R3 Product conducted in Texas have proven that it is environmentally sound, more affordable than traditional asphalt paving materials and has comparable engineering qualities. Pending rule changes by the Railroad Commission of Texas to reclassify treated cuttings as reuse material may allow and encourage the industry to safely recycle a drilling waste into a recyclable product. This paper will address the progress in Texas.

INTRODUCTION

Texas is an oil and gas state--has been and will continue to be for decades. The oil and gas exploration and production industry drives the economy providing countless jobs, valuable natural resources, and a tremendous tax base. While the general public reaps the benefits, our industry is also scrutinized as one of the most prevalent polluters because of the large quantities of waste it generates. Wastes such as oil and water based muds and associated cuttings, produced water and sands. Historically, these wastes have been disposed of using varying methods including, land farming, pit disposal, slurry injection, landfilling, thermal treatment, incineration, evaporation and salt cavern disposal (1). While the E&P waste disposal industry is mature and fairly well-defined, and an integral part of the oil and gas business, it for the most part has not evolved as far as technology advancements.

The Railroad Commission of Texas (RRC) encourages the oil and gas industry to minimize waste by following the Waste Management Hierarchy of Preference (2) as follows:

1. source reduction,
2. recycling,
3. treatment, and
4. disposal

For example, during drilling operations, operators seek options to minimize waste generated at the source. One method is the use of mechanical means to separate the undesirable cuttings (waste) so that the drilling fluids may be reused. Once wastes are minimized at the source, the remaining solid wastes, meeting RRC criteria, are treated and disposed onsite (i.e. land application, burial, injected), or transported to a commercial facility for treatment and disposal. Surprising enough, recycling of these waste solids rarely occurs.

E&P waste recycling operations are not new. In fact, companies have been recycling waste since the 1950's. There are recyclers permitted by the Railroad Commission to process waste materials and have had varying degrees of success--mostly for the recovery of oil--because of the recent oil price increases. Oil, a non-renewable resource, is recovered for resale, however, little has been done for the reuse or recycling of the remaining treated solids destined for disposal. The treated waste solids are a non-renewable resource as well, and in prolific oil and gas areas, are generated in substantial volumes. At times, these treated waste solids have been used for levee material, firewalls, pads and road base mostly within the generators' facility. For the most part these treated materials are not reused. Why? Consider the following:

- End users of the recyclable product may require larger volumes than the recycler has access to

- End users of the recyclable product may require stricter engineering product specifications than the recycler can provide or obtain

- Recyclers may lack the experience or the technology to manufacture a properly engineered recyclable product

- Transportation costs of recyclable product may be prohibitive

- Recycling industry has lacked standardized rules
- Recyclable product has lacked regulatory definition
- Generators have been reluctant to recycle E&P waste, as they do not want their name associated with the waste once it has been applied to the ground…the issue--liability.

US Liquids of LA, L.P. (USLL) is an environmental waste management company that treats and disposes of exploration and production waste. USLL owns and operates facilities in Louisiana and Texas with two of those facilities in South Texas. The USLL Rincon (Starr County) and Zapata (Zapata County) facilities have managed waste for over 10 years. Treatment at these facilities includes the separation and recovery of oil for resale and removal of water for disposal. The solids undergo a land treatment process within the cells to degrade remaining hydrocarbons, assisted by disking and tilling. Once the solids are treated to a total petroleum hydrocarbon (TPH) compliance limit of 50,000 ppm, the solids are destined for disposal in onsite landfill cells. Over 400,000 cubic yards of E&P waste materials have been placed in the disposal cells throughout the life of these facilities.

Recently, USLL surveyed the industry, asking key players what they consider the most important issue regarding waste disposal. The answer was obvious. Liability. This paper describes the steps USLL has taken to develop its R3 Initiatives and more specifically what USLL has done to convert E&P waste materials into a recyclable product so that the generators' liability will be minimized or possibly eliminated.

What was once waste in a landfill now has the potential of becoming a repository of aggregate to be mined and used as feedstock for the manufacture of a commercially viable recyclable road base, referred to as the R3 Product.

DEVELOPMENT OF THE R3 TREATMENT
Reduce, Reuse and Recycle

USLL's South Texas facilities receive large volumes of E&P waste, primarily oil based drilling muds and cuttings. To achieve R3, the waste must be **reduced** by properly segregating and separating the waste materials. The oil must be recovered and **reused** and the treated solid waste **recycled** into a product.

Markets

No matter how environmentally conscience or noble the intent of any recycling effort, success cannot be achieved without a viable and continuing market for the end product.

Prior to taking on an endeavor of this magnitude, USLL conducted a market study to understand and define the potential uses of the R3 Product. Market development began with an inventory of USLL materials and of the requirements necessary to move the project forward.

Prospective customers were identified including the state of Texas, counties, cities, oil and gas operators and ranch owners. These potential end users stipulated the following criteria:

- location of product utilization must be relatively near the feedstock repository,
- sustainable quantity of the recyclable product must be available, and
- provide a cost competitive product to what currently exists in the marketplace

The market study also identified that the South Texas area was experiencing a shortage of economical aggregate, an escalation of rock and asphalt prices, a shortage of pozzolon and prohibitive transportation costs; while the area was planning infrastructure growth for the construction and improvements of several thousand miles of roads.

The state of Texas, specifically the TxDOT, was easily determined to be the number one potential end user of the R3 Product. Historically, traditional road base products used in the South Texas TxDOT District are imported from areas as far as Central Texas and Southern Mexico making product transportation cost prohibitive. TxDOT became very interested in the R3 Product once it was learned that it would be manufactured within 25 miles of their District sub-office.

With an inventory of over 400,000 cubic yards of high quality, downhole bedrock aggregate at its South Texas facilities, USLL's objective was to:

- prove the ability to manufacture a product and meet both engineering and environmental specifications
- sustain long term operations
- maintain a low cost operation
- provide a competitive economical product to what currently exists in the marketplace
- commit and comply with the health, safety and environmental regulatory requirements

Proposed Regulations

The Railroad Commission of Texas regulates the treatment and disposal of oil and gas waste, as described and defined in Statewide Rule 8 and 30. It also regulates the recycling of the same waste via minor permits and/or the RRC Surface Waste Management Manual - Application Information for Permit to Treat Oil and Gas Waste for Use as Roadbase (3).

USLL conducted an extensive search at the state level for existing recycling rules. Even though the RRC maintained jurisdiction over E&P waste and had an existing regulatory framework, USLL believed that the rules lacked definition, were not standardized and did not provide direction to one applying for a recycling permit. The

rules certainly did not encourage the generator to recycle its waste. In November 2005 and with the support of the RRC, USLL drafted commercial recycling rules and submitted a petition for rulemaking that USLL believed would provide consistency, uniformity of regulatory criteria and establish clear guidance for those in the E&P recycling business. USLL proposed that the rules be included in Chapter 4 entitled "Environmental Protection (4)." The rules were published in the Texas Register in June 2006 and included a 30-day comment period.

One of the most significant excerpts from the proposed rule is the definition of recyclable product. The proposed rules intend to define "recyclable product" to mean a reusable material that has been created from the treatment and/or processing of oil and gas waste as authorized by a Commission permit and that meets the environmental and engineering standards established by the permit for the intended use as a legitimate commercial product. "**A recyclable product is not a waste**, but may become a waste if it is abandoned or disposed of rather than recycled as authorized by the permit (4)". As of this writing, the rule has not been promulgated, but the intent of the language is that once an E&P waste is recycled into a product, the operator's liability is greatly minimized and essentially eliminated as now the recycler is responsible for the product it manufactures.

In the interim, an operational decision was made by USLL to move forward with a "Road Base" Pilot Project at the USLL Rincon facility and lay the ground work for a full scale recycling operation. To get started, USLL applied for and received a minor permit while concurrently applying for a full commercial recycling permit in addition to its existing commercial disposal permit. The key issues in the minor permit were to 1) protect the environment; and 2) manufacture a product that met engineering and environmental specifications.

In addition to the RRC regulations and requirements, TxDOT has an established program for accepting recyclable products for the use in road construction. This program includes engineering and environmental specifications that must be achieved.

The DMS-11000 (5) governs the process for evaluating the environmental factors associated with nonhazardous recyclable materials (NRMs) not addressed in other TxDOT specifications.

TxDOT's approval criteria for the use of a NRM product is dependent on two factors:

1) Engineering – product must meet applicable department engineering specifications and other engineering evaluations deemed necessary by the TxDOT

2) Environmental – poses an acceptable level of potential environmental risk, following an evaluation of its environmental characteristics

NRM Product Approval Process:

To be eligible for use on TxDOT projects, the NRM product must:

- meet all applicable department engineering specifications and other engineering evaluations deemed necessary;

- contain only NRMs that meet the standards listed under Item 6, "Control of Materials," Article 6.9, Recyclable Materials of the Standard Specifications for Construction and Maintenance of Highways, Streets, and Bridges;
- contain only NRMs that are managed and protected from loss, as would be raw materials, ingredients, or products;
- be used without the need for short-term or long-term management, such as special worker protection precautions, deed restrictions or notices (i.e., institutional control requirements associated with the reuse of contaminated media as discussed in 30 TAC 350.36), tracking, monitoring, special handling after the project life, or special engineering controls;
- not present an increased risk to human health, the environment, or waters in the state when applied to the land or used in products that are applied to the land.

The DMS-11000 provides for an eligibility process. In the process, bench scale recyclable products must be formulated, developed and manufactured and extensive tests performed on those products. The product specified by the TxDOT--Special Specification 3157.

Recyclable Product Development

With the markets established, the regulations identified and the product specified, the recyclable product development began. USLL selected Raba Kistner, an engineering, environmental consulting and construction management company located in San Antonio, to perform bench scale tests. Mix designs were created by experienced, non-biased engineers, which included the comparison of various drilling waste/asphalt mixtures with traditional mix designs. The development goal was to meet engineering specifications, comply with environmental criteria and maximize the use of treated waste material in the final recyclable product. As per USLL's RRC minor permit, the product criteria were as follows:

PARAMETER	LIMITATION
Compressive Strength by Method Tex-126-E	35 psi minimum
Hveem Stability by Method Tex-208-F	35
SPLP by EPA Method 1312	
Metals	
Arsenic	<0.50 mg/l
Barium	<100.00
Cadmium	<1.00
Chromium	<5.00
Lead	<5.00
Mercury	<0.20
Selenium	<1.00
Silver	<5.00
Benzene	<0.50

1:4 Solid: Solution 7 Day Leachate Test (LA 29-B Method)

Chlorides		<700.0
TPH		<100.0
pH	(Standard Units)	6 – 12.49

TxDOT, Special Specification No. 3157 required:

- Minimum requirements for compressive strength shall be 35 psi for secondary roads and 50 psi for primary highways.

- Minimum requirement for Hveem stability shall be a stability value of 35.

- Asphalt content shall be determined according to product specific mix design requirements.

- Gradation,

Sieve Size	Percent
1 3/4 inch	100
No. 4	60* maximum
No. 40	50* maximum

* at the discretion of the Engineer

To meet the above criteria, Raba Kistner proposed a formulation that included a course aggregate, a pozzolon, an asphalt emulsion in addition to the E&P treated waste material or NRM. The aggregate is a native caliche located nearby the repository. The pozzolon consisted of cement kiln dust and commercial asphalt emulsion.

As per the DMS-11000, a recyclable product can be compared to "traditional material being replaced." The R3 Product was compared in side-by-side engineering and environmental comparisons to materials such as:

- "SS-1h mixture", a product prepared to TxDOT 3157 (i.e., oil field materials, native caliche, pozzolon and an asphalt emulsion binder). SS-1h is a water based asphalt emulsion containing no VOC or solvents.

- "MC-30 mixture", a product prepared to TxDOT 3157 (i.e., oil field materials, native caliche, pozzolon and an emulsified asphalt). MC-30 is a "Cut Back" emulsified asphalt, commonly used by TxDOT, which contains a medium weight petroleum hydrocarbon and used as a "Cut Back Solvent."

- "Type-D mixture", a hot mix asphalt prepared to TxDOT Type D specifications.

After extensive testing, the laboratory results proved that the bench scale recyclable products met or exceeded the minimum engineering and environmental requirements identified by all regulatory agencies.

Recyclable Product Application

Encouraged by the successful bench scale testing, USLL established a recyclable product launch. With the permits in place and customers established, the program began by sourcing experienced personnel in the management and operations of mixing plants and recycling projects, securing full scale equipment such as a crusher, screens, pugmill, feed bins, radial conveyors, weighting systems, silos, etc.

The setting for the R3 project (the "project") was at the USLL Rincon facility in Starr County. Over its history, this facility has disposed over 180,000 cubic yards of waste materials into its landfill cells. USLL's proposal was to incorporate the treated, nonhazardous oil field materials into specified grades of commercially viable asphalt paving products based on TxDOT Special Specification 3157 and Item 345 Modified Cold Mix/Cold Laid Asphalt Stabilized Base Course. USLL utilized the TxDOT DMS-11000 Guidelines to demonstrate that the subject products will meet these criteria and be protective of the environment, public health and the waters of the State of Texas.

Work and QA/QC Plans were drafted as part of the DMS-11000 submittal and internal operation documentation. The USLL QA/QC Plan was designed to document that the NRM Product passes TxDOT defined "acceptable level of potential environmental risk", and conforms to the DMS-11000 Eligibility Criteria. The QA/QC Plan was designed as a risk management tool and as an in-house check list that provides defensible documentation of the product's environmental and engineering characteristics. The objective of this plan is for all R3 Product to be warranted to comply, as much as practical, with project specific and overall TxDOT and TRRC requirements.

The NRMs to be excavated from the repositories for use in the R3 Product have data on file indicating that they are nonhazardous in accordance with the RRC analytical requirements of the USLL minor permit. The NRM sampling and testing protocol for the Pilot Project followed the RRC guidelines. Beyond the Pilot Project, the sampling and testing protocols will be amended as prescribed by TxDOT DMS-11000.

USLL emphasized that no R3 Product may be used on-site, or transported off-site, until engineering test data and environmental analytical reports have been received, reviewed and signed off by trained senior USLL staff at the site of production and that any R3 Product transported offsite would be documented on a Bill of Lading.

The Pilot Project is scheduled for the Fall of 2006 and will generate a production volume of 4500 tons. The R3 Product will be utilized on a Starr County road, a TxDOT production lot and for road materials within the USLL Rincon facility. Beyond the Pilot Project, it is intended to explore other potential materials that can be used as aggregates such as recycled asphalt pavement, cutlets, ceramic, and crushed concrete, to name a few.

CONCLUSION

USLL firmly believes that exploration and production waste streams must be handled as a waste first and its solids be treated to an acceptable compliance limit before using it as a feedstock for any application. It is also believed that the regulatory landscape must acknowledge that when a waste is properly recycled into a commercially viable product that the generators' liability is absolved.

The RRC proposed rule making for commercial recycling is taking E&P generators and the waste industry closer to achieving those goals.

When manufacturing a recyclable product, the environmental and engineering analysis must prove that the product is cost effective, meets or exceeds the engineering requirements of the traditional materials being replaced and is environmentally acceptable, complying with the permits and requirements of all three regulatory agencies, the Railroad Commission of Texas, the Texas Commission on Environmental Quality and the Texas Department of Transportation.

Environmental recycling projects will not succeed without market sustainability. The market demands a quality product. No product, no market. The USLL R3 Process is based on an "Engineering First" principle. By following sound business management procedures, maintaining client relations, working with suppliers and buyers as a team, then recycling oil field waste can be a beneficial path forward to the current waste management practices.

The purpose of the USLL R3 Technology was to develop processes to manufacture engineered and environmentally sound recyclable product from treated exploration and production waste and encourage recycling for use as levee and road base materials. It is believed that the R3 Process meets those goals.

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3. RRC Surface Waste Management Manual - Application Information for Permit to Treat Oil and Gas Waste for Use as Roadbase
4. Railroad Commission of Texas, Chapter 4. Environmental Protection, Subchapter B, Proposed new rules in new Subchapter B, commercial recycling
5. Texas Department of Transportation, Environmental Manual, DMS-11000 Evaluating and Using Nonhazardous Recyclable Materials Guidelines, (August 2004)

CALCULATION OF ENERGY REQUIREMENTS AND AIR EMISSIONS FOR DRILL CUTTINGS MANAGEMENT

Diana García and Mukesh Kapila, M-I SWACO

Residual drilling fluids and cuttings represent a large volume of wastes generated from drilling operations. In order to reduce potential environmental impacts, recycling and waste treatment options are employed. Different factors such as economic, operational and environmental limitations are involved in selecting the best technology for a particular area.

Drilling waste management is the planning and implementation of a cautious waste collection, treatment and disposal plan. Within the planning, detailed analysis of the treatment and disposal options is performed. This analysis evaluates the feasibility, potential liability, energy requirements, air emissions and cost of treatment and disposal options.

The objective of this project is to model and analyze the energy requirements and air emissions of various waste management systems which would allow the user to evaluate the most suitable option for the management of drilling waste. While the model can accommodate numerous possible combinations of equipment and methodologies of managing drilling waste, four examples are presented in this paper.

ENERGY CONSUMPTION

The energy calculations are based upon fuel consumption (in terms of fuel usage rate) of the equipment and activities associated with each part of the drilling waste management process including collection to final disposal or treatment method. The fuel consumption was calculated by multiplying the time of equipment operation by the fuel consumption rate specific to the activity or equipment involved. In situations where power is generally supplied, a generator running on diesel fuel was used to calculate emissions. This may not be applicable in all applications but provides a conservative calculation of emissions and energy consumption along with an easy side-by-side comparison of the various drilling waste management methods. The following sections present the assumptions and methodology used to calculate energy consumption. Calculations were made for an offshore project as well as an onshore project.

Discharge (Offshore)
If the cuttings are considered low environmental risk and depending on local regulations, they can be disposed into the sea in certain regions. However, most require some pre-treatment to reduce the oil-on-cuttings to less than 6.9% by volume on a wet weight basis. The model uses the energy requirements of the discharge method based on the operation time of the cuttings dryer equipment required to reduce the fluid content of the cuttings.

Injection
In the injection process, the cuttings are converted into slurry, which is then pumped into a receiving formation at pressures exceeding the fracture gradient. For cuttings injection, the energy consumption was based on the circulating pumps used in the slurrification process; the injection pump and the generator fuel consumption.

Haul to Shore (Offshore Project)
Three different options to haul the cuttings to shore where analyzed: cutting boxes, dense phase conveying and slurry. The number of supply boat trips required to haul the waste to shore was calculated based on the capacity of the boat, in terms of the number of cutting boxes or volume, according to the desired option. The total energy consumption calculation includes the distance traveled by the boat, allowances for maneuvering, idling and loading operations at the drill site and in-port activities at the dock. Fuel requirements for cranes also were taken into account where applicable, using estimates of crane handling capacity.

For the dense phase conveying method, the calculations were based on the vessel capacity, the time to fill and the diesel compressor fuel consumption. For the slurry method, calculations were based on circulating pumps rate and diesel generator fuel consumption.

Haul to Facility
Once the cuttings are hauled to shore, estimates were made for the transportation to the facility and the disposal site. Total drilling waste volumes were used to determine the number of truck trips required. This calculation, in conjunction with the distance traveled between the port and the facility and disposal site, enabled the calculation of fuel usage.

Pre-Treatment
Some waste management methods require or are suitable for pre-treatment of the cuttings resulting in an overall volume reduction requiring less intensive treatment or disposal. There are a number of pre-treatment methods and it is not practical to model all of them. However, for the purpose of modeling, an allowance for the pre-treatment has been made by utilizing the cuttings dryer equipment where liquid/solids separation minimizes fluid content of cuttings and thereby possibly recovering valuable drilling fluid and minimizing overall volume that requires further disposal or treatment. For simplicity, the model does not take into

consideration the offsetting energy and emissions of any recovered fluid in the pre-treatment step.

Disposal

Disposal is considered as a non-treatment option. The number of truck trips necessary to dispose of the waste was calculated based on the truck capacity and the distance to the disposal site. The use of land-spreading equipment at the disposal site was based on the waste volume and the activity of the equipment.

Solidification

The solidification is considered as a non-treatment option. The waste is mixed with a material (activated lime, kiln dust, fly ash, cement, etc) to form a solid product that immobilizes potential contaminants. The energy requirements for this option were calculated based on the fuel consumption of a diesel generator and the number of processing days.

Waste-Soil Mixtures

Waste-Soil Mixtures is considered a non-treatment option. It consists of mixing the waste with soil or subsoil to decrease the concentration of potential contaminants. The chemical properties of the waste are adjusted to meet regulatory standards. Energy consumption for this non-treatment option was calculated based on the number of processing days and the use of land-spreading equipment.

Thermal Desorption

This process applies heat to cuttings to separate and recover hydrocarbons drilling wastes. Thermal desorption is a separation and recovery process resulting in three streams: water, oil and solids. The heating volatilizes liquid and the vapors are cooled and separated into water and oil phases. The water phase is used to cool and return moisture to the solid stream; the oil phase can be recovered and made into a new drilling-fluid system or used as a fuel source, while the solids could be disposed of or reused. Energy consumption for this treatment option are based on generator fuel consumption, processing rate of the thermal desorption equipment and burners fuel consumption. For thermal desorption equipment that do not utilize burners to generate heat such as hammer mill technology, the equivalent fuel used by a generator to drive the rotor is used for simplicity.

Bioreactor

Biodegradation using a slurry bioreactor is a process that employs indigenous bacteria from topsoil that utilize the base oil as a primary carbon source. The cuttings will biodegrade rapidly when slurried with water, oxygen and nutrients. Factors to monitor during the bioreactor process include aeration, mixing, nutrients and bacteria colony strength. Energy consumption

for the bioreactor was based on diesel generator fuel consumption and processing rate to degrade the drilling waste.

Composting

This process consists of mixing the cuttings with a solid organic substance that is degradable (e.g. straw, wood chips, livestock bedding) and nutrients such as animal manure, to ensure the optimum carbon:nitrogen ratio. The blended material is placed in small heaps in long rows. Energy consumption for composting was based on diesel generator fuel consumption and number of treatment days.

Vermiculture

In this technique, worms are used to aid the decomposition process in biodegradation. The worms eat the waste and bacteria in the worms' intestines degrade the organic components. The residue is excreted as worm cast which acts as a soil improver and fertilizer. Energy consumption was based on the number of treatment days and diesel consumption of the equipment used.

Landfarming

In this technique, the cuttings are applied to a soil surface and plowed to ensure adequate mixing and aeration. The rate of degradation is controlled by using the correct levels of nutrients, soil moisture and air. Energy consumption was based on the number of treatment days and fuel consumption of the equipment used.

AIR EMISSIONS

Air emissions of operations associated with each of the methods are estimated using emissions factors related to the production of air pollutants to the period of time that the equipment is operated and the amount of fuel consumed. The calculations involve emissions factors for nitrogen oxide (NO_x), total hydrocarbons (THC), sulfur dioxide (SO_2), carbon monoxide (CO) and total suspended particulates (TSP).

Carbon dioxide (CO_2) emissions were also included in the calculations. For the biodegradation methods, the calculations include the emissions of methane (CH_4) as part of the THC emissions. Tables 1 and 2 show the categories and emissions factors used.

Table 1. Emission factors for cuttings management activities						
Category	Emission Factors					
	Units	NO_x	THC	SO_2	CO	TSP
Supply boats						
Transit	lb/gal	0.3917	0.168	0.02848	0.0783	0.033
Maneuvering	lb/gal	0.4196	0.226	0.02848	0.0598	0.033
Loading/Unloading	lb/gal	0.4196	0.226	0.02848	0.0598	0.033
Demurrage	g/bph-hr	14	1.12	0.931	3.03	1
Barge transit	lb/gal	0.3917	0.168	0.02848	0.0783	0.033
Supply boat crane	g/bph-hr	14	1.12	0.931	3.03	1
Barge crane	g/bph-hr	14	1.12	0.931	3.03	1
Trucks	g/mile	11.23	2.49	N/A	8.53	N/A
Wheel tractor	lb/hr	1.269	0.188	0.09	3.59	0.136
Dozer/Loader	lb/hr	0.827	0.098	0.076	0.201	0.058
Diesel Generator	g/bph-hr	14	1.12	0.931	3.03	1
Source: Table IX-4, EPA-821-B-0-013. December, 2000						

Table 2. Emission factors for greenhouse gases

Table 2. Emission factors for greenhouse gases[1]		
Category	Units	Factor
Diesel emission factor for CO_2	tonne CO_2/kWh	0.00025
Bioremediation emission factor for CO_2	tonne CO_2/tonne waste	0.00888
Bioremediation emission factor for CH_4	Tonne CH_4/tonne waste	0.00527

EXAMPLES

Four different scenarios were used as examples to illustrate the functionality of the model. Two of these examples were run for an offshore project and two for an onshore project. The scenarios are:

Offshore Scenario 1. Cuttings are pretreated using the cuttings dryer on site and then discharged or injected.

Offshore Scenario 2. Cuttings are pretreated using the cuttings dryer on site, and then hauled to shore using the dense phase conveying method. Two treatment options are analyzed: Thermal Desorption and Composting.

Onshore Scenario 1. No pretreatment on site is applied to the cuttings. The cuttings are hauled using cutting boxes. Three different options are analyzed: Solidification, Waste-Soil Mixtures and Thermal Desorption.

Onshore Scenario 2. Cuttings are pretreated using the cuttings dryer and hauled to either a disposal facility or an injection site.

The main operating assumptions used for the scenarios are presented in Table 3:

Table 3. Basic operating assumptions

Description	Value	Units
Total waste generated	1,500	bbl
Boat capacity	3,000	bbl
Boat round trip distance	100	miles
Truck capacity	120	bbl
Round trip distance to facility	20	miles
Treatment days for biodegradation techniques	20	days

Offshore Scenarios

For the offshore project, the following results were established.

Table 4. Energy consumption results for offshore project scenarios

Energy Results	Scenario 1		Scenario 2	
	Discharge	Injection	Thermal	Composting
Diesel consumed (gal)	57	996	9,615	5,280
Energy consumed (kWh)	2,178	37,905	365,999	200,960

Table 5. Emissions results for offshore project scenarios

Emissions Results (tonnes)	Scenario 1		Scenario 2	
	Discharge	Injection	Thermal	Composting
NO_x	0.0409	0.712	1.57	1.20
THC	0.00327	0.0569	0.362	2.84
SO_2	0.00272	0.0473	0.108	0.0826
CO	0.00885	0.154	0.342	0.261
TSP	0.00292	0.0508	0.118	0.0918
CO_2	0.544	9.48	91.5	54.5

The results for the treatment options represent the total of hauling, treatment and final disposal. The following Figures show the results obtained for the offshore project scenarios. For the thermal desorption, the graphs include also the hydrocarbons recovered in the treatment.

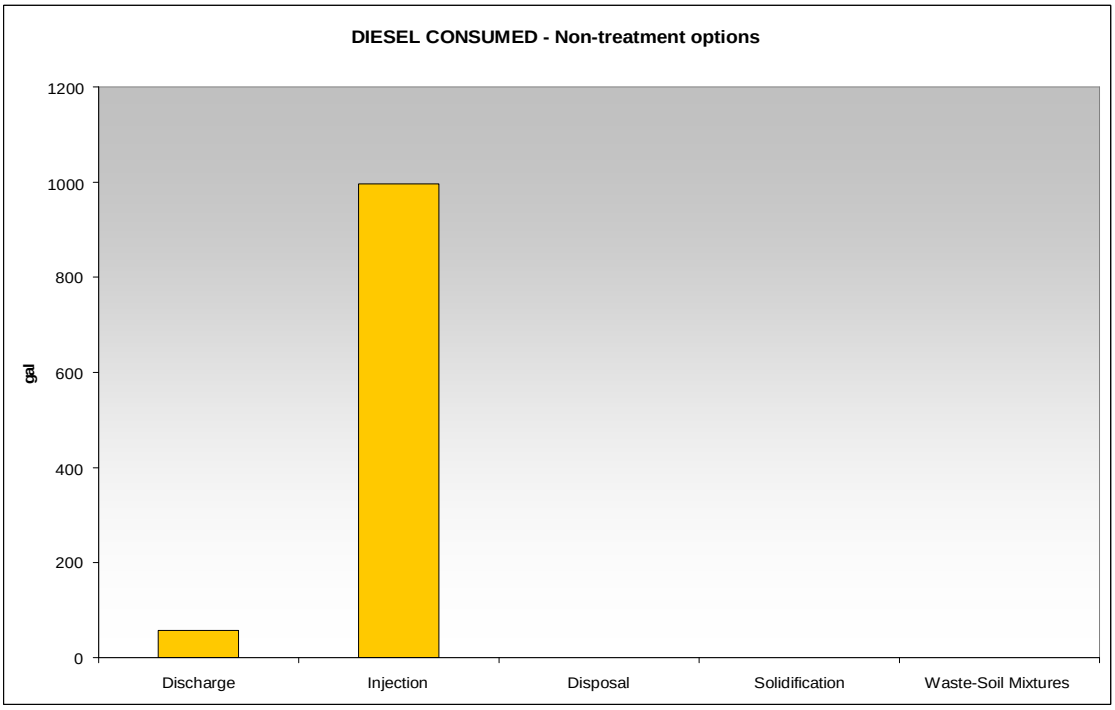

Figure 1. Diesel consumed for offshore project scenario 1.

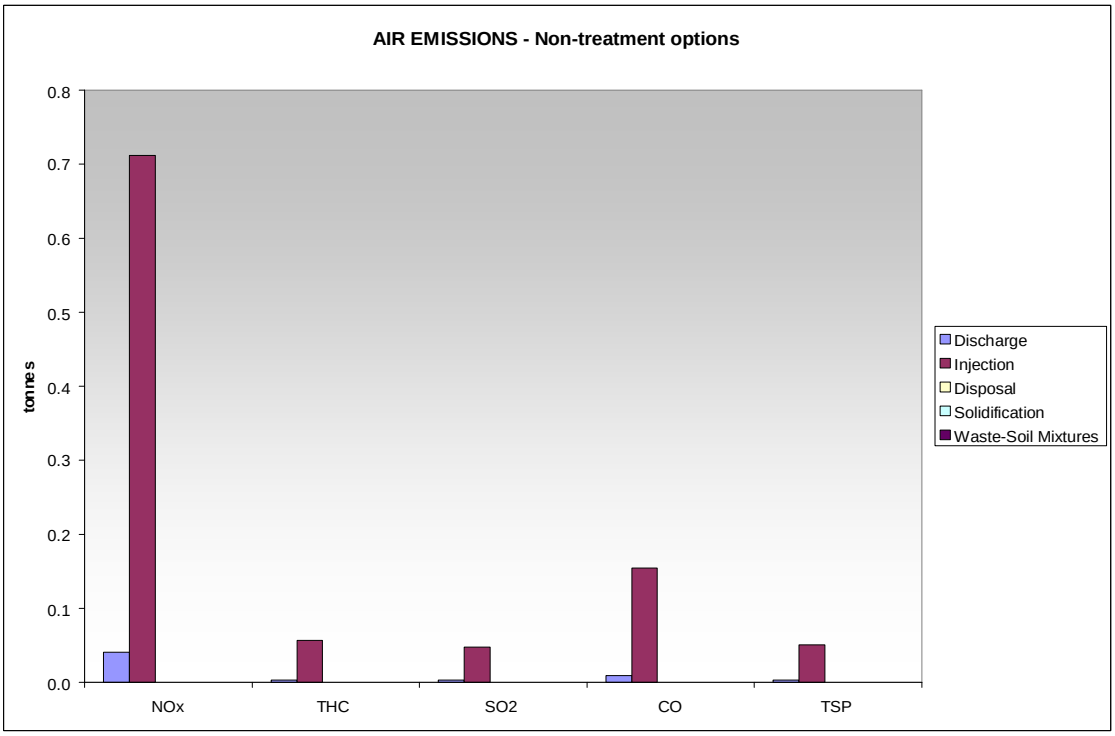

Figure 2. Emissions for offshore project scenario 1.

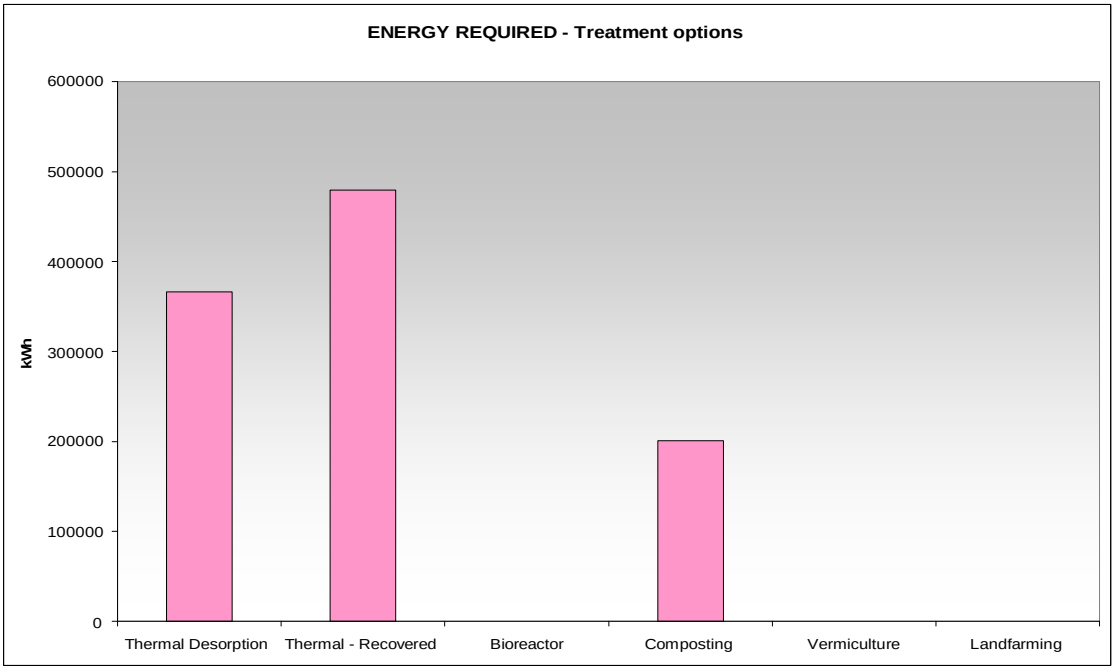

Figure 3. Energy consumed for offshore project scenario 2.

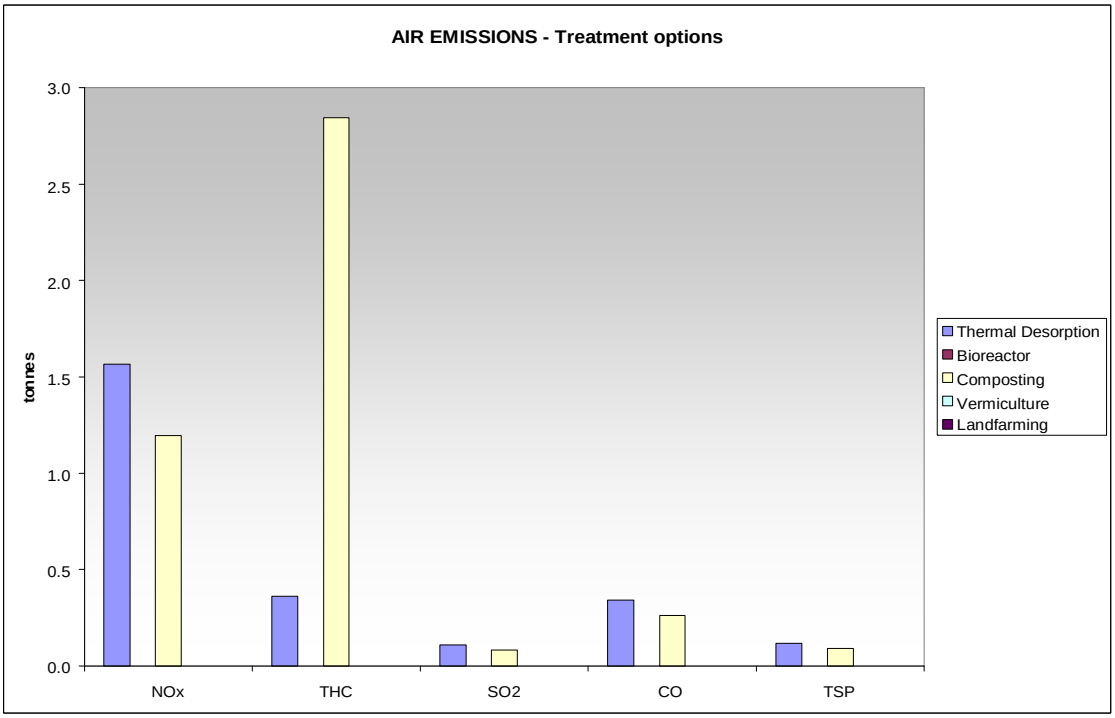

Figure 4. Emissions for offshore project scenario 2.

Onshore Scenarios

For the onshore project, the following results were established:

Table 6. Energy consumption results for onshore project scenarios

Energy Results	Scenario 1		Scenario 2	
	Solidification	Thermal	Injection	Disposal
Diesel consumed (gal)	1,934	5,989	1,309	1,155
Energy consumed (kWh)	73,601	227,982	49,813	43,962

Table 7. Emissions results for onshore project scenarios				
Emissions Results (tonnes)	Scenario 1		Scenario 2	
	Solidification	Thermal	Injection	Disposal
NO_x	0.390	0.759	0.789	0.0641
THC	0.0291	0.0599	0.0616	0.00537
SO_2	0.0263	0.0517	0.0521	0.00410
CO	0.112	0.193	0.173	0.0432
TSP	0.0278	0.0541	0.0560	0.00426
CO_2	18.4	57.0	12.5	11.0

The following Figures show some of the results obtained for the onshore project scenarios.

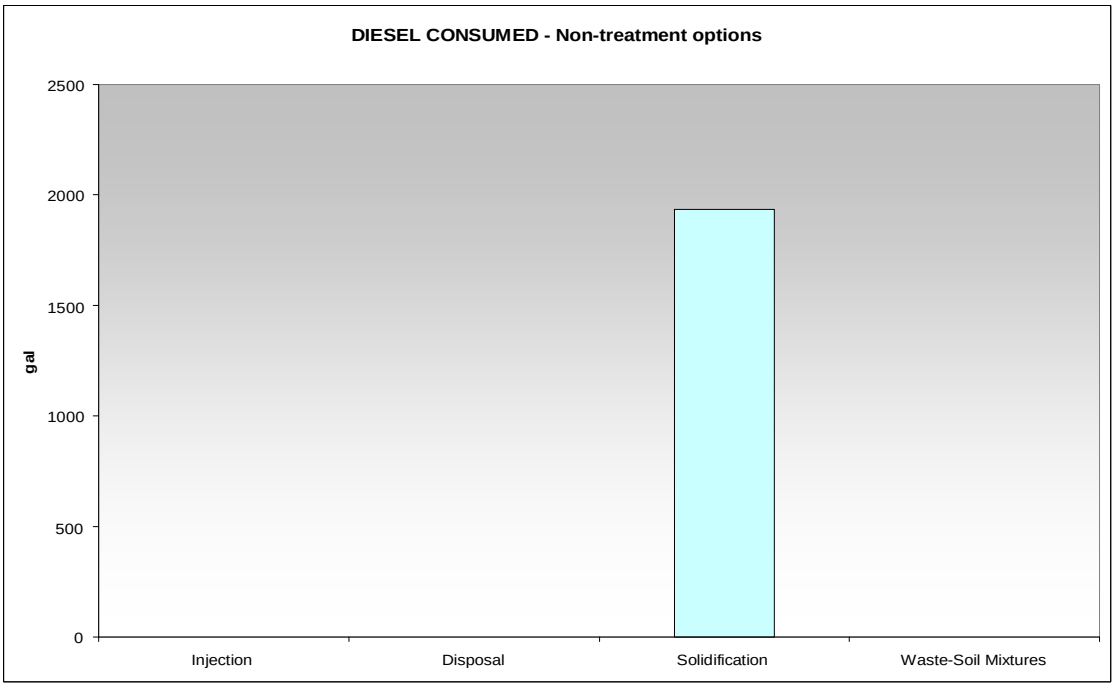

Figure 5. Diesel consumed on solidification for onshore project scenario 1.

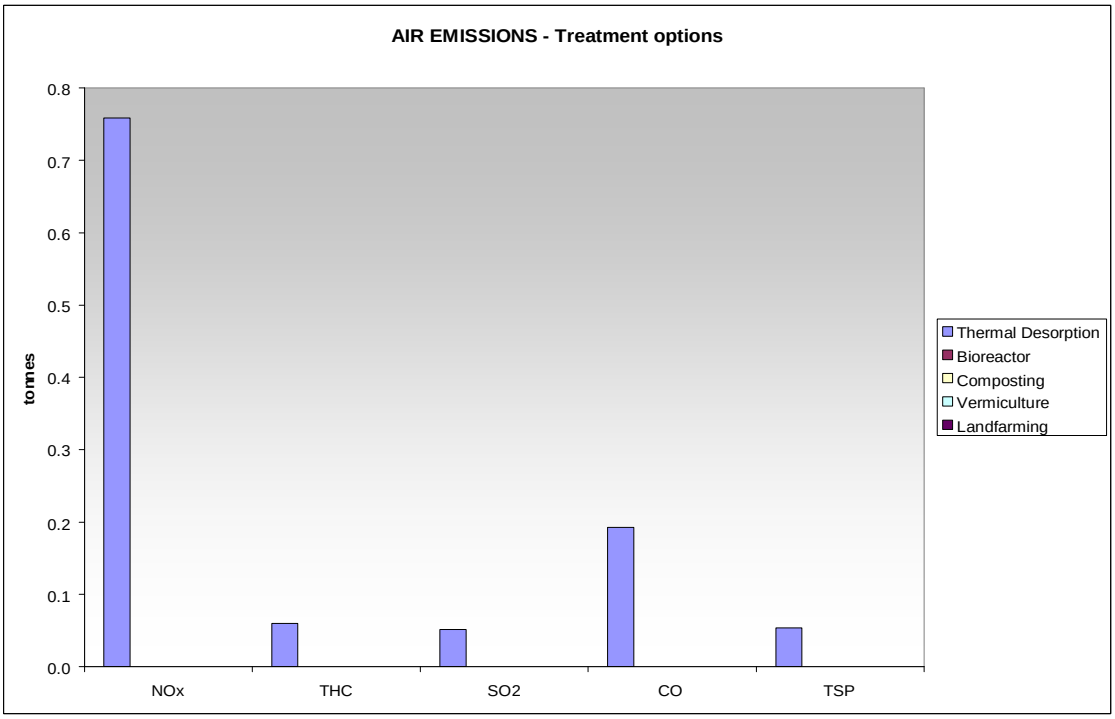

Figure 6. Emissions related to Thermal Desorption for onshore project scenario 1.

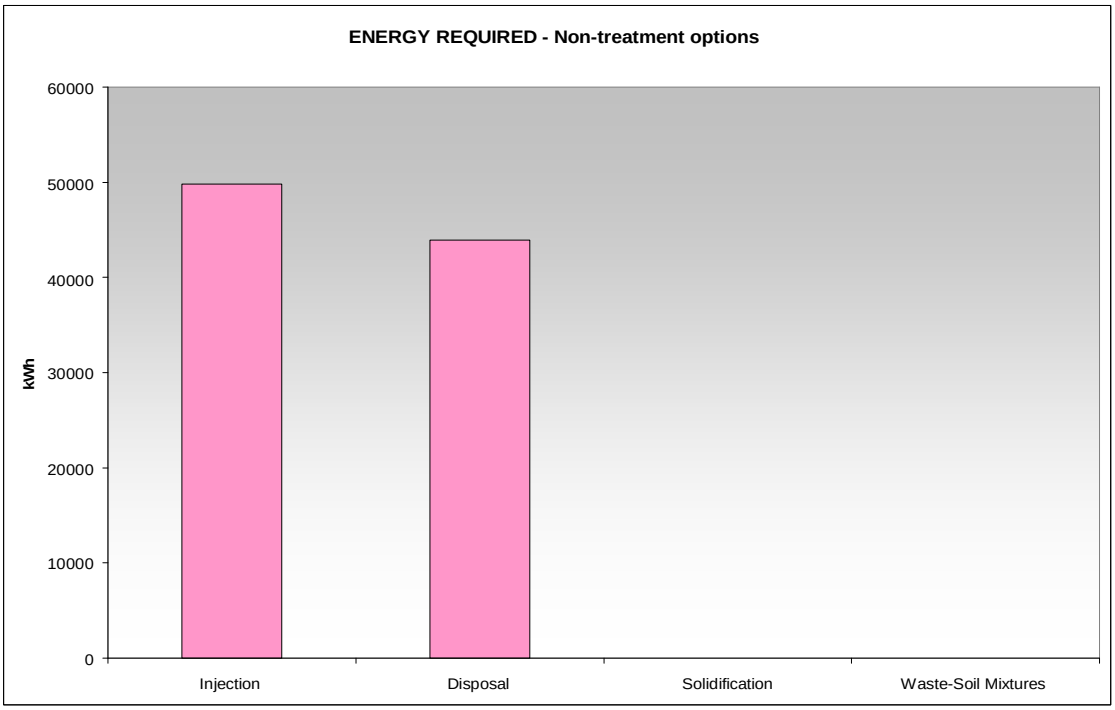

Figure 7. Energy consumed for onshore project scenario 2.

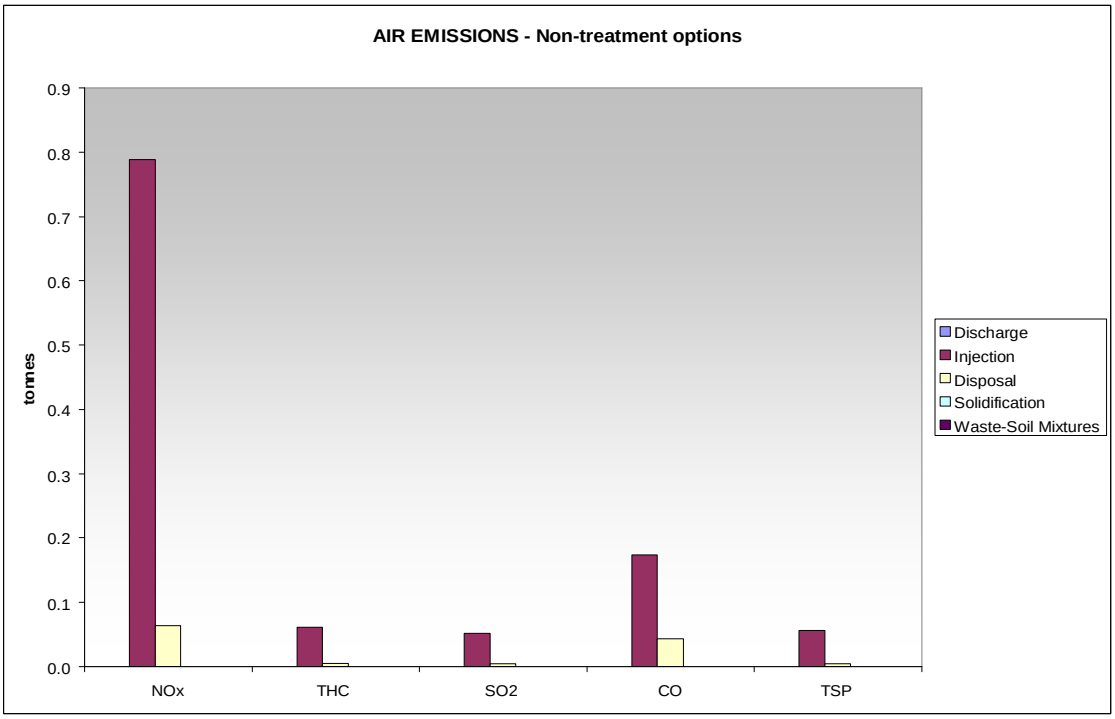

Figure 8. Emissions for onshore project scenario 2.

REMARKS

The model provides an excellent tool to analyze energy requirements and air emissions for a number of combinations, giving the user the possibility to compare between the different options and techniques available for waste management. It could be extensively used in places were diesel/energy consumption or certain environmental regulations become an important factor when evaluating the drilling waste management.

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Theoretical and Practical Models for Drilling Waste Volume Calculation with Field Case Studies

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ABSTRACT

The volume of drilling waste generated when drilling a well is an important and costly factor, especially when the waste must be transported, treated, or disposed off-site. This paper discusses various methods for calculating or estimating the volume of drilling waste generated, both onshore and offshore. The various methods are compared to a mathematical computer model that has been developed. Field case studies are used to illustrate the techniques and their accuracy or reliability.

DISCUSSION

There are a number of methods that can be used to estimate the amount of waste generated from drilling operations. One method is to use offset well information normalized to the specific well to project the amount of waste that could be expected on the future well. Once the offset data is collected and the waste information determined, the waste data is normalized by comparing it to the hole volume. In some cases, the waste data must also be normalized by time, as well, to account for other factors, such as storm water and process wash and cooling water.

There are several sources of well data that can be used to estimate the waste. These are:

- Pit volume
- Fluid deliveries
- Mud usage mass balance
- Waste hauling data

All of these methods require some pre-planning in order to effectively use them.

The amount of waste can also be estimated by using recently developed computer programs. These programs require the user to understand certain principles, but can be used to predict the effects of changing conditions on waste generation.

Estimating Volume in an Earthen Pit

When drilling an exploration or production hole onshore, earthen reserve pits are frequently used. While serving many purposes, one of the primary purposes is to collect and hold all of the drilling associated waste generated from the drilling operation. From that standpoint, estimating the amount of material contained in the pit is an estimate of the waste generated during drilling, assuming that the pit only contains drilling waste.

The method used to estimate the volume of waste in the pit is similar to gauging a tank to estimate the amount of fluid in the tank. First the empty pit volume must be known. At the final condition (after drilling) the volume of empty pit is determined. The difference is the estimated volume of waste.

This may seem an easy exercise at first; however pits are built in a wide variety of shapes. Besides the common rectangular shape, there are variations with a wall or levee down the middle. These are referred to as “horseshoe” pits. In the horseshoe pit, the solids are discharged into one end of the horseshoe. Sludge and fluid flow towards the other end with solid particles settling along the way. Fluid is recovered at the opposite end of the horseshoe. There is also a double horseshoe design, where there is an inner horseshoe pit and an external horseshoe pit. This configuration is designed to hold two different types of fluid, such as fresh water and brine.

One example of a pit investigation where the amount of waste contained in earthen reserve pits was performed in Wyoming. In this case, a single horseshoe pit was being used on a single well drilling location. The basic mode of operation was “circulating the pit”. In this system, an initial load of “reserve” water is brought to the pit. Conventional mechanical solids control equipment is not used (or is by-passed). Instead, returning fluid laden with drilled cuttings particles is discharged directly to the earthen reserve pit. The pit is designed to allow the low gravity solids to settle in the first part of the pit. Fluid continues to flow to the “deep” end, allowing solids to settle along the way. Fluid is recovered at the deep end and re-used in the drilling process. A diagram of this type of pit is shown in Figure 1.

This type of pit is constructed with sloped walls. The walls slope 2 feet horizontally for every foot of drop. This is commonly expressed as a 2:1 slope. This type of slope helps prevent wall sloughing or, in the case of plastic liners, it helps prevent puncturing.

One way to model the contents of this type of pit is create a spreadsheet that calculates the average content from one segment in depth to another. This method is shown in Figure 2. For a two-segment pit, such as the horseshoe pit, the fluid side segment and the solid side segment can be handled separately or one side can be doubled to obtain the total volume. Figure 3 shows the volume calculation for the example case in Wyoming.

In the Wyoming case, the pit surface dimensions were 160 feet by 90 feet. The depth was 12 feet, but the outage was 4 feet immediately after drilling. This means the pit was filled with 8 feet of material. In Figure 3 one can see that the total volume is estimated to be 16,840 barrels (2,677 cubic meters). Figure 4 shows a picture of the fluid side of a pit immediately after usage. Figure 5 shows the same pit on the solid (discharge) side.

In viewing this example, one can see that the estimate could easily be off by as much as 1,000 barrels. Notice for instance the solids delta formed in the upper right of Figure 5. This is a rough field estimate. It is perhaps more important to examine the purpose of making this estimate. The estimate is only useful in determined how much waste is generated in comparison to the hole volume drilled. In the example case, 762 barrels of hole volume was drilled. The estimated ratio of waste volume to hole volume is 22.1. For similar type of drilling where waste was removed from the location, volume ratios of as low as 5 have been recorded. The conclusion is that the “circulate the pit” method creates a large volume of waste (mostly water) that must be handled.

At the time this estimate was made, drilling operations consisted of single wells with single pits. The trend was toward multiple well pad drilling operations. This meant that pits would be used to hold the waste from multiple wells located on a single pad. If the “circulate the pit” method was used, then one could anticipate a very large pit being required, since multiples of a single well waste generation could be expected. If 10 wells were drilled at a ratio of 22 times hole volume, then almost 168,000 barrels of waste could be anticipated. If those same 10 wells were drilled at a ratio of 5 times hole volume, then only about 38,000 barrels of waste would be generated.

Estimating Volume from Fluid Deliveries

In some cases, the pit volume estimate does not work well. This may be because the pit construction details are not known or because the pit is used for several functions. In some areas, for instance, wells are immediately stimulated and flow is returned to the pit. In this case, waste volume can be estimated from the hole volume and fluid (water) deliveries to the location.

The theory in using this technique is that all fluid or water delivered to the location is used in the drilling process as either process water (wash water or cooling water) or drilling fluid. All of this fluid eventually ends up in the pit. The cuttings or earthen particles from the well bore also end up in the pit. So, if these two volumes are added, they should total the volume of waste left in the pit.

Figure 6 shows a summary of fluid deliveries to wells in West Texas’ Permian Basin. These wells are similar to the wells in Wyoming, in that they use the “circulate the pit” method. Two types of wells are shown. One type is a relatively deep well while the other type is similar to the Wyoming wells. Water deliveries are taken from delivery tickets supplied by the water hauling contractors. This makes the collection of data simple and easy for the drilling personnel.

Again, the primary conclusion that can be drawn from this data is in the relationship of estimated waste to the hole volume. In both types of well shown the ratio is about 20 times the

hole volume. While the data may be somewhat rough, it is accurate enough for most drilling purposes.

There are some cases in which water is not delivered by truck to the drilling locations. Some wells use water wells, either on-site or off-site (with water being delivered by pipeline). In these cases, a water meter can be used to measure deliveries. It is also possible to deliver the water to a tank and gauge usage each day by monitoring fill and usage. This method is similar to fuel usage on most drilling rigs. This method is certainly more difficult than the others due to the amount of water consumed.

Estimating Volume by Mud Usage Mass Balance

A technique often used in offshore drilling with non-aqueous fluid (NAF) is the mass balance on the mud system. In this system whole mud or fluid is delivered to the rig for usage. Mud may also be made on the rig. The amount of mud used is the difference between what is delivered or made and what is returned. This approach is shown in Figure 7. The amount of waste anticipated is the amount of mud used plus the amount of hole volume.

This system works on the theory that mud is lost with drilled solids being discarded. This may not always be the case. Some mud is lost in a variety of other ways. Some contractors perform the mass balance and, then try to "account" for the fluid lost by guessing at the other sources of loss. Unfortunately this tends to skew the waste estimate to an unrealistically low volume.

Figure 8 shows the fluid loss summary for a series of wells on a platform using NAF. The fluid usage numbers ignore any "accounting" by the service company. Waste generated while drilling with NAF has been recorded in the past to average between 2.5 and 3.5 times the hole volume. In Figure 8 the average estimated waste is 2.6 time hole volume. The wells were drilled in numeric order, so the trend of decreasing waste to hole volume is also significant. The indication is that with experience they were able to decrease waste amount by increasing solids control efficiency or drilling efficiency. These numbers were not tracked during the actual drilling operations, though, so the trend was likely missed.

Estimating Volume with Waste Hauling Data

The most reliable method, although it is not without fault, is to track waste by waste hauling data. One would think that this method is entirely accurate, but that would be in error. The fact is that waste being transported in boxes or tanks is still subject to error. Previous record comparisons between those kept at the rig and those maintained by the disposal company show significant variations. The most likely reason is simply not estimating the correct volume in each container, but sometimes whole containers are missed or assigned to the wrong well.

If planned correctly, each box is recorded along with the estimate of the volume or weight that it contains. Since weight is not usually available, volume is most frequently used. If pre-planning is not done, then the delivery records can still be used to estimate the amount of waste, but with a degree of uncertainty. If the total containers are known, then an estimated average amount per container is generally used. The sensitivity of the numbers can be obtained by using slightly larger or smaller amounts per container.

Figure 9 shows the summary of waste volume transported from the same platform as above, using an average "guessed" volume. The volume used was 15 barrels. The highest considered volume per container was 18 barrels. The lowest volume considered was 14 barrels. The volume obtained by this method was almost 37,000 barrels or 2.4 times hole volume. The

range could have been 20% higher or 7% lower. This would have yielded waste volumes from 34,000 barrels to 44,000 barrels (2.2 to 2.9 time hole volume).

The comparison of Figures 8 and 9 is interesting. First, the two methods used to estimate waste are relatively close. There is only about 5% difference using the two different methods. Second, the ratio of waste to hole volume using the fluid usage method showed a declining trend. There is no such trend using the waste hauling method. It is possible that some boxes of waste filled while drilling one hole (or interval) could have been attributed to another hole.

It has been suggested that the fluid mass balance method be applied to drilling discharges while drilling with NAF. These are not estimated now, but could be estimated in this manner in the future. When comparing waste volumes hauled to waste volumes by fluid usage, the effect of loss of circulation should be considered. Loss of circulation would result in higher fluid usage volumes, but would not be reflected in haul-off volumes. The same is true of discharge estimates where loss of circulation results in no discharge, but would result in increased mud usage. Loss of circulation "accounting" was not removed from the above fluid usage estimates and would have reflected somewhat lower waste volumes with the fluid usage technique.

Estimating Volume with Computer Predictions

Recently, computer tools have been developed that can predict waste volumes. These programs must be used by experienced users. If the wrong assumptions are made, then waste volume estimates could be grossly in error.

Almost all mud usage and waste volume calculations use the same theory. The theory is based in water-based mud technology. In that technology, formation solids come to the surface, where some are separated by solids control equipment and some are left in the mud. The determination of each fraction is some form of solids control removal efficiency. The solids being discarded along with associated drilling fluid is recognized as a portion of waste. The amount of drilling fluid required for dilution (and some form of dumping to make room for the dilution) is determined by the tolerance of the mud to drilled solids or low gravity solids.

All of these terms are used by all of the programs, although they may be expressed in different fashions. The expression is usually dependent on the point of view of the person developing the program. If the person is performing mud engineering calculations, then the emphasis may be on dilution volumes. The waste planning programs emphasize discard volumes, which are the sum of the liquid discards (to make room for dilution required) and solid discards from the solids control system (with associated fluid).

The programs currently being used can be simple or very complex. The more they try to mimic the way the system is being run, the more complex they become. The problem is that the solids control and drilling fluid system is extremely complex and prone to upsets. Any predictive system relies on a steady-state.

The same system is used with non-aqueous fluids (NAF) despite the fact that mud is not dumped with these systems. Adjustments to the normal factors can result in accurate waste volume estimates, but the logic is difficult to defend. Complicating this issue even further is the compliance test being used in the Gulf of Mexico. The compliance test indicates that best practices are being used to reduce the amount of NAF on discharged cuttings. This number does not indicate the volume of waste, but is frequently erroneously related to waste volume.

One computer program used to estimate waste volume is called "Providus" from Chevron. In this program, hole sizes and depths are input to determine the hole volume. Solids control efficiency, low gravity solids tolerance of the mud system and mud retention on discarded solids are used to estimate the waste volume in a simple model.

Figure 10 shows a waste volume estimate based on one of the wells using non-aqueous drilling fluid from the example platform used previously. Data from well #4 is used in the

program. The solids control efficiency used is high reflecting typical characteristics with NAF. The NAF tolerance to solids is also high. Retained mud on cuttings is low, as is typical. The waste estimate is 4,600 barrels or 2.7 times the hole volume (typical of NAF usage and waste generation). The two methods used from offset records indicated from 4,000 to 4,900 barrels of waste generated.

The circulating the pit method can also be estimated with a little ingenuity. In this case, the solids control efficiency is zero reflecting the lack of solids control. Since the fluid being returned to the mud is plentiful, a low concentration of low gravity solids (LGS) is used. The results are shown in Figure 11. The results from the computer model show that the ratio of waste to hole volume is anticipated to be 20:1. This is a close fit to the other offset records methods, but in reality is tricking the program some. The truth is that much of the waste comes from loading the pit with “reserve” water prior to beginning drilling. The pit acts as a one-gravity settling device that is somewhat efficient. But the results are the same.

FIGURES

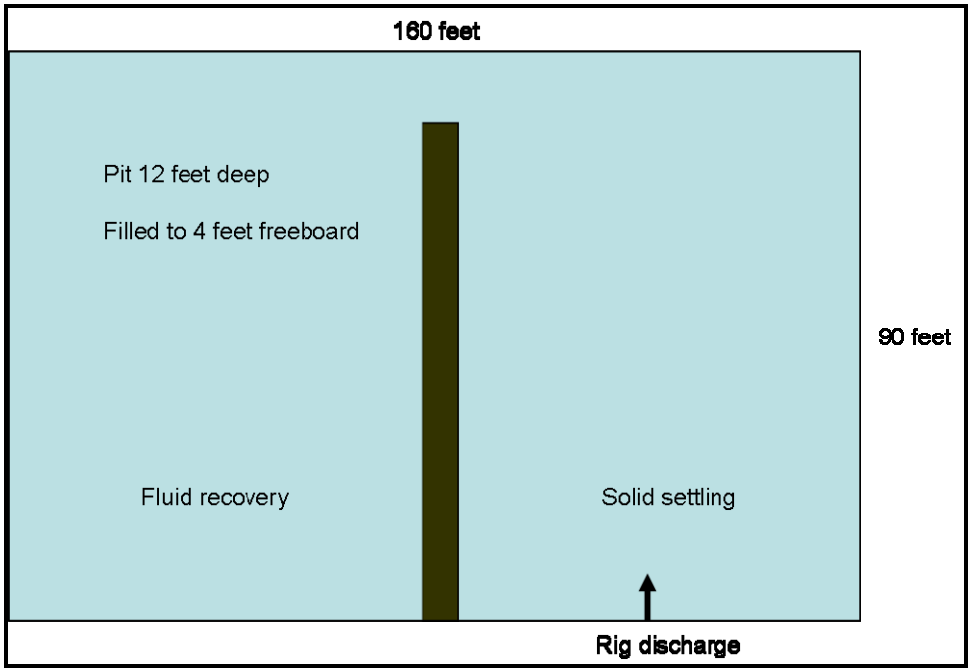

Figure 1. Single well pit being used in circulating the pit mode

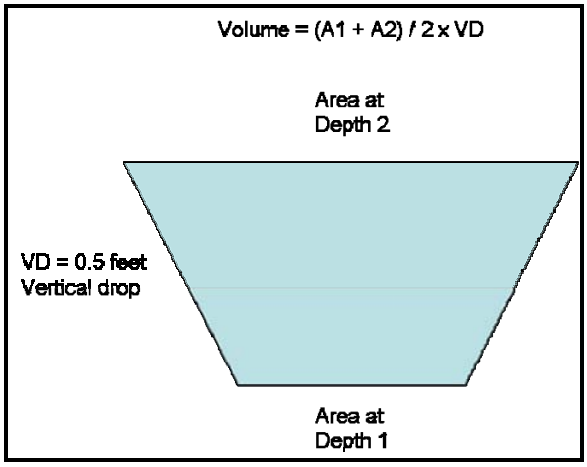

Figure 2. Volume calculation method for trapezoidal areas

	Depth (ft)	Length (ft)	Width (ft)	Square (sq.ft)	Ave Vol of section	Cum Cap. (bbls)		
0.0	0.0	90.0	80.0	7,200				
0.5	0.5	89.5	79.5	7,115				
1.0	1.0	89.0	79.0	7,031				
1.5	1.5	88.5	78.5	6,947				
2.0	2.0	88.0	78.0	6,864	3,411	10,806	← Capacity	
2.5	2.5	87.5	77.5	6,781	3,370	10,199		
3.0	3.0	87.0	77.0	6,699	3,329	9,599		
3.5	3.5	86.5	76.5	6,617	3,288	9,006		**Total Volume**
4.0	4.0	86.0	76.0	6,536	3,248	8,420	← Outage	**16,840**
4.5	4.5	85.5	75.5	6,455	3,208	7,842		
5.0	5.0	85.0	75.0	6,375	3,168	7,270		
5.5	5.5	84.5	74.5	6,295	3,128	6,706		
6.0	6.0	84.0	74.0	6,216	3,088	6,149		
6.5	6.5	83.5	73.5	6,137	3,049	5,599		
7.0	7.0	83.0	73.0	6,059	3,010	5,056		
7.5	7.5	82.5	72.5	5,981	2,971	4,520		
8.0	8.0	82.0	72.0	5,904	2,933	3,991		
8.5	8.5	81.5	71.5	5,827	2,895	3,468		
9.0	9.0	81.0	71.0	5,751	2,857	2,953		
9.5	9.5	80.5	70.5	5,675	2,819	2,444		
10.0	10.0	80.0	70.0	5,600	2,781	1,942		
10.5	10.5	79.5	69.5	5,525	2,744	1,446		
11.0	11.0	79.0	69.0	5,451	2,707	958		
11.5	11.5	78.5	68.5	5,377	2,670	476		
12.0	12.0	78.0	68.0	5,304	0	0		
12.5	0.0	0.0	0.0	0	0	0		
13.0	0.0	0.0	0.0	0	0	0		
13.5	0.0	0.0	0.0	0	0	0		
14.0	0.0	0.0	0.0	0	0	0		
14.5	0.0	0.0	0.0	0	0	0		
15.0	0.0	0.0	0.0	0	0	0		

Figure 3. Volume calculation for Wyoming pit

Figure 4. Fluid side of Wyoming pit after usage

Figure 5. Solid (discharge) side of Wyoming pit after usage

Well	Hole Volume (barrels)	Fluid Delivered (barrels)	Estimated Waste Volume (barrels)	Ratio	Average Ratio
1	1,083	26,910	27,993	25.8	
2	1,083	20,840	21,923	20.2	
3	1,083	24,070	25,153	23.2	23.1
4	718	12,930	13,648	19.0	
5	718	13,180	13,898	19.4	
6	718	13,340	14,058	19.6	19.3

Figure 6. Summary of fluid deliveries and estimated waste in West Texas

To starting volume

Add volume received

Add volume built

Subtract volume removed

Subtract ending volume

Total is volume used

Figure 7. Mud mass balance approach

Well	Hole Volume (barrels)	Fluid Used (barrels)	Waste Estimated (barrels)	Ratio (W:HV)
1	1,694	4,219	5,913	3.5
2	2,939	6,570	9,509	3.2
3	1,610	1,628	3,238	2.0
4	1,714	3,211	4,925	2.9
5	2,042	3,074	5,116	2.5
6	1,754	2,166	3,920	2.2
7	1,503	1,586	3,089	2.1
8	1,935	1,395	3,330	1.7
Total	15,191	23,849	39,040	
Average				2.6

Figure 8. Fluid usage volumes used to estimate waste volume

Well	Hole Volume (barrels)	Waste Transported (barrels)	Ratio (W:HV)
1	1,694	3,675	2.2
2	2,939	7,230	2.5
3	1,610	4,830	3.0
4	1,714	3,990	2.3
5	2,042	5,205	2.5
6	1,754	4,155	2.4
7	1,503	3,435	2.3
8	1,935	4,365	2.3
Total	15,191	36,885	
Average			2.4

Figure 9. Waste hauling data using estimated likely waste volume per container

« Return | Solids Control Efficiency | Math Calculator | Help | Waste Volume Calculator

Interval Number	Bit Size	Mud Type	Depth In	Depth Out	Interval Length	SCE %	Max. %LGS	Ratio Mud	Ratio Solids
1	16.000	O	1,913	4,111	2,198	85	15	1	1
2	12.250	O	4,111	12,117	8,006	85	15	1	1
3									
4									
5									
6									

For mud type enter **W** for water-based mud or **O** for oil-based mud (NAF)

	Water-Based Sections	Oil-Based Sections
Hole Volume	0	1,713
Waste Generated	0	4,624
Fluid Lost/Used	0	2,912
Ratio - R	0.0	2.7

Figure 10. Computer estimate of waste using NAF

« Return | Solids Control Efficiency | Math Calculator | Help | Waste Volume Calculator

Interval Number	Bit Size	Mud Type	Depth In	Depth Out	Interval Length	SCE %	Max. %LGS	Ratio Mud	Ratio Solids
1	11.000	W	0	1,200	1,200	0	5	1	1
2	7.875	W	1,200	10,300	9,100	0	5	1	1
3									
4									
5									
6									

For mud type enter **W** for water-based mud or **O** for oil-based mud (NAF)

	Water-Based Sections	Oil-Based Sections
Hole Volume	689	0
Waste Generated	13,778	0
Fluid Lost/Used	13,089	0
Ratio - R	20.0	0.0

Figure 11. Computer estimate of waste using circulating the pit

Analysis of Drilling Fluid Base Oil Recovered from Drilling Waste by Thermal Desorption

Paper and Presentation Prepared for 13th International Petroleum Environmental Conference, San Antonio, Texas, October 16th – 19th 2006.

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Abstract

In 2005 Halliburton began preparations for a major drilling waste management program. Instead of discharging drilling waste to the environment, the operator decided that oil-based mud cuttings would be brought to a central waste treatment facility and treated using thermal desorption technology. This technology reduces the residual oil on cuttings to a more acceptable level prior to disposal. In addition, the operator planned to use the thermally recovered base oil to build new drilling fluid.

Thermal desorption technology has been used widely in drilling cuttings processing; however there has been some concern expressed over the quality of oil recovered and its suitability for re-use. This has been a particular concern when using highly refined, ultra low aromatic, highly saturated, mineral- or synthetic- based oils. The issue is that the thermal energy required to distill enough hydrocarbons from the cuttings to render them suitable for disposal may result in some cracking or other thermal degradation of the base oil. It also may create aromatics and other undesirable unsaturated hydrocarbons that will adversely affect the toxicity and possibly even the performance of the drilling fluid.

As a result of these concerns, Halliburton and DuraTherm began a series of tests using the actual drilling fluid formulations and products that would be used in the field. We also used a pilot scale mini thermal desorption unit to recreate as closely as possible actual field conditions. The recovered base fluids then were analyzed for aromatic and unsaturated hydrocarbon content and suitability for reuse as drilling fluid. This paper will describe the results of the tests and operating conditions chosen for the project based on this testing.

Introduction

A major operator awarded a drilling waste management services contract to Halliburton in November 2005. The contract covered multiple drilling rigs, that combined would generate at least 50,000-75,000 MT per annum of cuttings contaminated with oil-based drilling fluid. In 2005, the cuttings were being discharged to the environment along with an estimated 12,500-18,000 m^3 (77,000-113,000 bbl) of drilling fluid base oil. While the environmental impact of this discharge was mitigated by the use of compliant oil-based

fluid, the economic impact in terms of loss of base oil was significant. Therefore, the operator elected to tender for thermal desorption services. Upon award of the contract, the operator requested that Halliburton define operating specifications for the DuraTherm thermal desorption technology that would optimize throughput and capacity and yet ensure that the oil recovered would be suitable for re-use in the drilling fluid. In response to that request, Halliburton and DuraTherm began the testing and analysis required to meet these objectives.

Thermal Desorption Technology

The use of thermal desorption technology or thermal desorption units (TDUs) to recover oil from drill cuttings has been well documented in the industry[1,2] and a detailed study of all available technology and processes was published by Halliburton in 2004.[3] In summary, thermal desorption of oil from drilling cuttings for environmentally acceptable disposal of the cuttings was identified as an option in the early 1990s. The technology used for this purpose evolved significantly in the intervening years. In Europe and South America, the processed cuttings typically measure less than 1% of Total Petroleum Hydrocarbons (TPH) before disposal in landfills and this was the target selected for the subject project.

Regulatory agencies in other areas have also set standards for the levels of TPH in cuttings prior to disposal or discharge to the environment. Some processes do not require thermal desorption technologies. For example, in the Gulf of Mexico the discharge of cuttings with TPH levels of either 6.9% or 9.4% by weight, depending on the synthetic oil selected, is allowed if other toxicity and biodegradation standards are met or exceeded. These levels of oil on cuttings can be attained with mechanical systems. However, the trend in environmental regulations is toward greater stringency and therefore an increased demand for minimal TPH levels in treated cuttings will drive the development of more oil-removal technologies.[4]

All thermal desorption processes evaporate the oil and water from the cuttings. The heat required to evaporate the oil and water provides enough energy to remove and separate emulsified oil as well. Free and emulsified oil and water are removed by distillation, and in the process, water evaporates first to produce steam. Oil has a higher boiling point and evaporates after the water. The production of steam can also assist in lowering the boiling point of oil.

The goal is to produce oil-free (or ultra-low TPH) solids for disposal by distilling off oils from the cuttings and recovering oil to be re-used for drilling fluid.

Base Oil Selection

The base oil for this project was selected in advance of the decision to use thermal technology and had been proven very effective in the drilling operation; therefore there was no option or consideration to change the fluid. The base oil is a highly refined

alkane (paraffin), 87% branched or cyclic, and contains no aromatic or unsaturated hydrocarbons. The physical properties of the fluid are summarized in Table 1.

Minimum molecule size	C12
Maximum molecule size	C24
Saturation*	100%
Aromatic content	0%

*100% saturation is stated on product MSDS, however testing of laboratory samples of base oil showed very small levels of unsaturated compounds (0.069%) – see Table 3.

Table 1. Physical properties of alkane base oil

Some cracking of base oils has been reported during thermal desorption operations, and some shift in analyses and the creation of new molecules such as aromatics has been shown to occur during thermal desorption. This shift and the creation of aromatics and other unsaturated compounds may negatively affect the toxicity of the fluid, making exposure more hazardous for personnel, and even negatively affect the performance of the drilling fluid.

Thermal cracking temperature is a function of molecule size. Larger molecules crack at lower temperatures. Hydrocarbons that are used as the base oil for drilling fluids contain relatively short-chain, small molecules that do not crack at the temperatures normally reached in thermal desorption units. Carbon compounds in the C20 to C30 range, of which some existed in this fluid, can crack at temperatures as low as 650°F (343°C). Further, some long-chain and large-molecule drilling fluid additives may also be present and could crack. It is also possible some drilling fluids additives may act as catalysts and lower the temperature at which cracking may occur. Therefore, the documented shift to lower-weight molecules may be the result of the cracking of crude in the cuttings, the cracking of additives or the cracking of the base oil itself.

When this shift is small, the oil is still reusable as a medium for makeup of drilling fluids and some loss of the volatiles created can be expected. This loss probably occurs on the shale shaker screens and other areas where the cuttings are exposed to the atmosphere. The loss of volatiles in turn raises the flash point of the recovered oil, which is often higher than that of the virgin base oil.

Laboratory Testing and Results

The first step of testing was to establish the baseline Gas Chromatogram (GC) analysis for the base oil. This was done by DuraTherm and Halliburton independently and also supplied by the operator as part of the tender documents. An example of the GC analysis of the base oil is shown as Figure 1.

The next step was to determine the boiling point of the oil and therefore the operating temperature of the thermal unit. The material safety data sheet (MSDS) provided indicated that the dry boiling point of the oil was 620° F (327° C) and this was verified in laboratory testing (Table 2). As the testing indicated that only 90-93% of the oil would be recovered at the originally proposed operating temperature of 600° F, it was decided to run the tests at 650° F. If these were unsuccessful the tests would be repeated at 625° F.

However, operating the unit at a lower temperature so close to the actual boiling point of the oil would increase the required cuttings residency time in the TDU and therefore could negatively impact treatment rates. From a process perspective, the best scenario was to operate at highest possible temperature without cracking the oil.

IPB	492° F
5%	498° F
10%	502° F
20%	512° F
30%	520° F
40%	528° F
50%	538° F
60%	546° F
70%	560° F
80%	572° F
90%	594° F
93%	608° F

Table 2. ASTM D-86 Method for Distillation of Petroleum Products

Once the initial operating temperature for the TDU process was set at 650° F, the next stage was to determine the optimal sweep inside the TDU. The options included 1) using nitrogen (removing oxygen from process) or 2) using the steam sweep that DuraTherm recommended and had used in their drill cuttings operations to date. The decision was made to use a lab-scale TDU to test both scenarios measure their effect on the recovered oil.

Once the operating parameters were agreed, Halliburton prepared a relatively simple, lab standard, 80/20 oil water ratio drilling fluid using the selected base oil and sent this to DuraTherm' facilities in San Leon, Texas. DuraTherm then mixed the fluid with sand to simulate cuttings. They ran the samples under the different conditions through their unique mini desorber at 650° F and collected and analyzed the oil samples. These samples were also sent back to Halliburton's Houston laboratories where the analysis was repeated.

DuraTherm's mini desorber is an electrically heated, insulating heat jacket surrounding a quartz tube that allows DuraTherm to recreate field TDU conditions in the laboratory (Figure 2). Ten years experience with the mini desorber indicates minimal difference between the laboratory and field results. In some cases the field results may be better because the field unit works under a slight negative pressure, which slightly reduces the boiling point of the oil.

In a process closely resembling that used with TDU units in the field, DuraTherm was able to split the recovered oil from the mini desorber into two phases: V1 and V2, representing two collection points within the TDU. Usually V1 and V2 oils are combined and re-used. However, as it was felt that V1 oil would have the least thermal degradation a sample of V1 oil was also provided to Halliburton for additional testing and analysis.

The data provided by DuraTherm is presented in Table 3. The base oil tested was the combined V1 and V2 recovered oil.

Compound	Lab Standard	Nitrogen Sweep	Steam Sweep
Unsaturated Hydrocarbon	692 ppm 0.069%	4664 ppm 0.466%	1484 ppm 0.148%
Aromatic	0 ppm 0%	2733 ppm 0.273%	612 ppm 0.061%

Table 3. DuraTherm results of mini desorber tests

Further analysis of the oil by Halliburton focused on V1 fluid. As much as 85% of the fluid was in the V1 cut. It was possible that an even cleaner product could be recovered and re-used as drilling fluid, while the V2 fluid, if not needed or desired, could be blended with diesel and burnt as fuel for the TDU. Table 4 shows the results for aromatic content of the recovered oils when analyzed by Halliburton and Figure 3 shows the n-alkane distribution pattern.

Compound	Lab Standard	V1 Only	V1 and V2
Aromatics	0.0%	0.01%	0.04%
Oxygenated hydrocarbons (<=C8)	0.0%	0.02%	0.10%
C8 Olefins	0.0%	0.0%	0.05%

Table 4. Analysis of recovered oil

Following discussion of this data with the operator, the formulation of the selected drilling fluid was raised as a point of concern as particular additives used in the operations could crack or act as catalysts. If this were the case, then it was necessary to rerun tests using the same products.

A "typical" formulation was agreed with the operator and the fluid mixed at Halliburton's Houston laboratory. The tests were re-run by DuraTherm with the steam sweep. Table 5 shows the formulation that was submitted to DuraTherm and Table 6 shows the primary fluid properties.

Product	**Concentration m^3 or kg/m^3**
Base Oil	0.625
Primary Emulsifier	7.1
Secondary Emulsifier	15
Lime	28.5
Wetting Agent	7.5
Water	0.122
Viscosifier	28.5
Suspension Agent	15
Filtration Control Agent I	17.5
Filtration Control Agent II	17.5
Mud Conditioner	2.5
LCM I	25
LCM II	10
Sweep Material	0.12

Bridging Agent	10
Barite	480
Calcium Chloride (97%)	26.6

Table 5. Formulation submitted to DuraTherm

Plastic Viscosity at 120° F, cP	34
Yield Point at 120° F, lb/100 ft^2	18
10 Second Gel. lb/100 ft^2	11
10 Minute Gel. lb/100 ft^2	20
Electrical Stability, Volts	494
Oil / Water Ratio	85/15
Water Phase Salinity, mg/L	200,000
Mud Density, lb/gal	10.9
Calcium Chloride (97%)	26.6

Table 6. Fluid properties

This fluid was then mixed with sand to recreate cuttings tested in the mini desorber by DuraTherm. The results are presented in Table 7.

Compound	Standard	Nitrogen Sweep	Steam Sweep	Steam Sweep 2
Unsaturated Hydrocarbon	692 ppm 0.069%	4664 ppm 0.466%	1484 ppm 0.148%	360 ppm 0.036%
Aromatic	0 ppm 0%	2733 ppm 0.273%	612 ppm 0.061%	821 ppm 0.082%

Table 7. Results of mini desorber tests including new formulation

Results

In summary, the oil recovered by the TDU process was determined to be suitable for re-use in the drilling fluid.

The laboratory standard base oil sample was 99.931% saturated. Nitrogen stripping resulted in a fluid with 99.533% saturated compounds and steam stripping resulted in a fluid with 99.85% saturated compounds. The lab standard contained no aromatics, while fluid recovered with steam stripping had an aromatic content between 600-800 ppm depending on the fluid formulation used. This represents a very small change in the fluid (six- to eight-hundredths of one percent).

Conclusions

Testing and analysis showed that the thermal desorption technology selected for this project and processes recommended by Halliburton and DuraTherm could meet the target TPH of <1% and that the recovered oil would be suitable for re-use as drilling fluid base oil. The testing also gave Halliburton operating parameters that could be implemented in the field to prevent any significant cracking of the oil and ensure suitability for re-use. Based on this analysis, a maximum TDU operating temperature of 650° F has been selected and the TDU will operate under the steam sweep recommended by DuraTherm.

It is expected that the field units will give better results than the mini desorber for a number of reasons, including the ability to control temperature in the actual TDUs much more accurately, improved control of the steam sweep and the existence of a slight negative pressure inside the field TDU.

It should also be noted that multiple treatments of the oil will not degrade the oil any further. Over time the unstable, volatile compounds will most likely be lost to the atmosphere during circulation of the drilling fluid or they will crack further to gases and be consumed within the TDU.

Oil quality in the field will be closely monitored at Halliburton's laboratory on location. Adjustments can be made as needed, including the isolation of the V1 oil which, with just 0.01% aromatics, has a slightly better profile than the V1+V2 oil combined. The V2 oil can then be burned as fuel for the TDU if necessary.

It was observed during the testing that certain characteristics of base oils would make some fluids more suitable for thermal recovery than others, and that base oils could be chosen for projects that could actually lower the thermal energy required to reach the target of <1% TPH. This would reduce operating costs and also the volume of emissions generated by the thermal processes.

Subsequent to completing this study, Halliburton began an in depth study of many different base oils used in drilling fluids, details of which will be published in a later paper including a recommendation for a "thermal desorption fluid" specifically designed to be recovered via thermal desorption with minimal break down or change in the fluid properties.

Acknowledgements

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Figures

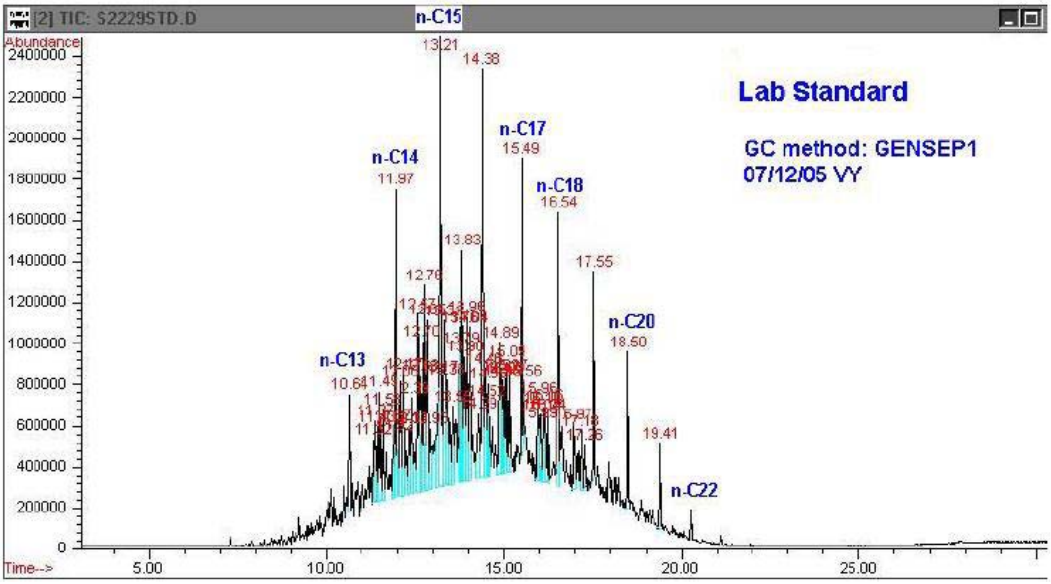

Figure 1. GC/MSD data for base oil

Figure 2. DuraTherm mini desorber

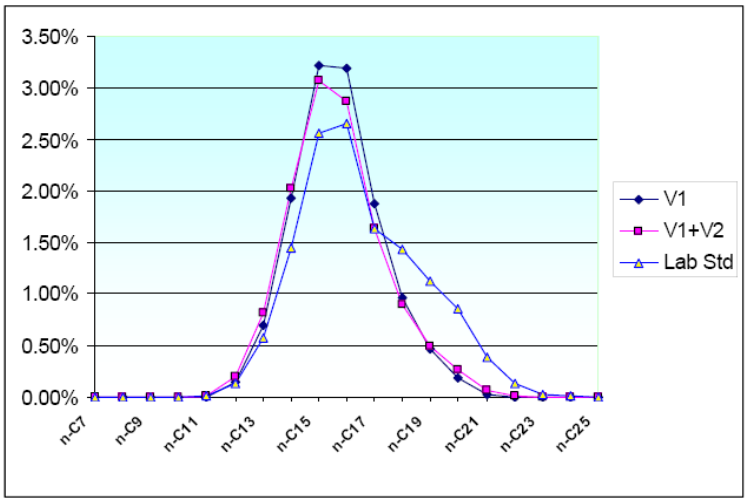

Figure 3. Distribution of n-alkanes in V1, V1 and V2 combined and the laboratory standard base oil.

ORGGANOCLAYS CAN CUT THE COST OF CLEANUP OF PRODUCED WATER, WASTEWATER AND GROUNDWATER BY 50%

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ABSTRACT

Organically modified clays (organoclays) are well known to the oil well drilling industry where they are used as viscosifiers of the drilling mud and to prevent fluid loss. What is less known is that they have been used for some 20 years for the cleanup of water, and lately, as components of permeable barriers and for sediment stabilization.

Their primary function is to remove organic compounds of low solubility from water, particularly oil, creosote, PNAH's and PCB. It is well understood that activated carbon is susceptible to blocking of its pores by large organic hydrocarbons of low solubility such as the ones mentioned above. Organoclays remove oil from water at seven times the rate, as does activated carbon. Similar removal capacity advantages occur with other compounds such as PNAH, PCB, chlorinated phenols and others. The best system for the removal of fuels and BTEX's from water is the organoclay/carbon system, because the organoclay will preferentially remove toluene and xylene leaving the GAC free to remove benzene, thus preventing the "roll off" phenomena. Lastly, the organoclays also remove small amounts of heavy metals from water.

This paper will discuss organoclays, what they are, how they work, and present laboratory data and case histories.

INTRODUCTION

When bentonite or other clays and zeolites are modified with quaternary amines they become organophilic. Such modified bentonites are used to remove mechanically emulsified oil and grease and other sparingly soluble organics. If the organoclay is granulated, it is placed into a liquid phase carbon filter vessel to remove FOG's and chlorinated hydrocarbons. In this application the clay is mixed with anthracite to prevent the early plugging of the filter by oil or grease droplets. In batch systems a powdered organoclay is employed.

Organoclay removes mechanically emulsified oil 500% to 700% more effectively than activated carbon alone. Oil and grease and other large sparingly soluble chlorinated hydrocarbons and NOM's (Natural Organic Matter) and PNA's (Polynuclear Aromatics) blind the pores of activated carbon (and ion exchange resins and membranes) reducing its effectiveness significantly. It is, therefore, economically advantageous for the end user to pre-polish the water before it enters carbon vessels. Operating costs can often be reduced by 50% or more.

NATURE OF ORGANOCLAYS

Organoclays consist of bentonite modified with quaternary amines. The major constituent of bentonite is the clay mineral montmorillonite which has an ion exchange capacity between 70-90 mg/gram. The nitrogen end of the quaternary amine is exchanged on the clay surface, rendering the clay organophilic. This means that swelling in water is minimized but swelling and gelling in organic fluids such as diesel fuel, gasoline, and others is greatly enhanced. This ability has resulted in the use of organoclay powders as thickeners in paints, greases, lubricants, etc. When organoclay is placed into water, the amine chains will stand up and extend into the water. As mechanically emulsified oil, fats, greases, and lubricants pass by these chains, they partition into the organics holding the organics by coulombic forces (Electrostatic, Van der Waal). This activity takes place at the surface of the clay platelets, in contrast to activated carbon, where adsorption takes place inside the pores. When an oil droplet or some other large organic molecule is passed through an activated carbon column, the droplet will either fill the pore or sit on top of it, blinding the carbon and preventing removal of such items as VOC's, which is the reason for using carbon in the first place. The blinding of the carbon results in frequent change outs, making recycling of the water uneconomical. The end user may simply choose to have the water hauled away by tanker truck. An example of a tank car wash operation looks as follows: A company spends $2,000 a month on water at an average cost of $2.00 per 1,000 gallon. It uses about one million gallons per month. This water is probably hazardous, so the company pays another $0.12/gal for hauling charges amounting to $120,000 per month. The total cost is now $122,000 a month.

The reason the company would not run the water through carbon columns is because there are some 10 ppm of oil in the water. Now if they first pass the water through an organoclay column, at a flow rate of 25 gpm, 24 hrs a day, 7 days a week, it would only require 2000 lbs. of organoclay per year in a vessel 4 feet in diameter with a 3 foot 6 inch bed depth. The total capital cost would be about $5000.00, and if they decided to add one or two activated carbon vessels, the capital outlay would only be approximately $15,000.00. Considering that most of the effluent water can be recycled, eliminating hauling altogether, it is obvious how quickly such a system would pay for itself.

The organoclay/anthracite system blends organoclay with anthracite to prevent early clogging of the pores, and when blended, they remove 50-60% of their weight in oil. Common applications for water treatment with organoclay are: Ground water remediation, wood treatment (creosote), boiler feed water, storm water runoff, heavy equipment and vehicle cleaning, industrial waste water, and any water that contains oil and grease.

Organoclay is used as a post polisher to oil/water separators and as a pre-polisher for activated carbon, as well as ion exchange resins, membranes, ultra filtration systems, and air strippers to prevent fouling. Powdered organoclays are used with rotary vacuum filters and in batch treatment systems to remove traces of oil, other organics and heavy metals.

This article presents research data and case histories from different situations.

CASE HISTORIES FOR STANDARD FLOW-THROUGH APPLICATIONS

A. Ground water in an Army Corp. of Engineers site in Alaska was contaminated with diesel fuel. Three vessels filled with activated carbon were set up and ground water was passed through. The carbon lasted for two days when breakthrough occurred. The carbon was replaced and three vessels with organoclay/anthracite were placed in front of the carbon. After three months of pumping, the site was clean and neither the organoclay nor the carbon were spent.

B. A foundry in Illinois had set up a water treatment system consisting of various settling and coagulation tanks, an oil/water separator, and a sand filter followed by an activated carbon vessel. The purpose was to remove solids, oil and grease, phenolics and some heavy metals, primarily lead. When the foundry used more than 1,500 gpd of water, an event which happened frequently, they would be out of compliance with regulations which resulted in fines. To remedy the situation the sand in the sand filter was replaced with organoclay/anthracite. In spite of varying flows, the foundry has been in compliance ever since.

C. Chlorinated hydrocarbons and PCB needed to be removed from sediments of a river in western New York as part of an NYSDEC consent order. The plan was to dewater the dredged sediment and clean up the effluent water. The contractor set up two multi media sand filters, each including pea gravel to cover the laterals, grade 68 sand, plus organoclay/anthracite. This was followed by two vessels filled with activated carbon. The organoclay/anthracite removed the oils and other hydrocarbons while the carbon removed the remaining PCB. The effluent quality fulfilled all NPDES requirements and the project was a complete success at a much lower cost than if activated carbon had been used exclusively.

ORGANOCLAYS REMOVE SPARINGLY SOLUBLE CHLORINATED HYDROCARBONS

A comparison between organoclay powder and activated carbon powder in the efficiency of removing phenolic compounds is shown in Table 1.

Another case of ground water at a RCRA site in New Jersey showed similar results is shown in Table 2. The primary purpose of the organoclay/anthracite was to remove oil and protect the carbon.

In some cases the organoclay removed all the toluene. This data indicates that pretreatment with organoclay helped the activated carbon considerably in removing chlorinated hydrocarbons. If there were benzene in the water the carbon would be extremely efficient in removing all of it due to the pretreatment with the organoclay. Laboratory data is shown in Table 3.

The next case, in Table 4, shows the data from sump sludge water that was passed through an organoclay/anthracite bed.

CASE HISTORIES SHOWING PESTICIDE AND PNAH REMOVAL

A. A lab trial showed powdered organoclay to be very efficient in the removal of pesticides such as: Alachlor; Diazinon; Metolachlor; 2,4-D; Trifuralin; 2,4,5-T' and others from water. Note, these are chlorinated hydrocarbons.

B. A ground water was contaminated with 100 ppm of fuel oil, of which 10 ppm were BTX's, while the other 90 ppm consisted of polynuclear aromatic hydrocarbons such as anthrazine, naphtalene, paraffins, and waxes. Originally two activated carbon vessels were used for pump and treat clean-up. The carbon had to be changed every two weeks. Additionally, after exiting the carbon vessels, the water still had a sheen of oily material, probably paraffin and waxes, which the carbon did not remove at all. Then a vessel filled with organoclay/anthracite was placed in front of the carbon. Now the GAC is changed every four to six months while the TOC analysis shows non-detect.

HEAVY METALS REMOVAL BY ORGANOCLAY

A. Anions

Two grams of organoclay when treated with a specific amine will remove 17 ppm of arsenite from water spiked with 20 ppm of arsenite. Similar results are also achieved with selenium or hexavalent chrome. To achieve such results, specific quaternary amines must be used. However, some reduction of all of these anions is achieved when using standard quaternary amines. These results propose that partition is not the only mechanism that operates in the removal of organic compounds. Anion exchange with the chlorine end of the quaternary amine, identical to the mechanism that operates with anion exchange resins is the second removal mechanism. This theory is supported by the high removal capacity of organoclay for chlorinated hydrocarbons. Anion exchange resins use quaternary amines with exchangeable chlorine and hydroxyl ions for removal of hexavalent chrome and arsenite.

B. Cations

Table 5 shows removal of heavy metals by organoclay/anthracite from the same sump sludge water as Table 4.

Two mechanisms again seem to be responsible for the removal of heavy metal cations by organoclay/anthracite. Bentonite, after it is modified with quaternary amines, still retains some 40% of its original cation exchange capacity, or 30-40 mg/gram, allowing it to act as a cation exchange resin. There is also some evidence that the iron in the water, at a certain pH, precipitates onto the anthracite with other metals co-precipitating. A word of caution is appropriate: We do not recommend the design of a system for metals removal alone. Only 30% of the clay/anthracite mix is organoclay, thus under standard flow conditions adsorption capacity is limited. The organoclay eventually becomes coated with oil resulting in loss of its exchange capacity. This ability of the organoclay to remove metals is, however, an added benefit for the clay/carbon system.

When combined with other media, the following scenario occurred in one case: Tumble water from a plating operation contained oil and some 2 ppm of zinc. (Discharge permits require less than 1 ppm of zinc.) Two 55 gallon drums with internals were set up preceded by an oil/water separator. The first drum was filled with organoclay/anthracite and was used as a post-polisher after the oil/water separator. The second drum was filled with natural zeolite which removed the zinc. The organoclay prevented the oil from plugging the pores of the zeolite. The plating fabricator is now in compliance with regulations and the media only needs to be changed every six months.

In another finding, a foundry detected organically bound lead in its rinse water. A three-step procedure was instituted: first an organoclay/anthracite vessel was used, followed by activated carbon, and finally followed by a vessel with an anion exchange resin. It operated successfully and placed the foundry into compliance with discharge permits.

It has also been found that organoclay/anthracite is excellent in removing colloidally bound metals such as nickel and cadmium. The mechanism here is believed to involve the zeta potential of the clay resulting in adsorption rather than an exchange mechanism. The anthracite may also be involved in this phenomenon.

Furthermore, even bioremediation can benefit from pretreatment with organoclays. One situation involved a ground water containing oils. An oil/water separator was installed including a mechanism which added an emulsion breaking polymer. This was followed by a tank into which bacteria were added to remove the remaining oil and was followed by an air stripper and an activated carbon tank. Given the

relatively high flow rate, the bacteria hitched a ride on top of the oil droplets passing through the entire system and coating the media in the air stripper, rather than digesting the oil. Placing a tank filled with organoclay in front of the air stripper would have eliminated this problem. The bacteria could have eaten the oil that was collected on the organoclay (hopefully they would eat only the oil, leaving the quaternary amine in place) providing some regeneration.

MORE CASE HISTORIES

1. An organoclay wastewater treatment system was used at several natural gas compressor stations.

Oil leakage and spills, when servicing compressors together with maintenance wash down water, are being satisfactorily treated with oil removal systems that consist of a wastewater holding tank with an oil drain off valve, a coalescing oil/water separator fitted with an oil skimming weir, an effluent holding tank, and two tertiary polishing filters.

The first filter is bedded with organoclay/anthracite media which has a very high affinity for sorption on oil and grease and other sparingly water soluble contaminants. The effluent from the first filter then flows through a GAC (granulated activated carbon) filter to remove more soluble "light ends" before being discharged.

Routine system maintenance is minimal and the filter medias have provided excellent bed life. The media lasts longer than one year. Effluent quality is low to non-detect allowing re-circulation of the water if desired.

2. A refinery in Canada discharged boiler feed water through a lime softener and desired to recycle the water. The water contained 8 ppm of total organic carbon, of which lube oil was 3 ppm, with spikes of 9 ppm. The remainders where chelating agents and amines used for scale prevention. Several ppm of iron were also present. The water runs at 30 psi and a temperature of 170 degrees F.

A vessel with 10,000 lb organoclay was installed. Since this is boiler feed water, extensive backwashing was required to remove any suspended clay fines that add silica to the water, and to remove salts such as sodium chloride, which is commonly associated with bentonite. The silica content stabilized at 5 ppm, which was acceptable, and the conductivity also decreased to acceptable levels.

After the system was brought on line, the oil content of the water was less than 0.5 ppm. The iron content was much lower but not measured. The system has lasted for over a year with no change out. The organoclay not only removes the oil, which means the water does not have to be reheated very much, perhaps by 20 degrees F, but also the iron. The iron precipitates onto the anthrazite at a pH of 7.8. This results in co-precipitation of other heavy metal cations which is a nice side benefit.

PRODUCED WATER CASE STUDY

An oil field produced water at a site in central Michigan containing 500 ppm of residual oil.

Problem:
Dispose daily of 3,500 bpd water containing 500 ppm oil into a water injection well. Injection rates where reduced constantly because oil in the water plugged the pores in the down hole formation.

Every three months the operator had to engage a work over rig for three days, and inject hydrochloric acid and xylene-based solvents into the formation to restore permeability at a cost of $7,500 every two months plus down time.

Solution:
Set up an oil/water separator at well head followed by a three ft. vessel containing 1,200 lb Oilsorb Organoclay.

Goal:
5 ppm oil, which was easily achieved. A 100 times reduction. Water injection rates remained constant.

Installation costs:	$5,900	Includes O/W separator	$2,000
		Skimmer	$500
		Pump	$400
		Filter	$3,000

Organoclay: $1,500 plus freight

Replacement of Organoclay: Every three months at a cost of about $2,000
plus disposal fee of spent clay of $40

Cost Savings: $6,000 every three months or $24,000 per year
plus down time of three days
Change out time is four hours max vs. three days.

SUMMARY AND CONCLUSIONS

Pretreatment of ground and wastewater with granular organoclay to enhance the life of activated carbon is a useful and established practice. Prevention of fouling of ion exchange resins, membranes, and ultra filtration units is advantageous to the end user. Post treatment after DAF units and oil/water separators to achieve water quality that allows recycling and thus zero discharge is feasible and appropriate in today's environment. The fact that organoclays selectively remove chlorinated hydrocarbons further enhances the efficiency of a carbon pump and treat system. Good results in the removal of oil from antifreeze solutions and acids have also been reported. The organoclay/anthracite's ability to remove heavy metals is a beneficial side effect. Powdered organoclay can be used in batch systems and with rotary drum vacuum extraction systems. Efficient removal of creosote at wood treating operations by means of organoclay pretreatment has benefited such operations. In conclusion, the experiences described in this article suggest that organoclays should be a standard part of most pump and treat systems design.

Table 1. Non-ionic organoclays removal capacity of phenolic compounds was determined by batch tests.

Concentration:.....25 ppm in water

Phenol: 78.2% of organoclay weight.....Solubility: 86 g/l

2,4,6 Trichlorophenol: 98.3% of organoclay weight .....800 mg/l

3 Chlorophenol: 89.8% of organoclay weight .....27.7 g/l

Pentachlorophenol (PCP):.....87% of organoclay weight
This means that 100 grams of organoclay can remove 87 grams of PCP, solubility is 80 mg/l.

This data shows that the lower the solubility of the phenolic compounds, the higher the efficiency of the organoclay vs. activated carbon. Powdered organoclay removes 76% or more of its weight in oil from water.

Table 2. Organoclay/carbon sequence for the treatment of contaminated ground water. The oil content is not known.

Organic Compound	**Solubility (mg/1) at 20-25 Degrees C**	**Influent (mg/1)**	**Effluent organoclay**	**After carbon**
1, 1, 1 Trichloroethane	480-4000	26044	ND	ND
Trichloroethene	110	688	271	ND
1, 1 Dichloroethene	335	285	ND	ND
Toluene	535	967	242	ND
pH		8.64	8.01	9.2

Table 3. Indication that pretreatment with organoclay helped the activated carbon considerably in removing chlorinated hydrocarbons. Lab results obtained from a mini-column test (Alther, 2004, 2002).

	Solubility	**% by organoclay weight removed**
Benzene	1800 mg/l	39
Toluene	535	44
o-Xylene	insoluble	44
Naphthalene	34.4	24.3
PCB 1260	insoluble	52

Table 4. 300 gal of sump sludge water was passed through a vessel filled with 250 lb. of organoclay/anthracite over a period of one hour.

Organic Compound Solubility (mg/l)		Inflow Conc. (mg/kg)	Outflow Conc. (mg/1)
Oil and Grease		12	1
COD *		16,084 (mg/1)	202
BOD		429	120
Phenanthrene	1.29	40,000	<10
Naphtalene	34.4	29,000	<10
Fluorene	1.98	10,000	<10
Pyrene	0.14	8,000	<10
Benzo(A)Anthrazene	0.014	5,300	<10
Anthrazene	0.073	2,000	<10
Indeno(1,2,3,C,D)Pyrene	0.62	2,000	<10

Table 5. Removal of heavy metal cations by organoclay/anthracite. 300 gallons of sump sludge water were passed through 250 lbs. of organoclay during a period of one hour, or at 6 gpm.

Metal	Inflow Concentration (mg/kg)	Outflow Concentration (mg/kg)
Aluminum	1,035	0.5
Barium	3,470	0.05
Cadmium	2.53	ND
Chrome 3+	28.1	0.11
Cobalt	13.9	0.05
Copper	297	0.032
Iron	3,620	1.27
Lead	1,980	0.015
Manganese	63.3	0.42
Nickel	44.8	0.05
Tin	56.9	0.45
Zinc	512	0.04

Treatment of High Sulfite Refinery Wastewater by Conventional Activated Sludge

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ABSTRACT

A clean fuels project at a U.S. refinery included the addition of a gasoline desulfurization unit that generates SO_2 offgas. The offgas will be scrubbed in a caustic scrubber before released to the atmosphere. The SO_2 will primarily be converted to Na_2SO_3 (sodium sulfite) and to a lesser extent to $NaHSO_3$ (sodium bilsulfite) and $NaSO_4$ (sodium sulfate). The scrubber blowdown will require treatment to oxidize the sulfites to sulfate. Two options have been identified to treat the scrubber blowdown: (1) Oxidation in the Refinery's activated sludge wastewater treatment plant and (2) Oxidation in a new air oxidizing system. A preliminary evaluation of (1) indicated that the existing activated sludge system would be capable of treating the scrubber blowdown with minimal impact on its hydraulic and treatment capacity. However, there were some concerns regarding its implementation because of potential inhibitory effects, non-compliance with Whole Effluent Toxicity (WET) test, and incomplete oxidation of sulfites to sulfate in the activated sludge system. In order to address these concerns, a bench-scale simulation of the activated sludge system was operated for six weeks while being fed with wastewater from the Refinery. Results of the study are presented herein.

INTRODUCTION

The Clean Fuels project at the Refinery included the addition of a gasoline desulfurization unit that utilized a technology that generates SO_2 offgas that will be scrubbed in a caustic scrubber before release to the atmosphere. The SO_2 will primarily be converted to Na_2SO_3 (sodium sulfite) and to a lesser extent to $NaHSO_3$ (sodium bilsulfite) and $NaSO_4$ (sodium sulfate). The scrubber blowdown will be approximately 20 gpm and will require treatment to oxidize the sulfites to sulfate. Two options have been identified to treat the scrubber blowdown:

- Option 1: Oxidation in the existing activated sludge wastewater treatment plant
- Option 2: Oxidation in a new oxidizing system

A preliminary evaluation of Option 1 indicated that the existing activated sludge system would be capable to treat the scrubber blowdown with minimal impact on its hydraulic capacity. Also, the total air required for biological oxidation, nitrification, and oxidation of the sulfites to sulfates can be provided by the existing system by operating the two existing blowers. However, there were the following concerns regarding the implementation of Option 1:

- Potential inhibitory effects on the activated sludge biomass by the presence of high concentration of sulfites.
- Non-compliance with the final effluent permit limits including Whole Effluent Toxicity (WET) requirements.
- Incomplete oxidation of sulfites to sulfate in the activated sludge system.

In order to address these concerns, a bench-scale simulation of the activated sludge system was performed. A bench-scale activated sludge reactor was operated for six weeks while being fed with wastewater from the Refinery. The wastewater feeds were spiked with sodium sulfite and sodium bisulfite to obtain concentrations of 1,333 mg/L and 600 mg/L, respectively. The study methodology, test results, and conclusions of this investigative program are presented in this report.

TREATABILITY STUDY METHODOLGY

Description of the Bench-Scale Mesophilic Activated Sludge System

Twenty-four hour composite samples of API separator effluent were collected at the Refinery and sent to THE STOVER GROUP's laboratory for use as feed in a mesophilic activated sludge system. The purpose of this study was to simulate the treatment performance capabilities of the biological activated sludge system for treatment of the process effluent containing the added sulfite.

The study used a bench-scale, complete mix, continuous flow activated sludge system. The system consisted of a plexiglas internal recycle reactor with a 3.01 liter aeration reactor volume and a 1.33 liter settling compartment (clarifier) volume. Feed was pumped from a mixed feed tank to the aeration reactor, and the effluent flowed by gravity from the settling compartment to an effluent collection tank. The influent flow was calibrated and regulated at the desired flow

rate using a peristaltic pump and timer switch. Compressed air from an aquarium pump passing through a diffuser air stone was used to supply oxygen to the microbial population as well as to mix the reactor contents. An adjustable plexiglas baffle was positioned to keep the clarifier sludge from compacting too tightly inside the baffle opening but at the same time, to allow efficient sludge settling and recycle.

Bench-Scale Study Investigative Approach

This study was performed at THE STOVER GROUP's laboratory. The investigative approach for this study was to use the refinery (spiked sulfite) wastewater as the feed to the activated sludge reactor. The volume fed to the activated sludge reactor was three liters per day. The reactor was initially started with biological acclimated seed sludge (return activated sludge) from the refinery.

Refinery API effluent was shipped two to three times per week to the laboratory. These wastewater samples were characterized for the parameters listed in Table 1. All the wastewater samples contained adequate nutrients (nitrogen and phosphorus) for biological treatment, such that nutrients were not added to the wastewaters prior to feeding to the activated sludge system. The wastewater samples were spiked with gradually increasing doses of sodium sulfite (Na_2SO_3) and sodium bisulfite ($NaHSO_3$), until the desired study levels were achieved. Around two weeks time period was used to acclimate and stabilize the reactor, while the sulfite doses were increased to the desired study levels. After reaching the desired operating conditions, each wastewater sample was spiked with 40 ml of 10% Na_2SO_3 and 18 ml of 10% $NaHSO_3$ stock solutions per 3.0 liters of feed (1,333 mg/L Na_2SO_3 and 600 mg/L $NaHSO_3$). The acidity from the $NaHSO_3$ additions required alkalinity (NaOH) additions to the wastewater feeds in order to maintain acceptable pH levels in the activated sludge reactor mixed liquor. The spiked wastewater samples were fed to the bench-scale activated sludge reactor at conditions to simulate expected full-scale operations (Temperature = 36 ^{o}C, D.O. = 5.4 mg/L, MLSS = 3,000 mg/L, and F/M = 0.35).

The reactor contents were monitored daily for pH, temperature, and D.O. along with waste biomass volume, and feed volume (amount fed), as well as the effluent volume and pH. Dissolved oxygen uptake rates and microscopic (microbiological) analyses were performed three times per week. Settling tests were performed toward the end of the study to determine settling characteristics. Samples were taken of the mixed liquor and treated effluent for analysis to monitor loading rates and treatment performance. These samples were analyzed for the key operational/performance parameters. The parameters analyzed are presented in Table 1. Toward the end of the study, composite effluent samples were collected for WET testing.

TREATABILITY STUDY RESULTS

The characterization results of the twelve (12) refinery API effluent samples utilized for this treatability study are presented in Table 2. The test results indicate that all these samples exhibited consistent wastewater characteristics. A summary of the bench-scale reactor average operating conditions during the stabilized data collection period is presented in Table 3. A comparison of the bench-scale operating conditions to the full-scale operating conditions in Table 3 shows that both systems were operated under very similar conditions. The D.O. uptake rate in

the bench-scale system was approximately two times higher than the full-scale D.O. uptake rate due to the oxidation of the spiked sulfites. Operation and performance trend plots for this study are presented in Figures 1 through 8. Figure 1 presents the reactor MLSS and MLVSS during the study period. Figure 2 presents the F/M operating conditions in terms of both COD and BOD. Figure 3 presents the influent and effluent COD concentrations, and Figure 4 presents the influent and effluent BOD concentrations during the study period. Figure 5 presents the treatment performance of the system in terms of both total COD and total BOD. As can be observed in Figure 5, the treatment performance of the system was excellent throughout the study period.

Table 4 presents the treated effluent quality from this study after the stabilized operations data collection period. During this period, the average total COD and total BOD removals were around 86 percent and 98 percent, respectively. A high degree of nitrification was achieved in the bench-scale system with an average effluent nitrate-nitrogen concentration greater than 50 mg/L achieved during the data collection period. The average effluent tCOD and tBOD were 145 mg/L and 7.5 mg/L, respectively. The effluent sCOD concentrations observed during the study were affected by both the significant evaporation rate (due to the aeration and high water temperatures) and the mixed liquor volatile solids concentrations. When the MLVSS decreased below the target operating conditions, due to overwasting of biomass, the effluent sCOD increased. When the MLVSS were allowed to increase back up to the target operating conditions, the effluent sCOD decreased accordingly. The relationship of reactor MLVSS and effluent soluble COD are presented in Figure 6. The average evaporation rate (effluent compared to influent) during the study was around 25 percent. Therefore, the effluent COD concentrations measured during the study were around 25 percent higher due to evaporation.

Figures 7 and 8 present the influent and effluent TDS and sulfate relationships, respectively. The effluent TDS and sulfate concentrations increased significantly over the influent concentrations due to the additions of Na_2SO_3 and $NaHSO_3$ and the significant evaporation rate in the system, as previously discussed. The TDS concentrations were also increased by the additional alkalinity requirement to neutralize the acidity of the spiked $NaHSO_3$ additions. Between 6.0 to 10.0 milliliters of 1.0 N-NaOH were required per feed to neutralize the $NaHSO_3$ acidity. All the sulfites and sulfides in the influent along with the Na_2SO_3 and $NaHSO_3$ added to the influent feeds to the system were oxidized to sulfates. The influent and final effluent sulfate concentrations were around 700 mg/L and 3,500 mg/L, respectively. Therefore, the system effluent sulfate concentrations were around five times higher than the influent sulfate concentrations during the stabilized data collection period. A sulfur mass balance was also performed around the system. Both the influent and effluent sulfate, sulfite, and sulfide concentrations were converted to sulfur concentrations such that the mass balance was calculated in terms of sulfur. With one exception, during the data collection period the sulfur mass balance (influent sulfur compared to effluent sulfur) closed within 10 percent or less.

Results of the mixed liquor settling test are presented in Figure 9. The initial MLSS concentration used for this settling test was 2,980 mg/L. As can be observed in Figure 9, the mixed liquor exhibited excellent settling characteristics. The reactor mixed liquor maintained excellent settling characteristics throughout the entire study period. Periodic microscopic analyses were performed on the refinery mixed liquor throughout the study period. The mixed liquor from the refinery typically contained small to medium filamentous diffuse floc characteristics. It contained a significant amount of *Sphaerotilus natans* filamentous bacteria (predominant filament). It also contained *N. limicola* and Type 0041 filamentous bacteria.

Higher life forms typically observed included stalked ciliates, crawling ciliates, and swimming ciliates. Microscopic analyses of the treatability reactor mixed liquor were performed three times per week during the study period. The mixed liquor from the treatability reactor typically contained small to medium tight and compact floc characteristics. It contained significantly less filamentous bacteria than the refinery mixed liquor. The same types of filamentous bacteria were observed as in the refinery mixed liquor (*Sphaerotilus natans*, *N. limicola*, and Type 0041) with the *Sphaerotilus natans* being the predominant filament. Higher life forms were similar to the refinery mixed liquor with stalked ciliates, crawling ciliates, swimming ciliates, and rotifers routinely observed.

CONCLUSIONS

The bench-scale activated sludge simulation treatability study of the refinery wastewater spiked with sulfite accomplished the following objectives:

- Evaluation of potential inhibitory impacts of sulfite spiked wastewater on activated sludge biomass
- Impacts on Whole Effluent Toxicity tests
- Oxidation of sulfites to sulfates

The refinery wastewater contained excess nutrients (nitrogen and phosphorus) above the requirements for biological treatment. No carbonaceous BOD removal or nitrification inhibitory impacts of the sulfite spiked wastewaters were observed in the activated sludge process. However, both the effluent soluble COD values obtained and nitrification appeared to be sensitive to the MLVSS concentration. When the MLVSS dropped below about 2,000 mg/L, the effluent soluble COD and ammonia-nitrogen concentrations increased. When the MLVSS was increased above 2,000 mg/L, effluent soluble COD concentrations around 110 mg/L were achieved, along with complete nitrification and effluent ammonia-nitrogen concentrations around 1.0 mg/L or less. When allowing for the 25% evaporation rate through the system, this effluent soluble COD value would be around 80 mg/L. The effluent tBOD remained very good throughout the study period with an average value around 7.5 mg/L.

The biomass characteristics remained excellent throughout the study period. Excellent settling characteristics were observed throughout the study period. The microbiological characteristics (bacteria and higher life forms) also remained excellent throughout the study period. Routine microscopic analyses of the full-scale refinery mixed liquor and the bench-scale system mixed liquor were performed throughout the study period for comparison. The same types of higher life forms and filamentous bacteria were consistently observed in both systems. However, the bench-scale system consistently maintained better floc characteristics and significantly less filamentous bacteria. The bench-scale floc characteristics were tighter and more compact than the full-scale floc, which was more diffuse in nature. *Sphaerotilus natans* was the predominant filament in both systems; however, significantly less filamentous bacteria were observed in the bench-scale system mixed liquor. It appears that the high influent sulfite concentrations help control the filamentous bacteria without any negative impacts on the higher life forms along with an overall positive impact on the biomass flocculation characteristics.

After stabilized operating conditions were achieved, chronic Whole Effluent Toxicity (WET) tests were performed with *Mysidopsis bahia* and *Menidia beryllina*. The treated effluent from the sulfite spiked wastewater treatability system successfully passed the WET tests. The sulfites spiked into the wastewater were completely oxidized to sulfates in the bench-scale reactor. The treated effluent contained non-detected levels of sulfites and sulfides. A sulfur mass balance around the system closed to within about 10 percent or less. The acidity from the $NaHSO_3$ additions to the wastewater required additional alkalinity (NaOH) additions.

In summary, no negative impacts of the treatability of the sulfite spiked refinery wastewater were observed. However, both the effluent soluble COD and nitrification appeared to be negatively impacted with MLVSS concentrations below about 2,000 mg/L. When the MLVSS concentrations were above 2,000 mg/L consistent effluent quality was achieved, including complete nitrification. The bench-scale effluent quality successfully passed a WET test. The sulfite spiked wastewater provided positive impacts on the microbiological characteristics of the activated sludge biomass. The acidity produced by the addition of the $NaHSO_3$ to the refinery wastewater required additional alkalinity demands (NaOH) for biological treatment.

Table 1. Analytical Laboratory Monitoring Program

		Effluent	
Influent	**Reactor**	**Acclimation Period**	**Data Collection Period**
pH	TSS	pH	pH
tCOD	VSS	tCOD	tCOD
$tBOD_5$		sCOD	sCOD
tTOC		TSS	$tBOD_5$
TSS		NH_3-N	tTOC
TDS		NO_3-N	TSS
Anions		PO_4-P	TDS
Cations		Sulfur Salts	Anions
TKN		Sulfates	Cations
T-P		Sulfites	TKN
Sulfur Salts		Sulfides	T-P
Sulfates			Sulfur Salts
Sulfites			Sulfates
Sulfides			Sulfites
			Sulfides

Table 2. Process Wastewater (Refinery API Separator Effluent) Characteristics

	Concentrations (mg/L)	
Parameter	**Average**	**Range**
pH (su)	N/A	10.26 – 10.96
tCOD	666	400 – 764
$tBOD_5$	242	155 – 338
tTOC	181	97 – 210
TSS	92	47 – 135
TDS	2478	2210 – 2780
TKN	47.23	16.80 – 85.10
T-P	3.03	0.78 – 7.40
PO_4-P	0.40	0.11 – 0.63
Sulfate	704	626 – 846
Sulfite	7.57	0.48 – 14.30
Sulfide	6.2	1.0 – 15.2
Flouride	2.73	1.48 – 3.73
Chloride	488	361 – 607
Nitrate-N	1.73	0.13 – 4.26
Nitrite-N	0.71	0.30 – 0.99
Bromide	2.20	1.59 – 3.21
Lithium	<0.1	<0.1
Sodium	850	689 – 1610
Ammonium	15.73	3.90 – 42.80
Potassium	14.23	6.88 – 23.90
Magnesium	4.10	2.50 – 5.20
Calcium	39.0	16.1 – 69.4

Table 3. Reactor Operating Conditions During Stabilized Data Collection Period And Refinery Average Operating Conditions

Parameter	**Bench-Scale Average Values**	**Full-Scale Average Values**
pH (s.u.)	6.90 – 7.38	No Data
Temp (^{0}C)	30	36
MLSS (mg/L)	2,987	2,977
MLVSS (mg/L)	2,126	2,300
COD F/M	0.35	0.35
BOD F/M	0.13	---
HRT (Days)	1.0	1.0
D.O. (mg/L)	5.17	5.40
D.O. Uptake (mg/L/hour)	21.0	11.5

Table 4. Treated Effluent Characteristics

	Concentrations (mg/L)	
Parameter	**Average**	**Range**
pH (su)	---	6.80 – 7.54
tCOD	145	76 – 201
sCOD	129	75 –192
$tBOD_5$	7.5	4.4 – 12.5
tTOC	39.2	25.6 – 52.5
TSS	31	2 – 60
TDS	6173	5650 – 6540
TKN	15.6	2.2 – 45.1
T-P	3.3	0.1 – 6.6
PO_4-P	3.2	0.8 – 6.1
Sulfate	3469	3240 – 3720
Sulfite	<1.0	<1.0
Sulfide	<1.0	<1.0
Flouride	<0.05	<0.05
Chloride	643	504 – 744
Nitrate-N	51	40 – 64
Nitrite-N	<0.01	<0.01
Bromide	2.84	2.08 – 4.22
Lithium	<0.1	<0.1
Sodium	2131	1980 – 2290
Ammonium	6.7	<2.5 – 9.0
Potassium	17.2	9.3 – 24.5
Magnesium	9.84	7.35 – 15.0
Calcium	56.9	37.4 – 80.9

Figure 1. Reactor MLSS and MLVSS During Study Period

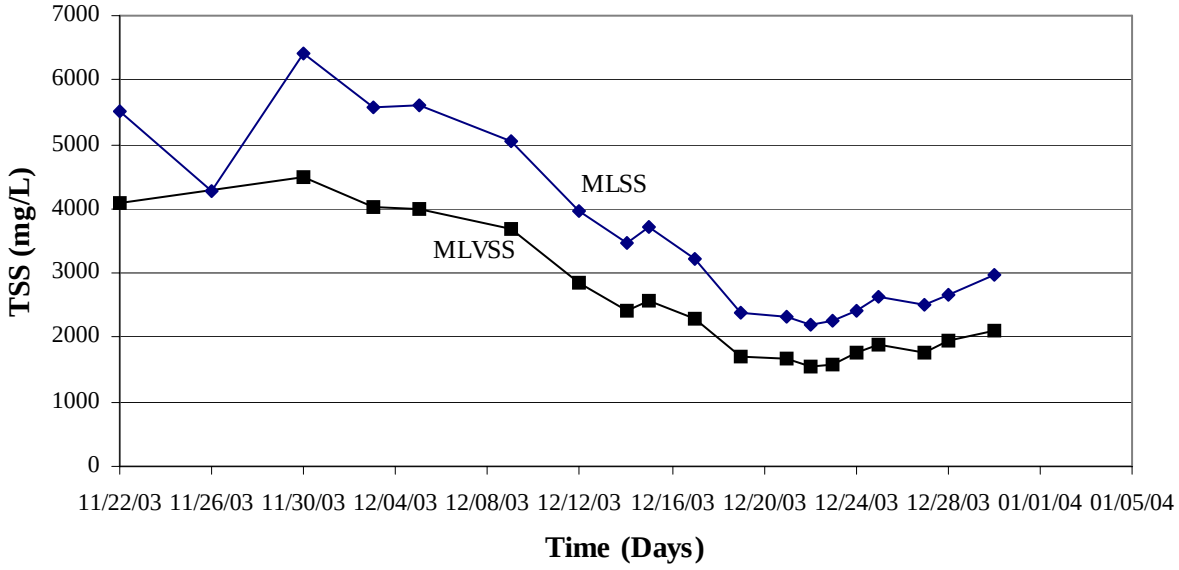


Figure 2. COD and BOD F/M Operating Conditions During Study Period

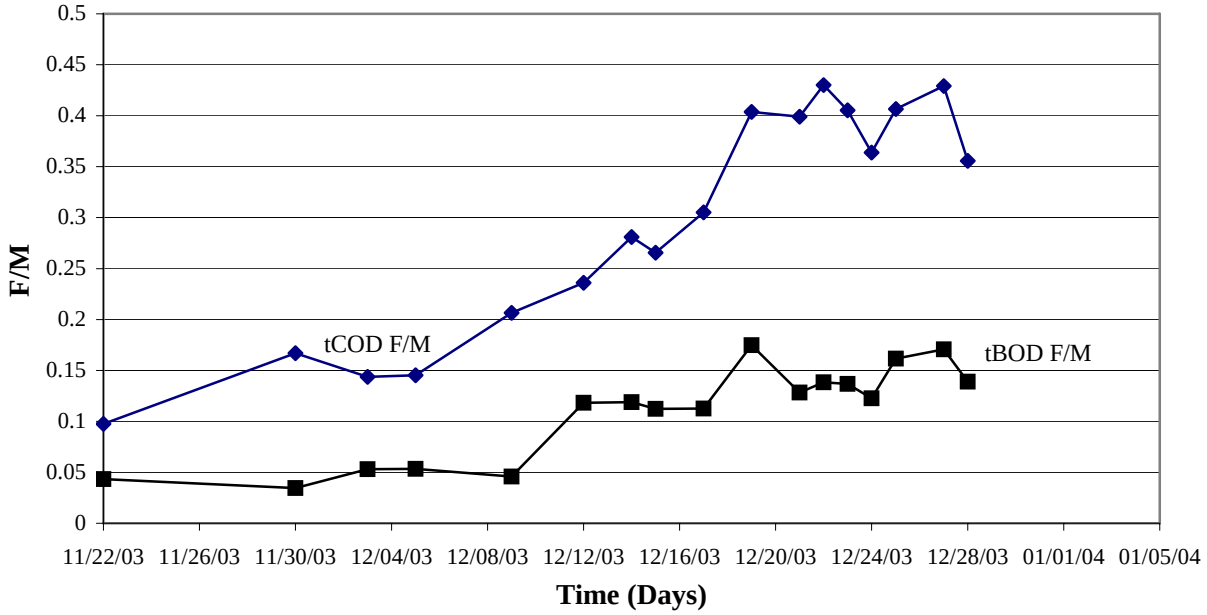


Figure 3. Influent and Effluent COD During Study Period

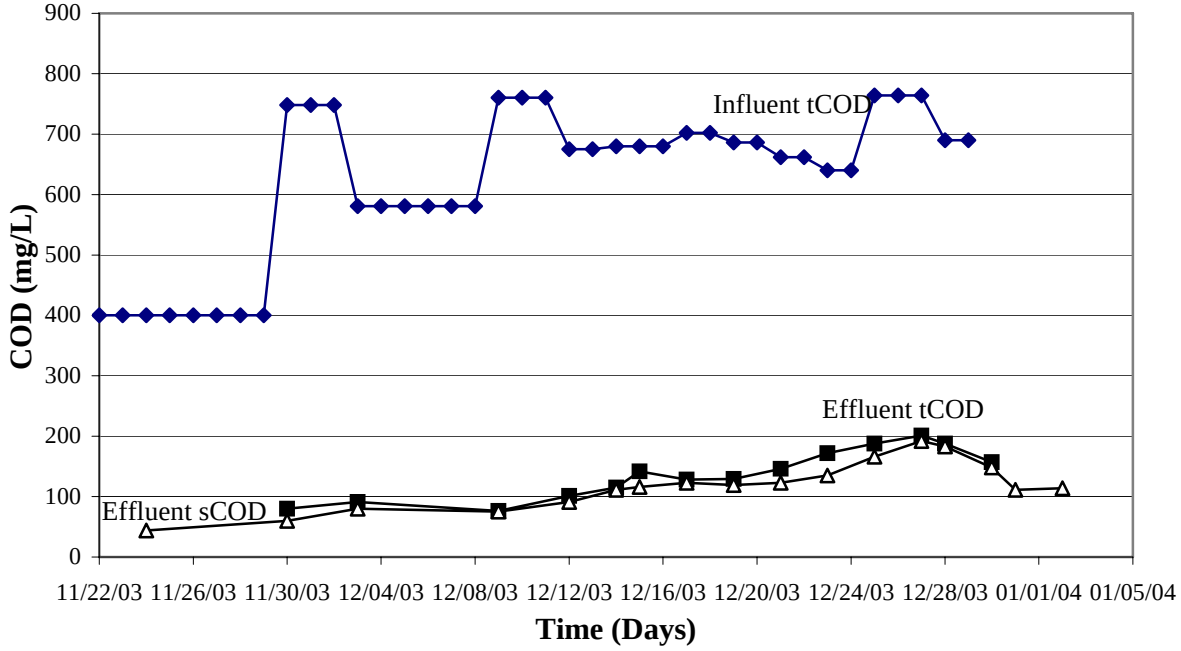


Figure 4. Influent and Effluent BOD During Study Period

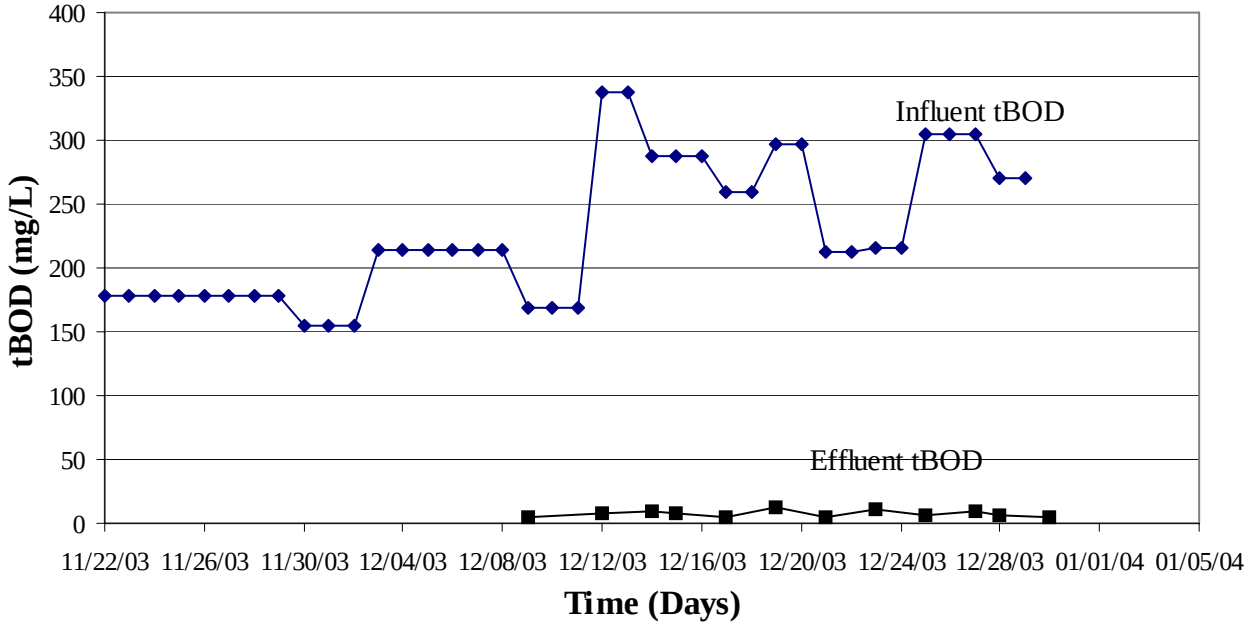


Figure 5. Treatment Performance in Terms of COD and BOD

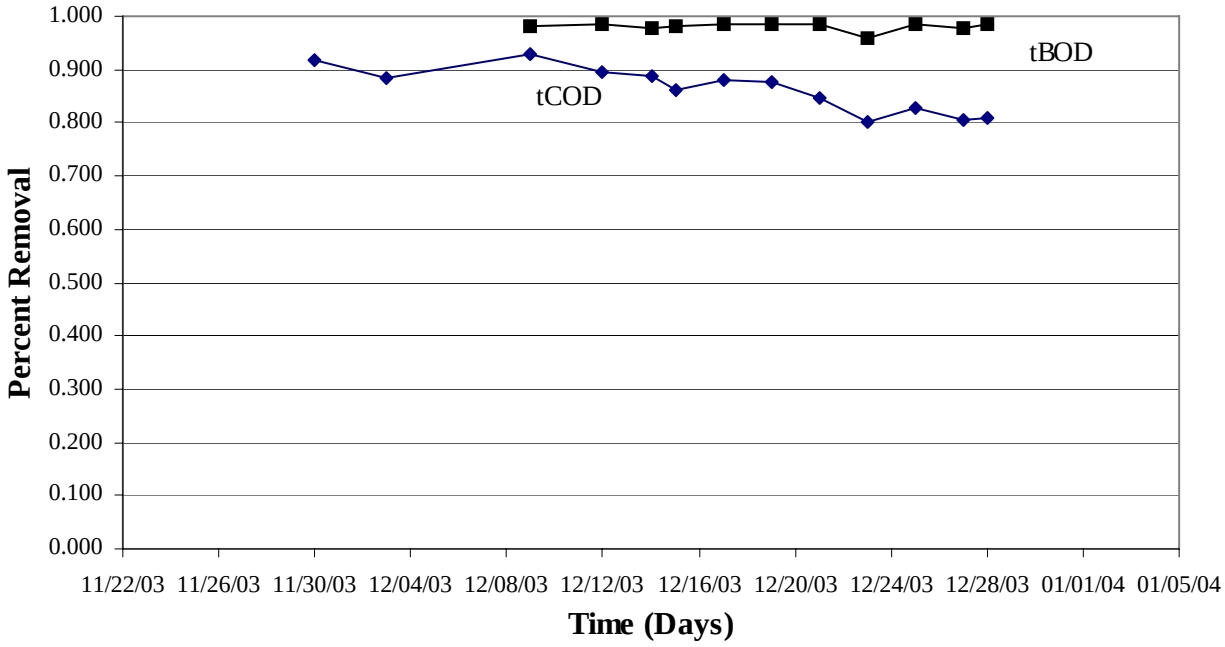


Figure 6. Reactor MLVSS and Effluent Soluble COD During Study Period

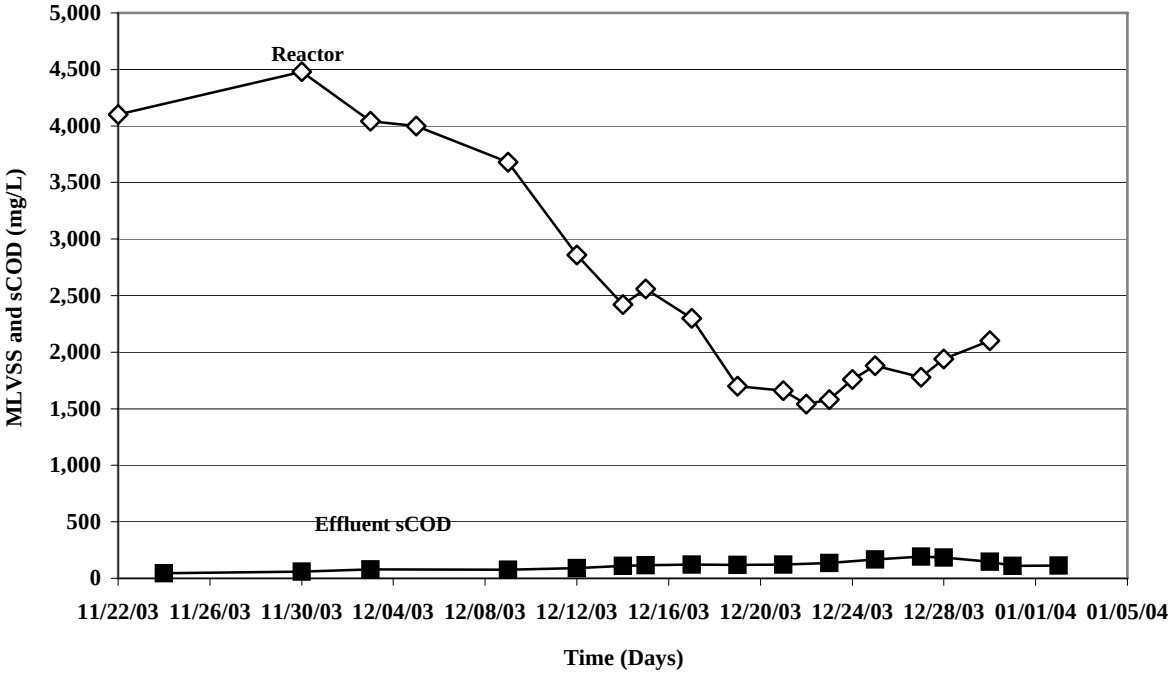


Figure 7. Influent and Effluent TDS During Study Period

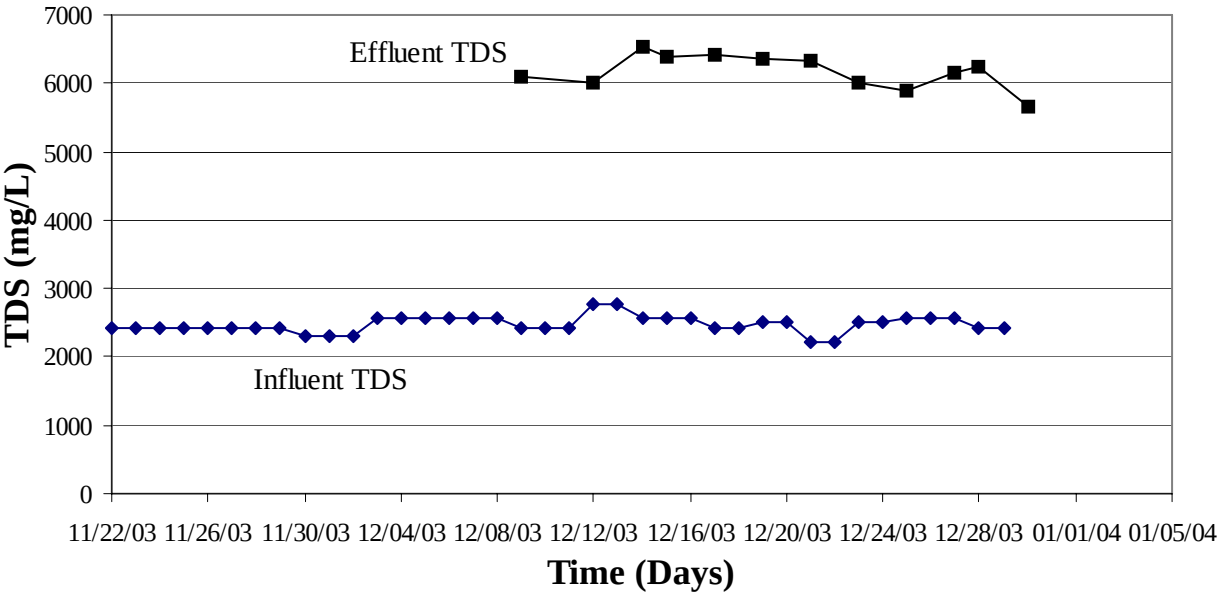


Figure 8. Influent and Effluent Sulfate During Study Period

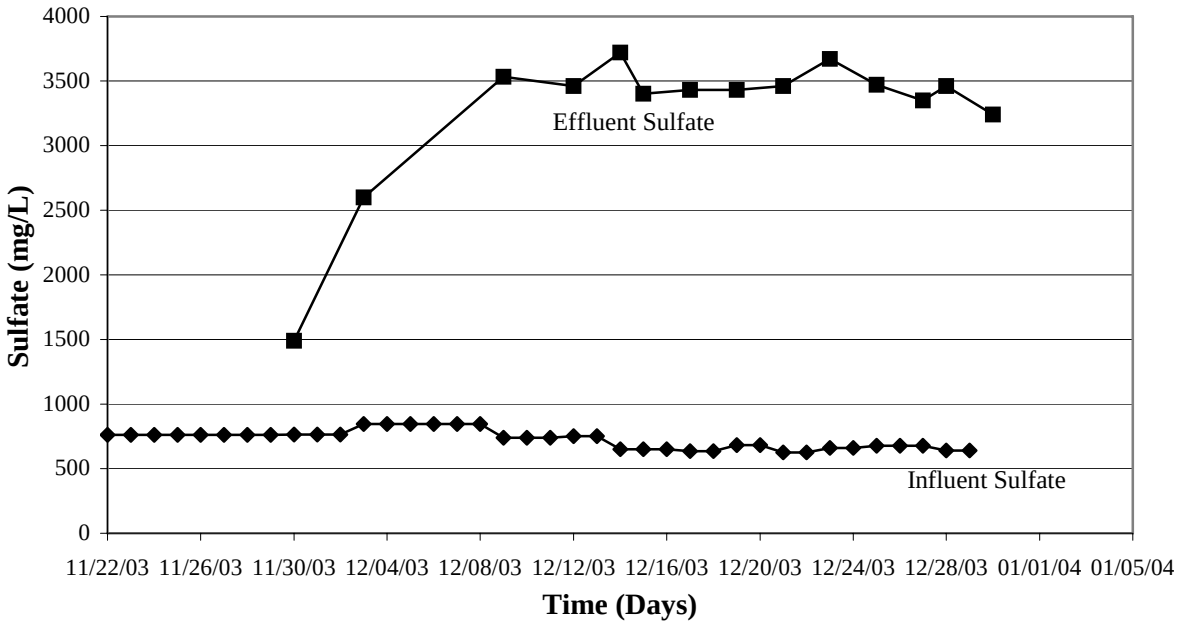
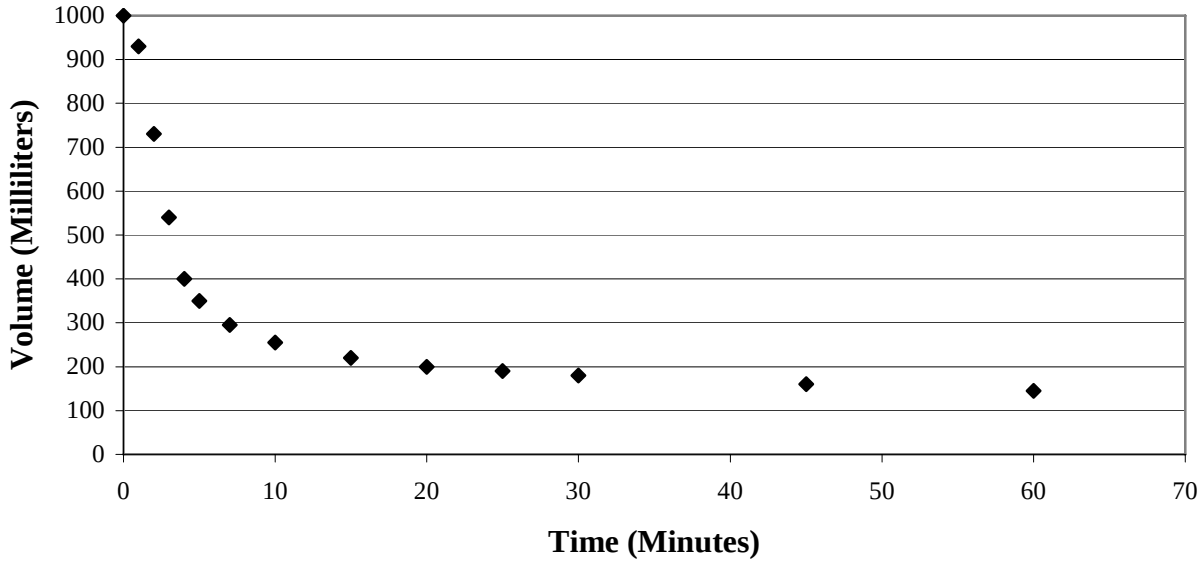


Figure 9. Settling Test



AltelaRain™ – State of the Art Produced Water Treatment Technology

INTERNATIONAL PETROLEUM ENVIRONMENTAL CONFERENCE

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San Antonio, Texas

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Abstract

Altela, Inc. provides products and services to customers in need of creating pure water from highly brackish and contaminated water sources. Altela has developed a fundamentally new water desalination product, the AltelaRain™ System, that inexpensively removes 100% of the dissolved salts and other contaminants from industrial waste waters and undrinkable brackish waters found throughout the world – representing the first new low-cost water desalination technology in the last 50 years. Altela has initially targeted the multi-billion dollar market for disposal of salt water co-produced with oil and natural gas production. By removing all contaminants from this dirty oilfield produced water, Altela converts these contaminated water liabilities into clean water assets, thereby removing our customer's high disposal costs and environmental liability by the present oilfield methods of reinjecting the water back into the ground or storage in large 'pits'. The AltelaRain™ System has successfully completed real-world oilfield beta testing. The beta water quality test results received from an independent water quality lab demonstrate the very high quality of treated water obtained from this simple, elegant technology for the treatment of highly challenged produced water. Total dissolved solids were reduced from 41,700 mg/L to 106 mg/L. Chloride was reduced from 25,300 mg/L to 59 mg/L. Similarly, benzene levels were reduced from 450 ug/L to non-detectable following AltelaRain™ treatment.

The Problem

Produced water is water trapped in underground formations which comes to the surface during oil and gas exploration and production. It occurs naturally in formations where oil and gas are found and, along with the oil and gas, is millions of years old. When oil or gas is produced, they are brought to the surface along with this produced water as a combined produced fluid. The composition of this produced fluid includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, produced solids such as sand or silt, and recently injected fluids and additives that may have been placed in the formation as a result of exploration and production activities.

Produced water indicators vary across (and even within) formation basins, depending on the depth of the well, geology, and environment of the deposit. In addition, formation hydrology often causes the quality of the produced water to change intermittently as the production well ages. The volume of produced water from oil and gas wells also does not remain constant with time. Traditionally, the water-to-oil ratio is the lowest when the well is new. As the well ages, the water-to-oil ratio increases, while the percentage of oil and gas similarly declines. For both oil and gas, the well's economic life is usually dictated by the amount of water produced – and its cost of disposal – rather than by the true end of oil or gas underground at the well. That is, by reducing the cost of produced water disposal, the economic reserves of oil and gas are increased in the U.S. Produced water is by far the largest volume of waste generated in oil and gas extraction operations. An average of over 7 barrels of produced water is co-produced with each barrel of oil produced in the United States, and, as oil wells age, the proportion of produced water co-produced continues to increase beyond that figure, sometimes to as much as 98% of the material brought to the surface. Oil wells in the U.S. may therefore be more realistically viewed as "dirty water wells", with the byproduct of oil representing only about 2% to 12% of the actual fluids lifted to the surface. Wells elsewhere in the world average about 3 barrels of produced water per barrel of oil, but still illustrate the point that, at most, only about 25% of an oil well's output is oil. Similar high ratios of gas to produced water production exist for production of natural gas. Overall, it is estimated that the United States oil and gas industry generates 15 to 20 billion barrels of produced water every year. To help put this in perspective, this is equivalent to about one-quarter-million acre-feet of water.

Produced water handling and treatment represents an $18 billion cost to the oil and gas industry in the U.S. alone. The cost of disposing of oil and gas produced water ranges from a low of $0.002 per gallon ($0.10/barrel) to a high of $0.24 a gallon ($10.00/barrel). By contrast, water for agricultural irrigation costs in the range of $0.0001 per gallon ($0.004/barrel) and municipal drinking water costs in the range of $0.003 per gallon ($0.13/barrel). The price of cleaning produced water is therefore as much as 80 times greater than municipal water, and as much as 2,600 times greater than agricultural irrigation water. The separation, handling, and disposal of produced water represent the single largest waste stream challenge facing the oil and gas production industry.

The Solution

Altela's patented AltelaRain™ technology uniquely cleans oil and gas industry produced water by removing its salts, residual oils and other contaminants - allowing it to be used on-site rather than requiring disposal in costly reinjection wells or evaporation ponds. In the arid western United States, purified produced water represents a new water supply and very desirable asset. Altela-cleaned water is attractive to ranch and farm landowners leasing their mineral rights to oilfield producers. In addition, drilling operators need clean water for fractionation and tertiary recovery operations. Presently, many producers are paying for dirty produced water to be trucked out and, at the same time, paying for clean water to be trucked in – the AltelaRain™ technology can eliminate both.

The Technology

The basic Altela technology is a simple and elegant process based on thermal distillation, which desalinates and decontaminates salty and polluted water in a fundamentally different way than the more familiar reverse osmosis and other membrane-based desalination technologies. In simple terms, the technology mimics nature's process of making pure rain water from seawater. What positions it as the first, truly new and disruptive water desalination/decontamination technology in over 50 years, however, is a scientifically complex, but inexpensively implemented, internal heat transfer process that allows the re-use of the latent heat of condensation over and over again to greatly offset the total latent heat of evaporation required in conventional thermal distillation. This internal heat transfer technology recaptures the energy used to evaporate water, thus yielding approximately 4 times the amount of distilled water per energy input as traditional distillation/evaporation techniques. Consequently, the AltelaRain™ technology yields energy costs that are approximately only 25% of comparable distillation/evaporation processes.

The water vapor from the evaporation chamber is transferred to the condensation chamber by a carrier gas, with the ability to absorb and desorb pure water from the produced water several times over, resulting in extremely high energy efficiencies, Figure 1. Ambient air is brought into the bottom of the tower on the evaporation side of a heat transfer wall. The wall is wetted by saline feed water, which is fed into the evaporation side at the top of the tower. As the air moves from the bottom to the top of the tower, low-temperature heat is transferred into the evaporation side through the heat transfer wall, allowing the air to rise in temperature and evaporate water from the wet saline liquid which coats the heat transfer wall. Water concentrated in contaminates leaves from the bottom of the tower and warm saturated air rises to the top of the tower. Heat is added to this hot air by an external heat source (low grade, atmospheric pressure steam). This hotter saturated air is then sent back down through the tower on the condensation side of the heat transfer wall. The evaporation side of the tower, being slightly cooler than the condensation side, allows the air to cool and transfer the latent heat condensation from the condensation side to the evaporation side. Pure distilled water condensate leaves the condensation side of the tower at the bottom of the tower.

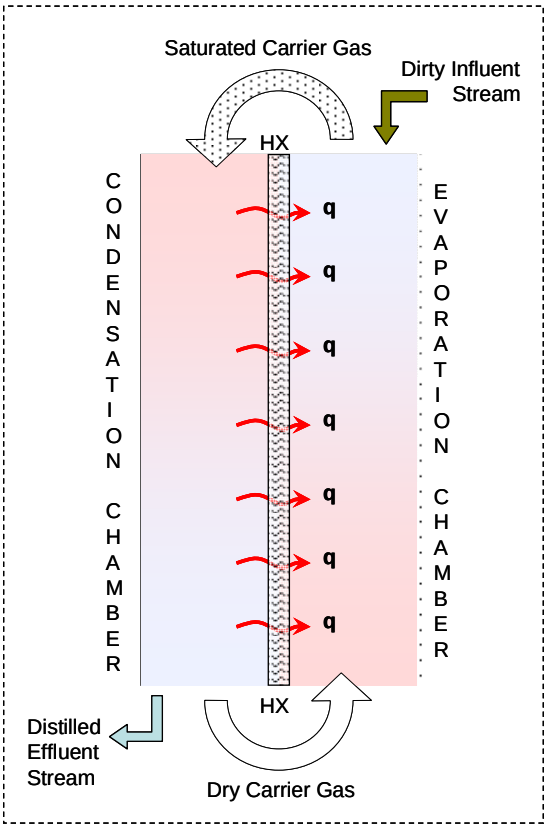

Figure 1: AltelaRain™ Process

Individual AltelaRain™ towers are approximately the size of a residential water heater and are capable of processing approximately 330 gallons per day (8 BPD) of water with salt concentration in excess of 150,000 ppm. The AltelaRain™ System can reduce effluent disposal volumes by as much as 90%. Since the treated water stream is distilled water, the quality of water from the AltelaRain™ System is extremely high. In summary, the key advantages of the AltelaRain™ technology include:

- Extremely high quality of treated water
- Relatively low cost

- High thermal efficiency
- Unattended operation
- No fouling
- No scaling
- No membranes to replace
- Near ambient temperature operation
- Operates at ambient pressure
- Uses waste heat to operate
- No pre-treatment
- No post-treatment

The AltelaRain™ System is highly scalable in size and can be produced in a variety of configurations to fit individual on-site needs. A smaller capacity system can be built and installed in a single 8 by 40 foot container. For higher volume applications, larger 180 to 250 BPD systems can be joined together to double or triple production capacity. Scaling up the volume of the system in this manner yields some cost savings on a per-barrel cost basis. The AltelaRain™ System is designed to minimize maintenance and operation costs. The use of plastics minimizes or eliminates many of the maintenance issues related to scaling, fouling or corrosion of metal systems. The moving parts in the system are few, and consist of proven, robust, off-the-shelf components, such as low pressure water pumps and air blowers. The system operates at ambient pressures and modest temperatures, and as such, has few mechanical failures in plumbing and related systems. The ability to remotely monitor the system allows field operators to detect system problems early and take remedial action before major failures take place.

Summary of Field Results

A beta pilot test using real oil-field produced water was conducted by Altela, Inc. employing the AltelaRain™ System for a conventional oil well located in southeastern New Mexico in early 2006. Coincident with this, Altela received from the New Mexico environmental regulatory authorities the first-ever permit issued for the surface discharge, on site, of clean water extracted from the highly brackish and contaminated produced water pumped from an oil or gas wellhead. The water quality test results received from an independent water quality lab demonstrate the very high quality of treated water obtained from this simple technology for the treatment of highly challenged produced water. Total dissolved solids were reduced from 41,700 mg/L to 106 mg/L. Chloride was reduced from 25,300 mg/L to 59 mg/L. Similarly, benzene levels were reduced from 450 ug/L to non-detectable following AltelaRain™ treatment. Detailed water quality data following AltelaRain™ treatment is outlined below in Table 1.

Table 1: AltelaRain™ Produced Water Pilot Test

	Water Contaminant (Analyte)	Symbol	Before Altela (mg/L) *except for Radium 226 and 228 which is in pCi/L	After Altela (mg/L) *except for Radium 226 and 228 which is in pCi/L
	Salts:			
1	Total Dissolved Solids	TDS	41,700	106
2	Chloride	Cl	25,300	59
3	Sulfate	SO4	81	0
	Metals:			
4	Arsenic	As	0.036	0
5	Barium	Ba	19.1	0
6	Cadmium	Cd	0	0
7	Chromium	Cr	0	0
8	Cyanide	CN	0	0
9	Fluoride	F	0.6	0
10	Lead	Pb	0	0
11	Total Mercury	Hg	0	0
12	Nitrate	NO3 as N	0	0
13	Selenium	Se	0.096	0.001
14	Silver	Ag	0	0
15	Uranium	U	0	0
16	Copper	Cu	0.02	0
17	Iron	Fe	38.1	0
18	Manganese	Mn	0.72	0
19	Zinc	Zn	0.01	0.03
20	Aluminum	A	0	0.3
21	Boron	Ba	44.8	0.2
22	Cobalt	Co	0	0
23	Molybdenum	Mo	0	0
24	Nickel	Ni	0	0
25	**BTEX:**			
26	Benzene		0.45	0
27	Toluene		0.45	0.0078
28	Ethylbenzene		0	0
29	Total Xylenes		0.76	0
	Radialogical:			
30	Radium 226		423	1.1
31	Radium 228		587	1.1

	Other:			
32	pH	pH	7.17	8.74

Conclusion

Oil and gas companies need lower cost methods for handling and disposing of produced water. Produced water handling and disposal is generally very expensive due to the large volumes of water that must be lifted to the surface, separated from the petroleum product, treated, and then injected into the ground or disposed of in surface evaporation ponds. In addition, environmental concerns are making it increasingly difficult to permit new surface ponds or injection wells. Historically, the produced water generated at an oil or gas site is stored on-site in large tanks. Oil and gas companies must pay for disposal trucking companies to visit the site multiple times per week, pump the produced water out of the storage tanks and transport the waste to commercial underground reinjection sites. These disposal trucks must often travel great distances to the reinjection sites. When these trucks are unavailable or during periods of poor weather, many well sites must be shut down due to the inability to store and/or dispose of the produced water on-site.

In addition, many oil and gas wells are simply "pinching back" production due to the inability of the on-site infrastructure to handle produced water volumes. Trucking costs alone can be in excess of $3.00 per barrel (bbl) and a disposal reinjection well can cost upwards of $4,000,000 to drill (assuming the ever increasing and costly regulatory compliance and environmental protests can be satisfied). In many locations, total produced water disposal costs are greater than $5.00 per barrel. Stated differently, the oil and gas industry spends as much as 80 times as much, per gallon, to get rid of dirty produced water as individuals pay for clean municipal water. Unfortunately, based on the high degree of complexity of produced water chemistry, produced water treatment technologies are presently not in wide use. Those that are have historically been applied only to mildly saline waters (almost drinkable before treatment, such as some coal bed methane produced water), and they have largely been developed by oil and gas operators on a case-by-case basis. Recent field tests of the AltelaRain™ System, conversely, demonstrate the technology's unique ability to successfully treat and purify a myriad of complex produced water chemistries while delivering the following inherent advantages to the produced water treatment industry:

Removal of Contaminants: AltelaRain™ represents a simple solution to removing all produced water contaminants, even in highly-challenged and extremely high-TDS conditions. Like all distillation based processes, the liquid water generated on the condensation side of the heat exchanger is pure and contains virtually no dissolved or suspended solids. The vapor phase water formed during evaporation is free of chemical compounds which have boiling points greater than or equal to that of water (at atmospheric conditions). As a closed-loop thermal process, the clean water vapor then condenses in the form of a very high-purity water stream. Like most thermal processes, water chemistry has only mild effects on system performance. Real world testing of the technology has revealed that highly volatile BTEX compounds typically found in produced waters do not condense in the distillate stream.

Flexibility: The low cost, scale-resistant materials used to fabricate AltelaRain™ towers enable AltelaRain™ Systems to be built that are modular and mobile, easily maintained, and capable of processing water with highly variable influent compositions. The modular design of an AltelaRain™ based system enables customization of each treatment system with little or no additional cost to oil and gas customers. For example, a system can be installed to minimize the effluent brine reject stream simply by re-configuring the physical layout of the primary system towers into differing series/parallel configurations.

Cost Effectiveness: Like other thermal processes, AltelaRain™ is simple, easy to maintain, and can operate unattended for long periods of time. However, unlike other desalination methods like RO, MSF, or MED, the primary treatment components are fabricated entirely from polymer (plastic) materials. This eliminates the need for costly influent pre-treatment components (such as filters, flocculants, and anti-scalant chemical additives). No metal is present on which corrosion and scaling can occur. Also, similar to other thermal processes, the major operating expense is the energy required to evaporate the influent water. Since the system operates at low temperatures, typically 180°F or less, it is possible to employ low grade sources of waste heat. Such operating scenarios dramatically increase the operating efficiency by further reducing the operating costs by virtue of the technology's unique ability to repeatedly 're-use' this low-grade heat multiple times by applying the exothermic heat of condensation to the endothermic heat of evaporation in a continual loop process.

Equity Considerations: AltelaRain™ based treatment systems typically require more physical space to treat a given volume of water than comparable reverse osmosis systems. This is a function of the low thermal conductivity of plastics relative to that of metal. This is generally a minor consideration in oil and gas locations, since well sites are located remotely with ample land available for the system's installation. Furthermore, many low cost construction techniques can be employed to erect temporary or permanent structures. Operation noise is minimal. A system that treats 90 BPD requires an area of 40' by 8'.

Environmental: The AltelaRain™ technology mimics nature's rain cycle and is inherently environmentally friendly. There are no pre- or post-treatment chemicals requiring handling or disposal. The pure distilled water stream that is generated can be reused for numerous beneficial uses.

Assessing and Controlling Emissions of Greenhouse Gases: A Pragmatic Perspective for the Oil and Gas Industry

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ABSTRACT

With last month's decision by California to begin to assess and regulate emissions of greenhouse gases, a whole new specter of environmental regulations may be casting its shadow over the oil and gas industry.

The purpose of this paper is to provide a pragmatic look at the recent California decision and similar initiatives being developed in other cities, States, and at the Federal level. The focus of the paper will be on the potential impact of these regulations on a representative oil and gas operation. Included in this presentation will be an assessment of different approaches for calculating emissions of greenhouse gases, an overview of such emissions for the oil and gas industry relative to other pollutant sources and a review of the issues involved in controlling and reducing these emissions in the future.

INTRODUCTION

The recent decision by California to begin to assess and regulate emissions of greenhouse gases can be interpreteed by some as a radical departure in legislation in the United States, where the focus is not on an exposure that will result in immediate danger to our nations residents, but to the long-term impact of releases on a future generation. However, such a legislation more likely represents the culmination of continuing concerns over the releases of Greenhouse Gases into the atmosphere.

With the potential impact of GHG controls within the United States growing, it is important to review the impact of upcoming regulatory interest on the Oil and Gas Exploration and Production Industry, and how such controls might affect continuing operations.

It is not the function of this paper to revisit all of the extensive efforts that have focused on grenhouse gas issues, but, rather, to try and place the available information into perspective as it relates to the oil and gas industry.

Greenhouse Gases

There are a number of chemicals that are classified as greenhouse gases, but the most important are carbon dioxide CO_2, nitrous oxide (N_2O), methane,(CH_4) and the class of compounds known as chlorofluro hydrocarbons, such as Sulfur Hexafluoride (SF_6). It is recognized that the greenhouse gas potential varies with the chemical.

The Global Warming Potential (GWP) represents the radiative effect resulting when the gas itself absorbs radiation (direct effects) or when it transforms into a chemical that does (indirect effect). It is presented as a ratio of the radiative effect of that gas relative to that of carbon dioxide. See Table 1. So from a Global Warming Potential perspecitve one ton of emissions of methane would be equivalent of 21 tons of emissions of carbon dioxide[1] .

Oil and Gas Production

Figures 1 and 2 present a summary of the oil and gas production for the nine top oil and gas producing states for 2004[2, 3]. These are Alaska, California, Colorado, Kansas, Louisiana, New Mexico, Oklahoma, Texas and Wyoming. So, when considering legislation by states associated with greenhouse gases, the activities of these states would be paramont.

STATE PROGRAMS

History/Politics/Legislation/Future

California's AB-32 signed by Governor Schwarzenegger on September 27, 2006 once again put the Sunshine State in the forefront of environmental protection. The bill, mentioned favorably by Tony Blair, New York Governor George Pataki, and Japanese Prime Minister Junichiro Koizumi requires a 25 percent reduction in carbon dioxide emissions by 2020 which effectively caps CO_2 emissions at 1990 levels. The bill includes provisions for achieving CO_2 reductions through market mechanisms as well as technology.

The CO_2 trading market is not new; seven Midwestern states are members of the Midwest Greenhouse Gas Registry, a program for voluntary CO_2 trading and nine northeastern states comprise the Regional Greenhouse Gas Initiative[1] or RGGI, formed in 2003, which uses a cap-and-trade system to reduce carbon dioxide emission from power plants.

In 2004, fifteen climate change bills were passed in eleven states. The bills' flavors varied: research, renewable energy portfolios, mobile sources regulation and CO_2 registries, but all were aimed at addressing greenhouse gases including CO_2. In 2005, despite the Federal silence on CO_2 regulation, 28 states had Climate Action Plans in place.

States like California, Washington and Oregon have begun to make head roads into CO_2 emissions control with established legislation capping emissions. California is in the process of convincing adjacent states and Mexican states that they should follow suit. Meanwhile, Texas, Wyoming and Utah are adopting a "wait and see" attitude.

At the Federal Level, the 2005 Energy Bill avoids any mention of climate change or greenhouse gas controls, the 2002 Climate Change Initiative sidesteps controls, the McCain-Lieberman Climate Stewardship Act aimed at capping power plant CO_2 emissions was defeated in 2003, and the US EPA does not regulate CO_2. However, the EPA's position has been challenged and is being challenged again at this time. In 1999 twelve states and three cities sued the US EPA claiming it had the authority and obligation to regulate CO_2. The EPA claimed the Clean Air Act did not give it the authority to regulate CO_2, and because CO_2 is not a pollutant with known health hazards, it does not fall under the Clean Air Act's purview. The EPA won the case in 2003 and a court of appeals upheld the decision in 2005. In August 2006, twelve states and ten environmental groups filed again[(4)]. These were Massachusetts, California, Connecticut, Illinois, Maine, New Jersey, New Mexico, and New York, Oregon, Rhode Island, Vermont, and Washington. Later, Arizona, Iowa, Minnesota, Wisconsin, Maryland, and Delaware--also joined in the lawsuit against EPA as have two electric utility companies, Calpine and Entergy Corp.

The Supreme Court will hear the case and is expected to render a decision in the Spring of 2007. Ten states joined the suit in support of the EPA's decision not to regulate greenhouse gases on the Federal Level. These were Alaska, Idaho, Kansas, Ohio, Michigan, Nebraska, North Dakota, South Dakota, Texas, and Utah

[1] Currently New York, Connecticut, Delaware, Maine, Massachusetts, New Hampshire, New Jersey, Rhode Island and Vermont. Maryland is slated to join in 2007.

When the EPA won its case not to regulate CO_2 in 2003, the scientific community was still relatively divided over the validity of global warming. Since that time, scientific inquiry has intensified and additional data appears to make the case for global warming stronger. The role of CO_2 in global warming is, by some accounts, much clearer now than a few years ago. The world-wide scientific community is less divided over global warming and management of greenhouse gases is becoming a focus of environmental and energy policies throughout the industrialized nations.

Emissions markets, which include CO_2 trading, are already in place in the European Union where CO_2 emissions are regulated and trading is not voluntary. The Kyoto Protocol, rejected by the US in 2001, was ratified by Russia in 2004 and became an official international policy in February 2005. The Kyoto Protocol requires industrialized nations to reduce CO_2 emissions by 10 percent of 1990 levels by the year 2012. European oil and gas companies are already addressing CO_2 emissions through technology as well as trading. The Norwegian company Statoil, has been injecting one million tons of CO_2 generated annually by its Sleipner off-shore platform back into the seafloor. They have avoided paying $53 million each year in taxes on CO_2 emissions. "Sequestration" of CO_2 is well proven and is used in the US to enhance oil recovery from waning fields, and as a CO_2 disposal method.

At present, power plants are currently the largest stationary source emitter of CO_2 comprising one third of all CO_2 emissions in the US. In an effort to get into the barn before the door shuts, utilities have accelerated their plans for building power plants to meet future electricity demands, According to some estimates, as many as 120 coal-fired power plants are currently on the drawing board nationwide. The demand for electricity is anticipated to increase nearly 50 percent over the next 25 years.

Yet, even without regulatory pressure, emissions from coal-fired power plants are being scrutinized and criticized by environmental groups, who have exercised some clout during the permitting process. For example, the Western Resource Advocates, in its attempts to fight Excel Energy's Pueblo Colorado plant, ended up settling out of court with the provision that Excel agree to account for the cost of global warming due to greenhouse gas emissions in its resource acquisition decisions.

The competition for power generation will be between renewables and natural gas. Wind, ethanol, biodiesel and even solar are currently receiving significant attention, funding, grants, and private investment. If greenhouse gas control continues to climb in national and global concern, then those options with the lowest CO_2 emissions will grow the fastest. The Bush administration, in May 2006, discussed an "Advanced Energy Initiative" which addresses the same four aspects of energy generation as the 2005 Energy Bill: nuclear power, research and development for cleaner coal burning plants, liquefied natural gas and renewable sources. The initiative also offers to "work… to boost oil and gas supplies to relieve high gas prices" through refinery permit streamlining, and increased off-shore drilling. While the initiative does not address climate change, its content implies that the US cannot continue to increase fossil-fuel based power sources with complete disregard for greenhouse gas emissions.

So what to watch for? Most of the oil and gas producing states have yet to actively participate in the greenhouse gas discussions. California and New Mexico have joined the lawsuit to require EPA to develop regulations of CO_2, while Texas and Kansas are supporting EPA in that lawsuite. The Supreme Court's decision on whether EPA can or cannot regulate CO_2 will be an important milestone in greenhouse gas emissions management in the US. Regardless of whether the EPA

regulates CO_2 emissions, the emphasis by state regulators and the Whitehouse on producing a larger percentage of our power through renewable sources and clean-burning power plants is being heard throughout the power producing industry.

GREENHOUSE GAS EMISSIONS

Emission Categories

The EPA has been preparing an annual summary of greenhouse gas emissions for a number of years. These reports present a relative comparison of the various sources to greenhouse gas emissions. Figure 3 presents a summary of the major sources of greenhouse gases between 1990 and 2004. Overall, emissions of CO_2 from fossil fuel combustion represent nearly two-thirds of the total emissions of greenhouse gases, up from 61 percent in 1990. Several categories have been combined in this representation. Coal mining includes active and inactive coal mines, Livestock includes both Enteric Fermentation and manure management, and natural gas systems include natural gas lines and petroleum systems.

Oil and Gas Operations

Greenhouse gas emissons from oil and gas operations, (essentially methane) decreased from 161.4 Tg (as CO_2) to 145 Tg, which is a reduction from 2.1 % of the total to 1.7 %. A further breakdown of the methane emissions from natural gas operations are summarized in Figure 4, while Figure 5 shows a similar distribuion of methane emisisons from petroleum prodction field operations.

Reductions in Greenhouse Gas Emissions

There are 10 potential sources of pollutants which may be generated in the exploration and production industry[5]: (*1*) unreacted raw materials; (*2*) impurities in the reactants; (*3*) undesirable by-products; (*4*) emissions from auxilliary equipment, such as engines and boilers; (*5*) off-spec product; (*6*) maintenance, ie, wastes and materials; (*7*) exhausts generated during start-up and shutdown; (*8*) exhausts generated from process upsets and spills; (*9*) exhausts generated from product and waste handling, sampling, storage, and treatment; and (*10*) fugitive sources.

There are two broad strategies for reducing emissions from a production facility[6]: (*1*) altering the design, operation, maintenance, or manufacturing strategy so as to reduce the quantity or type of air emissions produced, or (*2*) installing after-treatment controls to destroy or dispose of the pollutants in the generated air emission stream. As an example, in the first case, special efforts could be made to reduce the releases of methane containing gases during start-ups and shut-downs, maintenance or upsets. In the latter case, more of these gases would be sent to a flare, where they would be converted to CO_2.

Natural Gas Star Program

There have been extensive efforts focused on reducing the releases of greenhouse gases from oil and natural gas operations. Since 1995, the EPA with support from a number of trade associations has been assisting companies in assessing emisison reduciton opportunities through the Natural Gas Star Program[7]. Through this program guidance has been provided on calculating and controlling emissions and sharing experiences between facilities. Initially the emphasis of the program was focused on such sources of emissions as releases from well heads, losses from start-ups and shut-down and from upsets and spills. Through this program a significant reduction in methane emissions from natural gas operations has been achieved. The reductions through 2004 are summarized in Figure 6. Again, the largest reductions were from the natural gas production and transmission & storage sectors. The reductions from gas processing operations were much more modest.

Representative Natural Gas Processing Plant

The greenhouse gas emissions from a representative oil and gas processing plant were also estimated. This plant processed some 5.5 billion cubic feet of gas per year, and generated some one million bbls of liquids annually. The gas stream contained some 8 percent CO_2, which is reduced down to 3 percent before distribution. The plant contained boilers and heaters totalling some 60 MMbtu/hr, and ten engines that consumed some 55 mmcf/yr. The site includes a dehydrator as well as the amines plant. The emissions of presently regulated air pollutants are less than 100 tons per year, making this site a minor source of air emissions.

Figure 7 presents a summary of the calculated emissions of CO_2 and CH_4 for this facility[8, 9, 10]. The methane emissions total some 1300 tons per year, which is more than three times that of the regulated pollutants (NO_x, CO, SO_2, VOC, PM) combined. But, the CH_4 emissions are dwarfed by the emissions of CO_2, which totalled nearly 50,000 tons per year. When considering that the GWP of CH_4 is 21 tines greater than that of CO_2, the relative contribution as greenhouse gases of these emissions becomes more comparable.

An examination of the sources of these emissions (Figure 8) indicates that the the CO_2 emissions come primarily from combustion, and from the scrubbing operation in the amines unit. The CH_4 emissions are released in the tank battery (including flash emissions) and from auxilliary uses of the natural gas in the process, such as in pneumatic devices.

Some significant efforts at this facility were initiated to reduce the emissions of methane. In particular, the tank battery emissions were controlled, and the use of methane in the pneumatic devices curtailed and replaced with air.

With these modifications, emissions of CH_4 were reduced by nearly 80 %, and the total GWP reduced by 30% (Figure 9 and 10). However, to reduce the GWP of this facility further the CO_2 emissions would need to be curtailed, either by eliminating or modifying the combustion sources or by capturing the CO_2 released from the amines unit. Such emissions, if captured, would need to be sequestered.

CO_2 Sequestration

Executives at utility companies intent on building power plants and the Electric Power Research Institute are well aware of the global and now national move toward CO_2 regulation and have secured funding from congress for CO_2 sequestration at a demonstration plant called FutureGen. The utility industry knows that more expensive technologies such as coal gasification and circulating fluidized bed, which emit relatively low amounts of CO_2, may become the necessary options, making the cost to generate electricity from coal comparable to that of generating electricity from natural gas at current prices. Utilities at a local level have acknowledged that greenhouse gases need to be controlled and are taking action to meet what they view as inevitable national regulations. One such move was headed by the Colorado Springs Utilities department who have begun formation of a coalition of municipal utilities from Texas, Florida and Georgia to lobby Congress on the regulation of CO_2.

The result of pressure on coal-fired power plants to reduce CO_2 emissions, combined with the renewable energy bent of most State's Climate Action Plans puts renewables and natural gas at the forefront of preferred power generation options. Oil and gas companies are well ahead of the curve on sequestration. CO_2 injection to enhance oil recovery has been conducted since the 1970's. In 2004, the depleted South Liberty oil field near Dayton Texas received 1,600 tons of CO_2 at a depth of 5,000 feet. Kinder Morgan reportedly pipes 1 billion cubic feet per day of CO_2, much of it from Colorado to West Texas oil fields. Part of the cost of CO_2 sequestration revolves around its transportation. Solutions to this dilemma include construction of pipelines dedicated to CO_2 transportation, identifying reservoirs amenable to sequestration, and strategic location of power plants to take advantage of mapped reservoirs.

CONCLUSION

Reductions of greenhouse gases in the oil and gas industry may be looming on the horizon, either voluntarily, or at through regulations at the state or federal level. Over the short term, it appears that reductions of more than 10 percent of greenhouse gases can be achieved through control of methane releases. However, pragmatically, over the long haul, controls of CO_2 will need to be considered. With sequestration of captured CO_2 being the most likely option.

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11.

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Gas	GWP
CO2	1
CH4	21
N2O	310
SF6	23,900

Table 1: Global Warming Potential of Representative Greenhouse Gases Relative to Carbon Dioxide

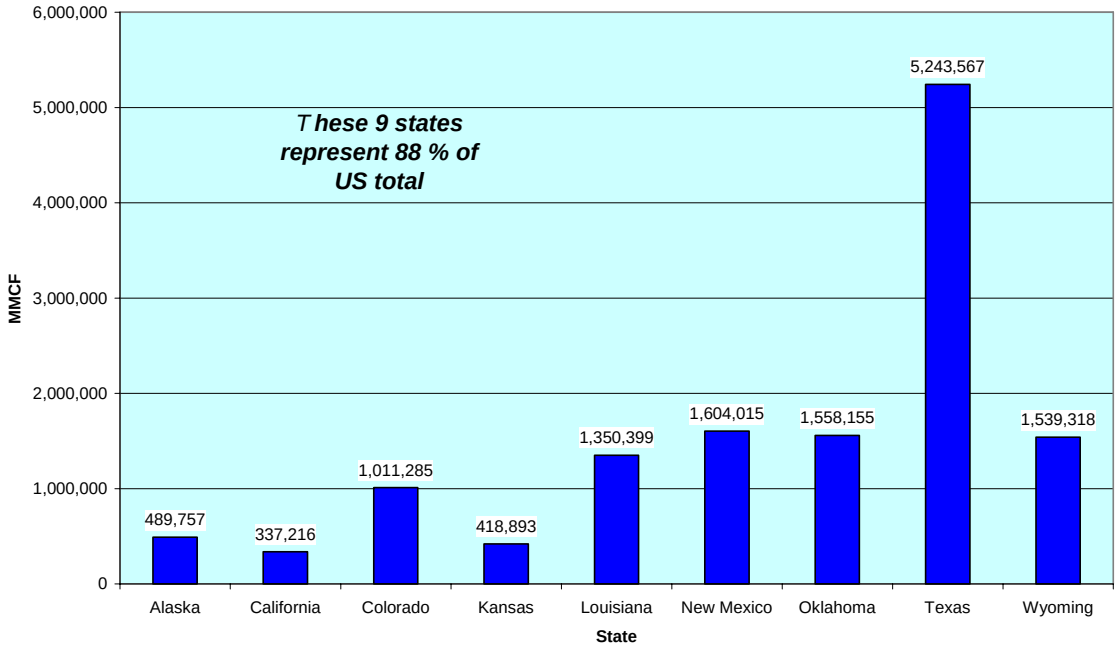

Figure 1: Annual US Production of Natural Gas -- 2003

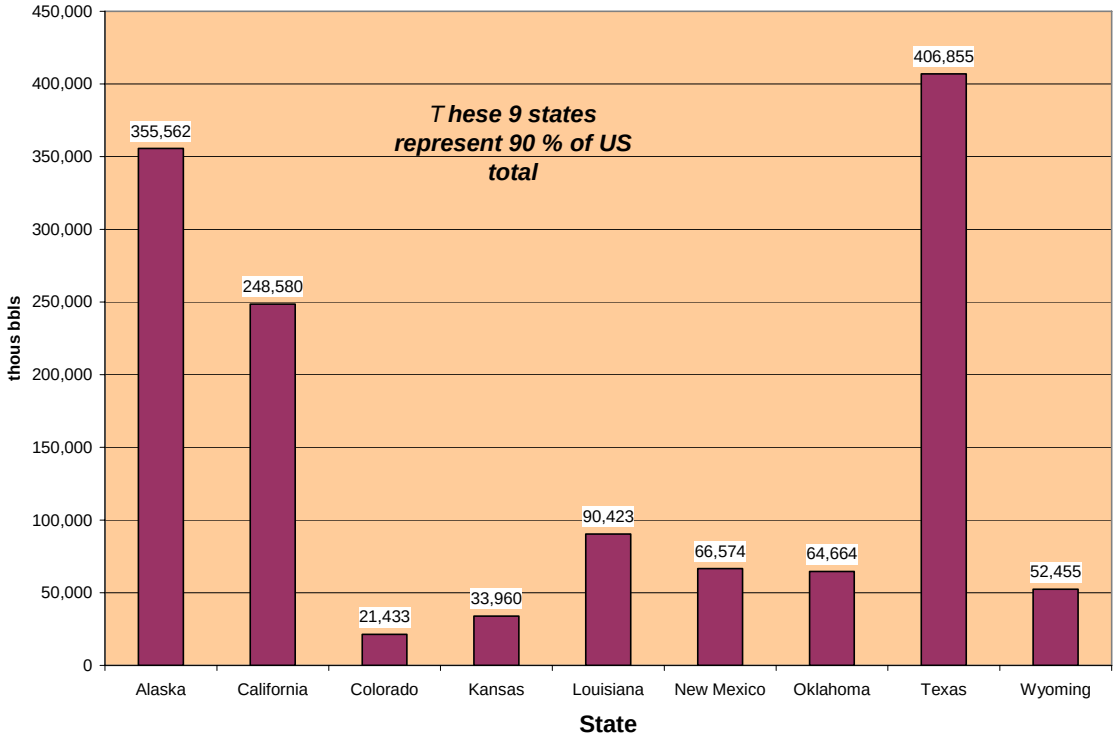

Figure 2: Annual US Production of Crude Oil --2003

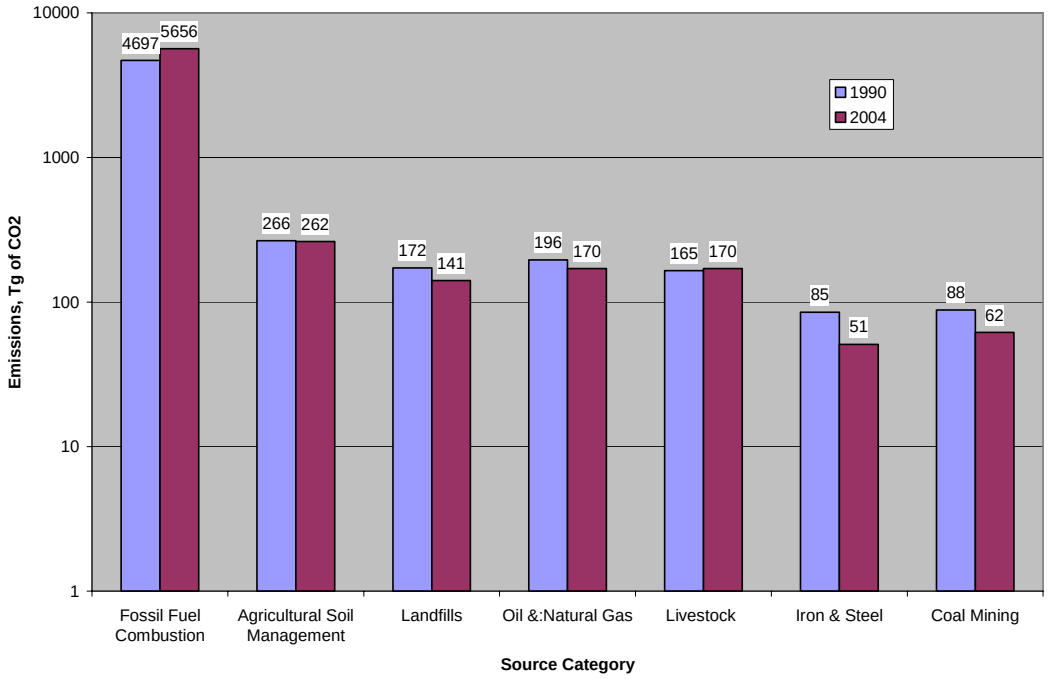

Figure 3: US Emissions of Greenhouse Gases, 1990 & 2004

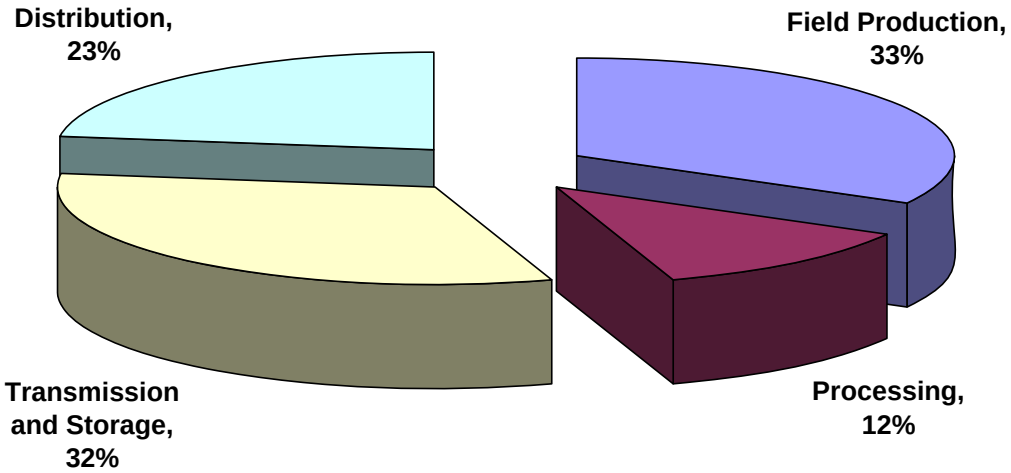

Figure 4: Distribution of Methane Emissions From Natural Gas Operations

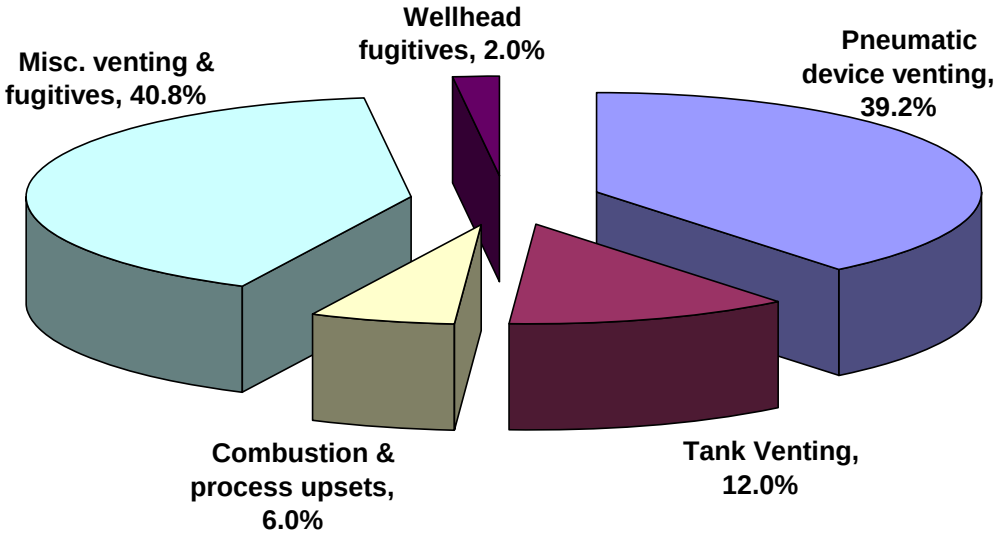

Figure 5: Methane Emissions From Petroleum Production Field Operations

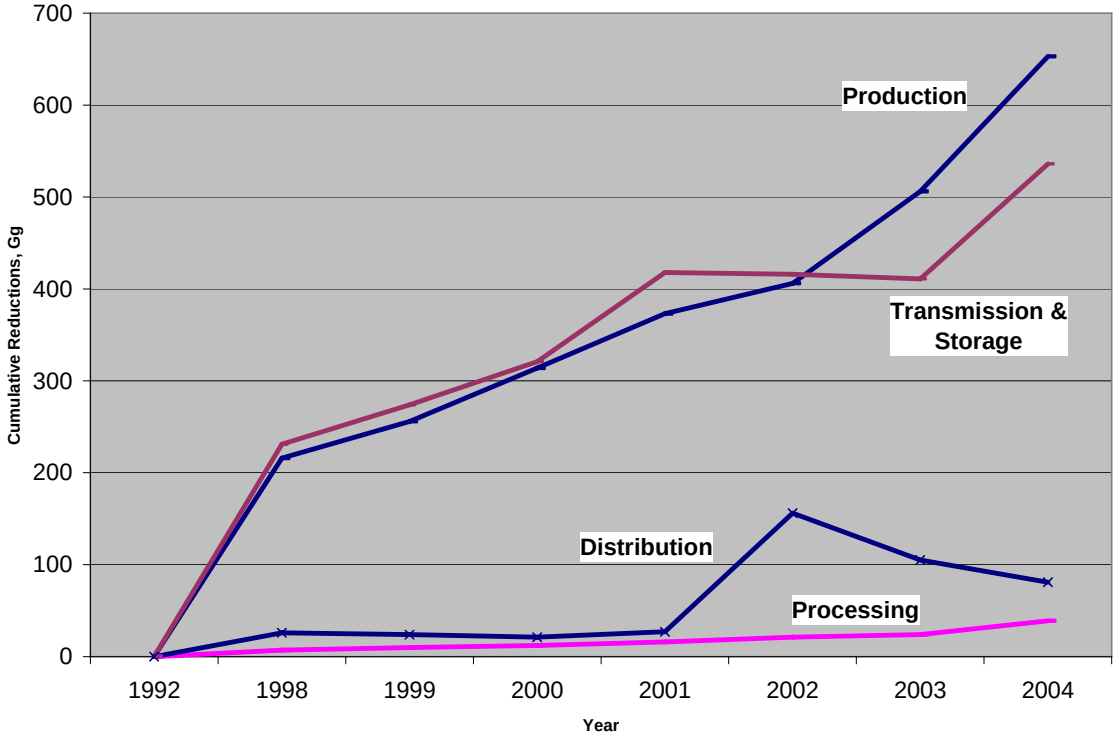

Figure 6: Methane reductions derived from the Natural Gas STAR program (Gg)

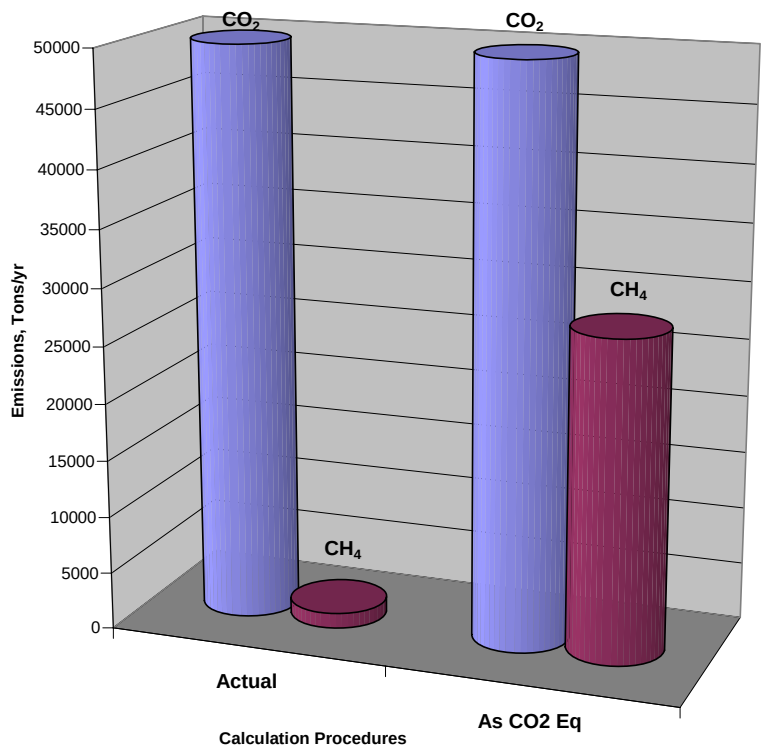

Figure 7: Total Emissions of Greenhouse Gases from Representative Gas Processing Facility

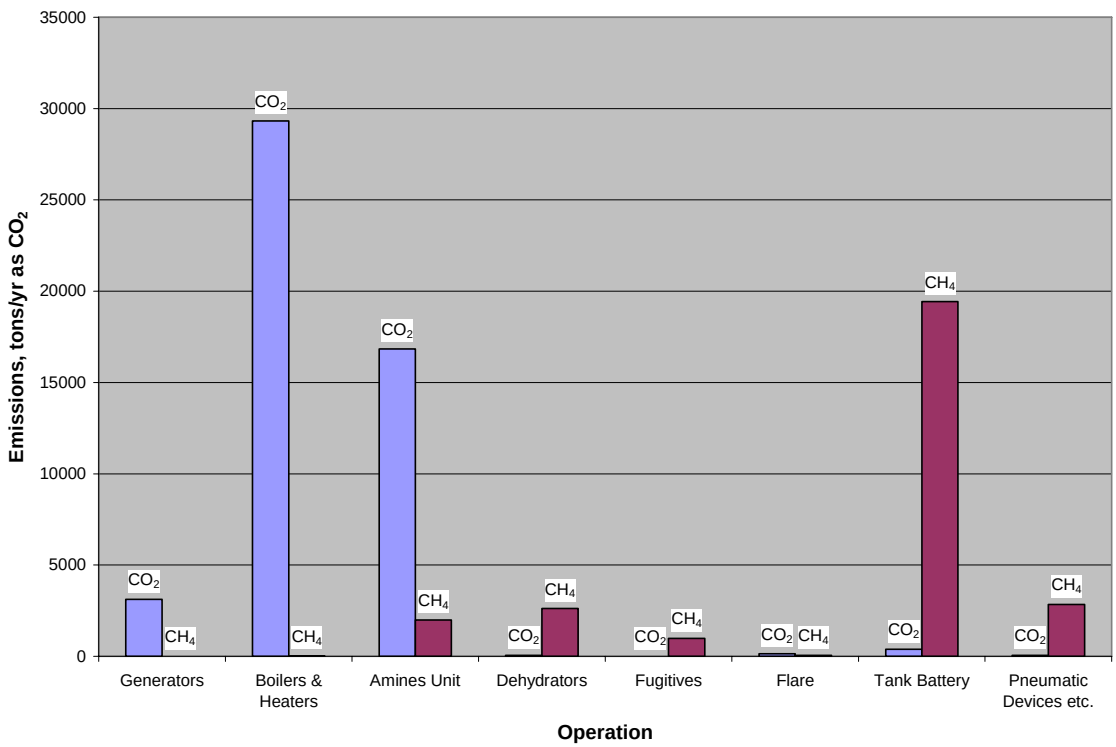

Figure 8: Distribution of Greenhouse Gas Emissions from Representative Gas Processing Plant

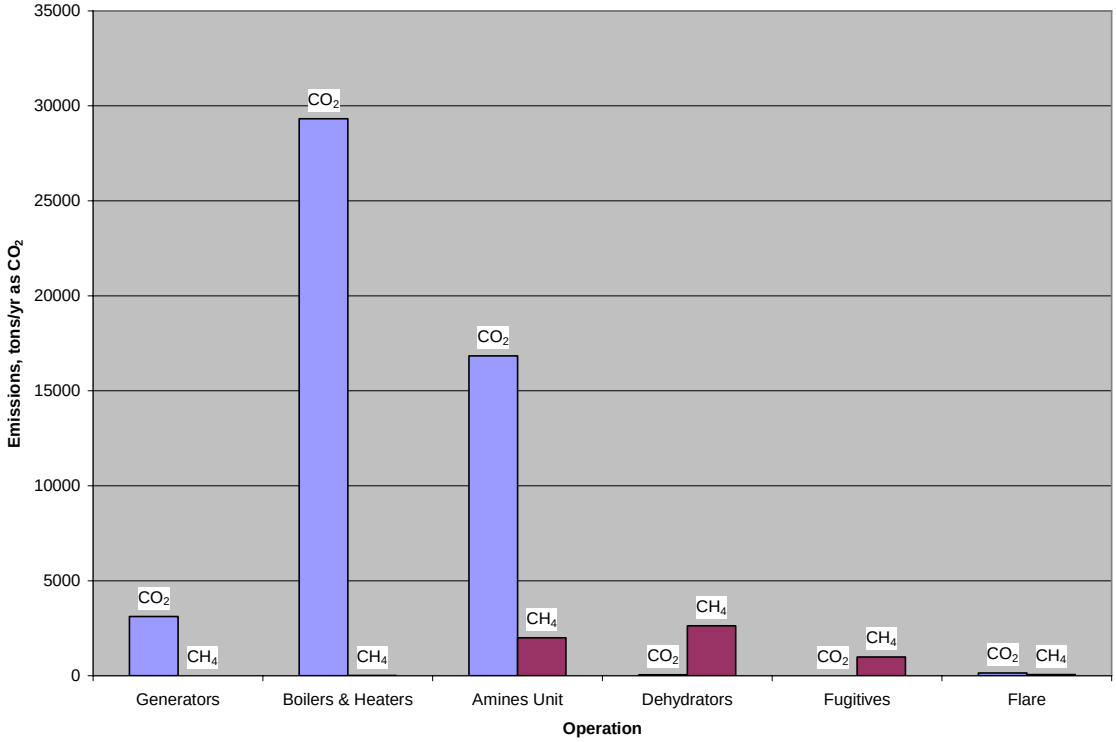

Figure 9: Greenhouse Gas Emissions from Representative Gas Processing Plant After Methane Controls

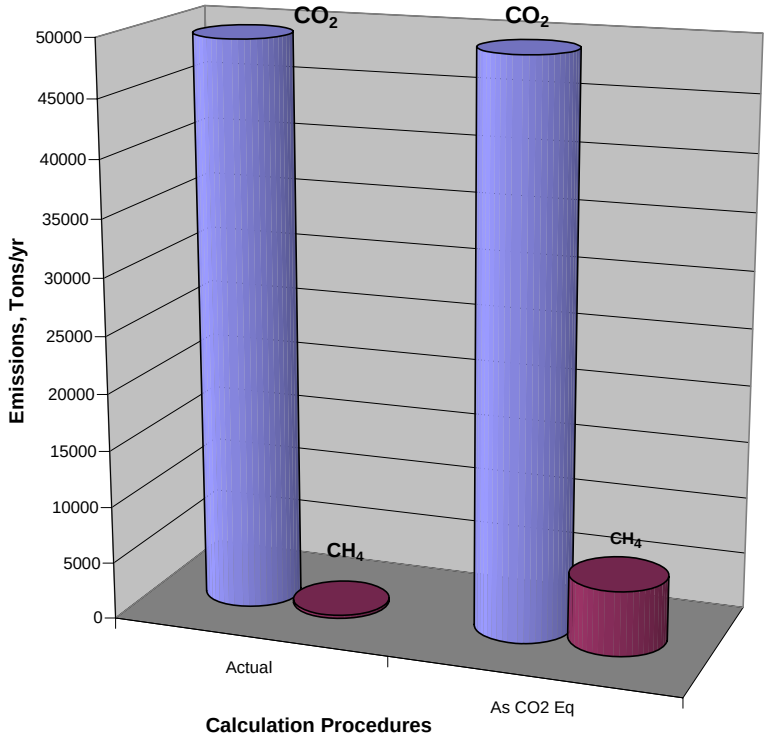

Figure 10: Total Emissions of Greenhouse Gases from Representative Gas Processing Facility, after Methane Controls

Sediments: An Emerging Environmental Issue

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ABSTRACT

In 1997 and again in 2004 the USEPA (EPA) issued major reports on the incidence and severity of sediment contamination within streams, lakes, bays and bayous in the United States. The EPA estimated that approximately 10% of the sediments underlying the nation's surface waters were sufficiently contaminated with toxic pollutants to pose potential risks to human health or the environment. Contaminants of primary concern were PCBs, mercury, other heavy metals, petroleum (oil & grease and PAHs), and pesticides-herbicides. The reports listed numerous geographic areas exhibiting elevated levels of these contaminates and identified large regions that have yet to be evaluated.

Currently the EPA is involved in the investigation and cleanup at over 200 sediment sites throughout the nation. Twenty percent of the sites on the U.S. National Priorities List have sediments issues of which at least ten are considered sediment "megasites" with projected cost of cleanup ranging from $50 million to nearly $500 million per site.

In December, 2005 the EPA issued a new guidance document for remediation of sediments at hazardous waste sites which may affect cleanup at numerous CERCLA and RCRA locations including some petroleum facilities such as E&P sites, refineries, storage terminals and chemical plants.

WHY FOCUS ON SEDIMENTS?

Our responsibility as scientists, engineers, managers, and stewards of our environment is to look forward. Our task includes understanding the physical, business, regulatory and political environments which influence the decision making process. This task also involves understanding that change is a never ending dynamic which requires adaptation and flexibility to address each stakeholder's interest. The strategic manager recognizes this dynamic and plans for how things will look like a year or five years from now.

In the corporate and regulatory regimes, environmental managers are generally involved in routine pursuits of compliance, prevention, assessment, remediation, and liability management. Historically, the media of interest focused on air, surface water, groundwater, soil… and sediments. The sediments part has traditionally been lumped with soil, and given little real attention. We suggest that the management of sediments is becoming a larger issue in the environmental arena and will continue to receive greater attention at all levels of the business and regulatory communities dealing with environmental issues. Following are some relevant facts:

- In 1997 and again in 2004, the EPA, on request of Congress and with the help of the United States Geological Survey (USGS) and the National Oceanographic and Atmospheric Association (NOAA), issued major reports on the incidence and severity of sediment contamination in the U.S. (Figure 1.)
- The EPA estimated that approximately 10% of the sediment underlying the nation's surface water was sufficiently contaminated with toxic pollutants to pose potential risks to human health or the environment.
- Currently the EPA is involved in investigation and cleanup at over 200 sediments sites throughout the nation.
- 20% (140) of NPL sites have sediment issues – 60 tracked on a National Basis.
- Ten are considered sediment "megasites" with projected cost of cleanup ranging from $50 million to nearly $500 million per site (Table 1).

The EPA evaluated sediment data at 19,398 sampling stations nationwide (Figure 2). Of those stations, the data indicate that 8,348 or 43% are probably associated with harmful effects on aquatic life or human health. 5,846 stations or 30% are possibly associated with harmful effects on aquatic life or human health, and 5,204 or 27% have no indication of associated harmful effects.

There are limitations to the data. As pointed out in the report, the sampling was not random, but biased towards areas where sediments were influenced by historical development. The data were also biased toward areas where state or local agencies had programs to gather sediment data. Further, there are uncertainties and variations in the tools used to assess sediment quality. As a result of the apparent bias, the EPA adjusted their estimate, stating that approximately 10% of the sediments under our nation's surface waters pose potential risk. Is this answer good enough? Will there be demand for better coverage? ... Better tools? ... Better data? What may that mean to the future?

WHAT MAKES SEDIMENTS DIFFERENT?

What makes sediments different? Isn't it just wet dirt? There are differences between sediments and soils. Sediments are usually associated with streams, rivers, bays, bayous and beaches. They may be encountered in urban, industrial, wilderness, wetland, or backyard environments.

Aside from obvious differences in sampling techniques (Have you ever tried to use a hand auger from a boat?), the extent of the areas and volumes involved tend to dwarf routine contaminated soil sites. The high water content and partitioning of contamination on to fine particles also create mobility problems both in sampling and in remediation if the sediment is disturbed. Also, treatment options developed for contaminated soils are frequently uneconomic or impractical for sediments. Lastly, decisions on the level of cleanup tend not to be based on simple MCLs (maximum contaminant levels), but are usually made on a preponderance of evidence and a risk evaluation based on local physical-chemical conditions, bioaccumulation factors, and potential risk to the food chain. Table 2 lists the differences between sol and sediment sites.

WHAT SHOULD WE DO?

Sediments are an increasing area of interest for regulatory agencies and nongovernmental agency (NGO) stakeholders. Stakeholder interests are diverse.

- Federal, state, tribes and local government
- Local residents
- Responsible parties
- Environmental groups
- Natural Resource Damage Trustees
- Meddlers
- Others

How can we position ourselves to handle the problems and to structure stakeholder interactions in order to make more informed, credible, and defensible decisions? The simple answer is to get educated, get involved, and work on communication skills.

There is significant crossover in the skills required to deal with surface water, groundwater and soils and the skill sets required to deal with sediments. Geology, engineering, chemistry, biology, and toxicology are some of the areas of expertise that are needed. However, the issues vary, and many of the terms are different. Excellent communication skills are needed to articulate the issues to the growing interest groups becoming involved in this issue.

Environmental scientists and managers need to become familiar with some new topics. For example, there are many avenues through which Polyaromatic Hydrocarbons (PAHs) may enter sediments. Petrogenic sources are those related to leaks and spills from pipelines or terminals, or other sources of unburned petroleum. Pyrogenic sources are those related to exhaust gases from trains, planes, ships and automobiles; to building fires or forest fires; and to old manufactured gas plants. Urban runoff may contain both petrogenic and pyrogenic PAHs. Some chemical fingerprinting techniques can distinguish pyrogenic from petrogenic PAHs, and perhaps even type a source.

There are cases where petroleum storage facilities were accused of being the sole or primary contributor of PAHs to harbor and bay sediments. The estimated cost of cleanup was substantial. The data, however, showed the PAHs in the sediment were primarily from pyrogenic sources. Determining the source of sediment contamination is a key in assigning appropriate liability, and in the design of remedial alternatives.

In dealing with sediments, we suggest learning more about the following terms;

- WRDA – Water Resources Development Act of 1992
- NSI – National Sediments Inventory
  - Contains 4.6 million records (sediment chemistry, tissue residue, toxicity) on
  - 50,000 monitoring stations in the U.S.
- ESGs – equilibrium-partitioning sediment guidelines (similar to MCLs for water)
- AVS – acid-volatile sulfides (molar values)
- SEM – simultaneously extracted metals in sediment (molar values)
- TBP – theoretical bioaccumulation potential
- BSAF – biota-sediment accumulation factor
- APC – Area of probable concern
- GLWQA – Great Lakes Water Quality Agreement (International agreement between U.S. and Canada)
- MNR – Monitored Natural Recovery

Fortunately, the EPA, USGS, DOD, SMWG (Sediments Management Work Group) and others have put forth a number of good documents to assist in understanding this growing area of interest. These documents have a wealth of information. The Sediments Management Work Group is an industry organization formed with the mission to advance risk-based, scientifically sound approaches for evaluation of sediment management decisions. The group's objective is to collect, develop, analyze and share data and information on the effectiveness of sediment management technologies and approaches.

A cooperative working environment between the EPA and the regulated community resulted in the recent USEPA document titled "Contaminated Sediment Remediation Guidance for Hazardous Waste Sites." The guide was issued in December 2005. It outlines data needs, discusses fate and transport of contaminants in sediments, covers risk evaluation methods, and outlines various cleanup options beyond dredging such as Monitored Natural Recovery, In Situ Capping, and Long Term Monitoring. This type of cooperation between stakeholders is key to maintaining a balanced approach to the long term resolution of this growing initiative.

Tables and Figures

Table 1. Superfund Sediment Megasites with estimated cost of cleanup.

Superfund Sediment "Megasites"

- Hudson River, NY - $460 Million
- New Bedford Harbor, MA - $361 Million
- Bayou Bonfouca, LA - $90 Million
- Marathon Battery, NY - $84 Million
- Triana/Tennessee River, AL - $80 Million
- Fox River, Greenbay, WI - $361 Million
- Silver Bow Creek, MT - $97 Million
- Commencement Bay, WA – $197 Million
- Bunker Hill (Coeur d'Alene Basin)
- Housatonic, MA

Table 2. Differences between soil and sediments

Differences between Soil and Sediment Cleanups

- Larger volumes of sediments
- High water content
- Fine particles tend to contain bulk of contamination
- High mobility creates problems in sampling and in remediation
- Sampling techniques are different
- Treatment options developed for contaminated soils are frequently uneconomical or impractical for treatment of sediments
- Decisions are usually made on preponderance of evidence and risk evaluation
- Disposal and material management issues
- Increased stakeholder (public) participation
- Long term management in remedy selections
- Significantly more costly

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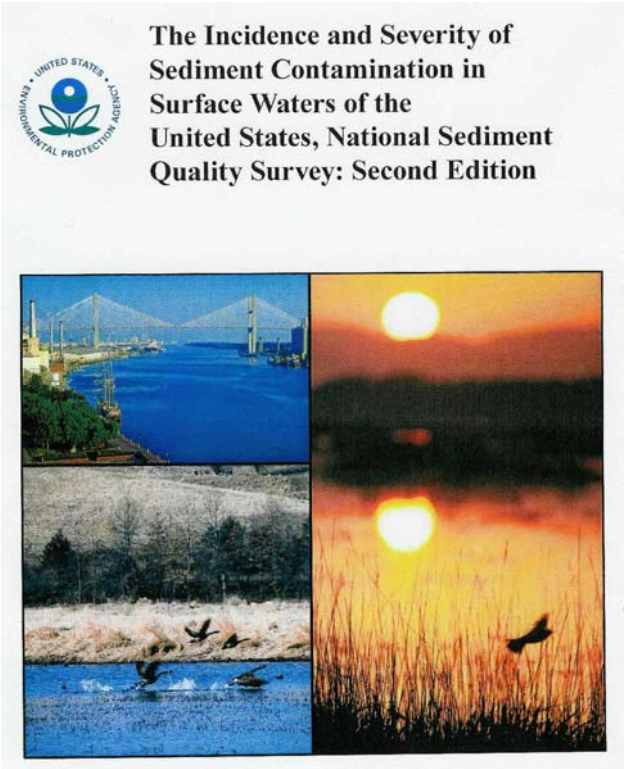

Figure 1. USEPA Report December, 2004.

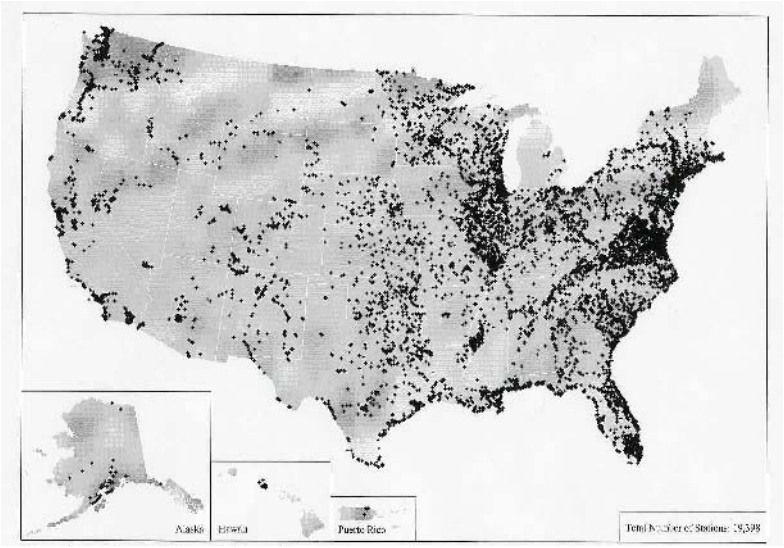

Figure 2. Sediment sample points.

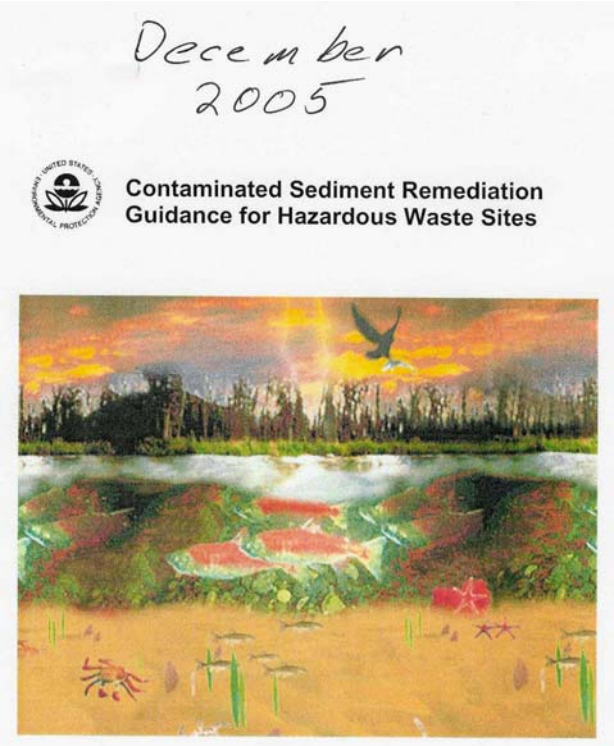

Figure 3. Contaminated Sediment Remediation Guidance for Hazardous Waste Sites.

An Interactive Integrated Information Data Management Process for Identification and Reduction of Liabilities

Margaret Roy URS Corporation Austin, TX; Pilar Odland URS Corporation Austin, TX; David Friday URS Corporation Austin, TX

ABSTRACT

The objective of the Interactive Integrated Information Data Management Process (IP) System is to provide a network of staff and tools not only to store data safely, but also to provide mechanisms to develop the objective of a sampling program, gather data, and verify and use data effectively. The URS IP System does not just manage data for environmental investigations; it can be a part of a larger strategy to manage liabilities. The identification of liabilities involves quantification of business related risk and estimates financial risk, using probabilistic techniques. Once the risks are identified, a strategy can be developed to mitigate these risks and focus resources. For instance, if a liability in a facility's environmental program is groundwater contamination that is discharging to a surface water body, the URS IP System will design the sampling plan, pre-load the database, verify that the data received is correct, validate the data, and then send the dataset for statistical analysis and/or to a geographic information systems (GIS). Significant data gaps can be identified and their related impact on financial risk assessed. As decisions are made and actions undertaken, the business risk model is re-run to measure the reduction in risk, to identify other contributors to risk, and to assess a cost/benefit relationship to determine if further action is required. The URS IP System calls upon multiple technical disciplines, an electronic database, and other computer based tools such as GIS, statistical software, decision theory techniques, and Monte Carlo simulations to design a data management program specific to your project or facility (long-term and short-term).

INTRODUCTION

Identification and management of environmental liabilities is an important consideration in redevelopment of industrial properties and on-going operations of current properties. Liabilities are defined not just in financial terms, but also in the non-financial terms such as public perception. This paper describes a fictitious site with attributes taken from multiple real-life sites and describes how the liabilities were managed in conjunction with a well thought-out sampling plan, laboratory quality assurance plan, and data management strategy.

Business risks can include strategic risk, financial risk, operational risk, commercial risk, and technical risk. In order to manage a company's risk, managers need to adopt a structured approach to the risk management process. Figure 1 shows the iterative and dynamic approach to identification and management of risk and liabilities. This methodology enables managers and decision makers to evaluate and answer three key questions:

1. Should I spend money?
2. Where or how should I spend it?
3. Have I spent it effectively?

Through the development of a business risk analysis, managers are able to gain an understanding of their enterprise risk by being able to 1) identify the most prioritize critical risk issues, 2) define acceptable and unacceptable risk, 3) develop a risk mitigation strategy, 4) implement the risk mitigation strategy in a manner consistent with their budgetary constraints, and 5) understand when there is no longer a benefit to implementing preventative actions. Risks can be quantified in two categories depending on corporate policy:

1. Quantitatively using costs; or
2. Qualitatively using an index.

Since many legal departments shun quantitative methods to assess risks, a qualitative methodology has been chosen to illustrate a risk index in this example. It is important to note that the indices must be objective to avoid manipulation or problem avoidance. The risk index is developed by reviewing the facts (see Figure 1) and then giving each category of risk a rating based on the facts. No half scores are allowed. As the site moves through the remediation process, the indices should be re-evaluated and corrected for current conditions (see feedback loops on Figure 1). This evaluation, over time, can be represented on a curve (Figure 2) and a determination made when activities no longer impact or reduce risk. As shown on Figure 2 when the costs reach around $40,000, there is no further significant reduction of the risk index and any money spent on the reducing the index would have little impact to the risk.

Quantitative methodologies allow more defined analysis of the impact. Uncertainty is represented by the magnitude of the standard deviations of the overall cost (see uncertainty bars on Figure 2). These cost curves, as conceptually demonstrated in Figure 2, are an excellent tool for purposes such as budgeting or defining risk tolerance vs. spending. The combined use of both curves provides an excellent management tool for environmental liabilities and risks. An applied example is presented below.

BACKGROUND

Bradley Chemicals was located in Holloway, Texas, along a navigable waterway. This company manufactured a wide variety of specialty chemicals for use in manufacturing industry from 1950 to 1985. Bradley Chemicals was closed in 1985 and the facility was sold to Junod Industries in 1987. Junod Industries planned to retool the 25-acre facility for pre-treatment of building materials for commercial and residential properties. Junod Industries felt that the purchase of the former Bradley Chemical facility was strategic because of its location along a navigable waterway. They would be able to move large amount of products in and out of the facility and to consumers quickly. Holloway, Texas, is located near several major ports and large cities along the Texas coast. The economy of Holloway was impacted when Bradley Chemicals closed. The re-opening of the plant could potentially provide a positive influence to the local economy and positive press for Junod Industries. Junod Industries is new to the area and wants to become known as a good corporate citizen.

Junod Industries purchased the properties and also took responsibilities for any environmental liabilities in the purchase. Junod Industries knew that there was a plume of solvents in groundwater, but felt that the technologies were available to remediate the contamination and would not be a hold up to the renovation and operation of the facility. Junod Industries was not aware of PCB contamination at the time of the purchase.

Figure 3 shows a layout of Junod Industries and the surrounding facilities. Richmann Refining is located adjacent to Junod Industries and also across the Dove River. Additionally, across the river and upstream is a pesticide and herbicide formulation facility.

Dove River is a tidally influenced navigable water way maintained by the Corps of Engineers. Downstream of the industrial park is the city of Holloway, Texas, with a population of approximately 50,000. Dove River is listed as impaired because of the pesticides and PCBs in fish tissue. There is data from groundwater taken from Junod Industries with detections of PCBs.

Business Risk Strategies for Junod Industries

Table 1 shows the risk categories and risk rankings for Junod Industries. Although there are numerous risk categories and potential liabilities possible in this example, three have been chosen for evaluation in this business risk analysis:

- Risk to Human Health;
- Natural Resource Damages;
- Public Perception.

As shown on Table 1, the lower the ranking the less uncertainty and a lower risk of a liability to occur and conversely, the higher the ranking the greater the uncertainty and, therefore, the greater the risk of a liability to occur.

Risk to Human Health

For the major category of protection of human health, the risks are further categorized into an understanding of nature and extent of the contamination and the potential for exposure. This human health category could apply to workers (e.g., health and safety) as well as residential exposure off site of the Junod Industries property.

If the concepts in Figure 1 are applied to the Human Health Risk Category, a review of the **Facts** show the following:

- Junod Industries knows that they have detections of PCBs, several chlorinated organics, and fuels in their groundwater. The available analytical data from several years ago shows that the detections and detection limits are above current screening criteria.
- They do not know the size of the plume or the direction of groundwater flow. From the general geology of the area, there are probably two groundwater zones.
- Depth to groundwater is only a few feet below ground surface in some locations and workers have been exposed to groundwater as it has seeped into trenches. During a recent construction project, fumes most likely from the groundwater overcame a worker as it surfaced into the trench.
- The facility gets its drinking water from a deep well on site. In addition, the drinking water for Holloway, Texas, is from wells located within a mile of the facility, but the wells are upgradient of known contamination.

An **Analysis** of the facts quickly shows Junod Industries that they need a well thought-out plan to address the groundwater nature and extent of contamination and protect the workers and residents from exposure. On Table 1, the initial ranking of the risk model shows a total initial risk ranking of 560.

Natural Resource Damages

Natural resource damage (NRD) is another major category that Junod Industries should consider in their uncertainty analysis since the site borders an impaired water body with active fishing advisories in place. Because of this, the site is highly visible to the regulators and trustees. Junod Industries can reduce their risk from costly NRD actions with understanding any potential contributions to past, current, and future impairment of the natural resources associated with Dove River. Legal actions against Junod Industries are possible.

If the concepts in Figure 1 are applied to the Natural Resource Damages Category, a review of the facts show the following:

- Groundwater most likely flows to Dove River.
- PCBs have been detected in the groundwater on Junod Industries.
- Pesticides were not used on Junod Industries property beyond application of pest control under manufacturers instructions. A pesticide formulation facility is located upstream of Junod Industries.
- The fish advisory is for pesticides and PCBs in fish tissue, especially predatory fish. The residents of Holloway, Texas, utilize the downstream portions of Dove River for recreation, including fishing.

An **Analysis** of the facts quickly shows Junod Industries that they need a well thought-out plan to address the potential contribution of groundwater contamination into Dove River, specifically the PCBs. As the groundwater investigation is implemented, Junod Industries will understand which PCB congeners are present in groundwater on-site. The additional cost of PCB congener analysis is determined to be acceptable for two reasons: 1) to achieve the detection limits necessary for the surface water criteria, and 2) to compare what is on site with what has been detected in the Dove River sediments and fish tissues. On Table 1, the initial ranking of the risk model shows a total initial risk ranking of 720.

Public Perception

Public perception is of importance to Junod Industries because they are dependent on local contractors to purchase their treated building products. Bad press could influence their sales in the immediate area. If the concepts in Figure 1 are applied to the Public Perception Category, a review of the facts show the following:

- There are activist groups in the general area who are concerned about the fish advisory.
- The local press ran positive articles about Junod Industries purchasing the property and indicated that the facility would be providing jobs and generating taxes.
- City and County government officials helped broker the purchase agreement for Junod Industries.

An **Analysis** of the facts shows Junod Industries that they need to develop a plan to manage their image for the local press and government officials. Junod Industries plans to participate in local social events and become well known as a corporate citizen while the environmental investigation is underway. On Table 1, the initial ranking of the risk model shows a total initial risk ranking of 80, indicating that they have a low risk ranking currently but will need to maintain their positive rating.

Junod Project Plan

From the risk analysis, Junod Industries knows that there are a variety of site characteristics that still have large amounts of uncertainties tied to them. A review of the facts helps Junod Industries prioritize activities:

1. Define Nature and Extent of Contamination;
2. Define complete human health exposure pathways;
3. Define the site's potential historical contamination contribution to Dove River;
4. Define and manage current releases into Dove River;
5. Maintain positive public perception.

This priority list will allow Junod Industries to design a programmatic remediation strategy that will not only maximize every dollar spent but also minimize liabilities. In particular, the programmatic strategy will allow Junod Industries to develop a system for managing the analytical data generated for the project that will be cost effective as well as help to characterize the site correctly. Junod Industries will manage the analytical laboratory and all of the analytical data generated for the project so that each data point is useful. The sampling plan, laboratory analysis quality limits, data validation procedures, and data storage are all laid out prior to

sampling. The database is pre-loaded to know what data to expect and prints out field logs and labels to minimize mistakes during sampling. The laboratory clearly understands what detection limits have to be met. The data validation will ensure that the data is acceptable to regulatory agencies as well as the public. The data will be stored in a secure database that can be accessed and updated as needed. The data will also be available for statistical analysis. Utilizing a well thought-out data management system reduces the need for re-sampling, and the database storage ensures that the data will be safe and available as future needs arise.

Re-Evaluation of Risks and Liabilities

As Junod Industries implements their project vision, they reassess and evaluate risks and liabilities as more facts become available. Once the initial risk analysis has been completed, Junod Industries has a clearer understanding of their site and a priority list of issues that is aligned with their strategic corporate plan. As Junod Industries implements their project vision, more facts will become available and the risk analysis can be reassessed. Table 1 shows the initial re-evaluation after the following facts have been established:

- Nature and Extent was defined.
- Human health exposure pathways on site are now actively managed through the facilities' health and safety program.
- PCBs and several chlorinated organic compounds most likely discharged to Dove River over a 10-year period. There are no other off-site releases current or historic.
- Any current releases are managed through an interim groundwater recovery system until a long-term system is in place.

Table 1 shows that Junod Industries has greatly reduced their risk and liabilities under the categories of human health and natural resource damages. Reduction of risk under the public perception category was not warranted. Using the risk analysis tools, along with smart data management and analysis tools, allowed Junod Industries to identify and prioritize risks and then to develop a spend plan based on risk tolerance and internal budgets to address the risks.

Figure 4 shows the risk index curve vs. cumulative money spent for the project. The spend is significant initially but levels out as additional data is gathered and analyzed and remediation activities are undertaken.

CONCLUSIONS

Three risk categories were chosen in this example that included areas not easily quantified, but that can have major financial implications to a company. A negative public perception and natural resource damage claims can have long-term impacts. Junod Industries recognized that these issues deserved a careful review in their business risk model early on in the process. These issues are inter-related and required a nimble and active method for evaluation before, during, and after project implementation.

Junod Industries took an eyes-open approach to this project and managed their costs as they managed their risk and liabilities. They utilized a data management system that made every analytical point count and they determined when additional data gathering would not reduce the risk index further. The decision to reduce the data gathering is determined by a company's risk

tolerance. In the case of Junod Industries, they are unable to totally remove all complete exposure pathways but are managing those pathways that are open through worker health and safety programs.

Although this example is greatly simplified, it does show that a company or facility can adopt a programmatic strategy to evaluate risks and liabilities that are aligned with its corporate goals. This evaluation allowed Junod Industries to have a complete understanding of their facility and the associated issues. In addition, Junod Industries will be able to design an efficient and cost-effective strategy for their facility that includes sampling, data management, and remediation activities. As a project progresses or circumstances simply change, those risk rankings can be re-evaluated.

Table 1. Junod Chemical Risk Categories and Rankings

Risk Category	Rank	Initial Score	20	40	60	80	100	Post Action Score
Human Health	2	160	No human health impact	Detections below industrial criteria	Detections above industrial criteria	Detections above residential criteria	NAPL and other detections above all criteria	120
		200	Delineation complete	Delineation mostly complete > 75%	Partial delineation > 50-75%	Partial delineation > 25% - 50%	Nature and extent not defined	40
		200	No complete exposure pathways	Insignificant but open exposure pathways	Potentially open and complete exposure pathways	Significant open exposure pathways	Multiple and active open exposure pathways	120
Total		**560**						**280**
Natural Resource Damages	3	300	No documented past releases, no past damages alleged	Past damage known, volume and timeframe known	Past damage known, one source, timeframe known, volume unknown	Past damage known, sources, timeframe known, volume unknown	Past damage known, sources, timeframe and volume unknown	120
		240	No current releases	Current releases after rainfall > 2”	Current releases after rainfall > 1”	Current releases with any rainfall	Active and open current releases	60
		180	No potential for legal action	Legal action threatened	Legal action threatened by stakeholders	Single-party NRD litigation	Multiple party NRD litigation	120
Total		**720**						**300**
Public Perception	1	40	No activist group(s) identified	Activist group(s) work cooperatively resolve issues	Activist group(s) negatively affect public perception	Activist group(s) threatened to file lawsuit	Activist group(s) file lawsuit	40
		20	Positive press	Neutral press	Local negative press	Regional negative press	National negative press	20
		20	Positive political	Neutral political	Local negative political	Regional negative political	National negative political	20
Total		**80**						**80**

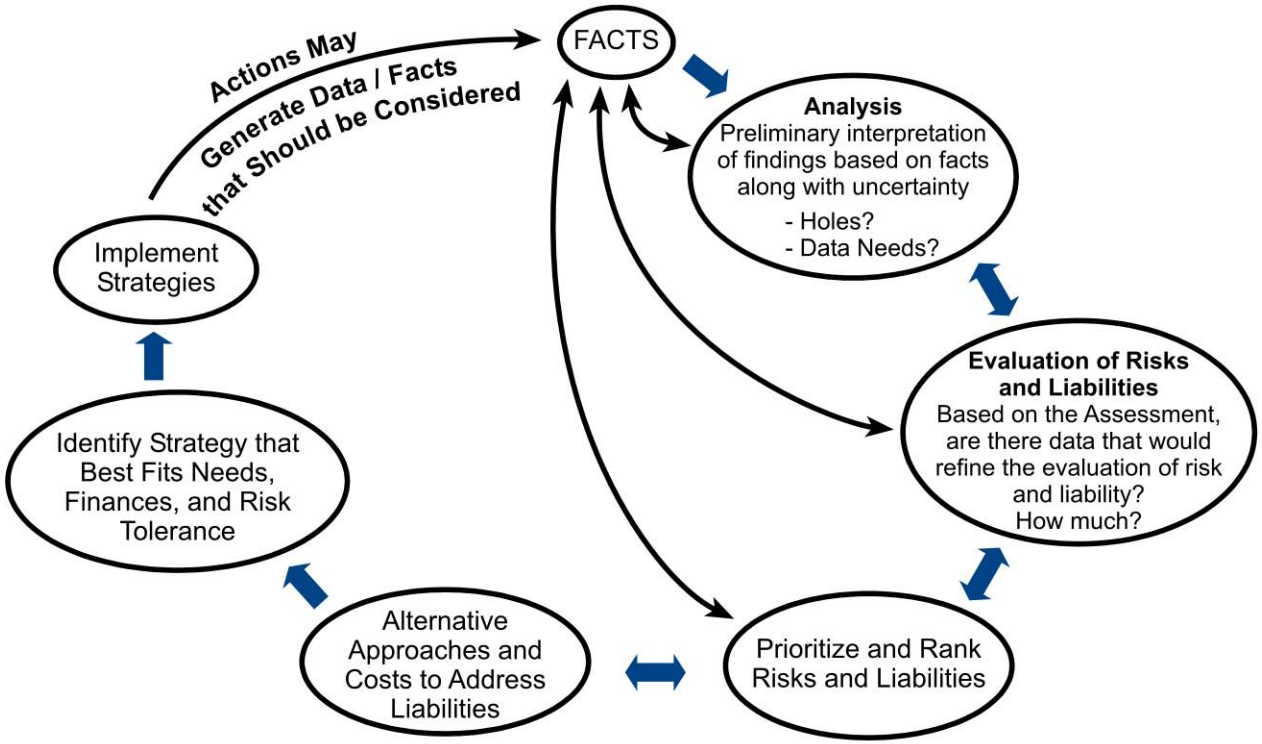

Figure 1.
Risk Liabilities Logic

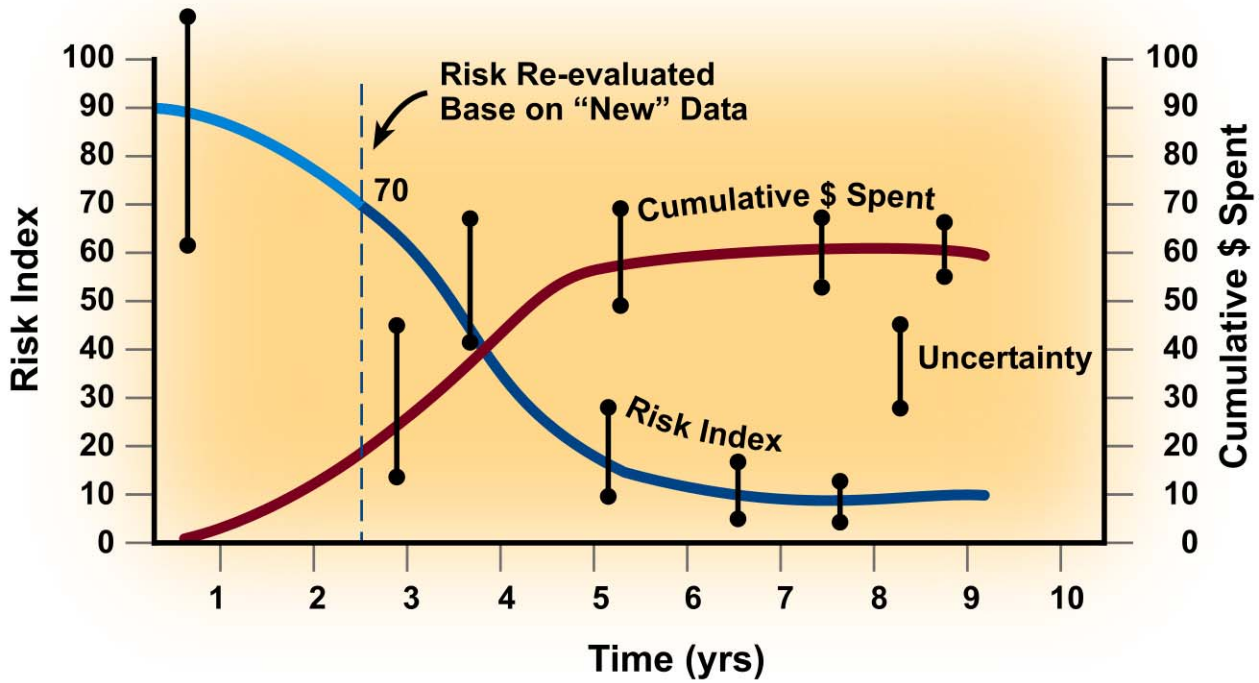

Figure 2.
Conceptual Risk Index vs.
Cumulative $ Spent

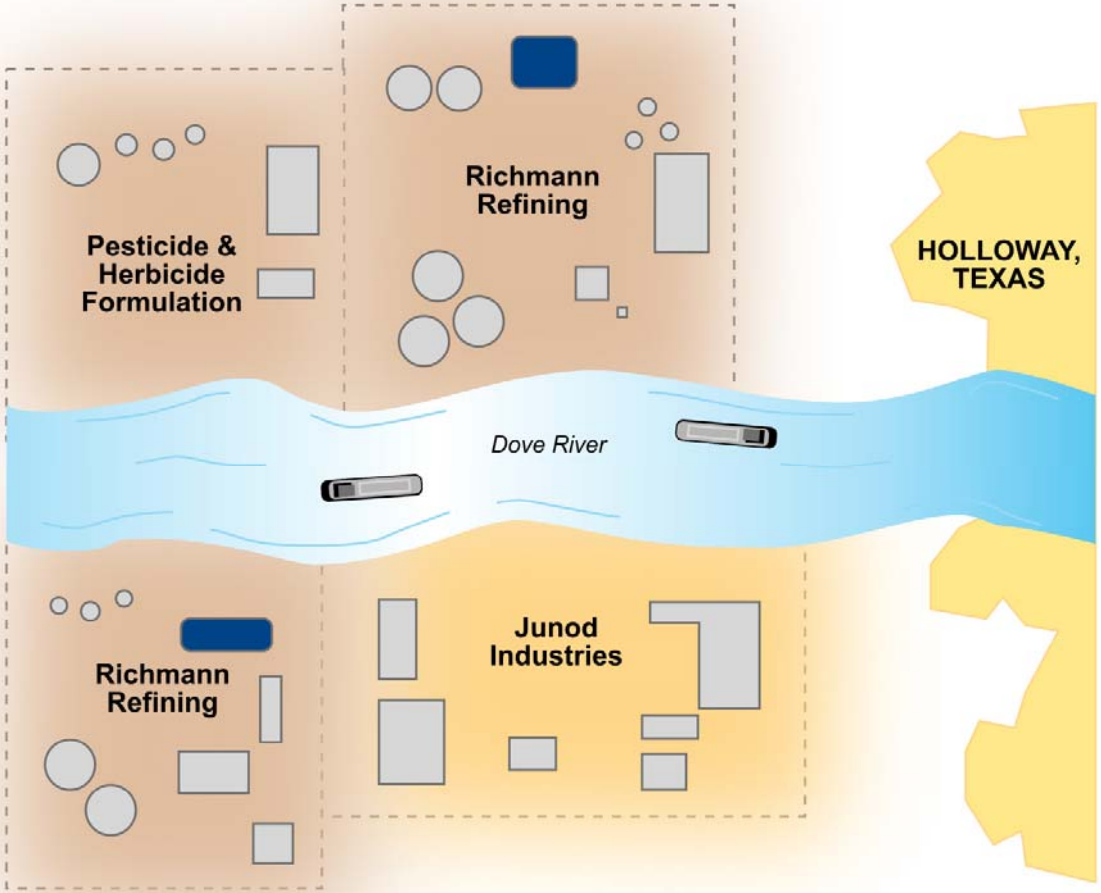

Figure 3.
Site Layout

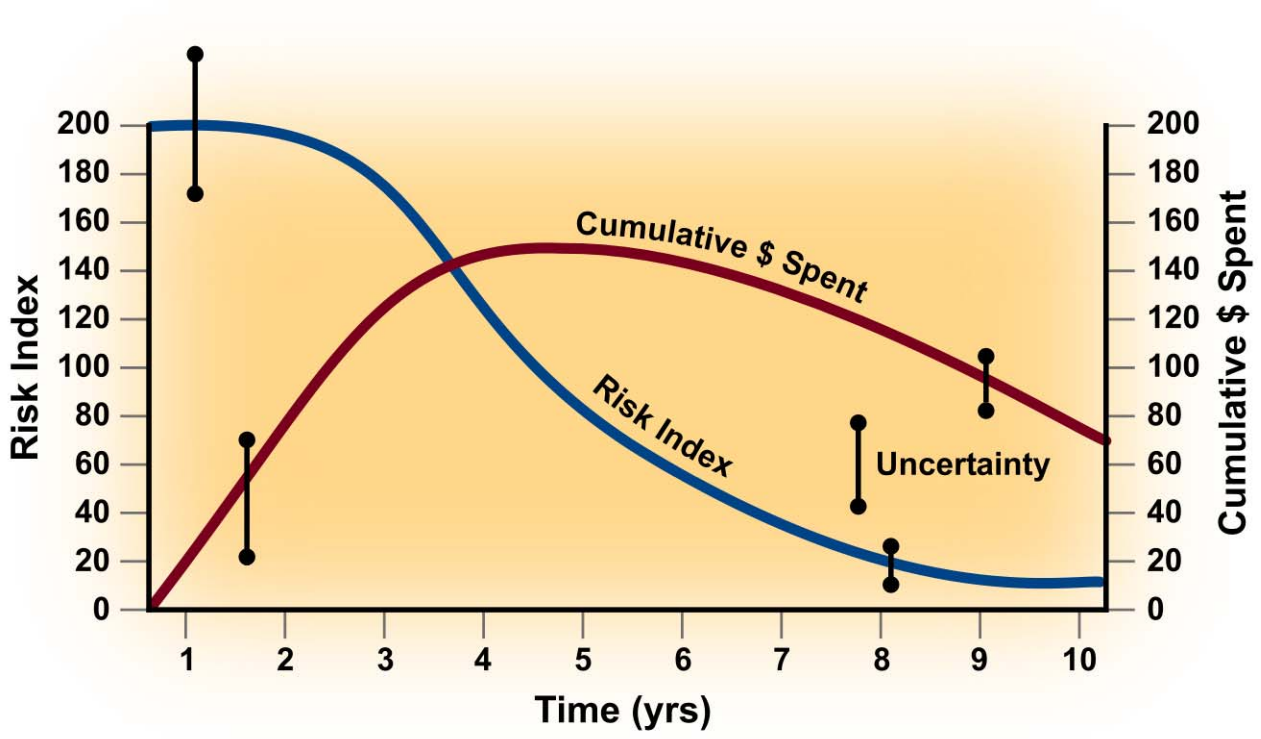

Figure 4.
Risk Index vs. $ Spent Over Time
for Nature and Extent

Mitigating Environmental and Site Liability through Electronic Data Management – A Case Study

Dean Novak, James Hatcher, Peloton; Carol Howlett, Trident Exploration

Abstract

Trident Exploration Corp. is a mid sized energy exploration company that was growing rapidly and needed a system to handle all of its site and environmental data. Due to the number of sites that were being drilling and acquired, the potential environmental liability was increasing and the current way of managing data (spreadsheets) was proving to be drastically insufficient. Trident implemented an electronic field and head office database to manage all of its site data from the transition of that site from early landowner negotiations to final reclamation sign off and all steps in the process in between.

With the system implemented Trident is now able to provide this information to all relevant parties with the touch of a button. Cost, liability and environmental detail can now be easily captured, managed, and reported by those who require it. This talk will describe how Trident has been able to manage and mitigate their environmental exposure through efficient data management.

Introduction

Trident Exploration Corp's sole business focus is the discovery and commercial development of natural gas in coal ("NGC") also known as coalbed methane ("CBM") resources in the Western Canadian Sedimentary Basin ("WCSB"). Trident has assembled its own WCSB land position of over 725,000 net acres. Trident employs approximately 300 office and field staff.

In the summer of 2005 it became apparent that the increasing level of activity, combined with increasing regulations for CBM developement, necessitated that better systems and processes were required to manage Trident's environmental information. Trident actively began an initiative to review their systems and processes with the goal of ensuring a high level of environmental performance, a reduction in their overall exposure to liability, and to streamline their regulatory permitting process for increased efficiency.

Challenges

Increased Public Focus

CBM development was relatively new in the area that Trident was operating. Previous CBM development in other areas, notably in Wyoming, had the effect of increasing public awareness and concern.

Increased Regulation

In part due to the increase in public concern, new government regulations were being introduced that would now require mandatory water well testing for all CBM wells. This was in addition to soil, water, and vegetation analysis that was part of the standard permitting process. A continuing trend by regulatory agencies towards 'self regulation' also meant that less environmental information would be submitted to government, but more detailed information would be required to be collected by industry – subject to audit.

Fragmented Information

Many different groups and departments within Trident collected, tracked, and managed various aspects of site permitting and environmental data. This data was captured in a variety of ways including spreadsheets, paper files, photographs, Word and PDF files, as well as hard copy files. This caused several problems:

- Accessibility of the data was difficult. Quickly finding the particular piece of information was problematic. The ability to analyze the data as a whole (to identify and action high priority sites for example) was also difficult.
- Integrity of the environmental information within the company was not optimal. Managing by spreadsheets often resulted in outdated or duplicate information or information where the source was unknown and undocumented.

- Poor information flow between various groups within the company, particularly between head office and field.
- An inability to effectively manage the increasing amount of activities and deadlines.
- Increased opportunity for error resulting in environmental and liability exposure.

Vision

SiteView

Trident had a vision of consolidating their regulatory and environmental information into a single system that would help them better manage their activities, as well as reduce their environmental and site liability. Trident had previously implemented an electronic well file system for their down-hole well information using a commercial software application from Peloton Computer Enterprises. They therefore looked to see if another software application from Peloton, (SiteView) could meet their requirements for managing regulatory and environmental information.

Growth

Trident was interested in a system that would not only fix the existing problems, but would also be able to accommodate for their expected future growth – they only wanted to do this once.

Consolidation of data

As a lot of different groups collected and relied on regulatory permitting and environmental data, by consolidating this data into one system the information flow between the different groups could be streamlined. This would also provide for one location in the company, where all site information would reside and would increase the ability to retrieve information (and be confident on that information) when required. Having a true database of site environmental information would also allow the company to better project, prioritize, and resource for upcoming activities.

Trident wanted to ensure that all environmental details on operations were properly stored to reduce their exposure to any issues. This would include storing information on:

- pre-site environmental assessments
- survey and construction activities
- water wells
- spill and contaminations
- reclamation/remediation activity

Consistency of data and processes

There was a desire to standardize on consistent terminology and process. Having a system that would help enforce what and how information is recorded would help increase confidence that when required, the proper information could be retrieved. There would be less dependency on which people 'did a good job recording information' and which didn't, as the system would help everyone to conform to the same expectations.

'Structured' and 'non-structured' data

Trident wanted the ability to put data that was of a consistent format (structured data), into a single database that would enable them to track and analyze, and report on it. If consistent data such as permit dates, water analysis, soil analysis, mud types and amounts, etc. could be stored in a database, then the ability to accurately retrieve, report, and plan upcoming activities would increase. It was also recognized that there was important 'unstructured' data that would also need to be stored for each site file. This type of information included a wide variety of documents, both from internal sources or from external sources such as regulatory agencies or outside consultants. These included scanned survey plats, aerial and satellite photos, PDF's, spreadsheet, and word documents.

Environmental CheckList

TRIDENT EXPLORATION CORP.

Report Date: 9/27/2006
Page: 1 of 2

Site Name: 981384 HAYNES 13-28-38-24 W4M, S02751-00

Project Name	Land Use	Environment Status	Lease Construction Status	CMS Project Area	UWI
981384 HAYNES 13-28-38-24 W4M	WELLSITE & ACCESS ROAD	Land	Sent to Permit/License		-28-038-24-4

Problem Site?	Quality Control Returned (Operations Only)
No	

Location

Loc Type	Des	Legal Location
WELLSITE & ACCESS ROAD	13-28-38-24 W4M	-28-038-24-4

Survey/Environmental Checklist

Type	Access	Wellsite	Status	Com
Native prairie?	No	No		
Parks or protected areas?	Yes	No		
Flood irrigated area?	No	No		
Alkaline flat or dry slough?	No	Yes		
Within 1 in 100 year floodplain?	No	Yes		
Historical resource area?	Yes	No		
Within 100m of water body?	No	No		
Within 50m of valley/coulee break?	No	No		
Significant elevation change?	Yes	No		
Weeds?	No	No		
Sandy soils?	No	No		
Water Act Notifications required?	No	No		
Sensitive wildlife or plants?	No	No		
Intermittent drainage or springs?	Yes	Yes		

Figure 1. An example of an Environmental Checklist report.

Workflow

Rather then just a database to store environmental information, Trident was looking for a system to help with process and work flow. The ability to assign tasks from one person or group to another, to schedule recurring audits or activities prior to upcoming deadlines was important. Having the system effectively report, or send alerts depending on the situation, would help ensure all environmental obligations are being met.

AFE

Job Type	Start Date	AFE #
Reclamation	4/9/2001	111
Construction	7/4/1999	222
Remediation	9/16/2000	2354234562345
Reclamation	4/9/2001	333
Reclamation	4/9/2001	999
Construction	7/4/1999	AFE17120

Milestones

Module	Module Status	Key Start Date	Expected Completion Date	Key Actual Completion Date	Comments
Reclamation	Ongoing	8/6/2006			

Activity	Completed Date	Duration	Notes

Module	Module Status	Key Start Date	Expected Completion Date	Key Actual Completion Date	Comments
Reclamation	Ongoing	8/1/2006			

Activity	Completed Date	Duration	Notes

Module	Module Status	Key Start Date	Expected Completion Date	Key Actual Completion Date	Comments
Construction	Ongoing	8/1/2006			

Activity	Completed Date	Duration	Notes
Reseed site			
Clean debris			

Module	Module Status	Key Start Date	Expected Completion Date	Key Actual Completion Date	Comments
Reclamation		8/24/2006			

Activity	Completed Date	Duration	Notes

Figure 2. An example of part of a report showing site activity milestones.

Field and Head Office

Keeping the growing number of field and head office people all working off the 'same page' was acknowledged as being a key requirement. Being able to have a portable field component that would provide those workers with the same up to date site information that head office had was important. Having a complete site history in front of them while on site, with all documentation at their fingertips, would provide a clear understanding on past site activities and would help in environmental reclamation or remediation work. As well, the ability to enter data on the go, and then transmit to head office would avoid consultants re-keying information at the end of the day. As Trident heavily utilized third party contractors, having them enter data directly into the system on behalf of Trident (while restricting access to other information) was important.

Water Well Details

Description	Type of Well	Well Depth (m)	Water Well Surface Elevation (m)	Distance From Well Center (m)
1	Active	7.50	5.00	100.0

Comment

Description	Type of Well	Well Depth (m)	Water Well Surface Elevation (m)	Distance From Well Center (m)
2	Active	1.50	3.50	250.0

Comment

Water Well Testing

Type	Sub Type	Vendor	Assessment Commitments Met
Water Well	Pre	Enviro-Field Services Inc.	

General Assessment Comment

Related Well	Test Progress	Date	Com

Type	Sub Type	Vendor	Assessment Commitments Met
Water Well	Post	Enviro-Field Services Inc.	

General Assessment Comment

Related Well	Test Progress	Date	Com
1	B. Test Complete	9/19/2006	
2	B. Test Complete	9/30/2006	

Figure 3. An example of a section of a detailed water well report.

Solution Implementation

Peloton worked with Trident to configure SiteView to meet their specific requirements. System fields were customized to reflect how they wanted to capture their information. Custom report templates were developed so that each group had reports that were specific only to their activities. Historical information, that which was in electronic format, was migrated into the new system. Permitting, construction, reclamation/remediation groups all began using the system. Subsequently other groups responsible for pipeline and facilities began to add their information to the system. Users also began to SiteView to track AFE budget and field cost estimate numbers.

Benefits

Overall, exposure to environmental issues has been lowered. Permitting requirements and missed deadlines are lower as there is a much more defined process, and a system to help everyone follow the same processes. Having a clearer picture on the outstanding sites that require activities has allowed for better planning and allocating of resources. Having a database of site and environmental information now makes it possible to query across all sites. Having the ad hoc query capability to quickly determine what sites might have a common issue, or what sites are coming due for an inspection is now available a the touch of a button. All rests on having confidence that if the information has been captured, it is in the system, and it is correct.

Conclusion

Oil and Gas companies have long had a centralized system to inventory the details on their well information and activities. By taking a similar approach with regards to surface activities with a site database that contains pertinent environmental information, benefits can be seen through more efficient processes, which drives better managed environmental activities, which lowers environmental liability.

Exploratory Well Site Reclamation And Restoration In Albania

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ABSTRACT

At present, Albania's infrastructure as well as regulatory guidelines or requirements for site reclamation and restoration, including waste management (storage, treatment, and disposal) are limited to non-existent. This paper describes Occidental Oil and Gas Corporation (OOGC)'s efforts, experience, and worldwide standard of care in site reclamation and restoration related to exploratory well development in Albania. Site reclamation and restoration associated with this well development consisted of: onsite stabilization of drilling mud, backfilling of the drill pits with stabilized mud, spreading and capping the stabilized mud, grading the site to original contour, and returning the site to the farmers for agriculture. OOGC's Worldwide Standard of Care consisting of a human health risk-based approach for waste management and protection of human health and environment, enabled the site reclamation and restoration activities.

OOGC's Worldwide Standard of Care included an early identification and screening-level evaluation of risks associated with the use of all materials and chemicals at the site, including drilling muds. Although technically and economically it would have been beneficial and preferable to use oil-based or potassium formate drilling muds, a conscious decision was made to use benign glycol-inhibited, water-based drilling muds for the protection of human health and environment. In addition, the spent drilling muds were stabilized using lime mixed with local clay soil to prevent mobilization of, and exposure to, their constituents. To further assure that disposal of the stabilized, benign drilling mud did not pose any adverse human health risk or exposure to animals, as part of the site reclamation and restoration and prior to backfilling and spreading, samples were collected, shipped under chain-of-custody, and analyzed in the United States for indicator chemical constituents following United States Environmental Protection Agency (USEPA)-approved methods.

The analytical results were compared to the Texas Risk Reduction Program's Tier 1 values for residential/agriculture land use scenarios to assure that the onsite disposal of the stabilized mud and site reclamation and restoration was protective of human health and the environment.

1.0 INTRODUCTION

At present, Albania's infrastructure as well as regulatory guidelines or requirements for site reclamation and restoration, including waste management (storage, treatment, and disposal) and health risk evaluation are limited to non-existent. Given this state of affairs, sites are typically closed with input from, consultation with, and ultimate approval of, local authorities, but without a process that evaluates the potential risks to current or future users. Such a practice, however established and prevalent in Albania, runs contrary to Occidental Oil and Gas Corporation (OOGC)'s Worldwide Standard of Care, which calls for a systematic site closure process integrating proper waste management, comprehensive human health and ecological risk evaluation, and surface restoration for subsequent beneficial use.

Accordingly, as OOGC prepared to close its former exploration site near Berat Albania, a screening-level human health risk evaluation was conducted to ensure that the site closure and restoration methodology adopted by OOGC did not pose an adverse health risk to current and future users of the site. This paper documents the risk evaluation conducted as part of the site closure process and the results and conclusions thereof.

The rest of this paper first discusses project and risk evaluation background in Section 2, and then describes our implementation in Sections 3 and 4. Section 5 presents our findings and conclusions and discusses the conservatism inherent to the risk evaluation process utilized at the site.

2.0 BACKGROUND

OOGC conducted a screening-level human health evaluation of its closed exploration site (site, drill site) located near Berat Albania. Since Albania does not have risk-based regulations or established health risk evaluation protocols, OOGC decided to use U.S.-based risk evaluation methodologies and regulatory standards for conducting this human health risk evaluation. After reviewing various United States Environmental Protection Agency (USEPA) and state risk-based programs, OOGC decided to adopt the Texas Risk Reduction Program (TRRP; 30 TAC 350)[1] for this project. TRRP was used because of its comprehensive, yet user-friendly framework in terms of its consideration of exposure pathways, exposure scenarios, risk-based exposure levels, chemical constituents, and health-protective standards (termed Protective Concentration Levels, or PCLs). TRRP uses a three-tier methodology for evaluating health risks, with process and agency scrutiny complexity increasing as the tiers increase. In order to maintain simplicity, TRRP Tier 1 was identified as the tier of choice for the Shpiragu site evaluation. While this choice afforded simplicity in terms of understanding the health risk evaluation process and its findings, it resulted in the evaluation being conservative (i.e., overly-protective) since this tier within TRRP utilizes default, conservative exposure parameters and scenarios that result in conservative PCLs.

As part of its oil and gas exploration plans, OOGC had excavated the side of a hill at the well site in order to accommodate its exploration pits and other surface infrastructure. The excavated soils were used to fill the portion of the site that was used to accommodate a fresh water pit and other infrastructure. The hillside that was excavated contained OOGC's now-abandoned well and associated drill and brine pits. Since the well did not produce as anticipated, OOGC decided to close the site. In compliance with its worldwide standard of care for closing former drill sites, OOGC stabilized the spent drilling mud on site using lime with local clay soil, and restored the side of the hill by capping the stabilized spent mud with native overburden (that was previously excavated and used as fill material on-site to accommodate the well pad) and improving the surface with dredge spoils from a nearby irrigation canal.

The stabilized spent drilling muds were situated below 35-45 feet of native overburden and dredge spoil, and located well above any groundwater-bearing units in the area. OOGC's site closure method was approved by the appropriate Albanian

authorities. Upon restoration of the surface, OOGC re-graded the land and returned it to the local community for farming and other agricultural uses.

3.0 SCREENING-LEVEL HUMAN HEALTH EVALUATION

3.1 Media Sampling

As part of the human health risk evaluation and in order to gain an understanding of the residual concentrations of Constituents of Potential Concern (COCs) in the stabilized spent drilling mud OOGC collected three grab samples of the stabilized drilling mud, one grab sample of the excavated native soils (for baseline purposes), and five grab samples of the dredge spoil for chemical analyses, as well as one grab sample of undisturbed native soils exclusively for geochemical analysis. The samples were shipped via common carrier and under chain-of-custody to an accredited, independent laboratory located in Houston, Texas. The samples were collected using protocols typically used in the United States and approved by the USEPA. In addition, samples of the dredge spoil were submitted to a local laboratory in Albania for pH analysis, to aid in evaluating mercury results.

3.2 Indicator Constituent of Concern (COC) Selection

The soil and spent drilling mud samples were analyzed for certain hydrocarbon and drilling mud indicator constituents (as indicators of potential hydrocarbon and drilling mud constituent presence), such as: Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX), Total Petroleum Hydrocarbons in the Gasoline, Diesel, and Oil ranges (TPH-GRO, DRO and ORO), as well as certain Metals, using USEPA-approved analytical methods. The undisturbed native soil sample was analyzed for carbon content (as fraction of organic carbon) using the Walkley-Black Method.

The dredge spoil samples were analyzed for COCs that are typically investigated at “brownfield” sites in the United States. The COCs consisted of: Pesticides, Herbicides, Polychlorinated Biphenyls (PCBs), 13 RCRA Metals (plus Barium and Mercury), Volatile Organic Compounds (VOCs), Semivolatile Organic Compounds (SVOCs), TPH-GRO, DRO, and ORO, and selected Polyaromatic Hydrocarbons (PAHs). These analyses were also conducted using USEPA-approved analytical methods.

Separately, in order to ensure that the actual constituents present in the stabilized drilling muds were addressed in the analyses listed above, OOGC reviewed available Material safety Data Sheets (MSDS) of drilling mud constituents. This review indicated that the constituents listed on the MSDS' were mainly naturally-occurring minerals and man-made polymers, which typically are respiratory system irritants and do not exhibit chronic toxicity. The principal constituents of the drilling muds, as listed on the available MSDS', were further compared to the list of chemicals for which PCLs have been developed under TRRP, and it was found that these constituents were not specifically listed (for such constituents TRRP requires that specific PCLs be developed with the regulatory agency's input; however, development of new PCLs was beyond the scope of the screening-level evaluation). Thus, the indicator COCs identified for this evaluation appear to be conservative, based on the drilling muds used at the site.

The soil, stabilized waste mud, and dredge spoil sampling results are shown in **Table 1.**

3.3 Environmental Setting/Exposure Assumptions

The following environmental setting and human exposure assumptions were used in the human health risk evaluation:

- The stabilized mud is situated under 35-45 feet of clean overburden; thus, potential for human contact with the spent drilling muds is unlikely;
- Future landuse is agricultural with no subsurface land use;
- Groundwater was not encountered on-site during previous excavation activities; groundwater has not been, and will not be, used at the site;
- The nearest water well (signifying regional groundwater use) is located within a population center (approximate pop. 700) located approximately 1.8 kilometers (just over 1 mile) away from the site;
- The spent drilling muds have been stabilized by OOGC to an extent that the COCs present in the spent muds cannot be altered environmentally (i.e., they cannot vaporize, leach, or become airborne);
- Based on a review of the MSDS' the COCs present in the spent drilling muds are not considered to exhibit chronic toxicity, or hazardous characteristics.

3.4 Exposure Scenarios

A site conceptual model (SCM) was developed using the above exposure assumptions regarding current and future landuse, current and future receptors, presence of contaminated (albeit stabilized media), potential for COC releases and associated pathways, and considering that the site restoration methodology adopted by OOGC resulted in an unlikely potential for human contact with the stabilized spent drilling muds at the site. Based on the model and as discussed above, the spent drilling muds is buried under 30-45 feet of clean soil overburden and capped with dredge spoils; groundwater use at the site is not likely; and the use of the site for agricultural purposes will only involve the site's surface/shallow soil. However, as a conservative measure, the health risk evaluation was based on the hypothetical exposure scenarios of farmers working at the surface and potentially coming into contact with the dredge spoils, as well as potentially coming into contact with residual COCs that may be present in the buried, stabilized, spent drilling muds. Further the potential for residual COCs in the stabilized muds and dredge spoil to leach adversely to underlying groundwater was also considered.

4.0 RISK-BASED STANDARDS

As stated above, the Texas Risk Reduction Program (TRRP; 30 TAC 350) was used to identify appropriate, published, human health risk thresholds for evaluation of COC concentrations potentially present in stabilized/spent muds, native soil, and dredge spoil , while recognizing that the site is located outside of the jurisdiction of this program (TRRP simply provided a readily-available means of evaluating potential human health risk on a screening-level basis).

Specifically, PCLs associated with direct exposure pathways (i.e.; incidental ingestion, dermal contact, inhalation, ingestion of vegetables), and protection of groundwater of varied classification (i.e.; groundwater from wells with high yield and low total dissolved solids content that can be used for drinking with minimal to no treatment [TRRP Class 1 and 2 resources], to groundwater from wells with low yield and high total dissolved solids content typically not used for drinking without treatment [TRRP Class 3 resource]), assuming residential landuse and a 30-acre source area size (which are typically the most-restrictive values) were used in this evaluation.

The result of 0.615 % (or 0.00615 g/g) obtained for the analysis of fraction of organic carbon in the undisturbed native soil sample was found to be within the range of default values of 0.002 to 0.008 g/g used by TRRP for calculation of the pH-specific Tier 1 PCLs, thus indicating that these TRRP default levels generally correspond to those that might exist at the site. In addition, pH-specific PCLs were developed for Mercury based on the lowest pH result (7.1 units) obtained for samples of the dredge spoil; TRRP equations and default values were used to develop these PCLs.

The use of residential PCLs to evaluate agricultural land use is conservative, as agricultural lands are typically classified as commercial/industrial under TRRP (see guidance document R-366/TRRP-7 "Land Use Classification") and thus, higher PCLs may apply. The identified PCLs for the soil, stabilized waste mud, and dredge spoil sampling results are presented in **Table 1**.

Additional conservatism exists in this evaluation since the PCLs used are designed to protect against potential health risks to individuals who live on the same residential properties for long durations (typically 30 years) and are considered to be exposed to site COCs for that entire duration by coming into daily contact with contaminated soil and drinking groundwater from underneath the site. As indicated before, and based on observations of area activities, such an exposure scenario is unlikely at the site since the farmers plan to use the surface of the land, which would consist of dredge spoils and native soils, and the stabilized muds would be located approximately 30-45 feet below the clean overburden. Further, observations of area activities indicated that there is/will be no known use of any groundwater that may be present underneath the site.

Table 1

SUMMARY OF MAXIMUM DETECTED ANALYTICAL RESULTS AND PCLs

Analyte	$^{Tot}Soil_{Comb}$ PCL	$^{GW}Soil_{Ing}$ PCL	$^{GW}Soil_{Class\ 3}$ PCL (mg/kg)	Stabilized Drill Mud	Soil Over Burden	Dredge Spoil
VOCs				**maximum detected result**		**(mg/kg)**
Ethylbenzene	4,020	3.82	382	0.0054		0.00099 U
Toluene	5,620	4.11	411	0.002		0.00074 U
Xylenes, Total	753	61.3	6,130	0.13		0.0019 U
TPH				**maximum detected result**		**(mg/kg)**
TPH (Gasoline Range)	1,100	33.0	3,300	0.19		0.025 U
TPH (Diesel Range)	2,000	99.0	9,900	220		20 U
TPH (Oil Range)	2,000	99.0	9,900	190		62 U
Metals				**maximum detected result**		**(mg/kg)**
Mercury (pH = 4.9) (1)	2.09	0.00391	0.391	0.371	0.16	
Mercury (pH = 7.1) (2)	6.80	1.98	198			0.0319
Arsenic	24.2	2.51	251	5.34	6.03	4.57
Barium	7,840	222	22,200	11200	13300	53
Beryllium	37.6	0.924	92.4			0.558 J
Cadmium	51.7	0.755	75.5			0.139 J
Chromium	23,100	1,200	120000	95.4	43.4	90.4
Copper	548	521	52,100	37	36.6	20.5
Lead	500	1.51	151	564	523	9.53
Nickel	832	78.7	7,870	191	71.2	171
Selenium	308	1.15	115			0.795
Silver	94.8	0.239	23.9			0.0755 J
Thallium	6.31	0.875	87.5			0.258 J
Zinc	9,920	1,180	118000	140	129	46.8 B
Pesticides				**maximum detected result**		**(mg/kg)**
4,4´-DDD	14.2	6.48	648			0.00031 JP
4,4´-DDE	10.2	5.89	589			0.00099
4,4´-DDT	5.39	7.37	737			0.0011
alpha-BHC	0.251	0.00396	0.396			0.00049
delta-BHC	2.85	0.0868	8.68			0.00046
Endrin aldehyde	19.4	314	31,400			0.00062 J
Heptachlor	0.127	0.0944	9.44			0.00084
Heptachlor epoxide	0.237	0.0291	2.91			0.00037 JP

2006 Texas Risk Reduction Program (TRRP) Tier 1 Protective Concentration Levels (PCLs); Residential Land Use; 30-acre source (mg/kg)
$^{Tot}Soil_{Comb}$: Combined incidental ingestion, dermal contact, inhalation, and vegetable ingestion exposure pathways
$^{GW}Soil_{ing}$: PCL protective of Class 1 and 2 groundwater that can be used for drinking
$^{GW}Soil_{Class\ 3}$: PCL protective of Class 3 groundwater that is not used for drinking
(1) Default value used.
(2) Mercury PCLs were developed for the dredge spoil based on measured spoil pH of 7.1 units
B: analyte detected in the associated method blank
J: analyte detected below the method quantitation limit
P: analyte coelution occurred; cleaner sample reported
U: analyzed for but not detected

5.0 FINDINGS AND CONCLUSIONS

A screening-level evaluation of human health risk was made by comparing site-specific COC concentrations obtained from the analyses of site soil, stabilized waste mud and dredge

spoil samples to TRRP Tier 1 PCLs. This comparison, summarized in **Table 1,** showed the following:

- All reported COC concentrations (detected, estimated or not detected) were below the corresponding residential/30-acre PCLs associated with ingestion, dermal contact, inhalation, and vegetable ingestion exposure pathways (i.e., the $^{Tot}Soil_{com}$ PCLs) or within the magnitude of concentrations observed in the native soil sample (the overburden sample).
- All reported concentrations (detected, estimated or not detected) were below or fell within a range of soil PCLs that are deemed to be protective of groundwater.

Based on the above findings as well as the exposure/COC assumptions, and site conditions used in the risk evaluation, OOGC concluded that the site restoration as undertaken at the Shpiragu, Albania site should not adversely affect human health.

6.0 REFERENCES

[1] Texas Risk Reduction Program (Title 30 Texas Administrative Code Chapter 350).

Dose – Response Relationship of Organisms in Soil with Heavily Weathered Hydrocarbons and Changes in Fertility Parameters

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ABSTRACT

The response of different types of organisms in soil containing highly weathered hydrocarbons was investigated. Heavily weathered oil was only slightly toxic to earthworms and bacteria; only above 50,000 mg/Kg TPH was a response observed in earthworms (*Eisenia foetida*, ~5 % mortality), and concentrations of ~30,000 mg/Kg were only slightly toxic to bacteria (Microtox). None-the-less, at even low concentrations, these kinds of hydrocarbons reduced vegetative growth, apparently by modifying soil fertility parameters. In soil contaminated with very weathered heavy oil range hydrocarbons, native marshy vegetation (*Cyperus laxus* Lam.) showed a reduction of 10 % in height at ~2,300 mg/Kg (r^2=0.976). Likewise, in soil contaminated with mid-range hydrocarbons which had been co-produced with and weathered in the presence of sulfur, ~2,600 mg/Kg showed a reduction in above ground biomass production in pasture (*Brachiaria humidícola*) of 10 % (r^2=0.982). These observations were correlated with a reduction in the field capacity of the soil (r^2=0.964) which showed a linear relationship with TPH concentration (r^2=0.993). These finding suggests that the principal mechanisms by which hydrocarbons affect soil organisms is qualitively different with fresh hydrocarbons and very weathered hydrocarbons, and that toxicity and field capacity are more appropriate parameters to use as soil remediation criteria.

Adams, R. H., Álvarez-Ovando, A. L., Escalante-Espinosa, E., and Gutiérrez-Rojas, M. 2006. Dose – Response Relationship of Organisms in Soil with Heavily Weathered Hydrocarbons and Changes in Fertility Parameters 13th International Environmental Petroleum Conference. International Environmental Petroleum Consortium, San Atonio, Texas, 16-20 Oct. 2006.

INTRODUCTION

Historically, many petroelum producing regions employed waste disposal and treatment methods which were inadequate to avoid severe impacts to soil. This is the case in the Gulf of Mexico región, especially in Tabasco and southern Veracruz area (1). With respect to determining appropiate clean-up criteria for sites with chronic contamination resulting in the last century, it is important to evaluate the impacts to soil organisms (2). It has been shown that the kinds of heavily weathered hydrocarbons present in old sites are very difficult to degrade (3), but have relatively low toxicity (4). In the present study the diferential response of earthworms, bacteria, and plants to the presence of heavily weathered hydrocarbons in the soil were compared. Also, the relationship between plant develolpment and impacts to soil physical-chemical properties was evaluated.

METHODOLOGY

In the first set of experiments, sediments were collected from a marshy area in which several grasses and *Cyperus* spp. were present as clusters in a heavily contaminated marshy area behind a refinery which was constructed nearly 100 years ago. The hydrocarbons contamination was due to chronic discharges over several decades (roughly eight) during which the hydrocarbons were weathered in a humid tropical environment. Oily mateial and sediments were collected as well as *Cyperus laxus* (Lam) plants. Contaminated soil was mixed with clean soil, peat and tezotle to obtain soil with a range of hydrocarbon concentrations. The soil prepared in this way was then used in dose response experiments with earthworms (*Eisenia foetida*), bacteria (Microtox bioassay) (5) and with the predominant native marsh plant, *Cyperus laxus*. In these experiments mortality, bioluminenscence and biomass production were observed, respectively.

In the second set of experiments, sediments were collected from a beach area in an artificial reservoir prevoiulsy used to contain waste water from a sulfur mine. This area had been contaminated with acid waste water which also contained hydrocarbons derived from the salt domes that were exploited for sulfur (the hydrocarbons were not recovered and were considered waste products by the mine operators). This area had been treated to neutralize the acidity but was still very contaminated with very viscous hydrocarbons which had been co-weathered in the presence of hydrocarbons for 10 – 20 years in a humid tropical environment. The sediment collected was very poor in non-petroleum organic matter and had a very high content of bentonite clay. This material was then mixed with red clay subsoil to obtain a range of hydrocarbon concentrations. The soil was placed in treatment cells of 0.4 m x 0.4 m x 0.2 m deep and planted with a tropical forage grass (*Brachiaria humidicola*) and aerial biomass was measured periodically by making cuttings and drying the material. This soil was also evaluated for field capacity according to ref. (6) and hydrocarbon concentrations by EPA method 418.1 (7).

RESULTS

Results of the earthworm bioassay are shown in figure 1. As observed in this figure, a typical dose–response curve produced which showed that even at very high concentrations of these heavily weathered hydrocarbons, there was relatively litte adverse affect to these organisms. At concentrations up to 5 % TPH very little affect was observed. However, the

affect to the native marsh plant from this area was much greater (see figure 2). Also, a typical dose-response curve was observed with a high correlation (r^2=0.976), but which showed a 10 % reduction in plant height at a hydrocarbon concentration of only about 2,300 ppm (0.23 %).

In the second set of experiments, a typical dose-response curve was also produced in humidicola grass (r^2=0.982), and also showing a 10 % reduction in biomass at a similar concentration (~2,600 ppm, 0.26 %), (see figure 3). These observations were correlated with a reduction in the field capacity of the soil (r^2=0.964) (see figure 4) which showed a linear relationship with TPH concentration (r^2=0.993) (figure 5). However, in the microtox bioassay in this study, at concentrations of roughly 3 % TPH the toxicity in the Mictotox bioassay was only slight, especially in comparison to the natural toxicity observed in mineral soils in the region (8).

CONCLUSIONS

The very weathered hydrocarbons investigated in this study showed relatively low toxicity to both bacteria and earthworms. Both of these organisms have high surface area in contact with the contaminated media and therefor would be expected to be relatively sensitive, especially earthworms which have both external and internal membranes exposed to soil surfaces. However, in the 3 – 5 % range of hydrocarbon concentration either no adeverse affect was observed, or it was very slight in comparison to the response to uncontaminated regional soils. Conversely, at very low concentrations, two vegetative species, a forage grass, and a native marshy species, showed reduced growth at concentrations as low as 0.23 – 0.26 % TPH, more than ten times less. It is to be expected that these kinds of organisms, with more resistant outer layers of cells would be less affected by potentially toxic substances. None-the-less, the opopsite was observed. At the same time, a very strong inverse correlation between field capacity and TPH concentration was observed which as also strongly correlated to a reduction in vegetative biomass production.

These observations suggest that heavily weathered hydrocarbons are indeed of low toxicity as observed by other investigators (4) but that this kind of hydrocarbon adversely affects plant growth by altering physical-chemcial parameters important for soil fertility. With this in mind it may be more prudent to concentrate on the restoration of these parameters in the soil, rather than on the reduction in total hydrocarbon concentration in remediation programs involving heavily weathered hydrocarbons.

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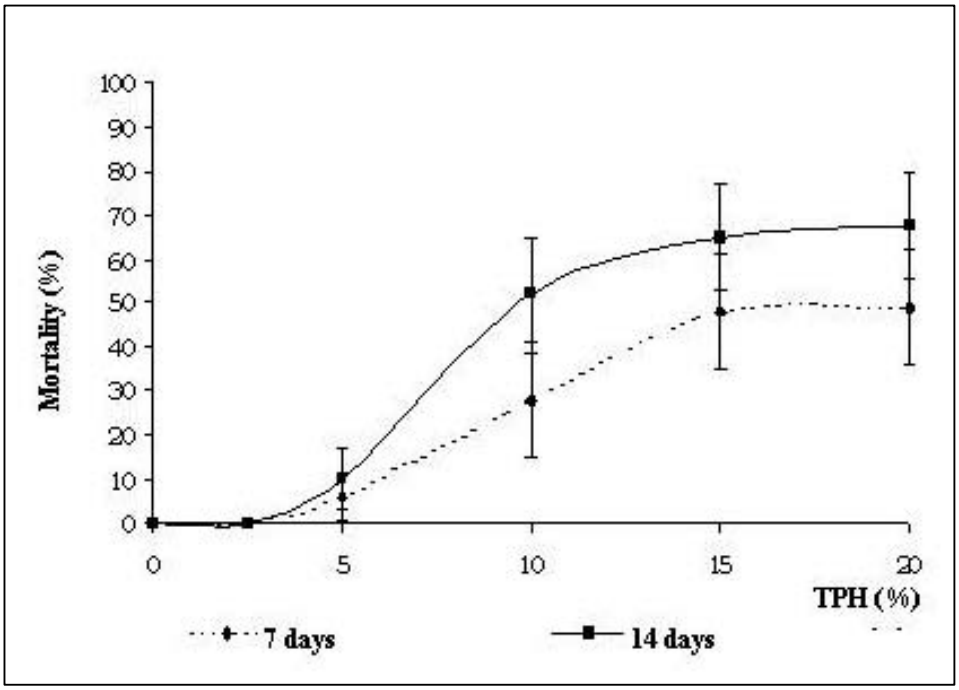

Figure 1. Mortality of *Eisenia foetida* L. at 7 and 14 days exposure to different hydrocarbon concentrations.

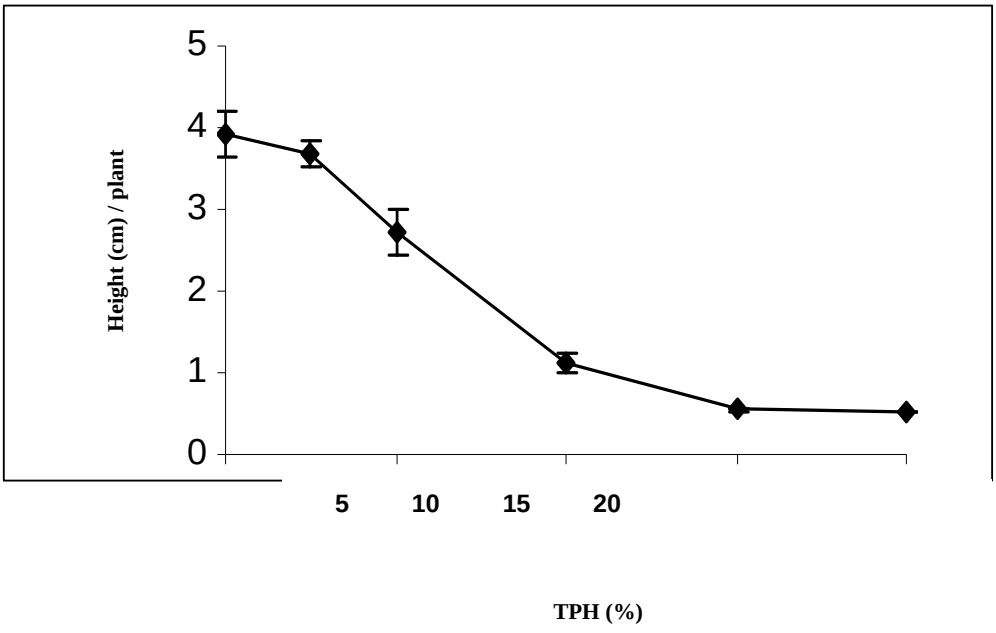

Figure 2. Plant height at different hydrocarbon concentrations.

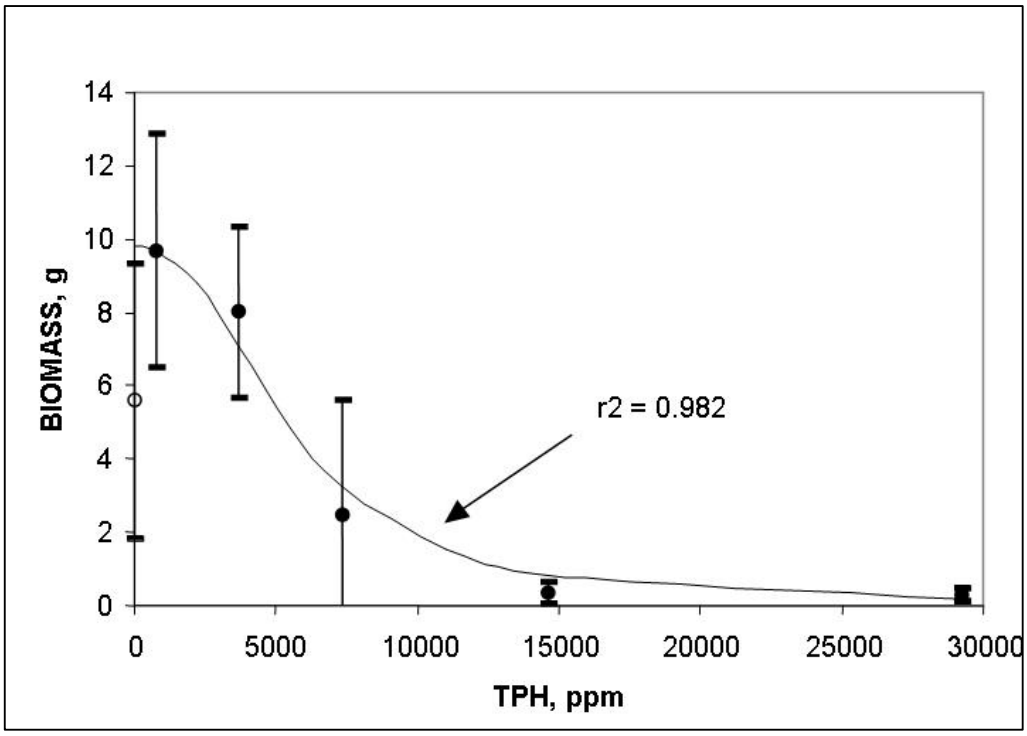

Figure 3. Dose-response relationship of humidicola grass in sediments with heavily weathered hydrocarbons.

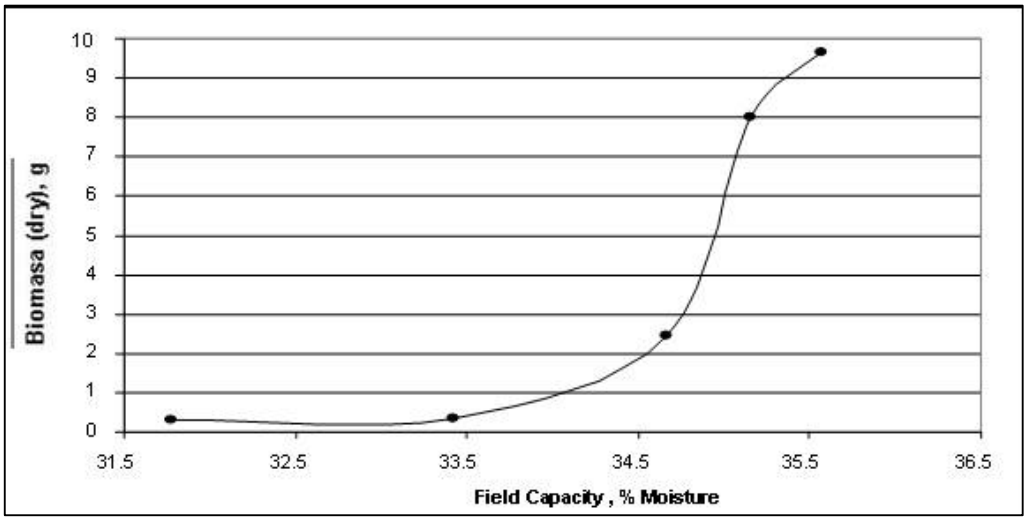

Figure 4. Biomass production in relation to field capacity in sediments with heavily weathered hydrocarbons.

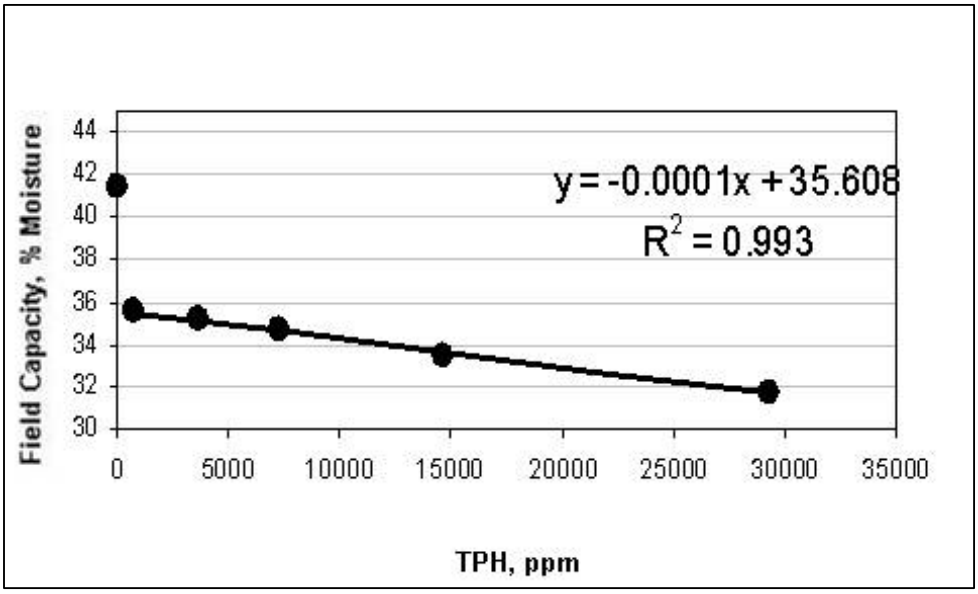

Figure 5. Relationship between field capacity and hydrocarbon concentration.

Utilization of Automated Oil Spill Detection Technology for Clean Water Compliance and Spill Discharge Prevention

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AUTOMATED SPILL ALARM FOR CLEAN WATER COMPLIANCE & DISCHARRGE PREVENTION

ABSTRACT: This paper discusses the development of an oil spill detection and alarm system that provides industry with a reliable, cost-saving mechanism for containing and/or preventing accidental discharges of hydrocarbon-based pollutants.

By utilizing an automated spill detection system, hydrocarbon releases are detected in real-time (analogous to a 'smoke alarm' for oil spills). Early warning and automated response capabilities allow containment of pollution before the environment, wildlife, public waterways, or commercial assets are damaged. This technology provides a new weapon in the pollution prevention arsenal, offering HSE personnel a critical compliance tool in accordance with NPDES, SPCC, and other regulations stipulating spill prevention, planning and response.

This paper details: 1) Development of a reliable, economical, optical, non contact, hydrocarbon pollution detection sensor, the "Slick Sleuth", 2) Performance results drawn from an array of performance tests and real-world deployments, 3) A variety of existing applications and deployment opportunities for which this new technology has proven to provide a reliable, easy-to-use tool for regulatory compliance and realization of cost benefits associated with minimizing spill risk(s).

Design features have evolved to reflect feedback from existing industrial users, as well as input from environmental consultants and regulatory agencies. These key system attributes include: 1) Near-zero maintenance, 2) Micron- level sensitivity for a comprehensive range of oils (from crude-oil to jet-A), and 3) Sensor/system flexibility and adaptability for a wide range of installation settings and application requirements.

Finally we describe how any entity that produces, stores, uses, or transports hydrocarbons, can best employ the detection sensor/alarm to realize cost-benefits, strengthen compliance, and eliminate the expense, environmental damage, and bad publicity inherent with any spill.

I. INTRODUCTION

Oil spills are a global concern and worldwide dependence on fossil fuels and oil derivative products are at historic highs for production, transportation, storage, and consumption. At the same time major offshore spills occasion headline-grabbing attention, while attention is intensifying with respect to oil and petrochemical spills [accidentally] discharged from inland and shore-side sources to inland waterways and along coastlines. In fact statistically, spills to freshwater and inland waterways result in comparable or greater damage than do marine spills [1], but have typically drawn less public attention. It's become evident to us that both offshore and onshore spills are of growing public concern, however innovation of the new methodologies and technologies necessary to protect ourselves and the environment from these sources of oil pollution are being severely outpaced by the growth, demand, and omnipresence of oil. With these premises in mind, the following describes our success in developing and introducing new sensor technology for the prevention, detection, and early warning/containment of oil spills. Our focus is on inshore and freshwater spills, with emphasis on industrial applications. We also examine inland and coastal waterway applications, as well as potential offshore uses.

This paper describes a rugged reliable spill detector that has been field-proven, complies with the US EPA's standard test procedure for evaluating leak detection methods, and is in the process of being patented. Details are provided regarding the scientific principle upon which the sensor is based (theory of operation), the sensor development process over the past few years, numerous applications for which this type of new sensor technology is optimally suited, and discussion of how this new sensor technology may be used to greatest advantage by different industrial entities (best uses and management practices) in a wide variety of applications and environments.

Prevention and early containment of spills benefits everyone: the public at large, stakeholders of watersheds and waterways, business interests (spills are expensive), the ecology of natural habitats, and the environment as a whole. Spill prevention through remote detection provides a proverbial "win-win" solution and, when implemented, greatly reduces the risk of significant spills and substantial harm. This practice is now validated by companies already using this new technology, who are demonstrating that real-time spill detection offers a powerful new tool for preventing and containing spills that would otherwise go undetected.

II. GOALS

In developing an oil spill detection sensor, our goal was to create an early detection mechanism for spills or discharges, accidental or deliberate, for both freshwater and marine environments. Since its inception, the scope of the sensor's design has evolved to address an ever-widening range of applications and system features. However, the fundamental sensor attributes we listed as goals at the outset remain at the core of the design: 1) reliable detection of oil sheens and slicks on water surfaces, 2) non-contact sensor design, facilitating highly-sensitive oil detection without the instrument contacting the target water/effluent, 3) impervious to environmental conditions, 4) remote & autonomous operation, 5) operable in excess of 5-meter range above fluid surface, 6) adaptable and scaleable, 7) easy to install and operate, and 8) a commercially viable, economical, low maintenance sensor package.

III. PRINCIPLE OF DETECTION

Oils are known to fluoresce, and the oil detection sensor we've developed detects the presence of oil by exciting and measuring fluorescence. Fluorescence is an optical phenomenon in which a compound absorbs light at one wavelength and emits it at a longer wavelength [2]. When fluorescent compounds are excited, some of the energy is absorbed through the excitation of electrons to higher energy states. Once the light source is removed the excited electrons fall back to their ground state, giving off light in the process. This process is very similar to what makes glow-in-the-dark materials possible, except it takes place in a much shorter time period. Because some energy is lost as heat in the absorption-emission process, the wavelength of the emitted light is always longer than the wavelength of the absorbed light. Typically the absorbed light is in the ultraviolet range and the emitted light is in the visible range. For example, oils typically absorb light between 300 and 400nm, and emit light in the 450 to 650nm range.

Fluorescence detection, or fluorometry, is by no means new technology in and of itself. Typically, fluorometers use spectroscopy methods for fluorescence detection in the form of flow-through or in-water systems. Often these comprise sophisticated lab-quality instruments, used either for scientific research or as in-line water analyzers, and as such tend to be prohibitively expensive and impractical for use as remotely deployed field units or in networked arrays. The flow-through technique is susceptible to bio fouling and oil staining on the sampling tube/mechanism and thus requires significant attention and ongoing maintenance. In-water sensors are of course subject to bio-fouling and troublesome installation and maintenance issues. By contrast, the design of this new spill detection sensor, while based on the same fluorometric principles, is a downward looking, non-contact, optical sensor, which is installed up to five meters above the target liquid surface and is free of these high-maintenance fouling effects and deployment limitations.

Within this sensor, a high power Xenon lamp is used to produce a high-energy light beam. This light is then filtered and sharply focused into a conical beam so only desired wavelengths of light are projected onto the target area. Any oil present in the target area will fluoresce and subsequently emit light of its characteristic wavelengths. This light is then processed by the sensor's proprietary scanning optics and digital signal processing system, which detects the fluorescence characteristic of oil.

The sensor's detection of oil is predicated upon differential measurement, meaning it is based on anomalous signal return within a target area when oil is present. Normal ambient conditions constitute the baseline reading or 'zero point', and a sensor state of "no oil detected". If oil is present, the signal return is greater than normal ambient conditions, triggering detection and an "oil detected" alarm state. If oil is present in varying amounts, the signal return is proportional to the amount of oil, or PAH/aromatic constituents, detected within the 'viewing' or sampling area.

IV. DEVELOPMENT

Using the basic physical principles of fluorometry, and the list of sensor attributes and objectives, we began the developmental stage by studying the physical characteristics of oil and conducting laboratory experimentation with various light sources, optics, and detectors. We focused our efforts on oils and petroleum-based fluids, commonly referred to as PAH (Poly Aromatic Hydrocarbons) and BTEX compounds (Benzene, Toluene, Ethylene, Xylene), that are either statistically most prevalent, or deemed of greatest concern by the industry (end users) and government experts with whom we consulted. These

include but are not limited to: crude, heavy fuel oil (e.g. “Bunker C”), lube oil, motor oil, hydraulic oil, turbine oil, diesel, jet fuel, naphtha, kerosene, mineral oil, various process oils, etc. We’ve also examined numerous food oils such as soybean, corn, and olive.

It is important to note that different brands or types of oil within these major ‘classifications’ (e.g. “diesel fuel-oil”) originate from many different sources, contain various additives, and consist of differing concentrations and compositions. From product to product within a given class of oils there is inherent variability in fluorometric characteristics and how the oil/pollutants will respond or ‘appear’ to the detector when excited with UV light. Rather than expending effort trying to analyze and classify small differences or degrees of variability, our primary focus was given to developing and testing a field sensor that qualifies the presence of a wide range of oils with high reliability.

For purposes of this paper, results are limited to the specific oils tested within the given set of conditions. We do find, however, that results gained from testing specific products against the detector can be used to successfully predict or infer successful detection of ‘related’ oils, regardless of slight variations from product to product. Moreover, for users interested in ‘detectability’ of particular oil(s) of concern, it has become a common exercise to test samples of oil against detectors in the lab, or on site in the field, to verify high probability of detection and to characterize and document detector proficiency for specific oil-based product(s).

Figure 2 illustrates one of our initial characterizations of oils when exposed to a broadband UV light source. The results are from tests performed during the development of the instrument. The tests were conducted using a laboratory light source and receptor, and while we have repeated this test with differing equipment and intent many times since, these results exhibit a representative estimate or benchmark for various oils’ fluorescence in the spectrum when irradiated with a UV light source. For reference, M. Fingas and C. Brown address a more thorough treatment of this topic in their paper entitled “Review of Oil Spill Remote Sensing” [3].

As the result of laboratory experimentation during initial development, a high-powered Xenon strobe was selected for the sensor’s integral light source, and was coupled with a suitable power supply. This same flash and power supply has proven to be highly effective throughout the sensor’s evolution. A key criterion for developing the flash assembly was enough output intensity to enable detection of small surface sheens from a distance of 5 meters above the target surface area. Presently this 5 meter limit is the approximate upper boundary for reliable detection; however ongoing tests confirm that this detection range may be increased in the near future.

Other critical components required for the output/optical subassembly are the parabolic reflector, which focuses/collimates the conical beam onto target area below, and band pass filters, which limit the energy output to the desired spectral range. Each of these components have been integrated, tested, and optimized based on extensive performance testing.

Similar to the development of the sensor’s optical subsystem, a proprietary set of photo detectors have been tested and integrated to provide the necessary receptor attributes that allow for accurate measurement of the presence of oil, based upon performance testing and field trials.

These subassemblies, along with requisite electronics and microprocessor, are compactly integrated within a stainless steel weatherproof enclosure (roughly 10x12x14 inches). The housing is also fitted with valve fittings and a vent, so that an air-purge system may be added to satisfy installation requirements in Class I Division II hazardous locations, such as are common in refineries and terminals. Subsequent sensor integration into an explosion-proof housing for use in Class I Division I environments is now nearing completion.

The initial system was designed for use with alternating current (AC) power, then later modified for operation with an integrated DC power source (e.g. batteries and solar panels) to facilitate deployments in remote settings. For installation convenience and other practical reasons (such as size and mitigation of electro-magnetic interference), the DC power system is now housed in a separate weatherproof enclosure that is collocated with the sensor, or installed away from the sensor to gain optimal exposure to sunlight for solar recharge. Similarly, when wireless communication is used (e.g. spread spectrum radio, satellite, cellular), the communications package is housed with the DC power supply and may be installed for optimal orientation.

Initial prototypes communicated using a basic RS232 protocol and a terminal program such as Windows Hyper Terminal. Typical field applications have since required us to add RS485 capability, as well as analog outputs such as 4-20mA and/or simple dry contact relays (switch closures) for integration with industrial process control systems. The detector's relay outputs may also be wired directly to controllers for uses such as actuating a valve, shutting off a pump, and/or activating audio/visual alarms whenever a spill is detected.

Wireless communication is required for many remote-monitoring applications. The automated detector has been designed to output compatible data, digital or analog, for use with any type of wireless telemetry (radio, cellular, or satellite) for real-time spill monitoring.

During the development period, InterOcean successfully completed proof-of-concept and prototype testing, conducted extensive lab- and field-testing (see Figures 3 and 4), and built first and second-generation production units that incorporated upgrades based on experience gained from real world installations and users. Critical (and much appreciated) feedback was gained from consultation with early customers such as Shell Oil (refinery applications) and Dominion Transmission (remote compressor station applications). They deserve credit for being on the leading edge in their respective industries, successfully implementing this new spill prevention and alert technology.

V. SENSOR PERFORMANCE: RESULTS & LESSONS LEARNED

Many problem-solving opportunities arose during the development process. One of the obvious challenges with an optical sensor is that it must have a clear 'view' of the area to be sampled. If the optical path is blocked, the detector is effectively rendered 'blind'. During testing and field experience we learned that the light beam is unaffected by light haze, smog or fog, but as a rule of thumb if the path interference is too thick for the human eye to see through, it will also affect optical sensor performance. For example we conducted a test using a large chunk of dry ice and tub of water with oil sheen. In this extreme scenario, a visually impenetrable fog was generated, which effectively prevented the sensor from being able to detect the oil sheen below. However this scenario has not existed or been presented as a problem in any existing field installations.

Partial path interference (physical blockage) does not necessarily disable the sensor's ability to monitor and detect oil. For example, in the photograph shown in Figure 5, the sensor is installed such that it is peering through a metal grate into a containment sump below. Although signal return is attenuated about thirty percent in this example (vis a' vis the grates partial blockage/impassability), the signal to noise ratio remains the same as with no grate. That is to say the 30% overall signal loss has no adverse affect on the detector's ability to reliably differentiate between clean and oil-polluted water

beneath the grate. A number of users have taken advantage of this capability, while others have simply cut a small window for the sensor to 'peer' through in grated-sump applications (refer to Figure 7, below).

While the sensor needs to be mounted roughly perpendicular to the surface below, we have learned that there is a tilt tolerance of about 15˚, which helps a great deal with certain applications such as buoy-based installations.

Naturally one of the biggest fears for sensor operators is false detection, and there are a few other substances that do fluoresce in a manner similar to petroleum-based fluids. For example, white paper and white fabrics can trigger a false positive (much as a white t-shirt glows under black light). Fortunately items that may cause false detection are few, and are not prevalent in typical installation environments. In the case of some non-oil substances known to fluoresce, for example fluids containing fluorescing rust inhibitors, varying the detector configuration can eliminate the possibility of a false positive. More common wildlife and debris such as birds, algae, seaweed, sea foam, driftwood, and plastic bags have not been problematic sources of false detection, and to date we have received no reports of any natural phenomenon causing false detection from users with sensors in field operation. Nor have ambient conditions such as sunlight, waves, or water currents been shown to have any adverse affect on detector reliability.

During installation and setup, taking a "baseline" measurement initializes the sensor. This measurement is internally recorded, and is used to establish normal operating conditions (either with clean water, or with a normal level of oily sheen or other chemicals/materials typically present).

As previously mentioned, this quick one-time process establishes the zero point or background level in order to account for ambient conditions, and to provide a baseline that contrasts with anomalous events, which are indicative of oil. Varying water level, such as tide or stormwater, causes this ambient baseline to shift up or down as water periodically rises and falls. In order to account for and cancel out this background shift (in applications where applicable), a feature called "adaptive baseline" is enabled. For example, in a cyclical tidal setting, or in applications where stormwater surge may occur, the adaptive baseline is utilized to normalize the effect.

An unexpected success of the sensor has been its ability to detect emulsified oils. For example, a prospective user was interested in evaluating the sensor's ability to detect small concentrations of emulsified oil (an interest recently promulgated by a costly pollution incident). They were particularly concerned with the sensor's ability to detect emulsified oil at a concentration of 0.1%, as this was the concentration of oil which had occurred during the accidental pollution discharge. The customer provided us with samples of various oils, which emulsified almost instantly when added to water. In testing the samples, the sensor easily detected each of the emulsified oils at a concentration of less than 0.1%, and was able to reliably detect one of the emulsified lubricants at a concentration of only 0.001%.

At the prototype stage the sensor was programmed to sample every 30 seconds, based upon preliminary user requirements. This proved to be impractical for installations where water was moving rapidly enough to transport broken spills past the sensor without detection. To overcome this we have since increased the sampling rate and conducted extensive tests using a flume (approx. 7 ft./minute flow rate). Based on our testing results, the sensor is now user-programmable for two higher sampling rate options. For "continuous" sampling a 2 Hz sampling mode is used. In this sampling mode the strobe is fired twice each second and the monitor outputs a value for each sample. Alternatively there is a 5-second sampling mode, in which the strobe takes a burst sample (typically 10 samples at 100msec intervals) once every 5 seconds, and the value output is an average of the periodic burst sample. Similarly the detector can be programmed to sample less frequently, as appropriate.

Another adaptation has been the development of a simple software utility program with which users interface with the detector. Use of the utility program is only necessary during initialization, to change monitoring parameters, or during troubleshooting. The simple point and click GUI allows users to adjust settings for sampling interval, flash rate, baseline measurement, detection offset/threshold, adaptive baseline, operating modes, logging features, etc.

VI. APPLICATIONS

Initial development of this oil spill detection system was based on the perception that spill monitors would be of utility in the coastal/marine environment, and in ports & harbor settings. For example single units or sensor networks could be strategically placed to monitor fuel piers and bunkering facilities, marine terminals, shipyards, naval installations, marinas, stormwater culverts/outfalls, etc., throughout a port. After extensive interaction with users and stakeholders, we now know that these do in fact constitute excellent applications for which these sensors are extremely well suited (reference Figure 9, Royal Australian Navy's marine terminal fuel pier installation). The range of applications we hadn't fully anticipated, but now know to be substantial, are in the realm of freshwater and inland waterways, particularly at or near petrochemical and industrial facilities. End users in this sector include: refineries, terminals, tank farms, power plants, paper and steel mills, heavy industry/manufacturing, water treatment plants, food oil plants, and more. Figures 5, 6, 7 and 8 exemplify typical installations in these sectors. Basically any facility that stores, processes and/or utilizes large quantities of oil is (or should be) concerned with real time detection. As such these entities and their key personnel are motivated to make use of "best available technologies" (BATs) and "best Management Practices" (BMPs) for early warning and containment of spills.

There is an immediate need at such plants and facilities to protect against spills going undetected and escaping into the environment. In part this need is driven by requirements for 'oil-centric' facilities to update their Spill Prevention Control and Countermeasure (SPCC) plans, as mandated by CFR, and overseen by the US EPA. For example, this type of sensor can be utilized in support of conformance with regulations listed in sections of CFR parts 112.7(a), 112.8(b), and 112.8(c) [4]. Detectors may also be used to augment an entity's strategy to meet their NPDES permit requirements and similar regulatory requirements, both local and international. Additional motivation can be attributed to the fact that spills are costly due to expensive cleanup, mitigation, fines, and bad publicity (there's motivation in not wanting to become tomorrow's headlines!). Thus there is ample justification for utilizing the early warning detection and alarm capabilities an oil spill sensor provides, to prevent or contain a spill before it becomes a disastrous event.

In addition to spill monitoring deployments along coasts and in ports & harbors, or installing spill alarms as safeguards along industrial spillways, a third major application is envisioned for remote spill detection sensors: protection of sensitive wildlife habitats and/or aquaculture/fish farms. In this scenario detector(s) are installed beyond or at the perimeter of a sensitive habitat such as an estuary, wetlands, bird sanctuary, or shellfish bed. If a spill encroaches upon the boundary of a protected area, on an incoming tide for example, the remote spill detector will alert designated personnel for immediate response. This will trigger the appropriate planned contingency response action in time to avert catastrophic damage and casualties to wildlife and natural resources.

In this scenario spill detectors could be incorporated into the areas contingency plan (such as the ACPs that exist for many designated sensitive areas in California), to provide the early warning defense mechanism that is needed, but currently does not exist. As part of a given contingency plan, designated spill responders will receive a spill alert in near real time, allowing them to deploy pre-positioned booms,

or implement pre-planned *time-critical* response activities, to protect sensitive habitat such as eelgrass and nesting areas that might otherwise be devastated. Strategic locations for sensor placement can be based on vulnerability analysis or environmental sensitivity index maps. Sensors are also a natural fit and are easily integrated into GIS-based monitoring and response systems, which are of increasing utility for habitat protection, resource monitoring, and contingency planning.

VII. CONCLUSION

The principle of detection upon which this sensor is based is not new science; however, the methodology and application of this technology in this sensor package is new. In meeting our design goals, and having successfully produced a non-contact spill detection system, we feel optimistic and reassured that this mechanism will prove invaluable in each of the applications discussed. And of course our work is not done…

Planned improvements for this system include continued refinement of the optics, increased signal to noise ratio, and increased detection range. Further to these system improvements, we anticipate adapting the current design for additional applications such as those in the offshore (eg. production platform) environment, and in the habitat protection scenario suggested above. Additional applications are sure to arise, including a pending first-time installation on a series of offshore loading buoys, slated to become operational in Autumn 2006.

There has been interest expressed as well in the ability to quantify the concentration of oil detected, or maybe even identify the type of oil, using this sensor. When we set out to develop this sensor, our primary intent was to qualify the presence of oil; Yes or No, Green or Red; and to sound an alarm when trace oil is detected (Yes/Red!). As such the detector is designed to qualify when oil is present. However, having received requests for PPM measurement from several sources, we are working to develop a meaningful correlation to enable quantification output.

Milestones include our having certified these sensors to comply with EPA defined standards, requiring successful completion of the US EPA's "Standard Test Procedures for Evaluating Leak Detection Methods". Another significant milestone is our having now successfully supplied customers with more than fifty systems to date. Success with users in real-world applications is always a big step in the progression of developing and introducing new technology products. We now have the assurances of a growing user-base to reference, and market sectors to build upon, as knowledge and acceptance of this new technology spreads.

New product features will evolve and new applications will emerge as feedback from end users and regulators continue to drive our further development of this system. A key component going forward will be to increase awareness of the availability and benefits of this new sensor technology, and to encourage widespread use and adoption of remote spill alarms as a best management practice, and as an integral part of stakeholders' spill prevention and response strategies. The future is now for utilization of new remote spill detection technology to aid in the prevention and early containment of oil spill pollution.

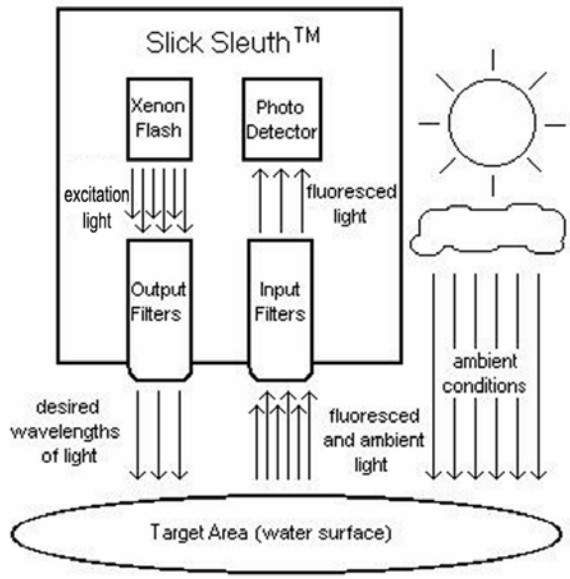

Figure 1. Basic operation of sensor.

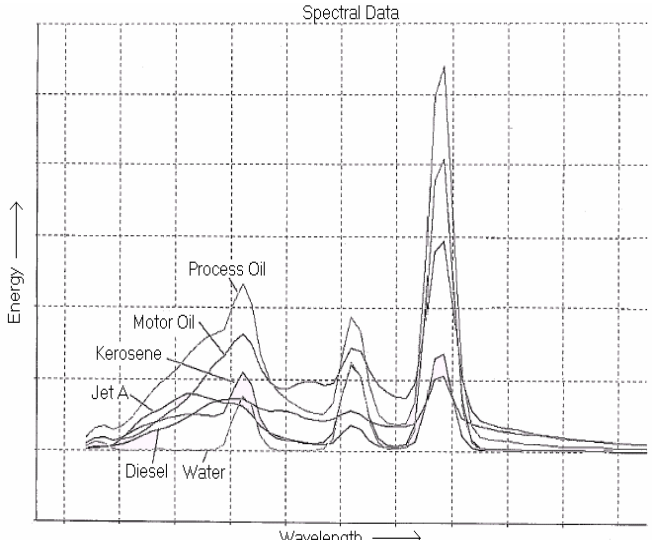

Figure 2. Relative fluorescence of various hydrocarbons

Figure 3. Prototype spill sensor.
Installed near fuel pier (background).

Figure 4. Early production unit.
DC/Solar power, radio telemetry.

Figure 5. Oil detector operating over stormwater sump. Real time output to nearby control center, and automated shutoff of sump pump.
Photo courtesy Dominion.

Figure 6. One of 5 units deployed at a Shell refinery (Australia) to monitor cooling water outfall channels. *Photo courtesy Shell.*

Figure 7. Unit deployed over deep sump at a GenCo in the USA. Automated control of sump pump discharge. *Photo courtesy Entergy.*

Figure 8. Discharge monitor installed at production facility in Ecuador.
Photo courtesv Occidental.

Figure 9. Slick Sleuth installed on fuel pier and marine terminal. Alarm output monitored using SMS messaging to key personnel. *Photo courtesy RAN*.

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Removal of Mercury and Arsenic from Produced Water

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ABSTRACT

Chevron (formerly Unocal) Thailand has been producing natural gas and crude oil in the Gulf of Thailand since 1981. Co-produced water is contaminated with hydrocarbons, mercury and arsenic. Where feasible, Unocal Thailand pursued a philosophy which entails re-injecting produced water back into the rock formations from whence it originated. Currently, over 50,000 bwpd are injected in two fields in legacy Unocal's contract area. Re-injection of all produced water is projected to be implemented by year-end 2007.

Overboard discharge limits for produced water are 40 mg/L TPH, 10 ppb Hg and 250 ppb As. Characterization of the produced water has shown that hydrocarbons are present as stabilized emulsions, mercury is primarily present in the elemental form, Hg, and arsenic is present as As^{3+}. A patented process was developed several years ago to remove these contaminants from produced water prior to overboard discharge. The process consists of a three-phase separator to remove gas and condensate. Water leaves the bottom of the separator and passes through desanding and deoiling hydrocyclones. The water then enters the chemical treatment process. In the chemical treatment process, an oxidant (NaOCl), ferric ions and a flocculent are sequentially added to the wastewater to form a floatable sludge consisting of ferric hydroxide, chemi-sorbed mercury, ferri-arsenate, and hydrocarbons. Bleach is added at the inlet to a degasser, ferric chloride is injected into the retention tank, and cationic polymer is added just upstream of the IGF (induced gas flotation) unit. The oxidation-reduction potential of the water is controlled by oxidant addition to allow As^{3+} to be oxidized to As^{5+} whilst maintaining Hg in elemental form. The water treatment process requires relatively short residence times between chemical additions and provides for large water throughputs (typically up to 20,000 bwpd).

In certain Gulf of Thailand fields, the concentration of Hg and As in the produced water is too high for the oxidant – Fe^{3+} – flocculent process to achieve clean water for discharge to the environment. New, improved technology has now been developed to process waters containing high concentrations of Hg and As. It consists of:

1. Installing desanding hydrocyclones to remove elemental Hg, HgS and sand particles to which Hg is attached.
2. Sequentially treating the desanded water with oxidant, ferric ions, a thiol, and the flocculent, or thiol, oxidant, ferric ions and flocculent. The new thiol addition step is especially effective in precipitating excess elemental Hg and any Hg^{2+} that cannot be removed using the oxidant – Fe^{3+} – flocculent process.

INTRODUCTION

The Gulf of Thailand forms a large embayment, over 700 kilometers (km) in length and 600 km in width, on the Sunda Shelf and opens onto the South China Sea (*See* **Figure 1**). The Gulf is relatively shallow with a maximum depth of less than 90 meters (m). Water depths in the northern and far eastern portions do not exceed 20 m for distances of 60 to 100 km offshore. Along the western shore, water depths greater than 20 m occur within 10 to 20 km of the coast. Only in the central 10 percent of the Gulf, 150 km from the Thailand coast, do water depths exceed 75 m.

Figure 1 - Map – Gulf of Thailand

Chevron Thailand's Unocal legacy offshore natural gas fields are situated at the northwestern edge of the deeper central portion of the Gulf, in waters ranging from 65 to 75 m (Figure 1). Oil and natural gas deposits in the Gulf of Thailand are contaminated with mercury and arsenic. The mercury and arsenic are thought to originate in coal, carbonaceous shale and tin (Type II) granites in or near high temperature producing reservoirs. Water co-produced with the hydrocarbons is contaminated both with stabilized emulsions and with the heavy metals (i.e., mercury and arsenic).

Unocal conducted a number of studies since the mid 1980's to better understand and quantify the impact of oil and gas operations in the Gulf of Thailand. Using physical chemical characterization data, a treatment process was designed and engineered to remove contaminants from the produced water for discharge to the environment. The treatment process has been operating successfully since early 2000 in legacy Unocal fields.

Although the total mass of heavy metals produced along with the natural gas, condensate and oil is not large, the metals concentration in the produced water can exceed Thailand's regulatory discharge standards. Unocal voluntarily committed to reduce the concentration of contaminants in the produced water to the following parts per billion (ppb) and parts per million (ppm) levels:

- Mercury (Hg) ….. < 10 ppb
- Arsenic (As) ….. < 250 ppb
- Hydrocarbons ….. < 40 ppm TPH (40,000 ppb)

CHEVRON THAILAND OPERATIONS

Unocal Corporation (now Chevron Corporation) has three decades of successful energy development history in the country. Gross natural gas production averages more than 1.2 billion cubic feet per day (bcfd). The company's cumulative natural gas production since the startup of operations in 1981 surpassed 4 trillion cubic feet (Tcf) (113 billion cubic meters [Bcm]) in May 2000. Legacy Unocal Thailand operates >134 platforms in the central Gulf of Thailand, supplying natural gas to generate 30 percent of the nation's total power demand (*See* **Figure 2**). Of the natural gas produced, more than 75 percent is used to generate electricity. The remainder is used for industrial fuel, transportation fuel, cooking gas and petrochemical feedstock.

Unocal legacy exploration and production covers 13 gas and condensate fields for its co-concessionaires, Mitsui Oil Exploration Co., Ltd., PTT Exploration and Production Public Company Limited (PTTEP), Amerada Hess (Thailand) Ltd., and Moeco Thai Oil Development Co., Ltd. This includes eight blocks in the Gulf of Thailand, covering 2.9 million acres (11,838 square kilometers) and three blocks in the Arthit Project, covering 988,000 acres (4,000 square kilometers).

Recently, Unocal legacy started its first crude oil production from the Gulf of Thailand. Gross oil production Yala-Plamuk complex is nearly more than 40,000 barrels per day (Bpd). Just north of the Unocal legacy assets, Chevron operates two oil fields, which are now combined since the merger of Unocal into Chevron. The Bongkot gas field shown in Figure 2 is operated by PTT, the national oil company.

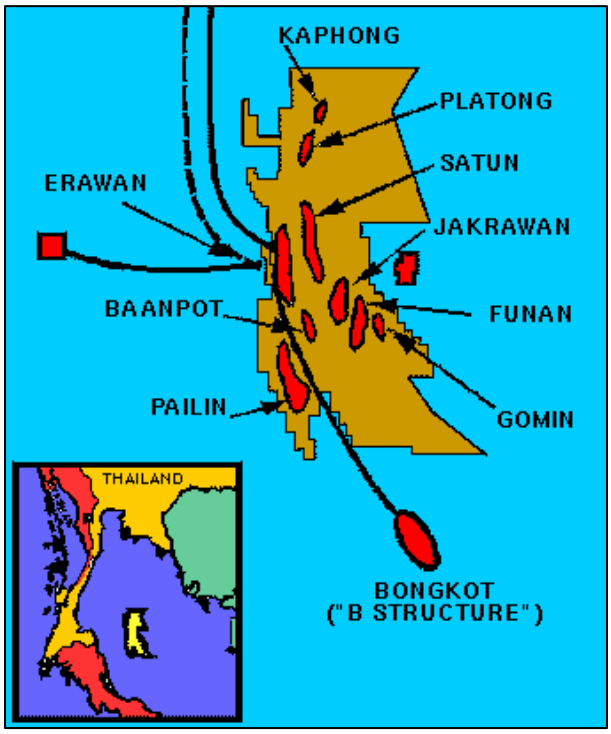

Figure 2 – Unocal Legacy Thailand Operations

GEOCHEMISTRY AND ORIGIN OF MERCURY AND ARSENIC IN GULF OF THAILAND

Mercury occurs naturally in several forms in the environment, including elemental mercury (Hg (0)), inorganic mercury (Hg (II)), and methylated forms (mono-methyl mercury and di-methyl mercury). Measurable levels of mercury occur in rocks, oils, condensate and gas in the Gulf of Thailand reservoirs, although concentrations vary widely. Mercury concentrations in rock cuttings from a series of Platong wells, for example, range from less than 100 ppb to

greater than 400 ppb, but are less than 600 ppb throughout the drilled section. Bedded coals tend to concentrate mercury with some shales and coals in the Gulf of Thailand containing about 65 times as much mercury as the surrounding shales. Worldwide, mercury-in-coal concentrations drop significantly with increasing rank level and this is expected to be the case in the Gulf of Thailand coals as well.

Three major origin "hypotheses" can be advanced to explain the occurrence and distribution of mercury in geochemical materials of the Gulf of Thailand -- the genetic, coal, and mineral origins. The genetic origin, which suggests a co-occurrence of Hg and total organic carbon (TOC) content in sedimentary rocks, derives from the observation that TOC contents and Hg concentrations in sedimentary rocks show good correlations. The coal hypothesis is related to the genetic hypothesis, and derives from the observation that certain coal-forming land plants act as concentrators of mercury present in the soils upon which they grow. The Hg is subsequently stripped from the coal by passing aqueous or hydrocarbon flows. The "mineral origin" hypothesis suggests that Hg leaves a mineral matrix and enters hydrocarbon solutions at high temperatures in the absence of sulfide. These three hypotheses depend critically upon the solubility relationships between Hg, water and hydrocarbons. Given the solubility of elemental mercury in both water and hydrocarbons, it is reasonable to expect elemental mercury to co-migrate with petroleum, either in aqueous solution or as a solute in hydrocarbons.

Indirect physico-chemical evidence suggests that mercury is produced primarily in the elemental state and that arsenic is produced as an AsH_3 gas. Since arsine is soluble in liquid hydrocarbons, it tends to concentrate in the condensate and pass into the produced water by a hydrolysis reaction. Mercury condenses in the gas as it comes up the well bore and is found to be largely associated with produced solids – although some free mercury droplets can be found, as can some soluble Hg^o. Table 1 summarizes water filtration data from three processing platforms in the Gulf of Thailand. Note that mercury is largely removable by filtration, while arsenic is not.

Table 1. Water filtration data

Operations	Mercury Concentration (ppb)	Arsenic Concentration (ppb)
Erawan Produced Water		
As Received	191 – 235	
3.0 micron filtrate	69	
0.45 micron filtrate	10	
Platong Produced Water		
As Received	155	
3.0 micron filtrate	12	
0.45 micron filtrate	<1	
Funan Produced Water		
As Received	11	382
5.0 micron filtrate	3.7	255

0.45 micron filtrate	1.9	251

PRODUCED WATER TREATMENT PROCESSES

Characterization of the produced water has shown that hydrocarbons are present as stabilized emulsions, mercury is primarily present in the elemental form, Hg, and arsenic is present as arsenous acid. A patented treatment process was developed to remove these contaminants from produced water prior to overboard discharge (**S*ee* Figures 3 and 4**). Where feasible, Chevron Thailand pursues a philosophy which entails re-injecting produced water back into rock formations from whence it originated. Currently, over 50,000 barrels of water per day (bwpd) are injected in two fields in legacy Unocal's contract area. Erawan Central Processing Platform (CCP) injects 98% of its produced water and South Pailin CCP has injected 100% since January 2003. Unfortunately, the re-injection of all produced water is not a simple task given the large geographic area over which gas production occurs. Funan, North Pailin, Platong and Satun discharge water overboard (5,000 to 20,000 bwpd) from each CCP. Re-injection of all water from central processing platforms is expected to be implemented by late 2007.

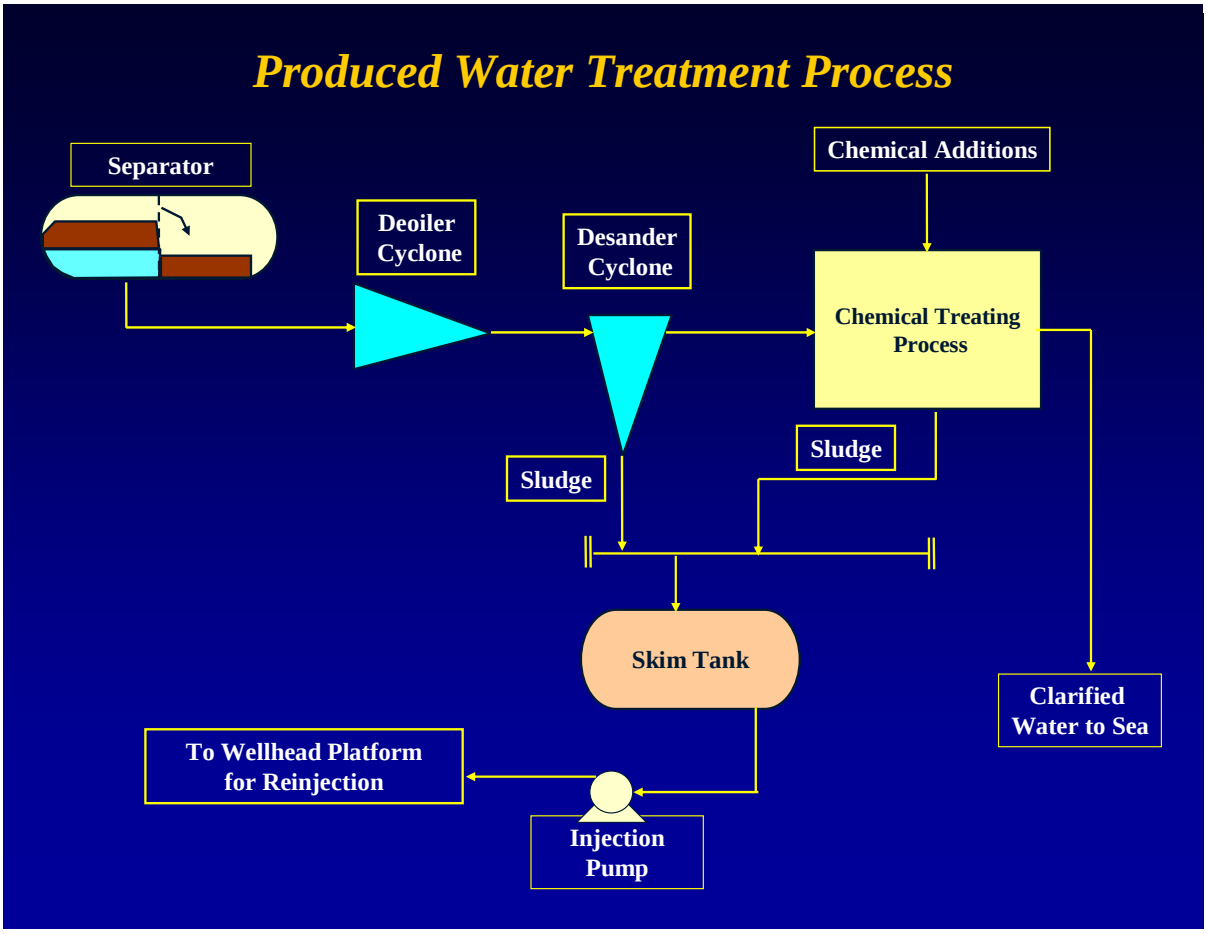

Figure 3. Original water treatment process

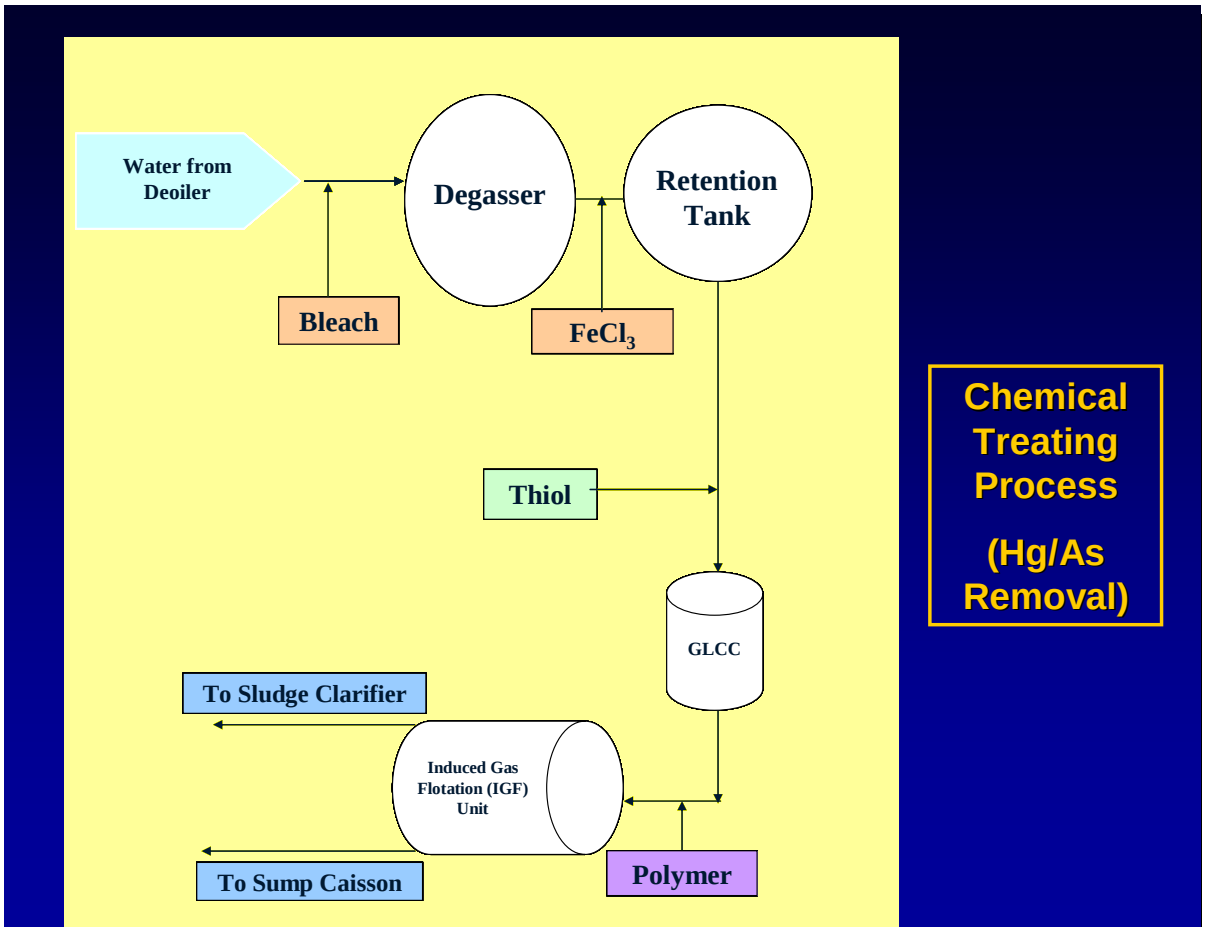

Figure 4. Chemical treatment portion of water treatment process

The process consists of a three-phase separator to remove gas and condensate. Water leaves the bottom of the separator and passes through desanding and deoiling hydrocyclones. The water then enters the chemical treatment process (***See* Figure 3 – Yellow Box**). In the chemical treatment process, an oxidant (NaOCl), ferric ions and a flocculant are sequentially added to the wastewater to form a floatable sludge consisting of ferric hydroxide, chemi-sorbed mercury, ferri-arsenate, and hydrocarbons. Bleach is added at the inlet to a Degasser, ferric chloride is injected into the Retention Tank, and cationic polymer is added just upstream of the IGF (Induced Gas Flotation) unit. The oxidation-reduction potential of the water is controlled by oxidant addition to allow arsenous acid to be oxidized to arsenic acid, whilst maintaining Hg in elemental form. The water treatment process requires relatively short residence times between chemical additions and provides for large water throughputs (typically up to 20,000 bwpd). The chemical reactions utilized in the process are:

$$NaOCl + H_3AsO_{3(aq)} = H_3AsO_{4(aq)} + NaCl$$

$$H_3AsO_{4(aq)} + FeCl_3 = FeAsO_{4(s)} + 3HCl$$

$$FeCl_3 + 3H_2O = Fe(OH)_{3(s)} + 3HCl$$

$$Fe(OH)_{3(s)} + Hg = \text{chemisorbed } Fe\text{-}O\text{-}Hg_{(s)}$$

In certain Gulf of Thailand fields, the concentration of Hg and As in the produced water is too high for the oxidant – Fe^{3+} – flocculent process to achieve clean water for discharge to the environment. New, improved technology has now been developed to process waters containing high concentrations of Hg and As. The new technology consists of:

1. Installing desanding hydro-cyclones to remove elemental Hg, HgS and sand particles to which Hg is attached.
2. Sequentially treating the desanded water with oxidant, ferric ions, a thiol, and the flocculent. The thiol may also be added just upstream or downstream of the desander, followed by the other chemicals. The new thiol addition step is especially effective in precipitating excess elemental Hg and any Hg^{2+} that cannot be removed using the oxidant – Fe^{3+} – flocculent process. We have recently identified a variety of thiols that are effective in decreasing Hg concentrations to below discharge limits. One of these thiols has also proven to precipitate a little additional As that is not precipitated by oxidation and Fe co-precipitation.

$$\text{Thiol} + Hg \text{ or } Hg^{2+} = \text{Hg-S precipitate}$$

where Thiol = dithiocarbonate; trithiocarbonate; sulfide, and the like

3. Re-injecting the Fe-As-Hg sludge back into rock formations from whence the water and petroleum were produced. To ensure that As and Hg will not be leached in the rock formations, the sludge may be "fixed/stabilized" with proprietary cement formulations or placed into steel containers for disposal in deep wells.

Produced water treatment analyses for Funan CCP (**Table 2)** and North Pailin CCP (**Table 3)** are shown below.

Date	TPH (ppm)	Hg (ppb)	As (ppb)	Comments
May - 2003	30	4	112	
Sep - 2004	24	9	505 *	Weak Bleach Injection
Jan – 2004	30	6	128	
May – 2004	30	3	194	
Sep – 2004	31	1	168	
Jan – 2005	35	4	221	
May – 2005	37	2	241	
Jul – 2005	35	2	138	

* Outside established limits

Table 2. Funan **c**entral processing platform (CCP) discharge water analyses

Date	TPH (ppm)	Hg (ppb)	As (ppb)	Comments
May - 2003	10	6	1,228 *	Insufficient NaOCl
Sep - 2004	19	37 *	87	Excess NaOCl
Jan - 2004	12	3	316 *	Start thiol
May - 2004	9	3	155	
Sep - 2004	16	10	380 *	Insufficient Fe 3+

Jan - 2005	7	5	253	
May - 2005	15	10	834 *	Insufficient Fe 3+
Jul - 2005	17	11 *	126	Excess NaOCl

* Outside established limits

Table 3. North Pailin central processing platform (CCP) discharge water analyses

Legacy Chevron oilfields in the Gulf of Thailand are required to meet produced water overboard discharge limits of 40 mg/L TPH and 10 ppb Hg, but no limit has been established for As. At one field, water is passed through a walnut shell filter, beds of Hg-A (sulfur impregnated activated carbon) and polishing cartridge filters. At the other field, water is discharged overboard from FPSO storage tanks after treatment with dithiocarbonate mercury precipitant and water clarifier. These treatment processes successfully remove TPH and Hg to the discharge limits. These fields will also switch to 100% injection next year.

SAMPLING PROTOCOLS

Overboard discharge limits for produced water are 40 mg/L TPH, 10 ppb Hg and 250 ppb As. Water samples are monitored daily for TPH on respective platforms. Closed drain sump caisson water samples are collected the 6th of each month and analyzed at Chevron's Songkhla central laboratory. Thailand Department of Minerals Resources personnel may also collect replicate samples for confirmation analyses. If produced water samples exceed any of the limits, a second sampling is conducted later in the month after adjustments to the water treatment process are made in an effort to comply with discharge limits.

SUMMARY AND DISCUSSION

Physical and chemical characterization data on the hydrocarbon emulsions, mercury species and arsenic species present in the Gulf of Thailand produced fluids were used to develop a produced water treatment process. The process has allowed legacy Unocal Thailand fields to comply with established discharge standards for produced water for total petroleum hydrocarbons (<40 ppm TPH), mercury (< 10 ppb) and arsenic (< 250 ppb).

The new desander - oxidant – Fe^{3+} – thiol - flocculent water treatment process has been operating relatively successfully at two fields since 2003. Further process improvements are being tested. We have attempted to develop continuous on-line Hg and As monitors to determine the concentrations of these metals entering the degasser. The monitors have been problematic and are not yet installed commercially. These monitors are needed to allow adjustment of chemical treatment rates to achieve desired metal discharge concentrations. In some fields, continuous, on-line TPH monitors are used to ensure that hydrocarbons are floated out of the IGF sufficient to meet sump caisson discharge limits.

Chevron Thailand is confident of their capability to meet the overboard discharge water quality specifications for the Gulf of Thailand.

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Mercury: Real Problems…Not Roman Mythology

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ABSTRACT

Some crude oils can contain a variety of mercury compounds: elemental mercury; mercuric chloride; mercuric sulfide; mercuric selenide; dimethylmercury; diethylmercury, etc., which can be damaging to refinery equipment and the environment. Mercury can also be a chemical component of a variety of complex asphaltenic and sulfur-containing compounds. It is important to understand that several of these mercuric compounds are volatile and can be distributed to refined products that can potentially impact product quality. Furthermore, mercury and mercuric compounds will also transition into the water phase. Removal of mercury in both of these phases represents some difficulties particularly with environmental discharge limits becoming more stringent.

This talk will focus primarily on chemical agents and aspects of mercury removal in the water environment as well as examining the chemical mechanisms of mercury complexation techniques.

INTRODUCTION

Mercury in Roman mythology was a major god of trade, profit and commerce. The word *mercurial* is commonly used to refer to something erratic, volatile or unstable. Hat makers long ago used mercury to in their work to make particular designs the hat maker wanted. As the hat maker's career progressed, he became more erratic, volatile or unstable. These symptoms as a result of mercury poisoning, have led to the banishment of most elemental mercury applications today as this element is being heavily regulated as an environmental and human safety hazard.

Increasing environmental concerns about heavy metal discharge have continued to fuel tightening metals discharge limits for oilfield production and refineries. Meeting lower limits will necessitate making changes to existing wastewater treatment systems and plant operations. For oil production and refinery applications, mercury and selenium are two very problematic metals to remove in the purification of industrial wastewater due to the low limits being specified, 50 parts per billion (ppb) or less.

Regulatory issues include the following for water, air and solid waste: Clean Water Act (CWA, Section 304), Total Maximum Daily Load (TMDL), Clean Air Act of 1990 (CAA, Section 112), National Emission Standards for Hazardous Air Pollutants, (NESHAP), Maximum Available Control Technology (MACT), and Resource Conservation and Recovery Act (RCRA).

The amount of mercury (1,2) in crude oil varies for 0.1 ppb to 3 parts per million (ppm) and when crude oil comes into contact with water, an entry of mercury into water-phase is introduced. Production of crude and natural gas also produces water. At most production sites, there are facilities for the separation of gas, oil and water. This "produced" water will have a variety of contaminates, including oil, sand, inorganic materials such as iron, sodium chlorides, hydrogen sulfide, and other salts and heavy metals such as nickel and mercury. Depending on the EPA, State and Local regulations, the produced water will have to be purified before being discharged in the environment. Wilhelm and Kirchgessner (2) have a review concerning discharging produced water for both onshore and offshore production facilities.

A second entry of mercury into water comes from refinery processes. In desalting applications, a small percentage of water (from 3 to 6% of the crude charge) is mixed with the crude feed slate of the desalter. Resolution of the emulsion is accelerated through the use of temperature (up to 275°F), an electric field (16,000 to 20,000 volts), and chemical demulsifier. With the water and crude oil being thoroughly mixed, this allows mercury to be transferred into the water phase. The mercury must then be removed before being discharged into the environment.

WHY TREAT METAL BEARING WASTE STREAMS?

Metals do not degrade readily in the environment and, therefore, are highly persistent. A number of heavy metals are human carcinogens and also have adverse effects on animals. Furthermore, metals can bioaccumulate in aquatic organisms and plants, posing a threat throughout the food chain. Some metals, such as arsenic, chromium and mercury, are readily transformed among various oxidation states, increasing their mobility in the environment. Human exposure pathways for metals include inhalation of dusts and fumes and ingestion of contaminated food, soil, ground water or surface water.

The metals occurring in waste streams that are listed as hazardous are:

Antimony	Chromium	Nickel
Arsenic	Cobalt	Silver
Barium	Copper	Selenium
Beryllium	Lead	Vanadium
Cadmium	Mercury	Zinc

PARTICULATE METALS REMOVAL

All discharge permits are based on total metals in the plant effluent. However, for treatment purposes, it is important to determine soluble and insoluble, or particulate, metals in the waste stream for treatment. In most applications, both particulate and soluble metals are present and must be removed at the same time.

In wastewater treatment applications, chemical treatment is used to remove oils, solids, and other contaminants. These chemicals have a cationic charge to neutralize the anionic charges on the surface of the contaminants. When there are heavy solids loading and/or hydrocarbons in wastewater, a large demand for cationic charge by the anionic surfaces of the particles is usually warranted. Since heavy metal removal agents are usually cationic in nature, they may be consumed by the solids and not be available to remove soluble metals. Thus, in applications with high solids and/or hydrocarbons, it is often more cost effective, first, to remove the solids and particulate metals with a coagulant (cationic) product, and then second, use the metal removal agent for soluble metal ion precipitation.

Other interferences for heavy metal removal operations include emulsion-stabilizing agents such as detergents and other water-soluble organics requiring a high cationic charge demand. Again, it may be necessary to pre-treat the water to remove charge demand before removing the heavy metals with a metal removal agent.

Table 1 gives a quick comparison of available precipitation technologies commonly employed today for soluble metal removal.

PRECIPITATION

The most widely used process for the removal of heavy metals from waste streams is chemical precipitation. This method is used by approximately 75 percent of the facilities that treat aqueous metal-bearing wastes. Chemical precipitation exploits the low solubility of certain metal complexes in solution that can be described by the following mathematical expression:

$$M(L)n = M^{n+} + n(L)^{-} \qquad (1)$$

$$[M^{n+}]\,[L]^{n} = Ksp \qquad (2)$$

where n = 2,3,4, etc., the brackets indicate molar concentrations, M is the metal species, L is the ligand, and Ksp is the solubility product. The smaller the Ksp, the greater the tendency for the metal-ligand complex to be insoluble. The precipitation reaction involves the alteration of the ionic equilibrium of the metal ion to produce an insoluble metal complex.

Chemical precipitation treatment depends upon one or more of the following variables: 1) maintenance of an alkaline pH through the precipitation reaction and subsequent settling; 2) addition of a sufficient excess of treatment ions to drive the precipitation reaction to completion; 3) addition of an adequate supply of sacrificial ions (such as iron or aluminum) to ensure precipitation and removal of specific target ions; and 4) effective removal of precipitated solids.

Precipitation techniques currently being practiced on aqueous metal wastes include hydroxide (e.g. caustic or lime), sulfide, and carbonate precipitation processes. Hydroxide precipitation is effective in removing arsenic, cadmium, chromium III, copper, iron, manganese, nickel, led and zinc. Sulfide precipitation is highly effective in the removal of cadmium, cobalt, copper, iron, mercury, manganese, nickel, silver, tin and zinc. Carbonate precipitation is effective in removing cadmium, nickel, and lead at a slightly lower pH than either hydroxide or sulfide techniques. Each of these processes has been reviewed in the literature (3).

SMALL ORGANIC PRECIPITATNTS

Small molecule organic precipitants such as alkyl dithiocarbamates (DTC), trimercaptotriazines (TMT) and trithiocarbonates (TTC) are used extensively in the metal finishing and electronics industries in the U.S. These precipitants react stoichiometrically with metal ions and show similar characteristics in use. In our discussion, we will use DTC as an example, keeping in mind that TTC and TMT show similar characteristics.

In treating dilute rinse waters containing low concentrations of metals, say below 50 ppm (mg/L), the resulting metal-DTC complexes form colloidal particles in suspension, i.e. particles that will not settle in a reasonable period of time. In some wastewaters, these particles are so small that they appear only as color, carrying metal ions into the effluent. Thus, sufficient removal of metal ions from plant effluent necessitates the practice of appropriate coagulation/flocculation techniques for colloidal suspensions.

Small organic molecule precipitation is difficult to optimize. This is because most wastewaters contain dispersants such as dissolved oils, organics and surfactants. These dispersants inhibit the aggregation of particles, increasing the dosage requirements for coagulants and sometimes, flocculants. Since these precipitants are negatively charged molecules, product overfeed tends to disperse the precipitate particles. In applications where the initial metals levels are less than 5 ppm, it is more difficult to achieve discharge limits using small molecule precipitants.

To summarize, disadvantages are:

1. Difficult to optimize coagulation/flocculation
2. Not effective for low-level metal removal.

POLYMER PRECIPITATION – NALMET®[6] 8702

A polymeric precipitant (Figure 1) reacts with soluble metals to form insoluble complexes with the same mechanism as the small molecule organic precipitants (Figure 2). However, because the metal binding groups are bound to a polymer (4), simultaneous metal precipitation and clarification occurs. Using this class of chemicals allows good solids/liquid separation and may not require optimization of a second chemical. This is dependent on the wastewater equipment in the system (typically clarifiers) as well as adequate retention time. In some applications, the clarifier effluent is sent to filters before discharge.

The NALMET product line is designed to react and remove a variety of heavy metals from wastewater, as shown in Table 2. More importantly, mixed metal contamination is not a problem using NALMET due to the chemical's ability to complex at pH as low as 7 to and as high as 9. This is vastly different than hydroxide precipitation where the solubility of the different metal hydroxides varies with pH, as shown in Figure 3. For example, a wastewater contains 10 ppm Cu, 5 ppm Ni, and 4 ppm Zn. The calculated theoretical dosage for NALMET 8702 is: (10 x 19.0) + (5 x 20.7) + (4 x 18.5) = 367.5 ppm.

NALMET removes the monovalent metals first, followed by divalent, as shown below. The metals are removed in descending order. Some overlap in selectivity does occur, especially when one metal is predominant in a waste stream.

Hg>Ag>Cd>Cu>Pb>Zn>Co(II)>Ni>Se(II)>Fe(II)>Mn

Mercury, in its various forms, has a great affinity for certain minerals, as well as protein and non-protein molecules in the body. Mercury (I) or (II) have a great attraction to the sulfhydryls or thiols. The mercury atom or molecule will tend to bind with any molecule present that has sulfur or a sulfur-hydrogen combination in its structure (5). For these reasons, NALMET reacts more rapidly with Hg (I) and Hg (II) than with other soluble metals, as shown in the list above.

Mercury in Refinery Wastewater

Most, if not all, of the mercury in refinery wastewaters is derived from crude oil (1). In desalter applications, water is mixed with the crude to help remove inorganic chlorides from the crude. If chlorides are not removed, then in downstream processes, gaseous hydrogen chloride is formed leading to severe corrosion. Furthermore, more than just chlorides are moved from the oil phase to the water phase. Other contaminates include oil from poor oil/water separation, solids, inorganic salts, inorganic mercury compounds, elemental mercury, as well as other heavy metals such as iron or lead. The spent desalter washwater called "brine" is then sent to the refinery's wastewater treatment plant.

The wastewater treatment plant (WWTP) must now remove the contaminants not only from the desalter brine, but also from all other wastewater sources such as cooling water blowdown, tank bottoms, stormwater runoff, etc. However, in nearly all cases, the refinery's largest contaminant in the water is crude oil. Desalter operations are optimized to limit the amount of oil in the wastewater. However, 5% washwater for 200,000 barrels of crude is still 420,000 gallons of water per day, not including any other process water streams. If the oil level in the desalter brine is 1000 ppm (0.1%), this is still **420 gallons of oil to the WWPT per day!**

Based on experimental data from our laboratory, agitation between the water and oil phases in the desalter is necessary to remove not only chlorides **but** also mercury compounds. Thus, the WWPT will not only have to remove the oil, but also mercury before discharging to the environment.

The effect of mercury being transferred from the oil phase to the water phase was examined in the laboratory to simulate the effects of the mixed valve in the desalter crude unit. As agitation is increased, the amount of total mercury in the water phase also increased, as shown in Table 3. Even very gentle agitation "rolls" removed one-third of the mercury from the oil

phase. As the agitation becomes more severe, up to two-thirds of the mercury is transferred. Based on these results, it is important for the refinery to optimize the removal of chlorides as well as mercury from the crude oil. However, it must be acknowledged that deionized water was used, and that different sources of washwater may limit mercury transfer.

Using NALMET 8702 on water samples containing $HgCl_2$ and Hg_2Cl_2 blend (500 ppb each), it was found that 6.0 ppm of chemical can precipitate 80% or 800 ppb. Higher dosages of 12 ppm gave 90% removal (100 ppb), and 18 ppm, 98% removal, (20 ppb).

Mercury Removal Experience

Currently Nalco is treating two solid waste incinerators in Europe and the quench water contains 720 ppb and 210 ppb mercury. Applying NALMET 8702 at a pH between 7-8 gives the following results:

Unit No. 1	Inlet	720 ppb	outlet 16 ppb	NALMET 8702: 15 ppm
Unit No. 2	Inlet	210 ppb	outlet 12 ppb	NALMET 8702: 25 ppm

This water contains no oil and is fairly clear prior to treatment. NALMET 8702 is fed upstream of the clarifiers, passed through small mixing chambers and sent to clarifiers for settling. An anionic flocculant is used as needed to help settling the precipitate. The water is then sent to multimedia filters to remove any small particles. The water is discharged meeting the >25 ppb specification.

We have several oil platforms in Southeast Asia that are using NALMET 8702 to remove mercury from their wastewater stream.

SUMMARY

NALMET 8702 is used to remove +1 and +2 heavy metals from wastewater streams in a variety of industrial applications. In particular, oilfield production in Southeast Asia and refineries using crude oil from Southeast Asia can have difficulty with mercury in the oil and wastewater applications. Polymeric dithiocarbamates, NALMET 8702 can remove mercury from the wastewater by precipitation, meeting the discharge specifications and allowing for the treated wastewater to be discharged to the environment.

Table 1. Comparison of Commercial Metal Precipitant Chemistries

	NALMET 8702	OH	Na_2S	$FeSO_4$	DTC	TTC	TMT	Ven Met
Chemical Cost	high	low	low	low	mod	mod	high	high
Sludge Disposal Cost	mod	high	high	high	mod	mod	mod	low
Treat Chelated Metals?	yes	no	no	maybe	yes	yes	maybe	yes
Low Levels?	yes	maybe	maybe	maybe	maybe	maybe	maybe	maybe
Mixed Metals?	yes	maybe	maybe	maybe	yes	yes	yes	maybe
Solid/Liquid Separation	easy	tough	tough	tough	tough	tough	tough	tough
Toxicity of product	mod	non toxic	human toxic	mod	high	mod	low	human toxic
Automation Available?	Nalmet 2000	pH	no	no	ORP	ORP	ORP	ORP
Ease of use	easy	easy	hard	hard	hard	harder	hard	hard

OH = hydroxide precipitation
DTC = alkyl dithiocarbamate
TTC = trithiocarbonate
TMT = trimercaptotriazine
Ven Met = sodium borohydride

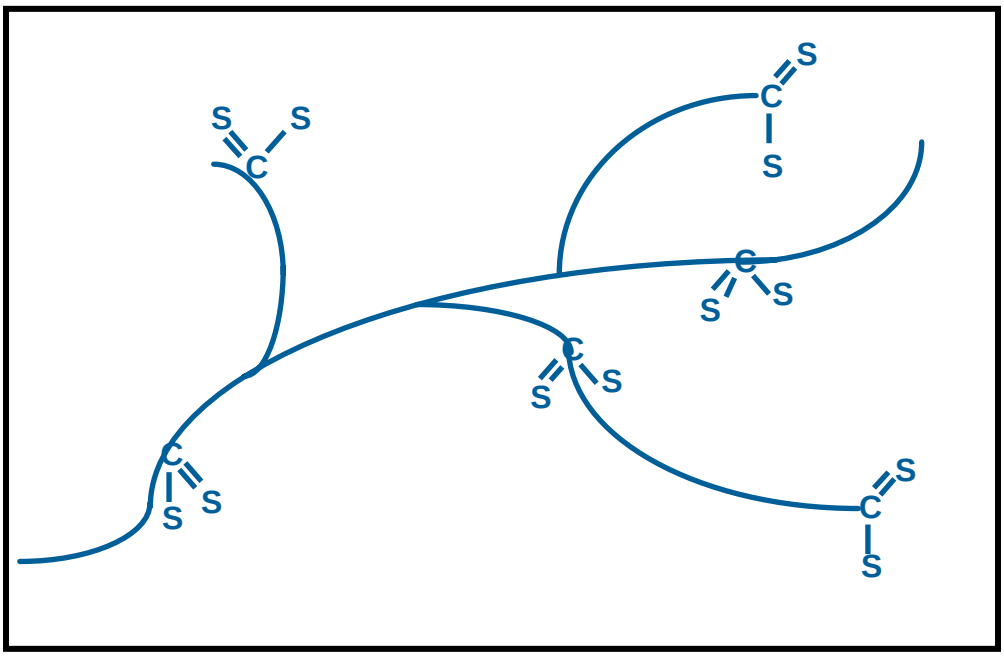

Figure 1. CS_2 Modified Polymer Backbone

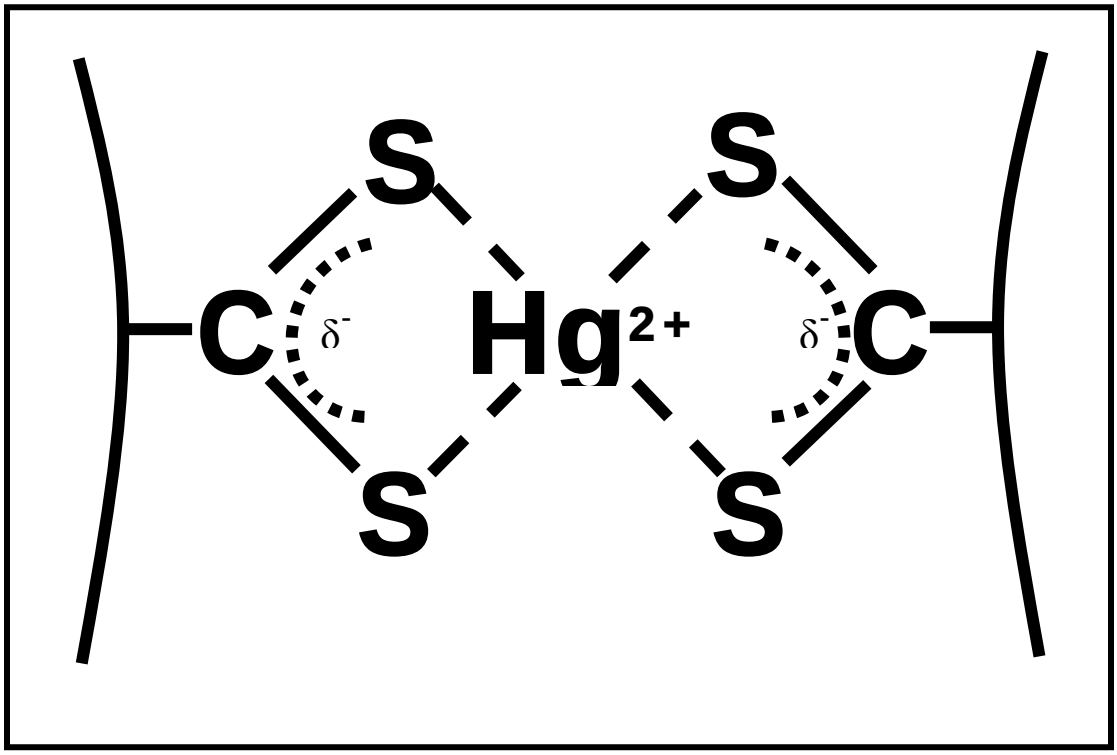

Figure 2. Metal Complex Schematic of Small Molecule and Polymeric Dithiocarbamates

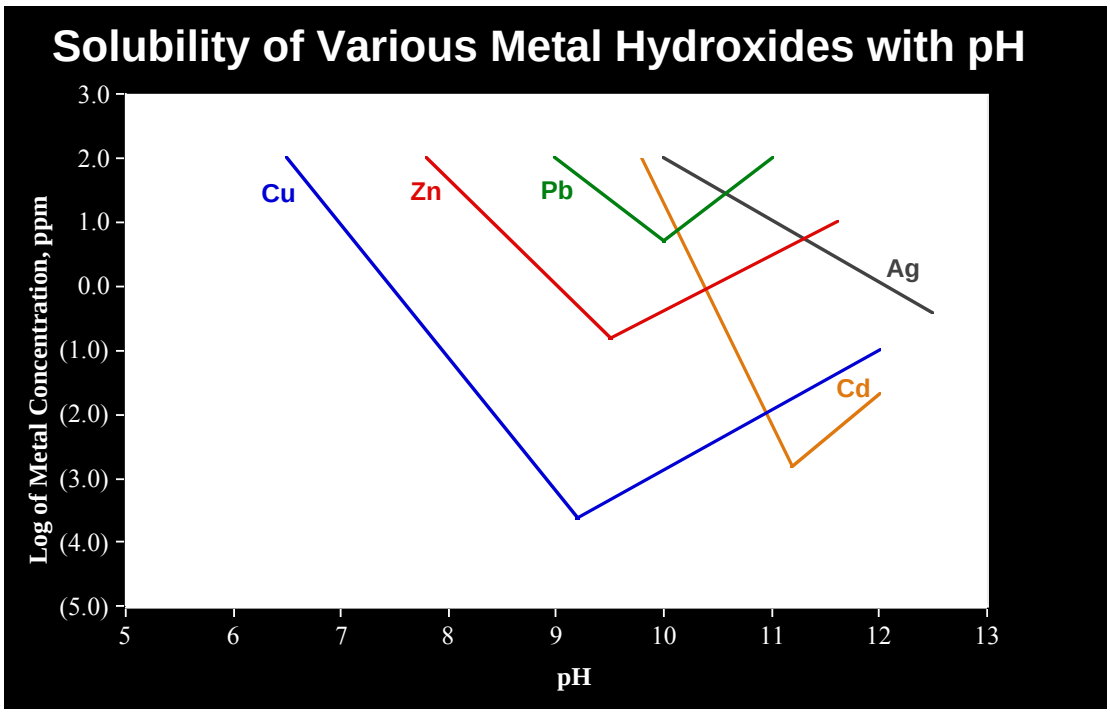

Figure 3. Solubility of Various Metal Hydroxides with pH (3)

Table 2. NALMET® Dosage needed to remove 1 ppm Metal.

Element	8702 ppm
Copper (Cu)	19.0
Lead (Pb)	5.9
Nickel (Ni)	20.7
Zinc (Zn)	18.5
Mercury (Hg (II))	6.0
Selenium (Se (II))	20.0
Silver (Ag)	5.6
Cadmium (Cd)	10.8
Iron (Fe(II))	21.7
Manganese (Mn)	22.0
Cobalt (Co)	20.6
Tin (Sb (II))	10.2

Table 3. Agitation studies for Mercury Removal from the Oil Phase

Hg ppb in Oil	Comments
1081.1	Raw Crude
607.7	20 very slow rolls
606.4	20 medium rolls
605.9	20 hard shakes
371.4	200 hard shakes
373.3	30 minutes on shaker "High"

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4. Siefert, K.S., Choo, P.L., Sparapany, J.W., and Collins, J.H., "Method for Removing Metals from a Fluid Stream", U.S. Patent 5,346,627 issued to Nalco Chemical Company, September 13, 1994.

5. Oji, L.N. "Mercury Disposal Via Sulfur Reactions," *Journal of Environmental Engineering,* **124**, 945-52 (1998).

6. NALMET is a registered trademark of Nalco Company.

HELICOPTER SURVEYS FOR LOCATING WELLS AND OILFIELD INFRASTRUCTURE

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Greg Hodges, Fugro Airborne Surveys

ABSTRACT

Prior to the injection of CO_2 into geological formations, either for enhanced oil recovery or for CO_2 sequestration, it is necessary to locate wells that perforate the target formation and are within the radius of influence for planned injection wells. Locating and plugging wells is necessary because improperly plugged well bores provide the most rapid route for CO_2 escape to the surface. This paper describes the implementation and evaluation of helicopter and ground-based well detection strategies at a 100+ year old oilfield in Wyoming where a CO_2 flood is planned. This project was jointly funded by the U.S. Department of Energy's National Energy Technology Laboratory and Fugro Airborne Surveys.

INTRODUCTION

Steel-cased wells have been located by ground-based electromagnetic (1,2,3) and magnetic surveys (4,5,6,7). The National Energy Technology Laboratory (NETL, unpublished results) has used ground measurements of total magnetic field intensity to locate oil wells where the steel casing had been cut off; some more than 3 m below the ground surface. NETL (8) also has used widely spaced airborne measurements of total magnetic field to locate oil and gas wells.

That ground and airborne magnetometry can detect steel-cased wells is well established and not the objective of this investigation. This investigation's purpose is to evaluate contemporary helicopter and ground-based magnetometer surveying systems for their ability to accurately locate wells, particularly wells in old oilfields where casing may be of varying length, diameter, and extent of corrosion. Further, the study intends to evaluate the ability of magnetometry to discriminate between well casing and other oilfield infrastructure such as steel pipelines, tanks, derrick anchors etc. An expected outcome of the study is the optimization of survey design (line spacing and direction; flight altitude).

Not all wells can be located with magnetometry. Very early wells had wood casing that exhibits no magnetic signature. Moreover, subeconomic wells may have had the steel casing pulled either for use elsewhere or for its scrap value. Therefore, a different detection strategy was needed for wells with no casing or non-magnetic casing. The hypothesis of this study is that leaking wells (both uncased and cased) as well as deep-seated fracture zones can be located by sensing volatile components from sedimentary strata that have migrated to the earth's surface via these pathways. Anomalous concentrations of light hydrocarbons, radon, or radon daughters on the surface can be indicative of leakage zones, either fracture zones or leaking oil and gas wells. The detection strategy is not new; soil gas sampling for light hydrocarbons has been used for many years as an exploration technique to evaluate oil and gas potential (9,10,11,12,13,14). Soil gas sampling has been proposed as a method for locating faults (15,16). Further, Armstrong (17) and Johnston and others (18) recommended the use of a portable hydrocarbon analyzer to reveal the exact location of wells because many abandoned wells have measurable methane emissions. On the ground, these techniques are time consuming, expensive, require landowner permission, and are only practical for small areas. Warner (19) and Van der Meer and others (20) proposed remote sensing as a prospecting tool for hydrocarbon exploration. The sensitivity of airborne remote sensing methods has dramatically increased in recent years. New, more sensitive sensing techniques now may allow leaking wells and other conduits for gas migration to be found based on the airborne detection of anomalous concentrations of these substances. Furthermore, airborne techniques allow larger geographical areas to be evaluated more quickly and inexpensively than ground-based searching. This is especially useful when evaluating

large fields, where the ability to locate CO_2 plumes in a timely manner translates to the more efficient deployment of resources in a sequestration or enhanced oil recovery (EOR) site.

This paper describes the results of helicopter and ground surveys of a one square mile area of the 100+ year old Salt Creek Oilfield near Midwest, Wyoming for the purpose of locating existing wells.

SURVEY DESCRIPTION

Site selection

Claims were first located in the Salt Creek Oilfield, about 40 miles north of Casper, Wyoming in the 1880's and the first major oil strike was made in 1908. Since then, the field has been in continuous production. Currently, Howell Petroleum, a wholly owned subsidiary of Anadarko Petroleum is in the process of refitting existing wells and drilling new wells to implement a CO_2 flood of this old field that will enhance oil production. CO_2 flooding of Phase I areas has commenced and the reworking of wells within later phases is ongoing. Because of the long production history at Salt Creek Oilfield, there are more than 3000 wells, many with unknown or inaccurately known locations. Howell Petroleum intends to locate, inspect, and, if necessary, refit or re-plug every well within the proposed CO_2 flood areas.

In 2004, NETL approached Anadarko about using the Salt Creek Oilfield as a site to test new airborne and ground-based strategies for locating wells. With the assistance of Anadarko personnel, a rectangular area (approximately one square mile) within the planned zone of CO_2 flooding was selected (Fig. 1). The area is representative of most of the Salt Creek Oilfield in terms of well density and infrastructure. However, the terrain within the selected area is more subdued, which benefited the ground investigations.

Technical approach

The objective of this study is to locate improperly plugged wells (with or without casing) that could allow CO_2 to move to the surface from injected formations. NETL's intention is to evaluate both airborne and ground-based well detection strategies with the expectation that a combination airborne/ground investigation will be required to search large areas yet provide the accurate locations needed for well refitting or plugging activities. Most wells in the Salt Creek Oilfield have steel casing. However, very early wells had wooden casing, and the steel casing has been pulled from some wells for use elsewhere. The selected study area contained 129 well locations listed in available well databases.

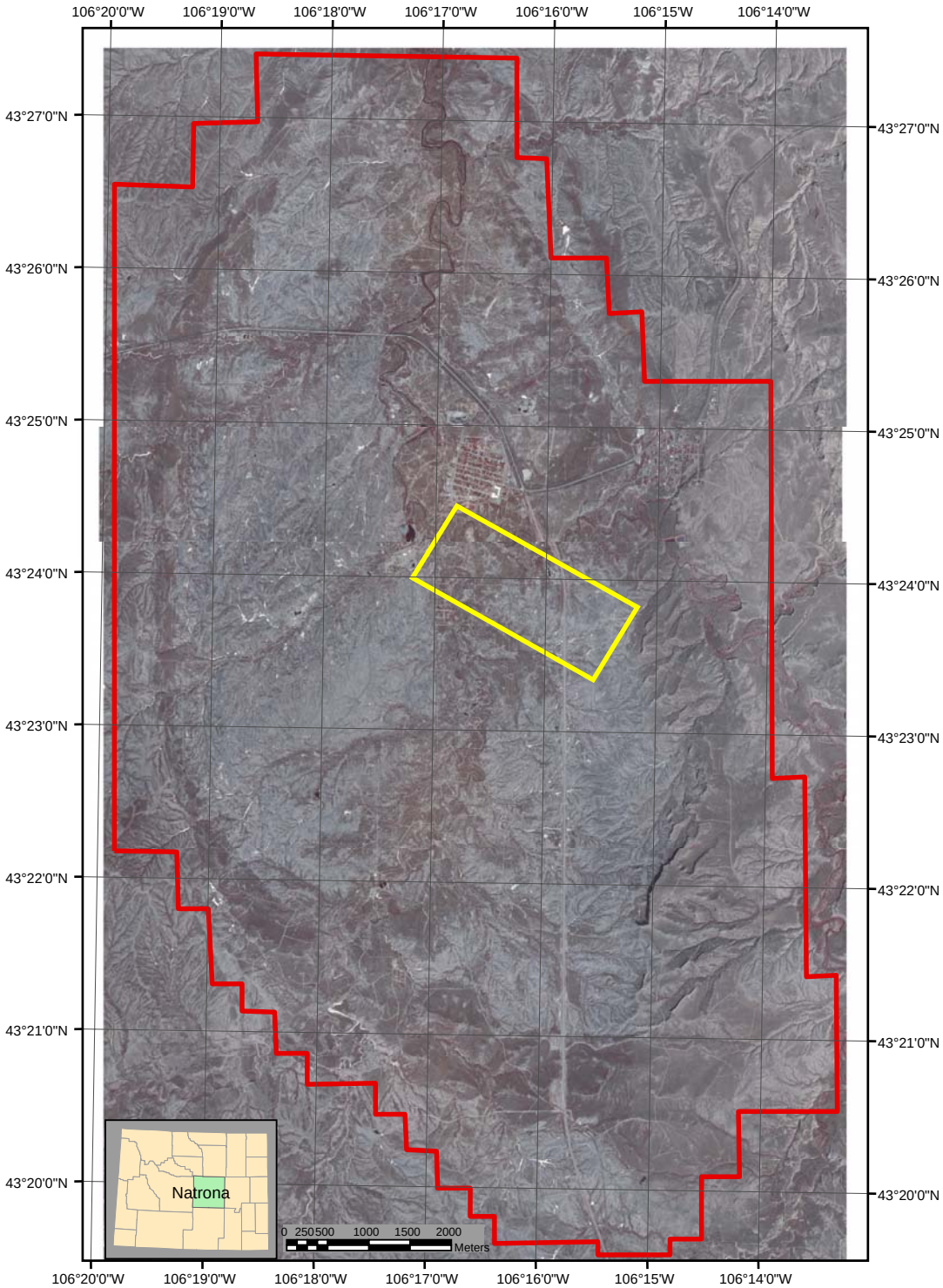

Figure 1. Air photo showing the boundary of the test area (yellow) and the boundary of the helicopter magnetic survey of the entire Salt Creek Oilfield (red) in Natrona County, Wyoming.

Wells with steel casing are located by their distinctive and strong monopole response in total field magnetic data. For this study, magnetic data were collected using airborne and ground vehicles equipped with two boom-mounted magnetometers. Airborne magnetic data were collected from the test area by Fugro Airborne Surveys using their Midas II system, a helicopter system with two cesium vapor magnetometers mounted on side booms (Fig. 2). Two Scintrex CS-2 magnetometers, each having an in-flight sensitivity of 0.01 nT and a sampling interval of 0.1 s were used. Sensor separation was 12 m, enabling the calculation of horizontal magnetic gradient. Real time compensation of the magnetic data for magnetic noise induced by maneuvering of the aircraft was accomplished using a flux-gate magnetometer. Corrections for diurnal variations in the earth's magnetic field were made using a magnetometer base station on the ground. Helicopter magnetic surveys of the test area were flown at altitudes of 35 m and 50 m in an NE-SW direction and an interline spacing of 25 m. Navigation and measurement locations were provided by differentially corrected GPS. Altitude was provided by laser altimetry. Following the completion of the test area flights, Anadarko Petroleum contracted with Fugro Airborne Surveys to fly a magnetic survey of the entire Salt Creek Oilfield. This flight was flown at a nominal altitude of 35 m in a north-south direction with an interline spacing of 25 m.

Ground magnetic surveys of about 10% of the test area were conducted using a Kubota RTV-900 four-wheel drive utility vehicle that was equipped with two boom-mounted Geometrics cesium vapor magnetometers (Fig. 3). The sensor separation was 6 m and the sensors were about 2 m above the ground on level terrain. Like the airborne sensors, the ground magnetometers had a sensitivity of 0.01 nT and a sampling interval of 0.1 s. Post processing of the ground magnetic data was performed to partially remove the magnetic response of the vehicle. Ground magnetic surveys were conducted in a northwest-southeast direction with a nominal interline spacing of 10 m. Measurement locations were provided by differential GPS that was also used in conjunction with a moving map-type presentation for navigation along a prescribed survey course.

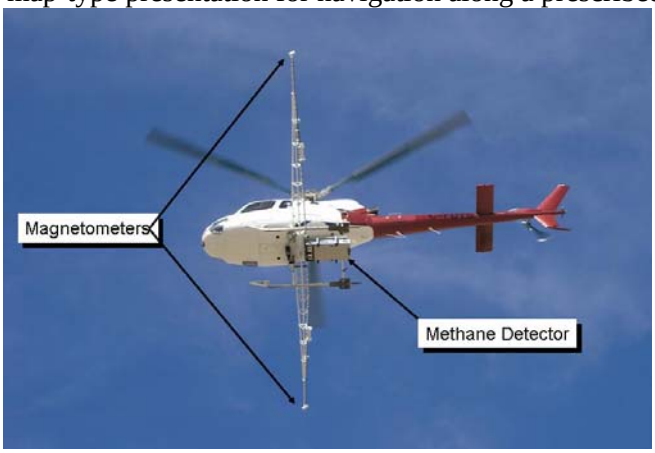

Figure 2. Helicopter with Midas II (magnetic) and LaSen ALPIS (methane) sensors.

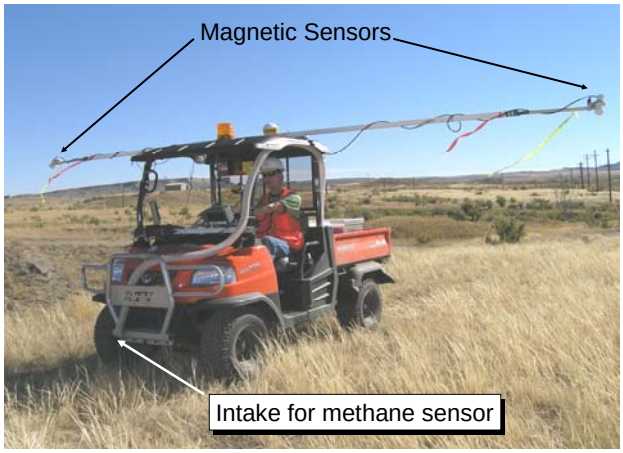

Figure 3. Four-wheel drive utility vehicle with Geometrics (magnetic) and Apogee LDS (CH_4. CO_2, and HC) sensors.

Detecting leaking wells (with or without casing)

To locate wells and fracture zones that may leak following CO_2 injection, NETL intends to detect downwind plumes of methane that already may be emanating from the well or fracture zone.

Helicopter, methane-sensing surveys of the study area were flown by Fugro Airborne Surveys using the ALPIS differential absorption lidar (DIAL) sensor developed by LaSen, Inc (Fig. 2). The ALPIS sensor was selected for this study because it was found to be one of the best sensors in a round robin test of remote methane-sensing technologies sponsored by the US Department of Energy and the US Department of Transportation (21). The ALPIS sensor uses two mid-IR laser beams: one with a wavelength in the methane absorption band and one with a wavelength outside the methane absorption band. Laser beams of both wavelengths are transmitted down from the helicopter to illuminate an area on the ground. After reflection from the ground, the beams are collected and the amount of received energy is measured. If the beams pass through a methane plume, the beam at the methane absorption wavelength will be diminished with respect to the beam that is not in the methane absorption band. Because changes in ground reflectivity and atmospheric opacity affect both beams equally, differential measurements made using the two-beam system can compensate for different atmospheric and ground conditions. However, one exception is that the ALPIS system does not provide accurate methane indications over highly reflective surfaces. Reflective surfaces, such as water bodies, saturate the instrument's sensors and prevent accurate readings. These data are removed during post processing. The ALPIS survey was flown at an altitude of 50 m, which resulted in an 8-m wide detection area (footprint) on the ground (measured perpendicular to and centered on the flight line). Interline spacing was 25 m so ground coverage was about 30%.

Ground methane surveys were conducted using a Kubota RTV 900 utility vehicle that was equipped with the Apogee leak detection system (LDS), a high-speed gas analyzer capable of measuring methane (CH_4), total hydrocarbons (HC) and carbon dioxide (CO_2) in sub part per million (ppm) concentrations at a sampling interval of 0.1 s (Fig. 4). Ambient air was drawn into the LDS system from the front of the vehicle by means of a hose containing an in-line fan and filter (Fig. 3). The LDS system uses an infrared analyzer to measure gas composition and has a computer-based data acquisition system for data logging and display. The computer monitor displays methane, total hydrocarbon, and carbon dioxide concentrations together with a moving map showing vehicle location. A differentially corrected GPS is used to determine the vehicle's location for navigation and sample location. The LDS was calibrated using certified calibration gases (Scott Specialty Gases) prior to the field work. The calibration was also verified at the end of the field program and found to have changed by less than 10%.

Fugro Airborne Surveys used an Ecureuil AS350-B2 helicopter for the magnetic, methane sensing, and radiometric surveys. Midas II magnetic surveys are routine services offered by Fugro Airborne Surveys. However, the methane sensing survey using the ALPIS system required the fabrication of a special bracket on the base of the helicopter fuselage and a special air worthiness certification. Two surveys of the test area were flown: the first payload consisted of the Midas II system and the ALPIS system and was flown at an altitude of 50 m with an interline spacing of 25 m; the second carried a payload of only the Midas II system and was flown at an altitude of 35 m and an interline spacing of 25 m. All helicopter surveys of the test area were flown in azimuthal directions of 120º and 300º to intercept methane or radon plumes driven by primarily southwest winds at this locality. However, the helicopter magnetic survey of the entire Salt Creek Oilfield, which was flown for Anadarko Petroleum with only the Midas II system on board, was flown in a north-south direction. The flight speed with the methane detection system was approximately 2.6 m/s, while the average flight speed with the Midas II only payload was 3.7 m/s.

RESULTS AND DISCUSSION

Airborne and ground magnetic surveys

Available databases containing well locations for the Salt Creek Oilfield were obtained from Anadarko Petroleum. When these databases were combined and duplicate entries eliminated, a comprehensive database was created that documented locations for 129 wells within the test area. An intensive ground search of the study area located 139 wells.

Total magnetic field intensity data from the magnetic sensors of the Midas II system were compensated for the magnetic effect of the aircraft and for diurnal variations in the earth's magnetic field. Processing algorithms were applied to these data to accentuate the distinctive monopole magnetic signature that is characteristic of vertical well casing and to obtain distinguishable magnetic anomalies of minimum radius that were located directly over wells and could be used to guide ground investigations. Two fast fourier transform (FFT) processing sequences were identified that when used together resulted in the most sensitive well detection capability with the most accurate well locations. One processing sequence was to take the FFT of the first vertical derivative data and to apply a log transform to the resulting data. When the transformed data were plotted on maps, a threshold was applied so that only the well anomalies were depicted. Processed data were then plotted as hill-shaded, color-scaled images. Images from magnetic data processed in this manner were found to enhance visualization of well casing irrespective of its age, diameter, and length. The second processing sequence applied a reduced-to-pole FFT correction to the compensated total magnetic field intensity data. The transformed data were then plotted as contour lines on the same map as the colored, hill-shaded well anomalies from the first processing sequence. Reduced-to-pole FFT data plotted as contours were found to provide a more spatially correct well location and were used to target subsequent ground searches to locate well heads.

Averaged two-sensor data

Initially, total magnetic field intensity data from the two Midas II magnetic sensors were averaged and reported at the location given by the GPS antenna on the tail of the helicopter. These data were processed, gridded, and depicted on a map of the study area in figure 4. The survey identified 127 distinctive monopole-type magnetic anomalies within the study area that were interpreted to be steel well casing. Additional processing to detect weak magnetic anomalies (lowering the magnetic threshold and applying logarithmic stretch) identified six more wells for a total of 133. Of the 133 wells interpreted from helicopter magnetic data, 34 were probable well locations not previously documented in available Anadarko databases. The ground search of the study area following the helicopter survey found 6 additional wells that were not detected using averaged two-sensor magnetic data.

Independent two-sensor data

Compensated total magnetic field intensity data from the two sensors were processed independently using location information from two boom-mounted GPS antennae located approximately 2 m inboard from each magnetic sensor. Using data from two independent sensors was expected to increase resolution by doubling the amount of magnetic data and to improve spatial accuracy by using location information that is closer to each magnetic sensor. Figure 5 is a map of magnetic data from two independent sensors. Although it is difficult to see at the resolution of this publication, maps made using independent (versus averaged) two-sensor magnetic data resulted in sharper, more intense anomalies over the well locations. Although maps made with the independent two-sensor data were visually more pleasing, the same number of wells (133 wells) were detected.

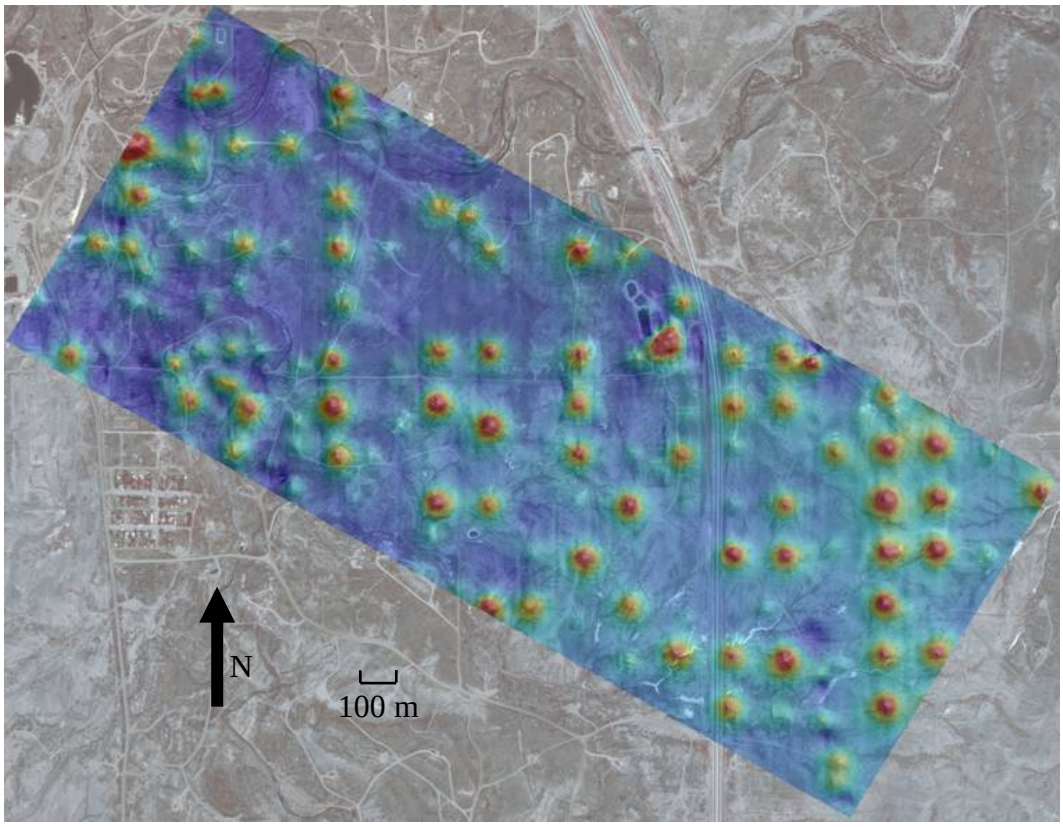

Figure 4. Hill-shaded, color scale map of averaged total magnetic field intensity data from two sensors collected at 35 m altitude and 25 m flight line spacing.

The effect of flight altitude on well detection

Two helicopter surveys of the test area were flown with a NW-SE flight line orientation and an inter-line spacing of 25 m. One flight was conducted at an altitude of 50 m while the second flight was flown at 35 m. Maps showing the processed and gridded two-sensor magnetic data for both flights are shown in figure 6. Even at the low resolution of this document, one can easily see that the lower flight provided sharper, more distinct anomalies. Closely spaced anomalies are not resolved at the higher altitude.

The effect of flight line orientation on well detection

One helicopter magnetic survey of the test area was carried out using NW-SE trending flight lines. A few days later, helicopter magnetic surveys of the entire Salt Creek Oilfield (including the test area) were performed using N-S oriented flight lines. Both surveys were flown with the Midas II system using 25 m inter-line spacing and a nominal flight altitude of 35 m. This provided an opportunity to examine the effect that flight line orientation had on the ability of helicopter magnetic surveys to detect wells. Maps showing the processed and gridded two-sensor magnetic data for both flight line orientations are shown in figure 7. The magnetic survey acquired using N-S flight lines was preferred because the well anomalies were more localized. Also the N-S surveys contained less striping, which indicated that magnetic compensation was better in that direction. Microleveling of the magnetic data could remove the striping from images and changing the illumination angle of the hill shaded image could make the striping less apparent. Flight line orientation is probably not critical to the ability of helicopter magnetometry to detect steel well casing.

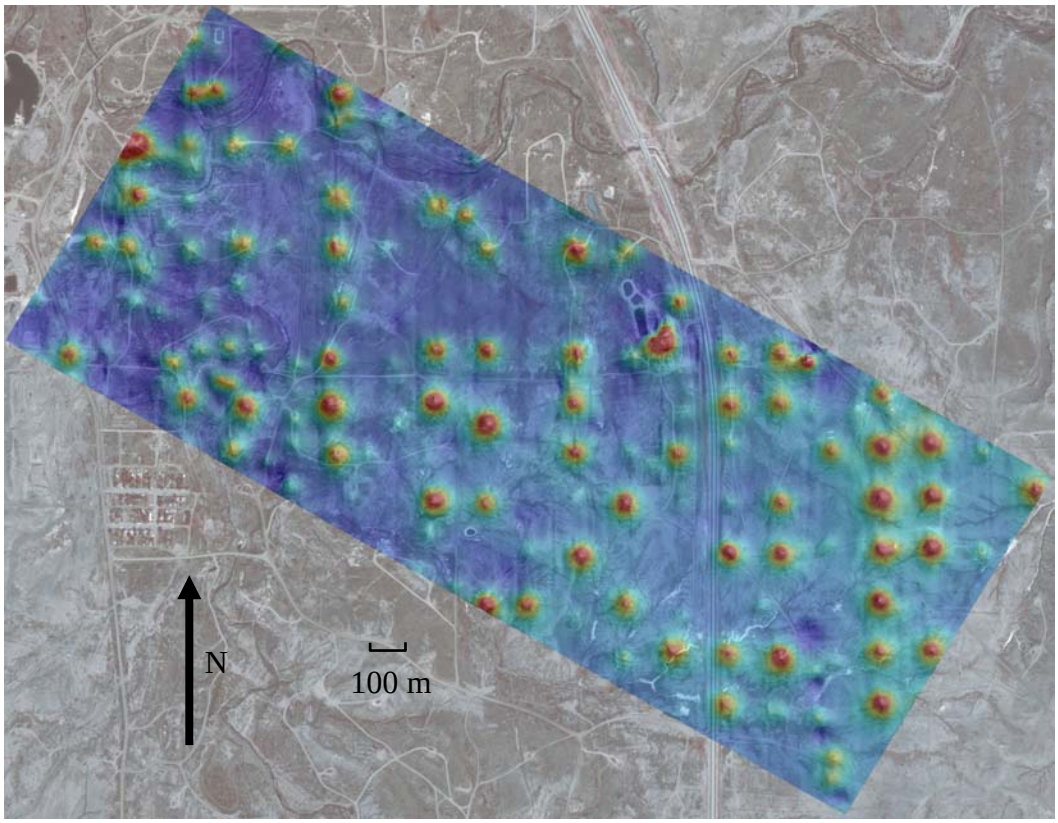

Figure 5. Hill-shaded, color-scale map of total magnetic field intensity data when the two sensors are treated as separate measurements.

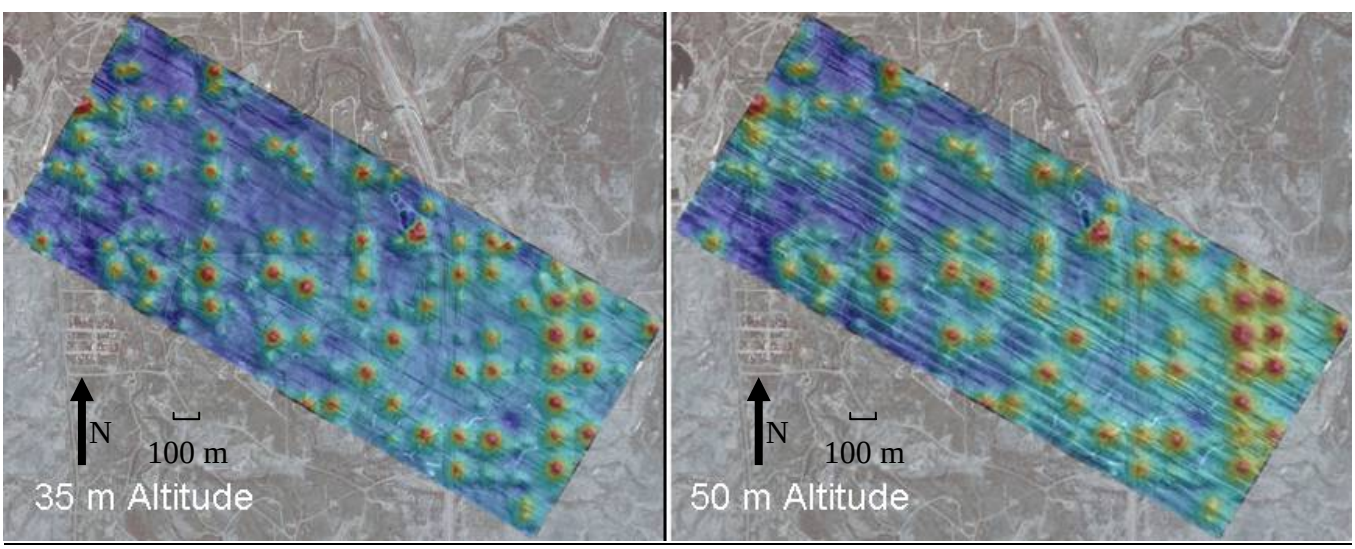

Figure 6. Comparison of the effect of altitude on the ability of helicopter magnetic surveys to detect wells. Hill-shaded, color scale maps prepared using independent two-sensor data.

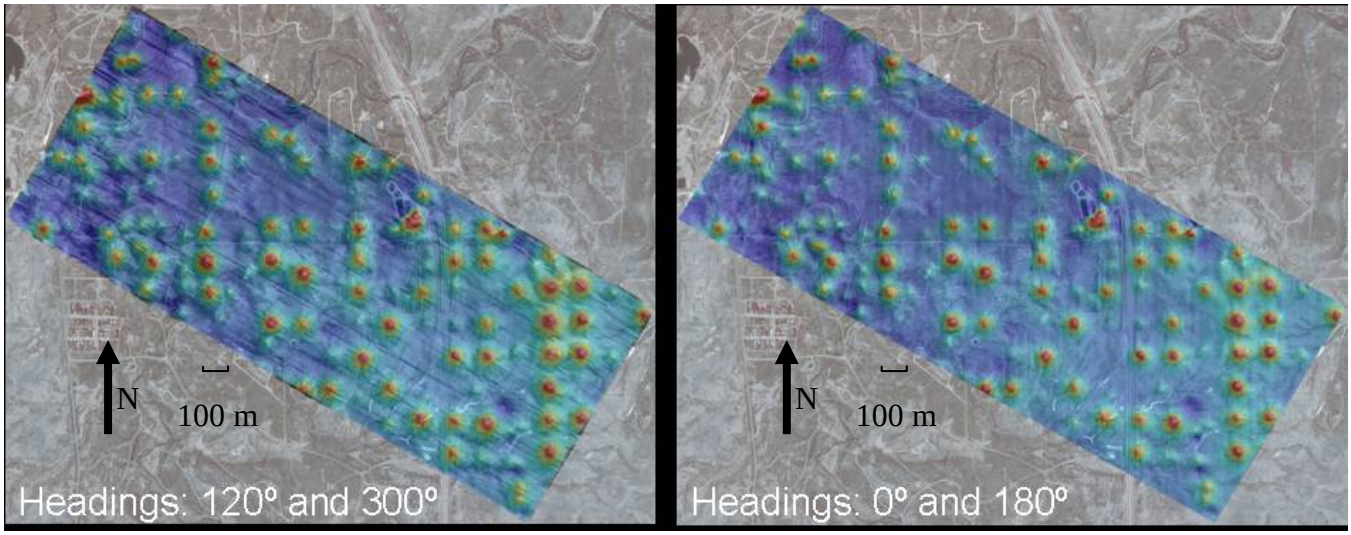

Figure 7. Comparison of the effect of flight line orientation on the ability of helicopter magnetic surveys to detect wells. Hill-shaded, color scale maps prepared using independent two-sensor data.

Ground magnetic surveys

Ground magnetic surveys were performed on two sub-parcels of the test area (Fig. 8) using two, boom-mounted magnetometers on a Kubota RTV 900 utility vehicle (Fig. 3). Nine magnetic monopole anomalies were found within these sub-parcels that were interpreted to represent the locations of wells. Only eight wells were detected within these sub-parcels by the helicopter survey. Pipelines and other oilfield infrastructure can be discerned in the ground magnetic data. The helicopter survey at 35 m altitude is less sensitive to the near-surface oilfield infrastructure (pipelines, etc) that can complicate well detection. However, selecting a minimal "dig" area to unearth the well head is best done by ground magnetometry, which provides a more focused anomaly.

Airborne and ground methane surveys

Helicopter methane detection surveys using the LaSen ALPIS sensor were carried out at an altitude of 50 m using NW-SE trending flight lines with 25 m inter-line spacing. The survey identified four methane anomalies (A, B, C, and D; Fig. 9) that were elongated in a NE direction by a consistent SW wind that was blowing during the survey. Methane sources were identified by tracing the anomalies to their origin in an upwind direction. The sources were found to be: A) a leaking gas line, B) a leaking well head, C) a leaking oil:gas:produced water pipeline, and D) an oil:gas:water separation facility. These findings were useful to Anadarko, who had repaired all leaks by the following day. NETL's purpose for conducting methane surveys was to detect leaking wells and fracture zones; conduits that are apt to leak when CO_2 is injected into underlying formations. Toward this purpose, the more subtle anomalies in the ALPIS data were examined and found to coincide with well locations, particularly those wells with pumping units.

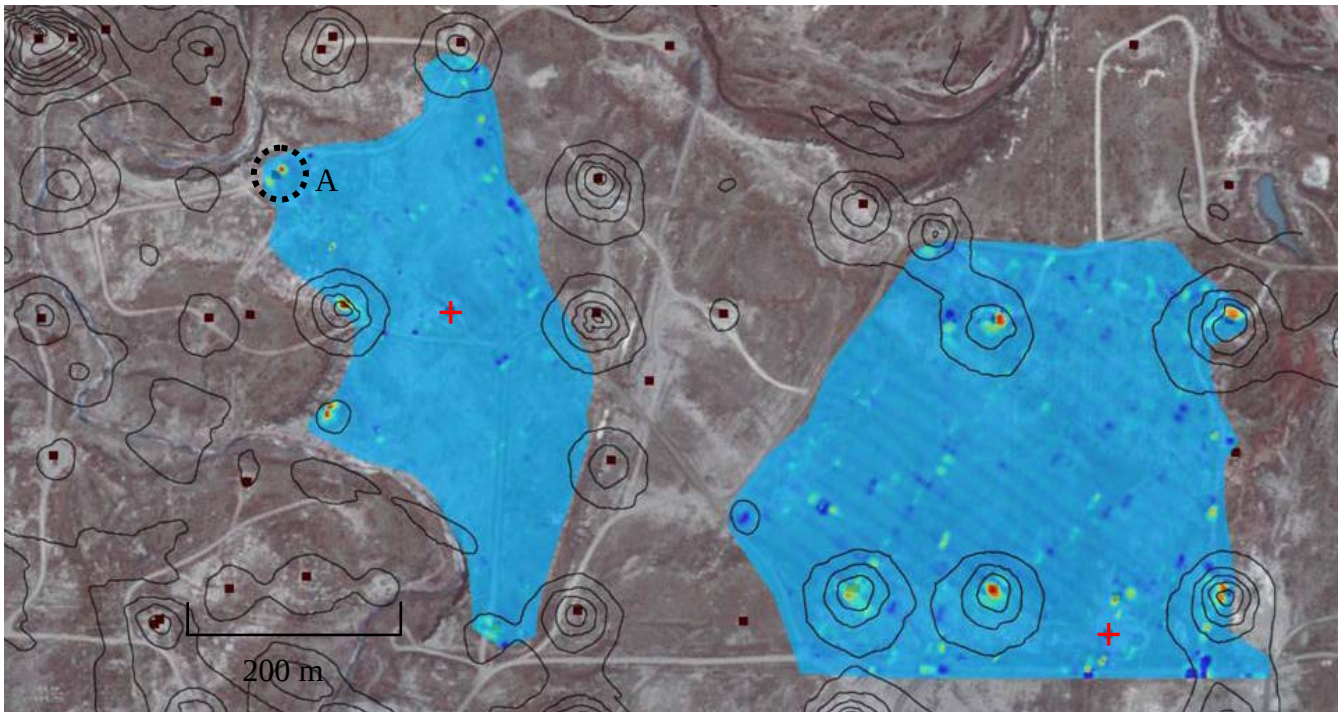

Figure 8. Map showing results of ground magnetic surveys (color scale) and helicopter magnetic surveys (black contour lines) for two sub-areas of the test area. One well (A) in Anadarko's database was detected by the ground survey but not the helicopter survey. Two wells (+) were listed in Anadarko's database but were not detected by either the ground or helicopter survey.

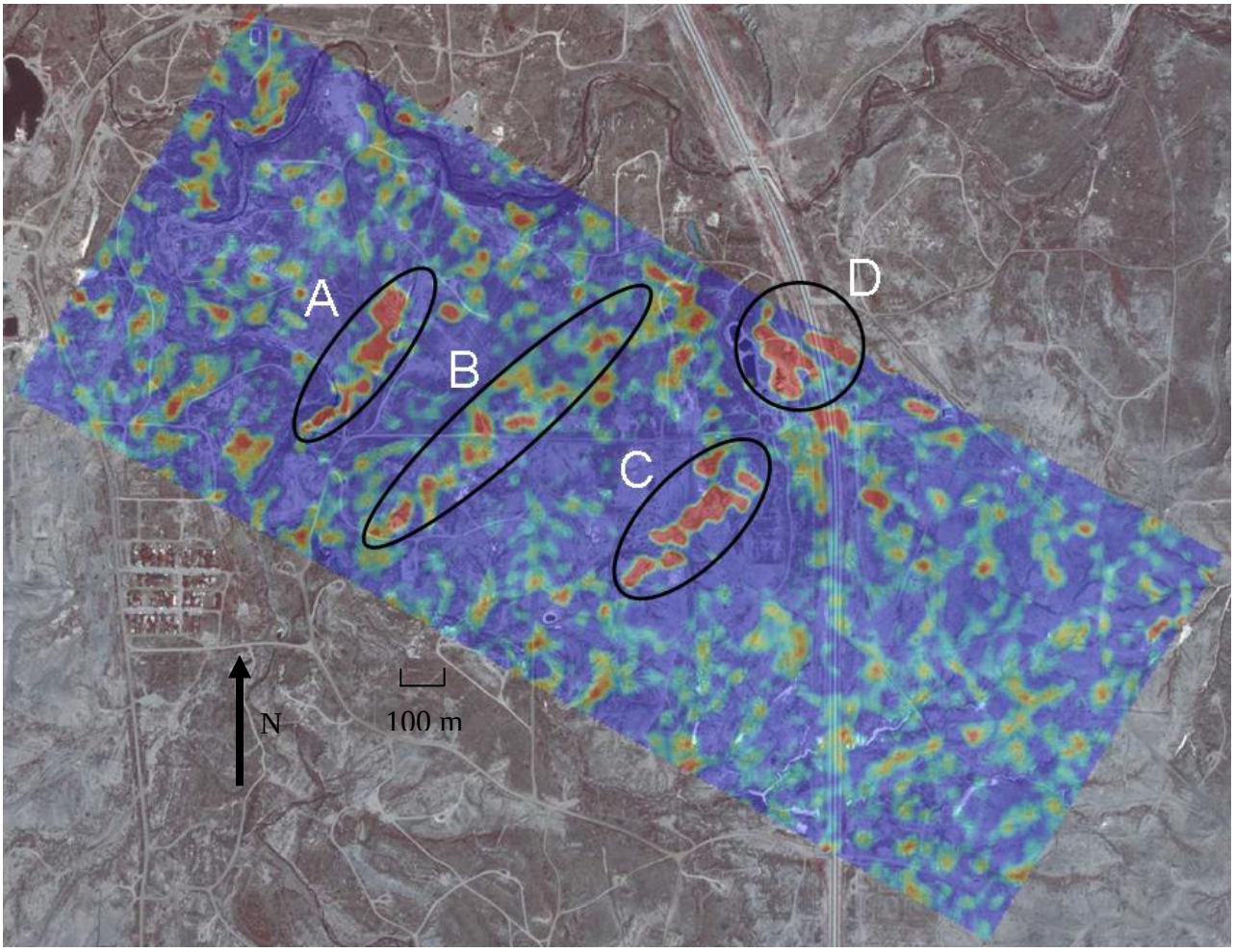

Figure 9. Helicopter methane (LaSen ALPIS) survey of study area. Warm colors indicate areas of higher methane concentrations. Methane anomalies designated A-D are discussed in text.

The ground methane survey was carried out using a Kubota RTV 900 utility vehicle equipped with an Apogee LDS. The first step in the methane ground survey was to survey all roads in the study area to intercept wind-blown methane plumes. When a methane anomaly was encountered, the vehicle was turned upwind and the plume was followed to its source, usually a well head or pumping unit. The ground survey independently located and identified the sources of the four strong methane plumes found by ALPIS in the helicopter survey. The location of methane sources as determined using ALPIS data was always within 20 meters of the actual source location. The Apogee LDS survey identified 29 locations where methane concentrations were more than 4 ppm, about twice background (Fig. 10). The methane emissions were generally found to coincide with the location of pumping units; almost all pumping units were the source of minor methane emissions that were detectable using the Apogee LDS. The ground methane concentration at the faintest ALPIS anomaly was measured by the Apogee LDS and found to be about 4 ppm or about twice background. All methane anomalies were traced to visible sources; no leaking boreholes or fracture zones were identified by either the airborne or ground methane surveys. No methane emissions were detected in the vicinity of wells designated as plugged and abandoned.

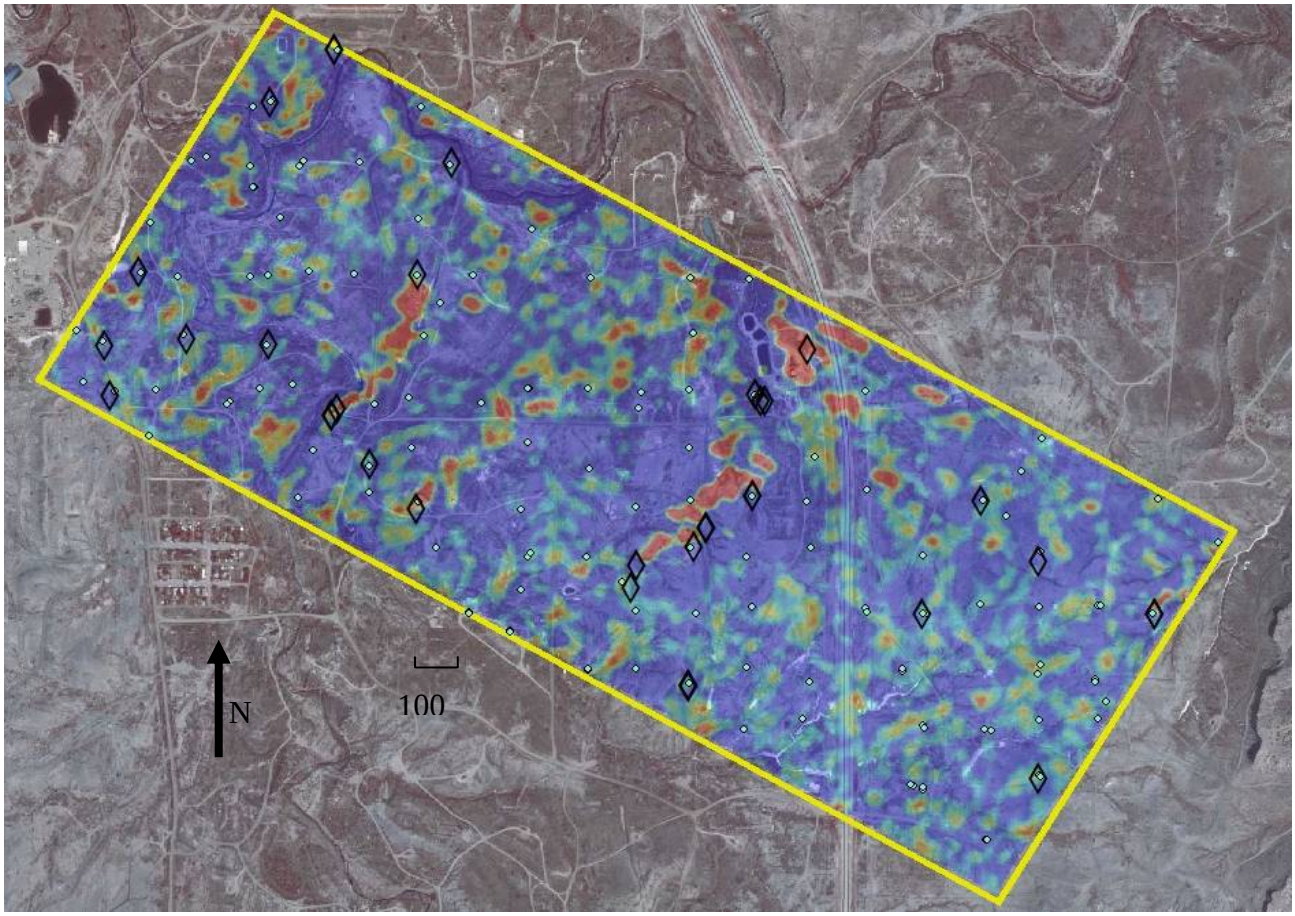

Figure 10. Map of helicopter methane anomalies (color map) that also shows the location of ground methane anomalies (black diamonds). Green dots depict the location of wells in the Anadarko database.

CONCLUSIONS

Helicopter surveys with two boom-mounted magnetic sensors located 133 wells within the test area where an intensive ground search of the study area found 139 wells. Initially, the helicopter magnetic survey only identified 127 wells but the number of detected wells was increased to 133 by lowering the threshold and applying a logarithmic stretch to the magnetic data. Magnetic data below an arbitrary minimum threshold value were not shown on initial maps to minimize the effect of near-surface ferrous objects, which were not the target of this survey. The threshold takes advantage of the fact that well casing exhibits much stronger magnetic response (at the altitude of the helicopter) than do near-surface ferrous objects. In subsequent maps, the threshold value was decreased and six of the twelve previously undetected wells were detected. However, a further decrease of the threshold value did not result in the detection of additional wells. Ultimately, the helicopter magnetic survey detected 95% of the known wells within the study area.

Subsequent ground magnetic surveys were conducted at the locations of wells that were not detected by the helicopter magnetic surveys. The ground magnetic surveys found that these wells did exhibit a typical well-type magnetic anomaly albeit the magnitude of the response was less than that of other wells. Calculating the upward continuation of the magnetic response from these well casings showed that they would not be detected at an altitude of 35 m. The conclusion is that future well detection magnetic surveys will be flown at a lower

altitude (reduce altitude from 35 m to 20 m) where possible to increase the likelihood that weak well anomalies will be detected.

This study found that better results were obtained when helicopter magnetic surveys were flown in a N-S direction and at an altitude of 35 m rather than 50 m. These results were expected. For surveys flown at higher altitudes, the magnetic anomalies are broader and less intense, which would result in a larger area for the ground search. The surveys flown at suboptimal headings exhibited more striping from the uncompensated magnetic effects of the helicopter. Although visually less appealing, maps produced from suboptimal survey orientation proved to be adequate for locating wells.

Helicopter, methane-sensing surveys using the ALPIS sensor detected four methane plumes within the study area and numerous lesser methane anomalies. Methane sources were located by tracing the plume to its origin in an up-wind direction. Locations determined in this manner were within 20 m of the actual source. The four most substantial methane anomalies were at well heads, pipelines, and separation facilities and were quickly repaired when identified. At present, not all sources of the more subtle ALPIS methane anomalies have been investigated. However, one ALPIS anomaly is at a pumping unit where the Apogee LDS system detected 4 ppm methane at ground level. It is remarkable that a 4 ppm methane plume could be detected from a helicopter at 50-m altitude. However, the concentration and thickness of the methane plume in the atmosphere between the ground and the helicopter (which would affect detectability) is not known.

Ground methane surveys with the Apogee LDS detected numerous methane sources originating from pumping units. The observation that methane anomalies were commonly associated with older pumping units was made but not investigated. If this observation is correct, the Apogee LDS may provide an effective means of determining when maintenance is needed on pumping units.

The helicopter magnetic surveys have aided Anadarko Petroleum's effort to locate and re-plug, as necessary, all wells before their planned CO_2 flood of parts of the Salt Creek Oilfield. The survey has provided the location of numerous wells that were not in available databases.

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The Use of ElectroChemical GeoOxidation for the Destruction of PAHs in Crude Oil

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ABSTRACT

ElectroChemical GeoOxidation (ECGO) is a powerful new electrochemical technology for the treatment and destruction of organic contaminants in soil. The process is being applied in Europe and the United States for the treatment, destruction, of a number of organic contaminants in soil at industrial sites. Over 2 million tons of soil has been treated using the ECGO process. The contaminants being treated include PAHs, BTEX, pesticides, and chlorinated chemicals such as TCE.

A study was undertaken by Electro Petroleum, Inc. to evaluate the use of ECGO for eliminating PAHs from crude oil. In this study eight crude oils were treated, at EPI's test facility, on cubic yard qualities of crude contaminated soil. At the start of the tests all of the crude oils contained measurable PAH concentrations. The test results showed that by using the ECGO technology PAHs could be electrochemically destroyed in the crude contaminated soils.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are found as a contaminate at many sites including hazardous waste site, in sediments, and at manufactured gas plant sites. The formation of PAHs has been traced to many sources including combustion sources or many found in nature occurring in sources such as crude oil (1). PAHs are a series of organic molecules having a structure of two or more hydrocarbon rings fused together to form a family of ringed compounds referred to as polycyclic aromatic hydrocarbons. Several of these molecules have been found to have a degree of toxicity and several have been found to be carcinogenic. Benzo [a] pyrene and Dibenz [a,h] anthracene are the most carcinogenic (2, 3). Although the family of PAHs is large, characterization is normally limited to the analysis of 16 of the "EPA PAHs". These are: naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Anthracene, Phenanthrene, Fluoranthene, Pyrene, Benz[b]anthracene, Chrysene, Benzo[b}fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indenol[1,2,3,-cd]pyrene, Dibenz[a,h]anthracene, and Benzo[ghi]perylene.

Crude oil has been a known source of PAHs. In a study completed under the Petroleum Environmental Research Forum Project, conducted by a consortium of oil companies, sixty crude oils from around the world were evaluated for their PAH content. The results of this study were reported on at the International Petroleum Environmental Conference in 1999 (3). A summary of the results of that study are shown in Table 1.

PAH contaminated soils have been treated by many methods including incineration, bio-remediation and by various oxidation techniques. A technique used extensively in Europe to treat MGP sites is ElectroChemical GeoOxidation, (4) which is an electro-chemical process which has been licensed by Electro-Petroleum Inc. for use in the United States. This process uses both low voltage and low current in a contaminated soil to promote the destruction of organic molecules by electrochemical means. The effectiveness of the process can be seen from the results as shown in Table 1 and 2.of using the process in Europe. The results from the tests at a Manufactured Gas Plant site in France demonstrated that the PAH content in the soil could be degraded dramatically in a period of 120 days.

Electro-Petroleum undertook a research project to evaluate the effectiveness of the ECGO process to destroy of PAHs in crude oil as part of its soil remediation initiative. Seven crude oils were evaluated in this test program.

EXPERIMENTAL SET-UP

Test Set-Up

The tests were conducted at Montech Research Laboratories, Butte, MT. Electro-Petroleum Inc. has since moved it research to Natural Resources Research Institute, University of Minnesota, Coleraine, MN. A special facility was constructed in which one cubic yard quantities of crude oil mixtures could be exposed to the electric fields required to effectively treat hydrocarbon contaminated soil using the ElectroChemical GeoOxidation process. A schematic of the facility is show in Figure 1 and a picture of the facility is shown in Picture 1. The facility measured approximately 10 meters by 10 meters and the depth of the matrix into which the crude

oil mixtures were placed was approximately one meter deep. Electrodes were placed in the matrix at either end of the facility and a direct current passed between the two electrodes. This arrangement allowed us to provide a uniform electric field across the test sample cells placed in the matrix. Seven crude oil samples were acquired from various California Oil fields and all oils were acquired as produced. Crude oil samples were sent to the test facility in lined steel drums. Produces water from the fields were also shipped to the facility, if available. The soil used in the test was washed sand having eleven percent silt content. Power was provided to the system using a Direct Current Power Supply acquired from ecp, Stuttgart, Germany.

Sample Preparation and System Operations

Approximately one cubic yard of sample was prepared by mixing batches of 86.5 kg of dried sand with 18 kg of formation water in a ½ cubic yard cement mixer. After the sand was fully wet 3 kg of crude oil was added to the mixture until homogenized. Since the majority of the crude oil was "heavy" crude it became necessary to heat the oil to a 175 degrees F prior to blending to facilitate mixing. After the mix was prepared it was placed in batches in a cell in the test facility until the pits were filled with the crude mixture. Six cells could be filled and tested at any one time.

The tests were run for a minimum of 124 days with samples being taken from each cell on days 50, 74 and 124 after the start of the test. Voltages across each cell were monitored through out the test period. An example of the voltages across each cell is shown in Figure 2 and it should be noted that the voltage gradients varied with the crude oil and the conductivity of each of the test mixes. Temperatures, Figure 4, were also recorded at each end of the cell and at the edges of the test building during the test. These temperatures were found to be close to the ambient temperatures in the matrix and the cells discounting the possibility of volatilization of the PAHs from the mix.

Sampling and Analysis

Samples were randomly cored through the depth of the sample and composited prior to sending them to a commercial laboratory for analysis. The samples were extracted and analyzed by GC-MS using EPA Method 8270.

TEST RESULTS

The results of the analysis are shown in Tables 5 – 8. The analysis indicates a steady decrease in the PAH content of the crude oil during the test. Within seventy four days the PAH concentration had been destroyed in all but Crude oil C. All PAHs had been destroyed or were no longer extractable from the crude oil C by day124.

CONCLUSIONS

The results of this study confirm that the PAH content of crude oil can be destroyed by the ECGO process under the conditions used in the test. This is consistent with the results observed in the application of the ECGO process at MGP sites in Europe.

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Table 1. Summary of PAH Content of 60 Crude Oils (3)

PAH content of 60 World Crude oils, All Data are Reported in mg/kg				
	Minimum	Maximum	Mean	Detection Frequency
Naphthalene	1.2	37000	422.9	60
Acenaphthylene	nd			
Acenaphthene	nd	58	13.9	48
Fluorine	1.4		73.6	60
Phenanthrene	nd	916	176.7	59
Anthracene	nd	17	3.4	24
Fluoranthene		26	3.9	24
Pyrene	nd	82	15.5	58
Benzo(a)anthacene	nd	38	5.5	40
Chysene	4	120	28.5	60
Benzo(b)fluoranthene	nd	14	3.9	60
Benzp(k)fluoranthene	nd	7	0.46	56
Benzo(a)pyrene	nd	7.7	2	45
Indeno(1,2,3-cd)pyrene	nd	1.7	0.06	4
Dibenzo(a,h) anthracene	nd	9.2	1	28
Benzo(ghi)perylene	nd	9.6	1.53	38

Table 2. Test results for PAH destruction at a MGP site in France

Test results for cell 1: French MGP Site mg/kg					
	P2000	Day 40	Day 75	Day 90	Day 120
Benzene	<0.01	<0.01	<0.01	<0.01	<0.01
Toluene	0.013	<0.01	<0.01	<0.01	<0.01
Ethylbenzene	<0.01	<0.01	<0.01	<0.01	<0.01
p,m Xylene	<0.01	<0.01	<0.01	<0.01	<0.01
o-Xylene	<0.01	<0.01	<0.01	<0.01	<0.01
BTEX	0.013	n.d.	n.d.	n.d.	n.d.
TPH	184	99	175	73	73
Naphtalene	0.1	0.1	0.1	2.0	<0.1
Acenaphtylene	1.9	5.0	1.1	0.1	<0.1
Acenaphtene	11	8.8	2.4	1.0	1.0
Fluorene	27.4	6.6	1.8	2.5	2.2
Phenanthrene	90.8	27.8	6.4	8.4	6.2
Anthracene	33.6	10.4	2.8	3.7	2.8
Fluoranthene	79.7	42.5	10.3	12.9	9.7
Pyrene	68	29.4	6.5	8.9	6.6
Benz(a)anthracene	46.6	17.4	4.4	5.7	4.1
Chrysene	40	12.9	3.6	5.5	3.4
Benzo(b)fluoranthene	27.8	8.5	2.1	4.4	1.7
Benzo(k)fluoranthene	18	5.7	1.7	3.0	1.1
Benzo(a)pyrene	33.9	9.2	3.5	5.4	2.9
Diben(a,h)anthracene	3.4	1.8	0.1	2.3	<0.1
Benzo(ghi)perylene	11.9	5.0	1.1	2.1	0.3
Indeno(1,2,3cd)pyrene	17.7	6.6	1.6	2.6	0.8
PAH tot.	**511.3**	**197.6**	**49.1**	**70.5**	**42.8**

Table 3. Test results for PAH destruction at a MGP site in France

Test results for cell 2: French MGP Site mg/kg					
	P6000	Day 40	Day 75	Day 90	Day 120
Benzene	0.031	0.025	0.01	<0.01	<0.01
Toluene	2.51	0.46	0.017	<0.01	<0.01
Ethylbenzene	0.01	0.01	0.01	<0.01	<0.01
p,m Xylene	0.015	0.033	0.01	<0.01	<0.01
o-Xylene	0.023	0.03	0.01	<0.01	<0.01
BTEX	2.58	0.55	0.017	n.d.	n.d.
TPH	380	459	316	327	242
Naphtalene	186	284	11.8	4.3	4.1
Acenaphtylene	162	218	8.9	3.0	2.5
Acenaphtene	151	70.7	7.9	1.3	5.4
Fluorene	315	339	15.5	9.4	8.9
Phenanthrene	683	717	27.9	27	24.6
Anthracene	330	246	11.5	17	8.3
Fluoranthene	706	643	31.5	46	29.8
Pyrene	417	350	14	29	13.1
Benz(a)anthracene	217	162	11.8	15	9.8
Chrysene	186	117	9.7	14.9	9.2
Benzo(b)fluoranthene	106	69.3	4.8	9.7	4.1
Benzo(k)fluoranthene	71	38.4	3.6	6.7	2.9
Benzo(a)pyrene	135	82.9	9.3	13.3	8.6
Diben(a,h)anthracene	12	51	5.1	1.6	4.2
Benzo(ghi)perylene	38	23.1	2.8	5.2	1.8
Indeno(1,2,3cd)pyrene	54	35.3	3.7	6.7	2.1
PAH tot.	**3769**	**3395.7**	**179.8**	**210.4**	**139.4**

Table 4. Temperature

Temperatures in Cells and at the E,W,N,S of the test building					
A_1	59.4	D_1	54.4	E	54.4
A_2	55.2	D_2	58.6	W	72.3
B_1	55.0	E_1	61.4	N	50.2
B_2	54.3	E_2	56.8	S	56.1
C_1	55.0	F_1	57.0		
C_2	54.9	F_2	54.8		

Table 5. Initial PAH content of crude oils used in the test.

Initial PAH content mg/kg							
PAH	Crude A	Crude B	Crude C	Crude D	Crude E	Crude F	Crude G
Naphthalene	nd	0.52	2.24	nd	0.09	nd	nd
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	6.5	nd	nd	nd	nd
Fluorine	nd	0.69	nd 1.38	nd	nd	nd	nd
Phenanthrene	51.9	12.1,14.45	5.2 1.97	8.4	1.4 , 1.01	1.3	nd
Anthracene	nd	nd	nd	nd	nd	nd	nd
Fluoranthene	1.2	0.35	nd	nd	nd	nd	nd
Pyrene	1.9	0.65	5.6 1.22	nd	nd	nd	nd
Benzo(a)anthacene	nd	0.42	nd 0.21	nd	0.44,0.06	1.2	nd
Chysene	1.3	0.47	7.2 0.74	1.8	nd	1.1	nd
Benzo(b)fluoranthene	nd	0.46	nd 0.16	nd	nd	nd	nd
Benzp(k)fluoranthene	nd	nd	nd 0.19	nd	nd	5.4	nd
Benzo(a)pyrene	nd	nd	nd 0.32	nd	nd	3	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	3.8	nd
Dibenzo(a,h) anthracene	nd	nd 0.31	nd	nd	nd	4.2	nd
Benzo(ghi)perylene	nd	0.31	nd 0.12	nd	nd	3.8	nd

Note: If duplicate samples were analyzed both results are reported. nd indicates not detected.

Table 6. PAH content of crude oil after 50 day of treatment

PAH content day 50 mg/kg							
PAH	Crude A	Crude B	Crude C	Crude D	Crude E	Crude F	Crude G
Naphthalene	nd	0.41	0.49	nd	0.11	nd	nd
Acenaphthylene	nd	0.15	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	6.5	nd	nd	nd	nd
Fluorine	nd	.023	nd	nd	nd	nd	nd
Phenanthrene	nd	0.22	nd	nd	2.45	nd	nd
Anthracene	nd	0.16	nd	nd	nd	nd	nd
Fluoranthene	nd	nd	nd	nd	nd	nd	nd
Pyrene	nd	nd	4.5 0.66	1.2	nd	nd	nd
Benzo(a)anthacene	nd	0.12	0.59	nd	0.64	nd	nd
Chysene	nd	0.18	6.7 0.57	1.1	nd	nd	nd
Benzo(b)fluoranthene	nd	nd	nd	nd	nd	nd	nd
Benzp(k)fluoranthene	nd	nd	nd 0.11	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd 0.24	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a,h) anthracene	nd	nd	nd	nd	nd	nd	nd
Benzo(ghi)perylene	nd	nd	nd	nd	nd	nd	nd

Table 7. PAH content of crude oil samples after 74 days of test

PAH content day 74 mg/kg							
PAH	Crude A	Crude B	Crude C	Crude D	Crude E	Crude F	Crude G
Naphthalene	nd	nd	nd	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	nd	nd	nd
Fluorine	nd	nd	nd	nd	nd	nd	nd
Phenanthrene	nd	nd	nd	nd	nd	nd	nd
Anthracene	nd	nd	nd	nd	nd	nd	nd
Fluoranthene	nd	nd	nd	nd	nd	nd	nd
Pyrene	nd	nd	1.9	nd	nd	nd	nd
Benzo(a)anthacene	nd	nd	nd	nd	nd	nd	nd
Chysene	nd	nd	2.4	nd	nd	nd	nd
Benzo(b)fluoranthene	nd	nd	nd	nd	nd	nd	nd
Benzp(k)fluoranthene	nd	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a,h) anthracene	nd	nd	nd	nd	nd	nd	nd
Benzo(ghi)perylene	nd	nd	nd	nd	nd	nd	nd

Table 8. PAH content of crude oil samples at the end of the tests day 124

	PAH content day 124 mg/kg						
PAH	Crude A	Crude B	Crude C	Crude D	Crude E	Crude F	Crude G
Naphthalene	nd	nd	nd	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	nd	nd	nd
Fluorine	nd	nd	nd	nd	nd	nd	nd
Phenanthrene	nd	nd	nd	nd	nd	nd	nd
Anthracene	nd	nd	nd	nd	nd	nd	nd
Fluoranthene	nd	nd	nd	nd	nd	nd	nd
Pyrene	nd	nd	nd	nd	nd	nd	nd
Benzo(a)anthacene	nd	nd	nd	nd	nd	nd	nd
Chysene	nd	nd	nd	nd	nd	nd	nd
Benzo(b)fluoranthene	nd	nd	nd	nd	nd	nd	nd
Benzp(k)fluoranthene	nd	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a,h) anthracene	nd	nd	nd	nd	nd	nd	nd
Benzo(ghi)perylene	nd	nd	nd	nd	nd	nd	nd

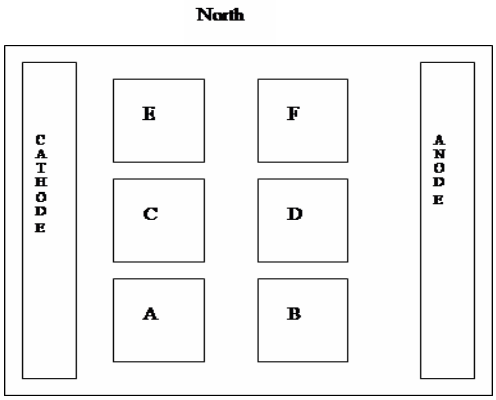


Figure 1. Test Cell Layout in test facility

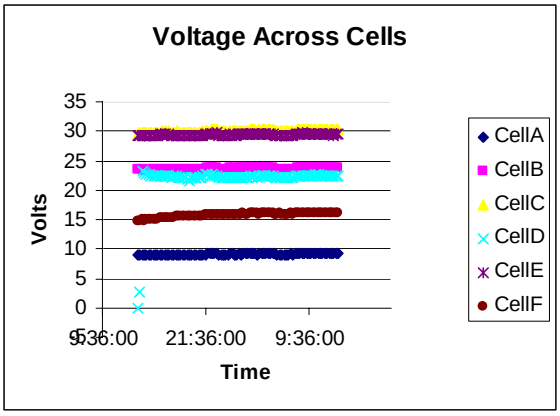


Figure 2. Voltages across test cells

Picture 1. Test facility

Picture 2. View inside test facility showing test cells

Picture 3. Crude Oil mixture in test cell

Combining Gamma Ray Logs with Boring Logs

By:

Leonard Billingsley

Frank Vernon

Oklahoma Corporation Commission
Petroleum Storage Tank Division

What Does the Gamma Ray Tool Detect?

- Natural Gamma Rays
  - “Energetic form of electromagnetic radiation produced by radioactive decay”*

*Wikipedia

What Produces Gamma Rays?

- Most common sources:
  - Potassium
  - Thorium
  - Uranium - Radium

Where Are These Elements Found?

- In zones containing potassium feldspars (i.e. granites, feldspathic sands)
- Volcanic and igneous rocks
- Sands containing volcanic ash
- Clays

The Gamma Logging Tool: What Does It Do?

- Detector is a thallium-doped sodium-iodide crystal
- Crystal emits light when it absorbs a Gamma Ray
- Light emissions are counted and ultimately displayed as counts per second (CPS) vs. depth on a graph
- This graph is then referred to as a Gamma Ray Log

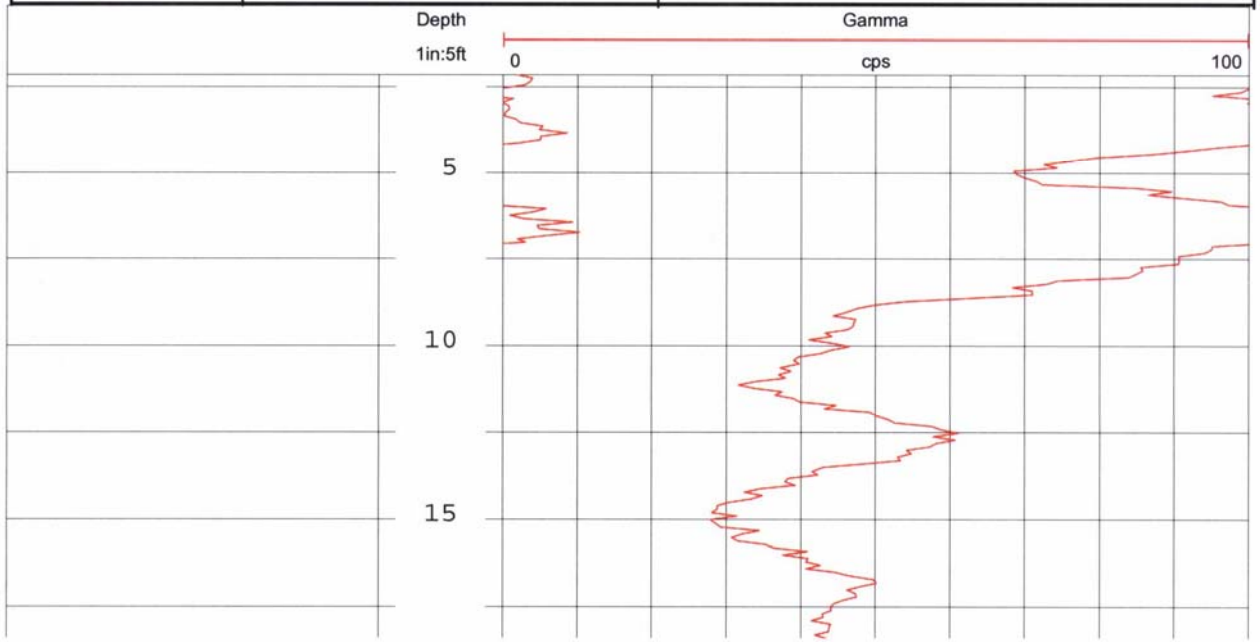
What you really need to know…

- “Any sufficiently advanced technology is indistinguishable from magic” - Arthur C. Clark
- The Gamma Ray log is magic
- The larger the Gamma Ray CPS, the larger the clay content…the smaller the CPS, the smaller the clay content
- Thus:
  - High CPS = Clay
  - Low CPS = Sand

Gamma Ray Log

COMPANY:	OCC
Location:	Elk City
Well	0303-060406-mw-9
Date	060406
BH Fluid	air
Casing	PVC
File Name	0303-060406-mw-9
Depth Driller	20
Depth Logger	18.9
Logged by:	l billingsley
Witness:	f vernon & k barron

OTHER SERVICES



Applications of Combining Gamma Ray Logs and Boring Logs

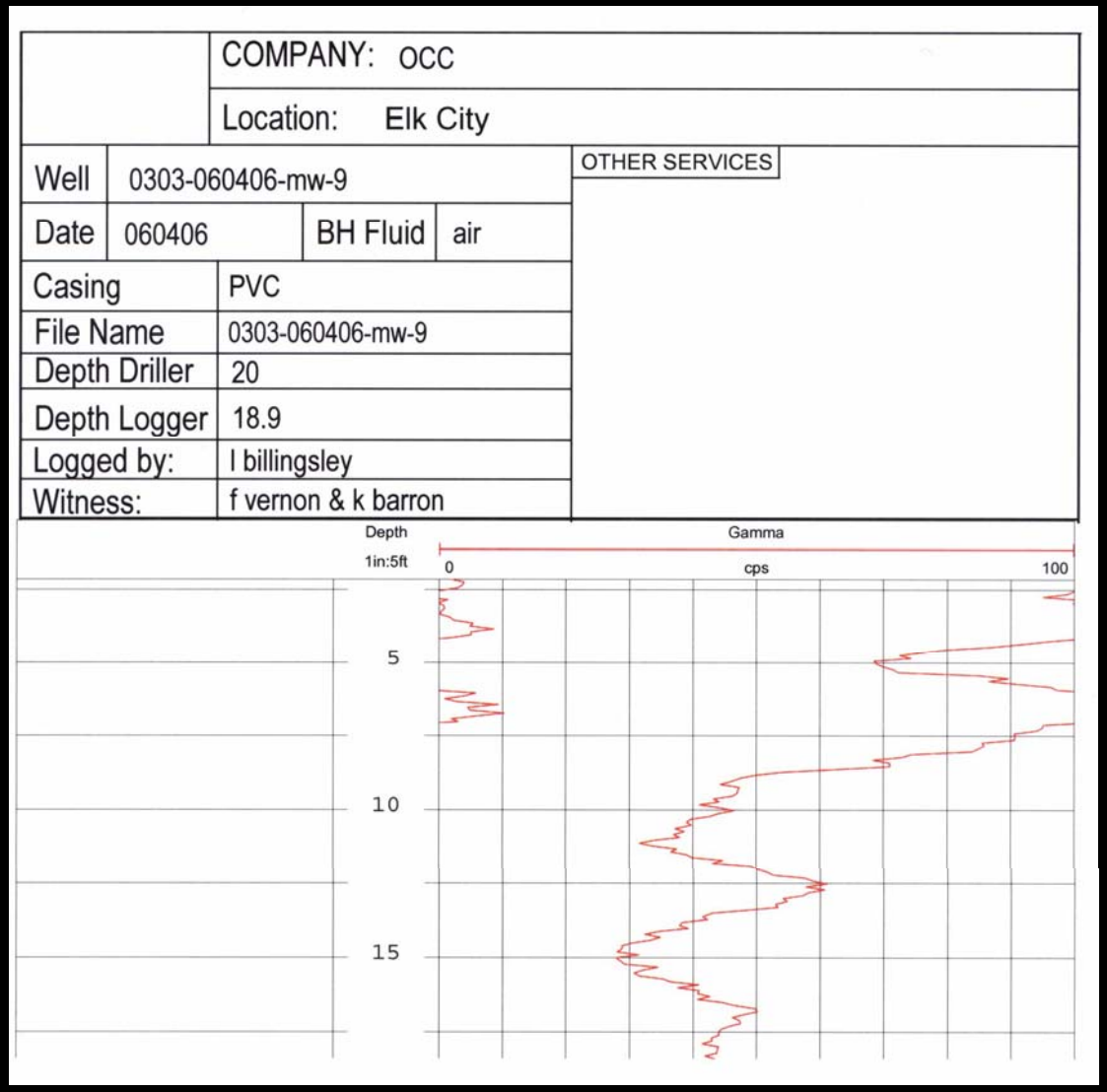
- Zone identification
- Zone correlation
- Zone content
- Seal identification
- Boring log interpretation
- Potential transport zone identification
- Potential source zone identification

Assumptions:

- Unconsolidated formation (can split-spoon)
- Sand and clay sequence
- Have field screening values
- Have cut-off values (OVM value between source and non-source interval)
- Contaminants are volatile organics
- Only natural radioactive sources are present
- Bentonite has a high K content
- Other exceptions

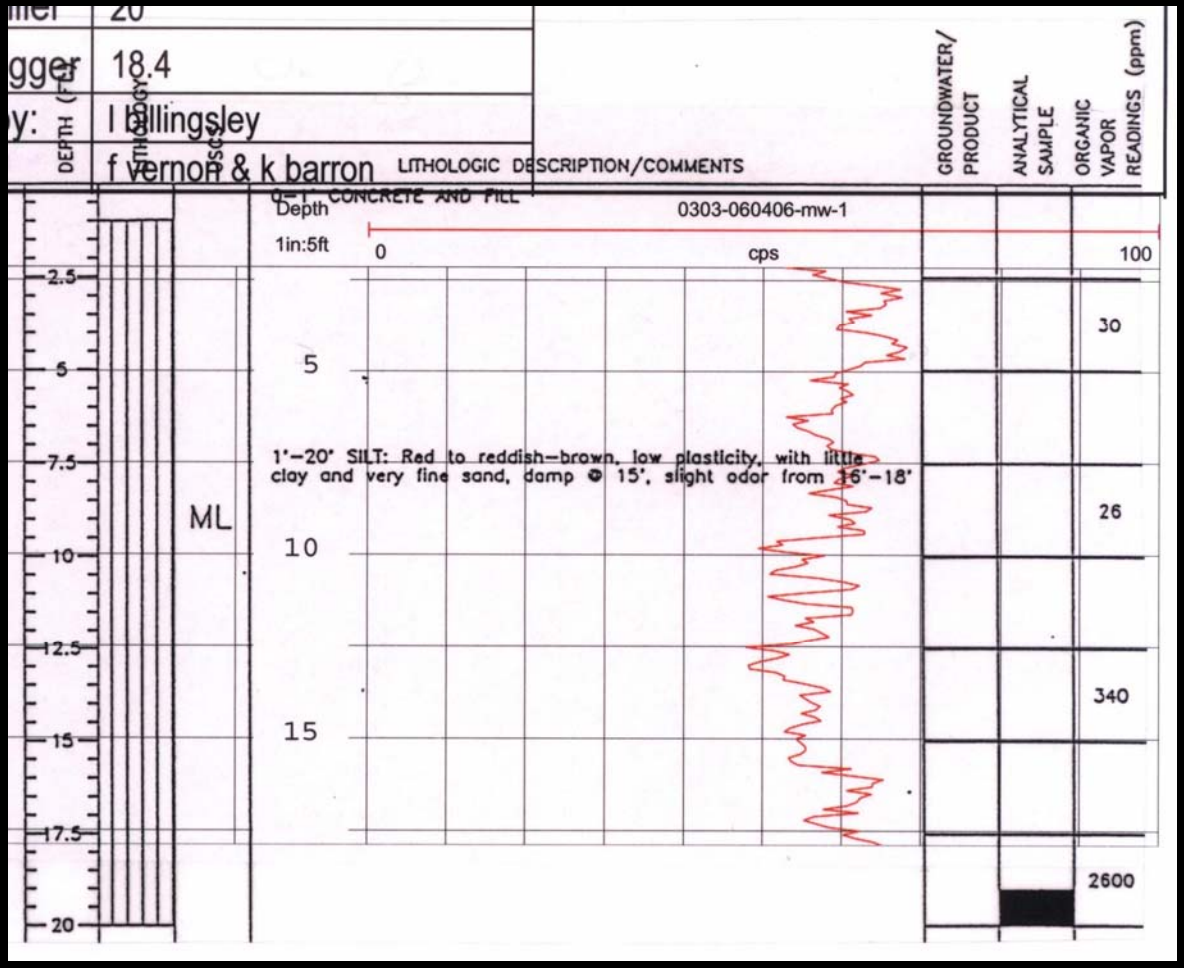
Zone Identification

- Seal
- Sand
- Clay



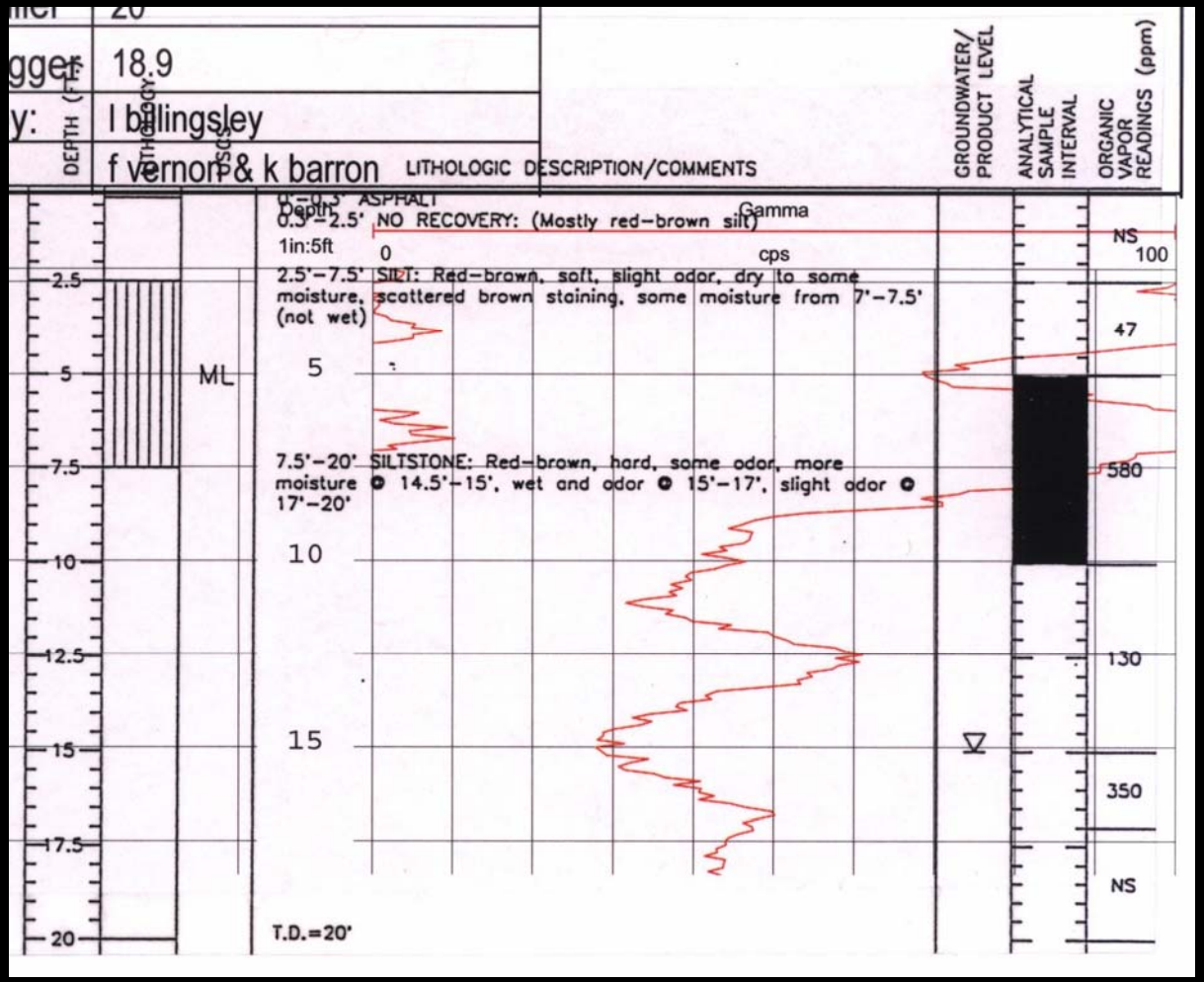
Zone Identifications

- Sample descriptions similar to the Gamma Ray log



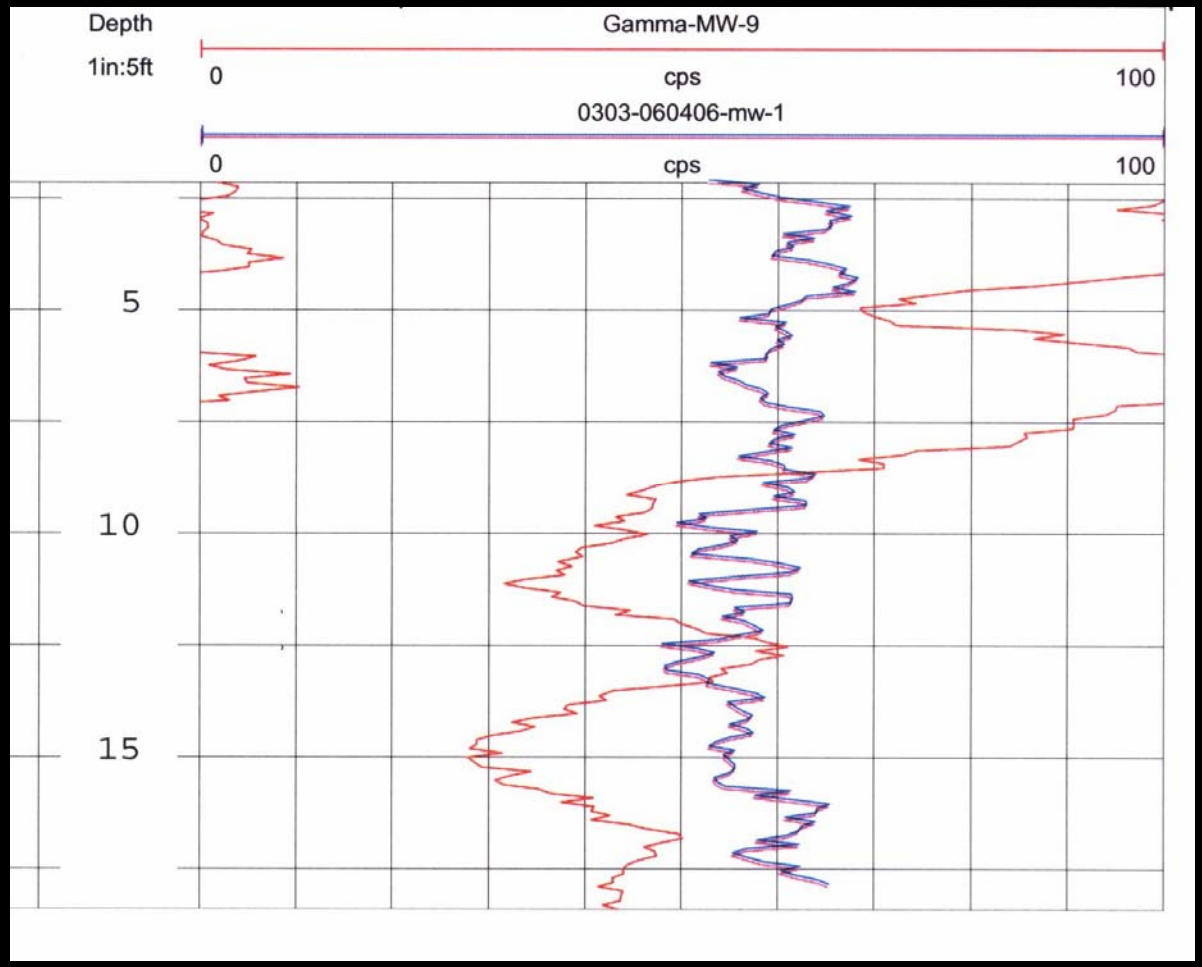
Zone Identifications

- Sample descriptions dissimilar from the Gamma Ray log



Zone Identifications

- Overlay of Gamma Ray curves for boring logs with similar descriptions



Potential Transport Zones

- Lower CPS zones

Potential Source Zones

- Lower CPS zones with high OVM values
- Medium CPS zone with high OVM values

Non-Source Zones

- When dealing with risk assessments, non-source zones are:
  - High CPS zones with high OVM values
  - Zones with low OVM values

Semi-Quantitative Analysis for Combined Gamma Ray and Boring Logs

1. Identify bentonite seal
2. Identify the range without the bentontite seal
3. Identify potential transport intervals
4. Identify potential source intervals

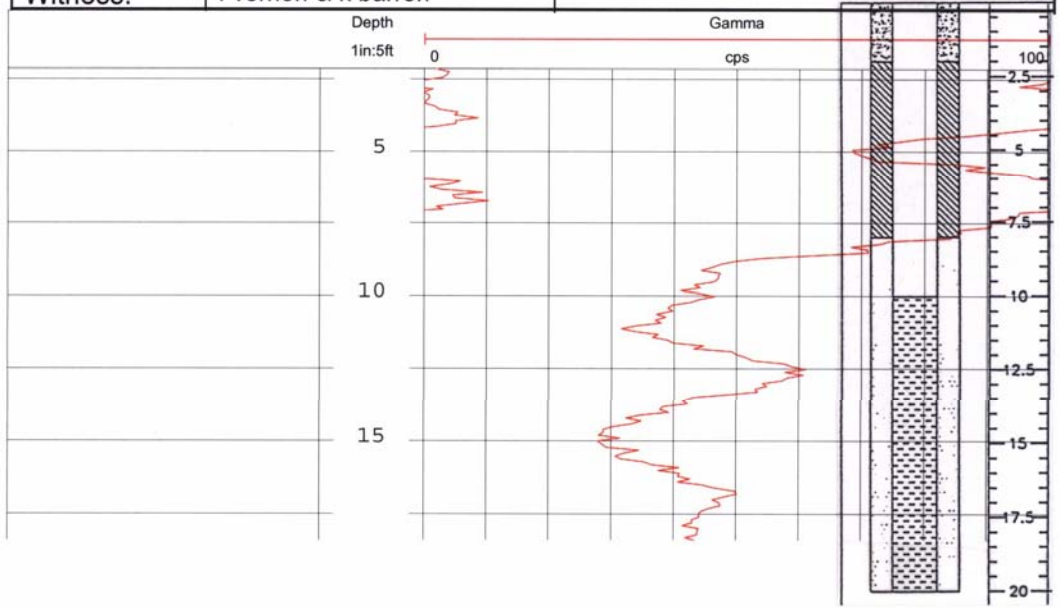
1: Bentonite Seal Identification

- Gamma Ray log with bentonite seal
- Gamma Ray log without bentonite seal
- Gamma Ray log with bentonite seal erroneously reported

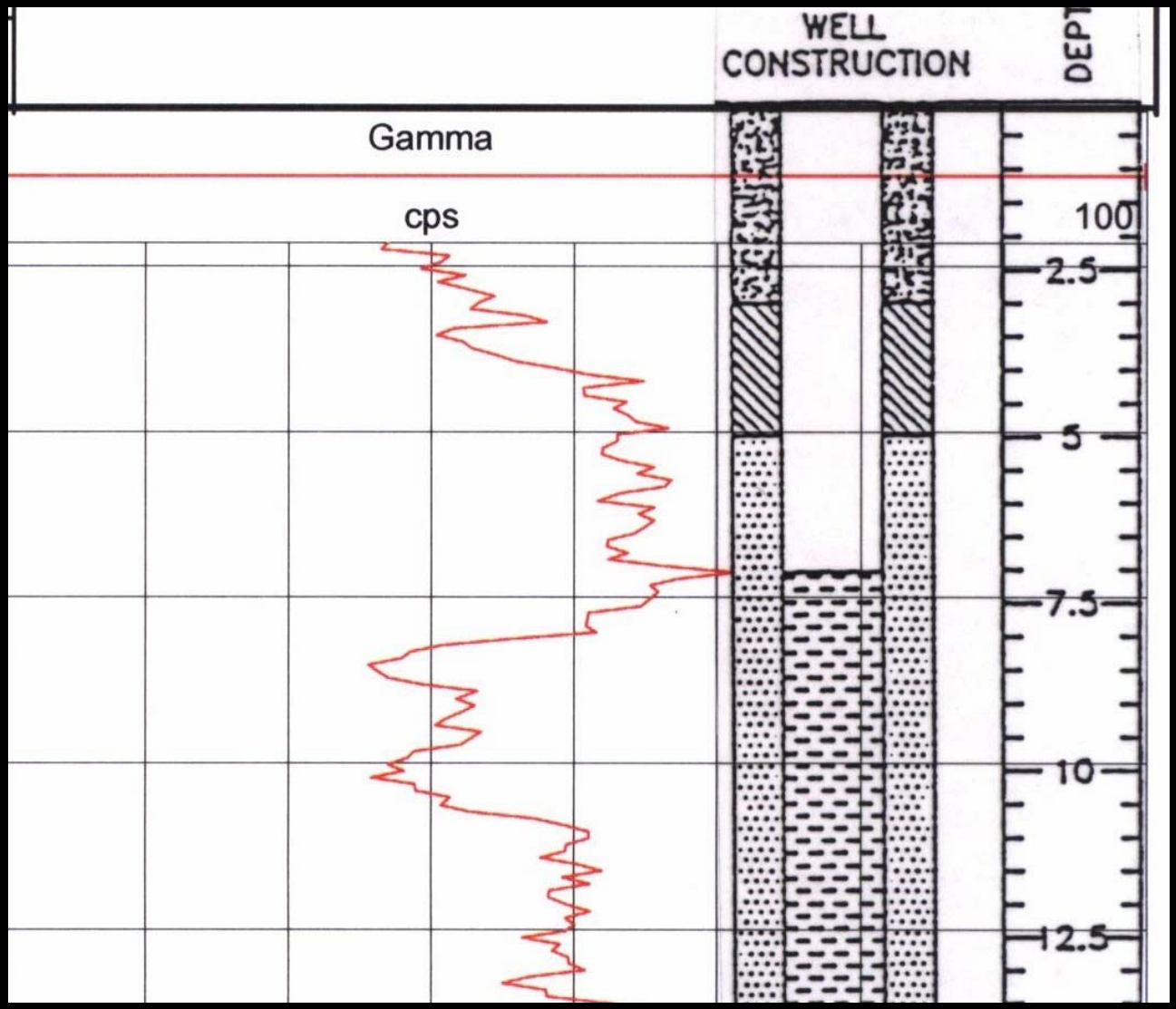
Gamma Ray With Bentonite Seal

COMPANY:	OCC
Location:	Elk City
Well	0303-060406-mw-9
Date	060406
BH Fluid	air
Casing	PVC
File Name	0303-060406-mw-9
Depth Driller	20
Depth Logger	18.9
Logged by:	I billingsley
Witness:	f vernon & k barron

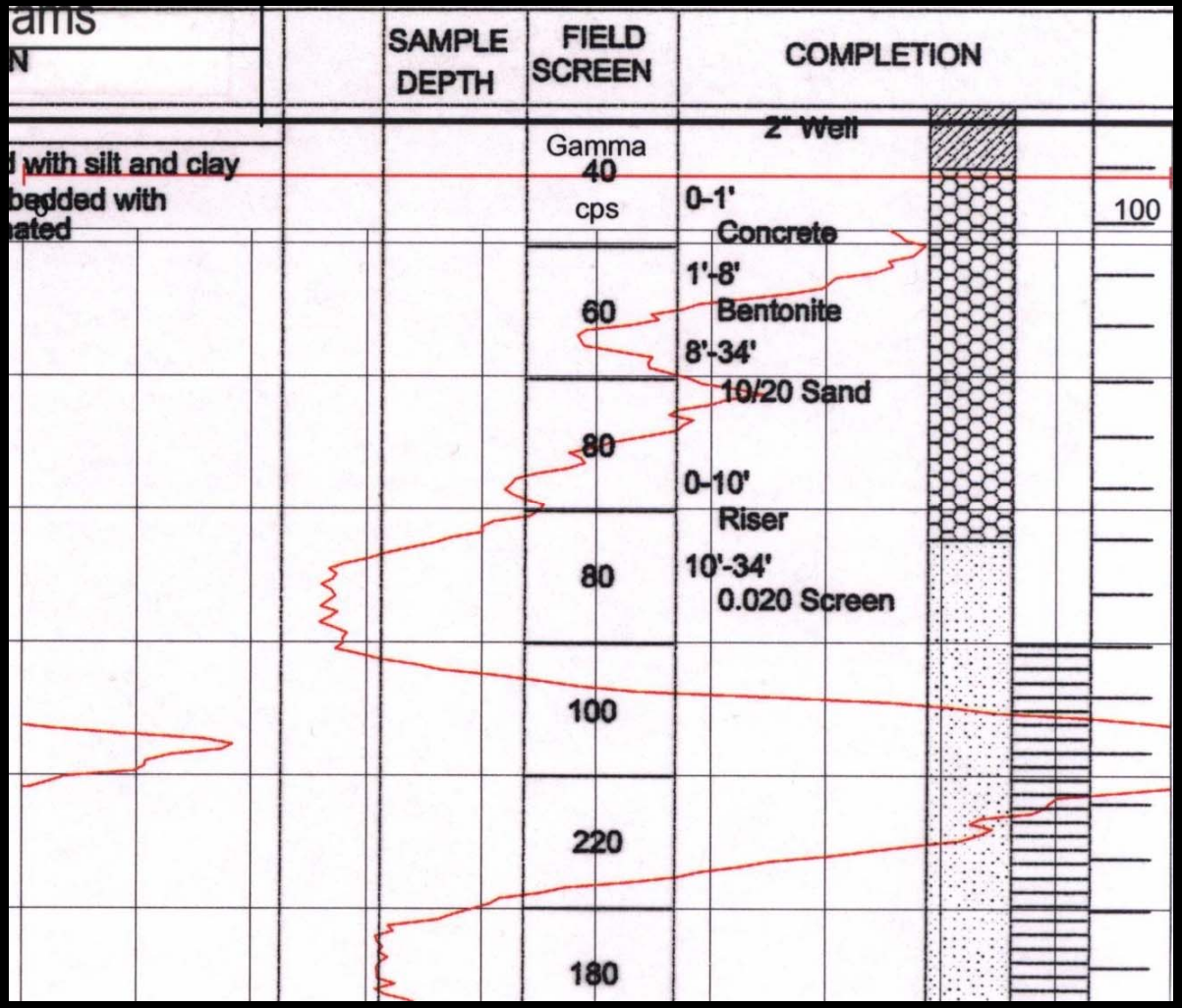
OTHER SERVICES



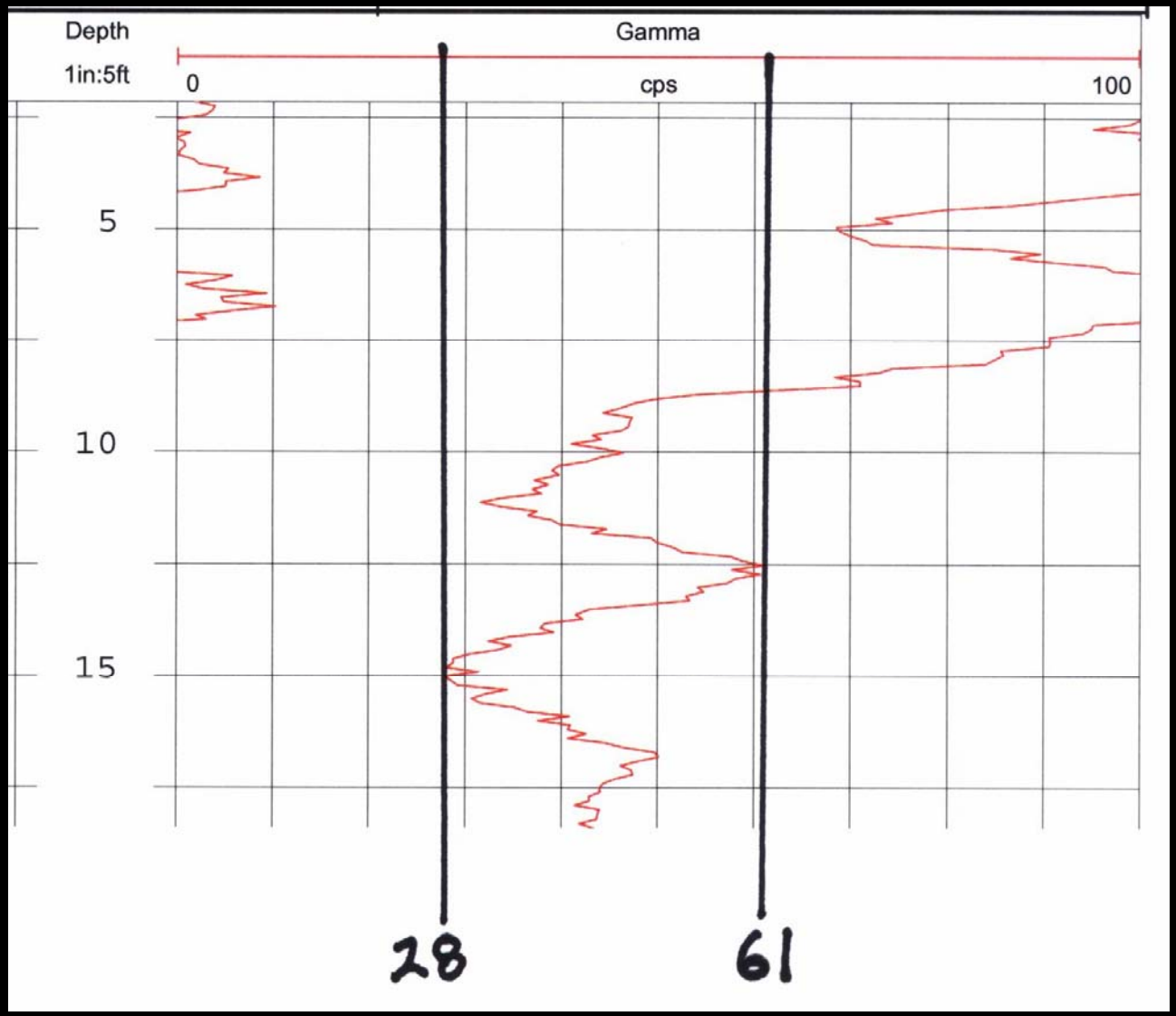
Gamma Ray Without Bentonite Seal



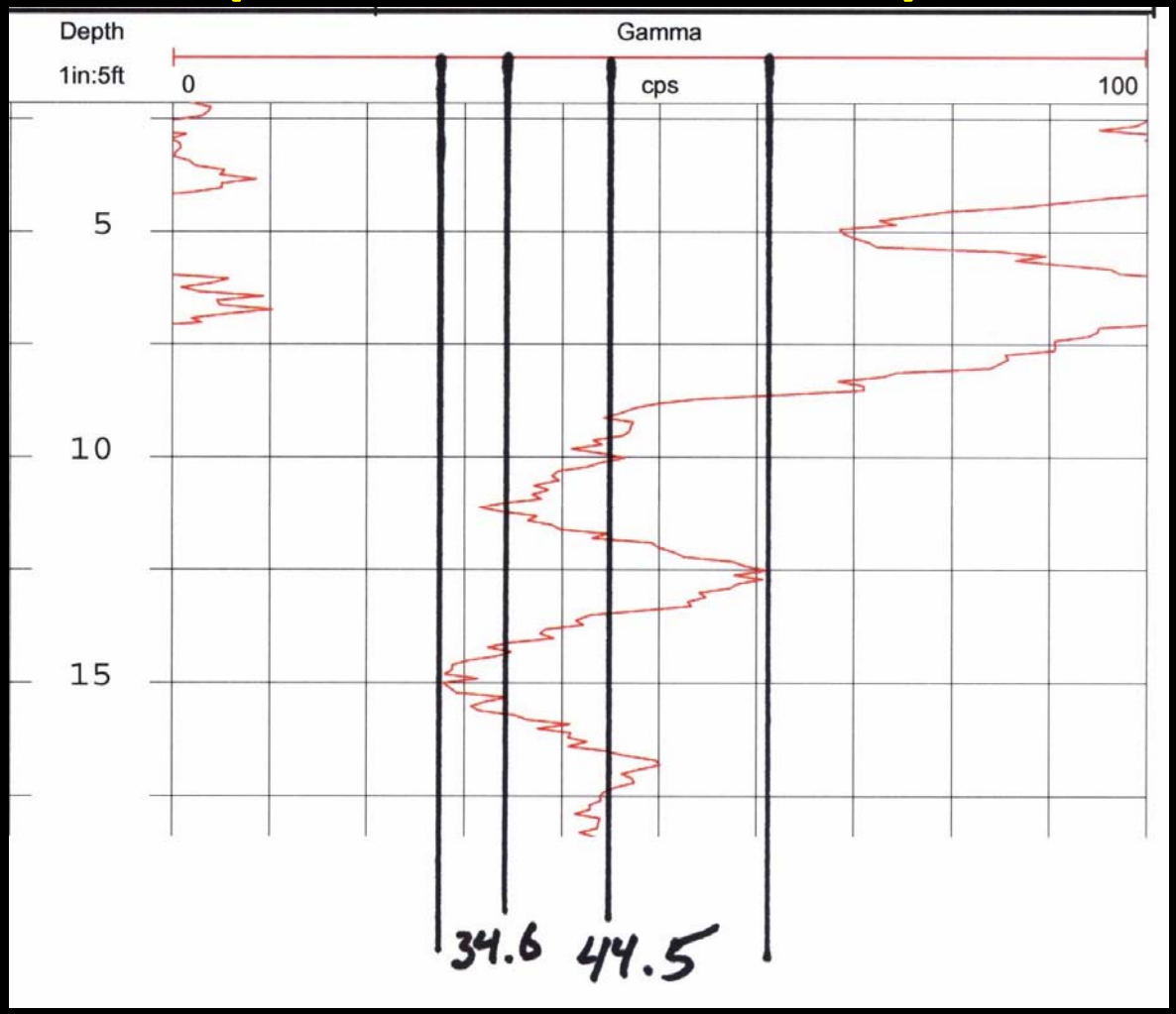
Gamma Ray Log With Bentonite Seal Erroneously Reported



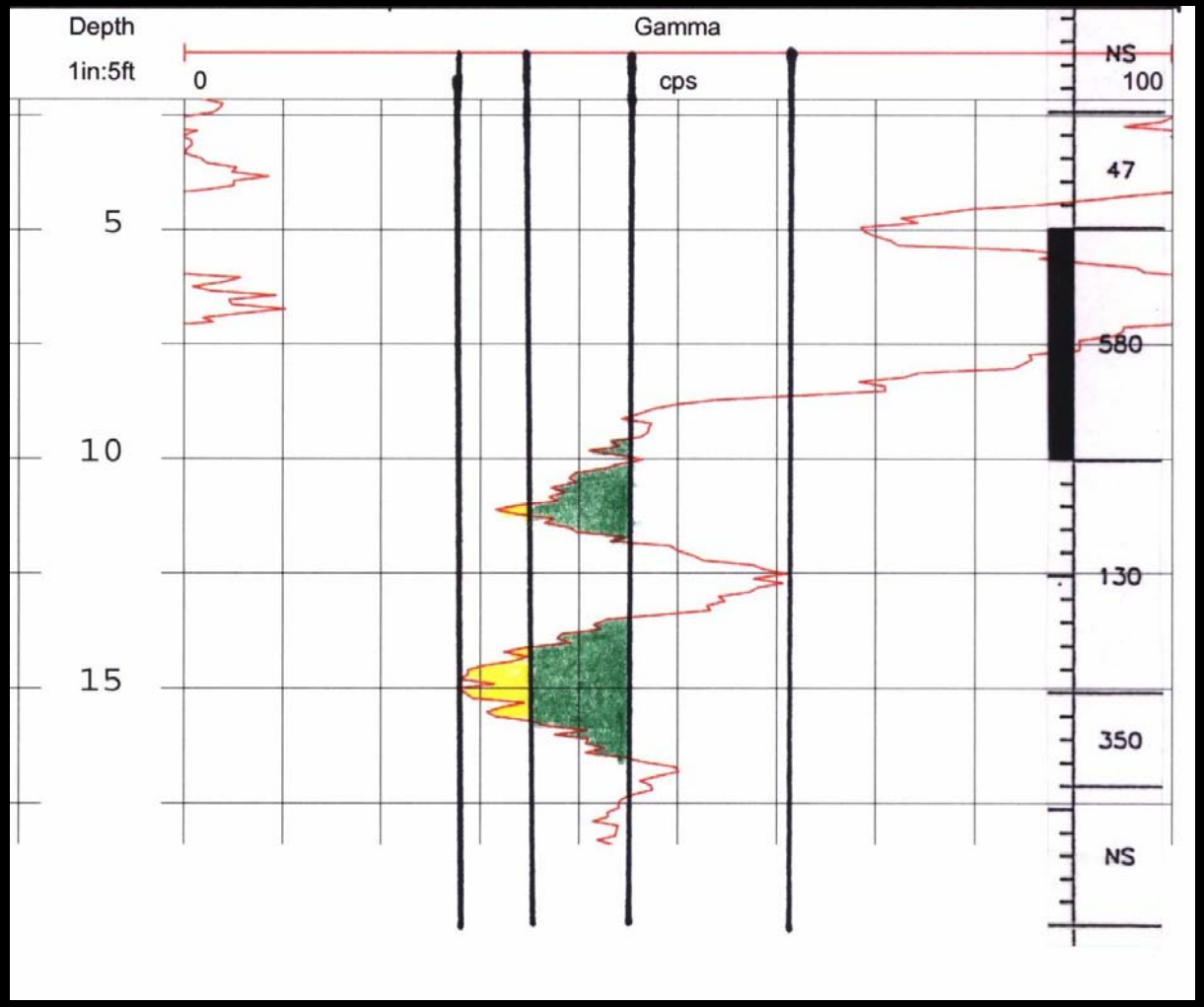
2: Identify the Range



3: Identify the Intervals (20% and 50%)



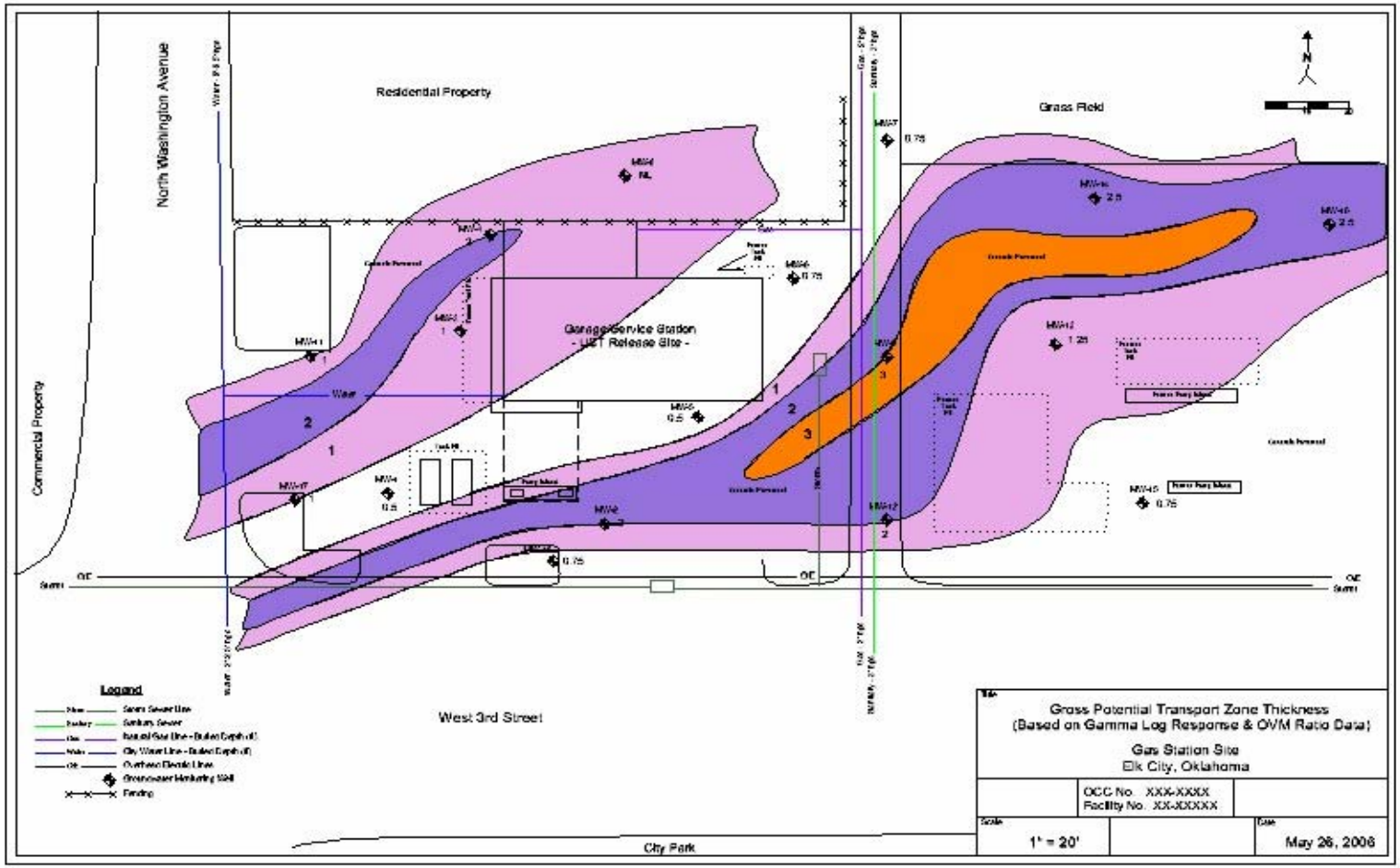
4: Identify Potential Transport and Source Intervals



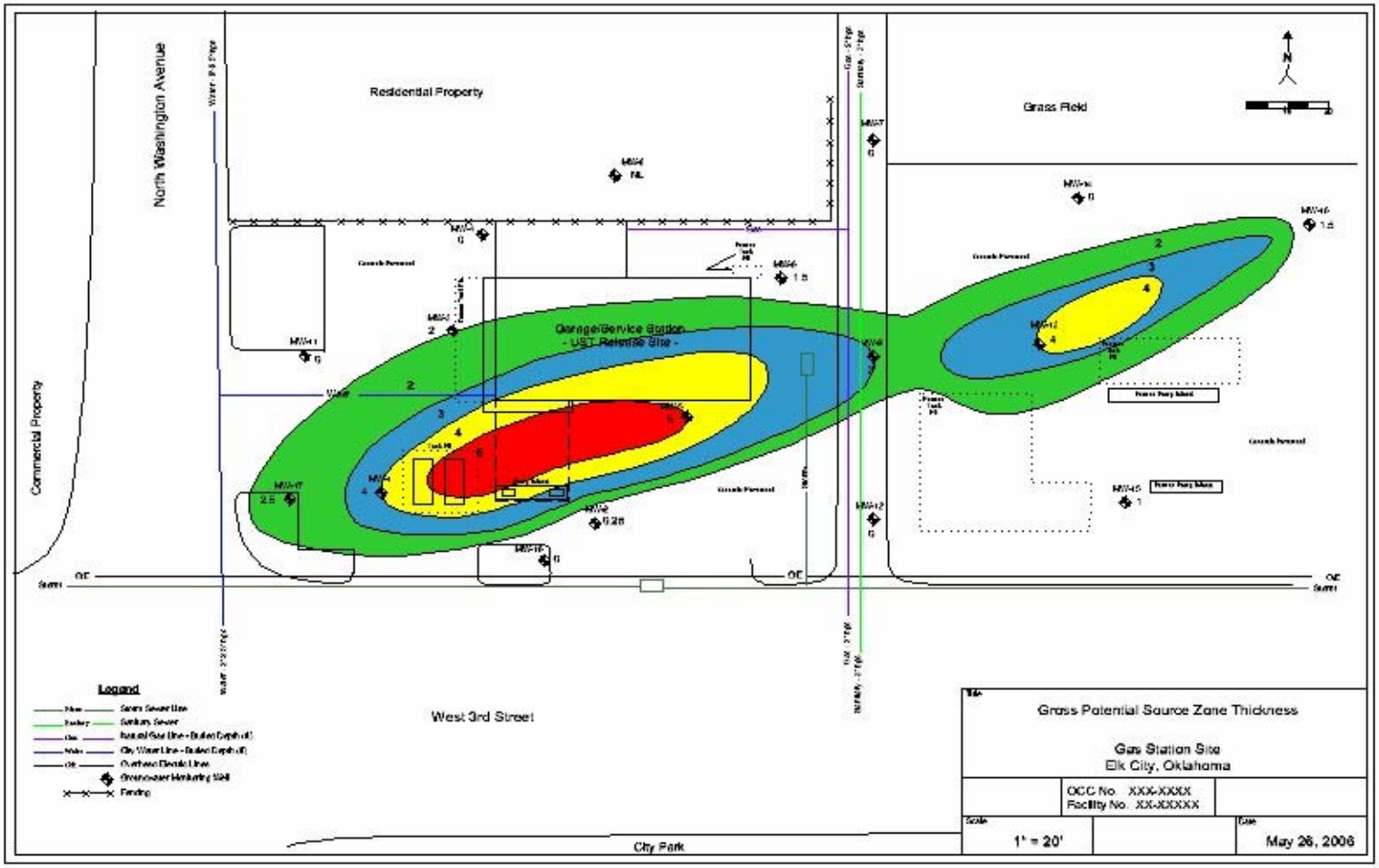
Semi-Quantitative Transport and Continuing Source Zone

- Potential transport zone isopach map
- Potential source zone isopach map
- Combined transport and source isopach map

Potential Transport Zone Isopach Map

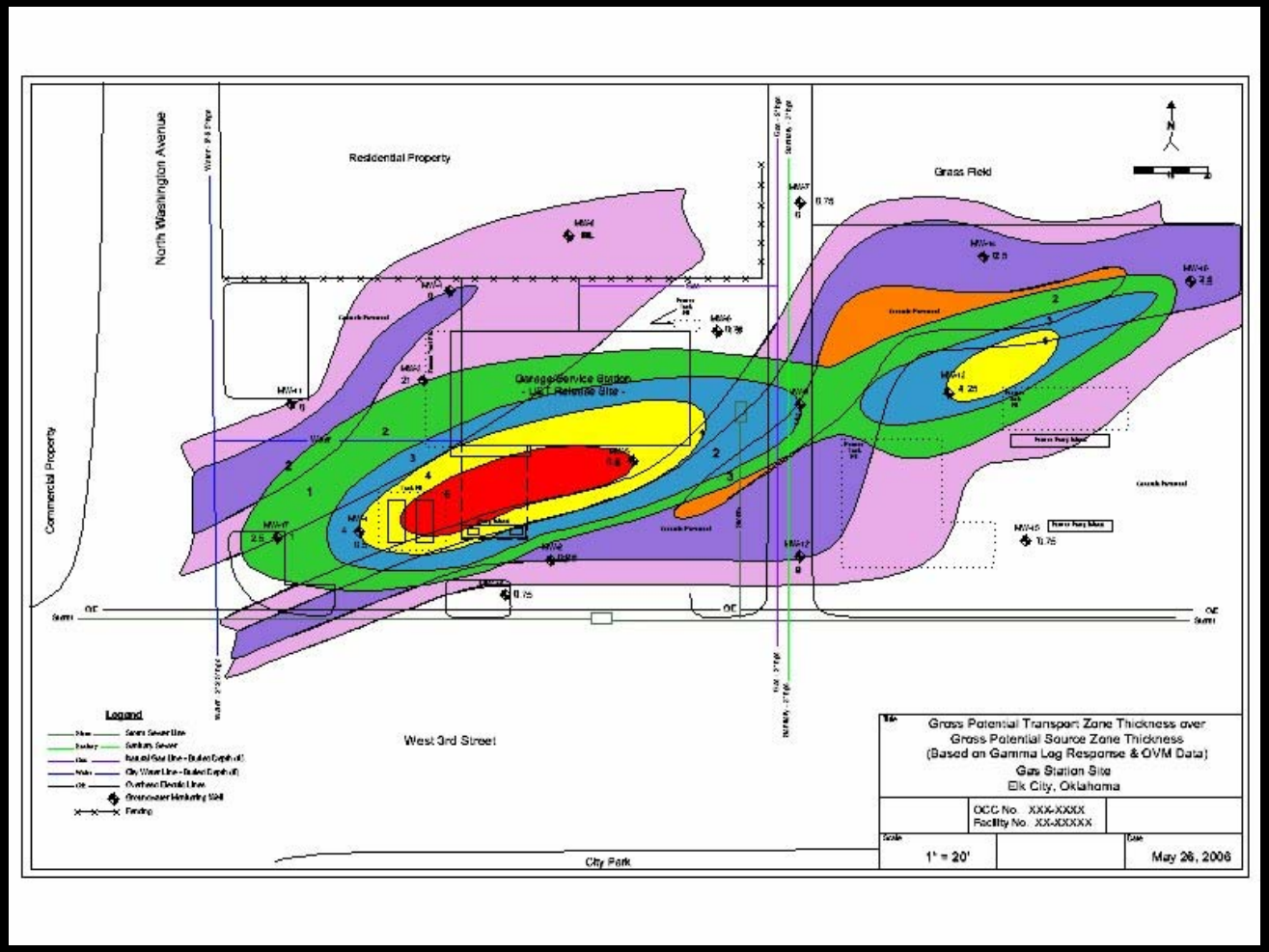


Potential Source Zone Isopach Map



Combined Transport and Source Isopach Map

- What does this map do for you?
- Where do you put your effort?



Conclusions: Combining Gamma Ray and Boring Log Data

- Allows mapping of potential contaminant zones
- Allows mapping of potential transport zones
- Identifies contaminant source zones for maps and cross-sections
- Leads to 3-D delineation models idenitifying the area of concern

Questions???

Thank you

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- Frank Vernon
  - 405-521-6719
  - f.vernon@occemail.com

DEVELOPING A NEW WATER RESOURCE FROM PRODUCTION WATER

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This paper will discuss a project in northern Colorado regarding the potential of the development of a new water resource. The paper will discuss a full scale plant demonstration on technology for treating oil production water to meet environmental standards and the subsequent development of this water as a new water resource for the western states. The paper will discuss the water quality testing results as well as the economic analysis for the subsequent sale of this water to environmental and commercial entities for beneficial use.

Introduction

Stewart Environmental Consultants, Inc. has been working on both oil production water as well as coal bed methane water for treatment and a proposed beneficial use of this water as a new water resource. This idea of beneficial use has been discussed by others but until our facility was built in Colorado, had never been actually completed.[1]

In 2003, Interior Secretary Norton announced a new Federal initiative to assist communities in addressing chronic water shortages in the West. In this initiative, areas where shortages are most likely were identified. To a large extent, these areas coincide with the states that produce oil and natural gas. The top producing states are Colorado, Texas, Louisiana, Alaska, Oklahoma, and California.

In 2002, 2.1 billion barrels of oil and 196 trillion cubic feet of natural gas were produced in the United States (API). These activities resulted in nearly 22 billion barrels of produced water.[2] Produced water is water that is generally mineralized and contains particulate and dissolved organics and brought to the surface with oil and gas operation.

PRODUCED WATER REMAINS A LARGELY UNTAPPED WATER RESOURCE

Despite individual efforts by the oil and gas industry to beneficially reuse produced water, and an increasing trend toward reuse and recycling, by far the most common method of disposal is subsurface injection in a Class II injection well. This disposal method is very costly and treats water as a liability rather than an asset. There appears to be several reasons why previous reuse efforts have had limited success, including:

- Unfamiliarity of the oil and gas industry with the intricacies of water marketing.
- Uncertainties related to the duration of the produced water supply.

---

[1] Water Rights and Beneficial Use of Produced Water in Colorado, Wolfe, Dick and Graham, Glenn, Ground Water Protection Council, Produced Waters Conference, 2002

[2] DOE – NETL, Produced Water from Oil and Natural Gas Operations – Setting the Context, Water Program 063, http://www.netl.doe.gov/technologies/oil-gas/publications/AP/Program063.pdf#search=%22produced%20water%20in%20the%20us%20water%20program%22

- Fluctuating oil and gas prices and the resulting fluctuation in the willingness to make capital investments in recycling technology.
- Wide differences between the desire for rapid development of recycling by private industry, once a “go” decision has been made, and the slow pace of development for public water infrastructure.
- The relatively poor source water quality of produced water and the need for extensive treatment.
- Risks associated with environmental and public exposure to treated produced water.
- The relatively low value placed on water, particularly in relation to the high value of oil and gas.
- Focus of time and capital by the oil industry on their core business – finding oil.
- Clean Water Act limits the discharge of produced water to surface water in the West.

In short, although there are significant technical, economic, environmental, and legal barriers to produced water development, the primary barriers are the institutional and communication differences between the private oil and gas industry and the publicly dominated water industry.

BENEFITS OF PRODUCED WATER DEVELOPMENT

Despite the barriers to development of produced water, the benefits are substantial and are both economic and technical.

The economic benefits of produced water treatment include:

- Adding a new water resource to the shrinking number of water resources available in the water-short West.
- Water is becoming an increasingly valuable commodity that is both transportable and in demand.
- Dramatically reduce the volume of produced water injected into disposal wells and eliminate this as a cost of producing oil and gas. This will reduce the energy loss due to this operation by as much as 20 percent.
- Minimize the cost and risk of the environmental impact of producing oil and gas by dramatically reducing the total use of chemicals in the recovery and treating process.
- Make better use of natural and financial resources by lowering the cost of environmental compliance.
- Reduce the demand for surface water resources by domestic and industrial users, which conflict with the maintenance of endangered species and wild rivers.
- Reduce some or all of the costs associated with the underground disposal of produced water including maintenance, acidizing, drilling new disposal wells, regulatory and administrative activities.

The technical benefits of produced water treatment include:

- Improve the efficiency of thermal oil recovery by decreasing the amount of steam required to heat the water along with the oil in the reservoir.
- Reduce the potential for reservoir damage by disposal injection.
- Reduce the recirculation of injected water into the oil producing horizons.
- Lower the energy demand for oil field operations through reduced water production and handling.

PRODUCED WATER RECOVERY WILL INCREASE DOMESTIC OIL PRODUCTION

In many oilfields, injected produced water flows to producing areas and increases the water content of recovered oil. For example, in the San Ardo Oilfield in California where produced water is reinjected, the water cut was less than 1 percent in the 1940s, but now is nearly 95 percent. Thus, water removal is the key to increasing production. If the reservoir could be dewatered, an estimated 150 million barrels of additional oil could be developed from this oilfield alone.

In reservoirs with thermally enhanced recovery, produced water reuse will also reduce heat requirements. By increasing the steam quality, the amount of steam required can be substantially reduced. Because these heat requirements represent a significant cost and recoverable oil reserves are based on production economies, more oil may be recoverable from existing oilfields.

EXAMPLES OF PRODUCTION WATER PROJECTS

There are three examples of production water projects that have been or are nearing completion.

Wellington Colorado Production Water Plant

The first project is near Wellington, Colorado. This project is treating oil production water as a new water resource. This new water resource will be used to augment shallow water aquifers to prevent injury to senior water users. The oil company is embarking on this project to increase oil production. A separate company will then purchase and utilize this water as an augmentation water source. This water will eventually be used to allow the Town of Wellington and northern Colorado water users to increase their drinking water supplies significantly. In this example, the Town of Wellington can increase their water supply by 300 percent due to this new water source.

The economic reason for this plant is as follows:

1. The cost of the production water treatment plant is approximately $2,000 to $3,000 per ac-ft of capacity. The operational costs for this plant is approximately $350 per ac-ft.
2. The cost of the reverse osmosis plant for the drinking water portion of the plant is $2,000 to $3,000 per ac-ft.
3. For the two plants, the cost for capacity is $4,000 to $6,000 per ac-ft.
4. The market for this water is $20,000 per ac-ft for the non-tributary water and the market for the finished water is an additional $15,000 per ac-ft.
5. Therefore, for an investment of $4,000 to $6,000 per ac-ft, the return is close to $35,000 per ac-ft.

We believe that the economic value will only increase in the future. This is due to the lack of water in the western United States.

San Ardo Oil Field

Another example of the beneficial use of production water is the San Ardo field near Monterey California. Research of this production water system is being conducted by Kennedy/Jenks Consultants of San Francisco, California. This oil field is currently utilizing 50,000 barrels per day for steam, but has over 100,000 barrels per day of water available for beneficial reuse. The end users of this water could be agriculture, groundwater recharge for salt barrier intrusion and environmental reclamation.

Coal Bed Methane Production Water

A third example would be the coal bed methane production waters that are being developed in the west. These waters need to be removed in order to develop the resource of the coal bed methane. This is a difficult water to dispose of due to the organics and mineral content of the water. Technologies have been developed to treat this water, but the beneficial use of this water has not been researched or developed. Potential uses of this water are for municipal augmentation of a new water resource, industrial and agricultural interests as well as environmental enhancement through the creation of wetlands and in-stream flows.

An example of this would be the Atlantic Rim area near southern Wyoming and northern Colorado. This water could be discharged to the tributaries of the Colorado River. Currently, a majority of this water has been classified as non-tributary by the two states. This will allow the potential for movement through interstate transfers of this water. For example, this water could be sold to downstream users on a lease basis.

The cost of treatment of this water for CBM production water has been estimated between $0.25 to $1.00 per barrel. The cost of deep well injection has been as high at $2.00 per barrel. This translates into a cost of $2,000 to $8,000 per ac-ft for treatment and $16,000 per ac-ft for disposal. The market price for this water is close to $20,000 per ac-ft for a long term lease. If the energy companies are currently paying $2.00 per bbl for disposal, then treatment would lower their overall costs. In addition, the first activity at a CBM facility is dewatering phase. If the water could be sold at this point, then the cost of development is greatly reduced.

A NEED FOR PRODUCED WATER RESEARCH

I believe that there is a real need for production water research. Presently, there is a lack of information on the amount of effort required to produce this water. I have been working on this effort in Colorado for over 5 years. Most of this time was spent obtaining regulatory approvals and working on the legal aspects of our project.

There are two bills in the US Congress that can be of assistance in this area. The first is HR 5110, which is authored by Colorado Congressman, Mark Udall. This bill asks for funding of this important new water resource. The second bill is by Senator Domenici of New Mexico. This bill is currently in committee but it is hoped that it will be able to move through the system within the next year. Both of these bills call for assistance in the regulatory areas of this program as well as funding of technical research.

CONCLUSIONS

Production water can be a new water resource for the western United States. This has been proven true for several areas in Colorado, Wyoming and California. There are several reasons that this should move forward:

1. Economically, this approach will be beneficial to the energy companies as well as the water providers.
2. The technology for treatment of these waters has been proven. There are issues with several aspects, but overall the technology exists for this type of production water treatment.
3. Communication of this issue is the largest hurdle to providing this new water resource. We need the energy companies and the water providers to communicate needs and requirements in order to make this new water resource a reality.

An Exciting New Produced Water Concentrator Technology for Tail and Brine Waters: AltelaRain™

October 17-20, 2006
San Antonio, Texas

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Abstract

Through the use of its proprietary, patented AltelaRain™ technology, Altela, Inc. desalinates and decontaminates highly challenged water sources without the energy intensive equipment, high temperatures, or high pressures of other water desalination technologies. Altela's System provides a unique solution for the desalination/decontamination of highly concentrate tail and brine water effluents including reverse osmosis coal bed natural gas produced water treatment systems. The AltelaRain™ desalination/decontamination system requires no expensive pre-treatment or post-treatment processes – extremely clean water is simply extracted from contaminated brines in a single, elegant step. This allows the AltelaRain™ System's operational costs to be far lower than those of competing technologies, especially in the realms of highly challenged produced water treatment. Altela has developed a mobile, scalable system that can be configured to be economically feasible for operation at individual well locations to treat as little as 20 barrels per day (BPD), or as much as 250 BPD. By further scaling larger modules together, AltelaRain™ Systems can also be configured to treat large volumes (in excess of 1,000 BPD) of tail water on-site. The AltelaRain™ System has successfully completed real-world oilfield beta testing.

The Company

Altela, Inc. provides products and services to customers in need of creating pure water from highly salinated and contaminated water sources. Through the use of its proprietary, patented AltelaRain™ technology, Altela desalinates and decontaminates highly challenged water sources without the energy intensive equipment, high temperatures, or high pressures of other water desalination technologies. The AltelaRain™ desalination/decontamination system requires no expensive pre-treatment or post-treatment processes – extremely clean water is simply extracted from contaminated salt water in a single, elegant step. This allows the AltelaRain™ System's operational costs to be far lower than those of comparable reverse osmosis, multi-stage flash, ion-exchange, or vapor compression technologies in the realms of highly-brackish and/or contaminated waters.

The AltelaRain™ System is an elegant solution for the desalination/decontamination of moderate volumes of challenged water, on-site where the brackish, salty and/or contaminated water is generated or stored. Within the water desalination/decontamination market, there are numerous, sizeable market segments with characteristics ideally suited to the AltelaRain™ System. These include the purification and remediation of:

1. Produced (formation) water in the oil, natural gas, and mineral extraction industries,
2. Highly salinated concentrate "tail-water" from large-scale reverse osmosis and other brine generating desalination systems,
3. Industrial waste water treatment, particularly in the semi-conductor and electronic manufacturing industries,
4. Cooling tower "blowdown" water from electrical power generating stations, and
5. Contaminated ground water.

Water & Environmental Challenges in the CBNG Fields

As noted above, the AltelaRain™ System is well suited for the treatment of highly salinated concentrate "tail-water" from large-scale reverse osmosis systems which recently have begun to be employed in the coalbed natural gas (CBNG) industry for the treatment of produced water. CBNG, the natural gas derived from water-saturated underground coal seams, has recently become one of the most talked about energy resources in the West. CBNG is classified as an unconventional source of natural gas. It is growing dramatically as a domestic source of natural gas at a time when demand is rapidly increasing and output from some conventional sources appears to have peaked.

As of the mid-1980s, CBNG was widely regarded as a hazardous byproduct of coal mining and was not traditionally considered a resource. CBNG was initially discovered during coalmining operations when fires or explosions of methane gas threatened the safety of miners. To mitigate the risk of explosions, methane began to be vented during mining operations. Later, these same companies began to capture this methane gas as a valuable asset. Interestingly, this in turn, resulted in ownership questions centered on whether the CBNG was part of the coal estate or part of the gas estate. In Amoco Production Company v. Southern Ute Indian Tribe, 526 U.S. 865 (1999), the Supreme Court ruled that CBNG is not included in the meaning of coal. CBNG is part of the gas estate, not the coal estate. The Court held that coal companies could vent the gas while mining, but the right to vent the gas does not imply ownership of it. This ruling, coupled with federal tax credits for exploration, has contributed to the CBNG boom.

Production of CBNG often involves significant amounts of produced water. CBNG operators typically drill surface wells into coal seams. These coal seams usually contain deep bedrock aquifers and large volumes of water. CBNG operators pump this water from the seam causing a reduction in pressure, thereby releasing methane to the surface along with significant amounts of produced water. U.S. Environmental Protection Agency guidelines define produced water as "water (brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water, and any chemical added downhole or during the oil/water separation process." Recently, the Ninth Circuit Court of Appeals found that CBNG water qualified as produced water under these same guidelines.1 Generally, neither the amount of produced water nor the quality of the water can be predicted prior to bringing the water to the surface.

Due to distinct variances in water quality, CBNG produced water is dealt with differently across the basins. Water quality indicators vary across and even within basins, depending on the depth of the methane, geology, and environment of the deposition. In the San Juan Basin of New Mexico for example, produced water is typically re-injected because of poor quality. Conversely, much of the produced water in Wyoming's Powder River Basin is useable for a variety of purposes. A major CBNG challenge has been managing the tremendous increase in produced water. Over the past three years within the Powder River Basin, approximately 5,500 new CBNG wells have been drilled and more areas of the basin have been opened to exploration.2 To support this dramatic increase in exploration, considerable infrastructure has been installed which in turn, has raised numerous environmental concerns. Demand for CBNG will undoubtedly continue. The Energy Information Administration, in its Annual Energy Outlook 2004, estimates that natural gas demand in the United States could be 31.41 Tcf by the year 2025. That is an increase of 38 percent over 2002 demand levels of 22.8 Tcf.

Management of produced water, including treated concentrate brine ("tail waters"), will continue to be a central development issue. CBNG development has produced important energy and other economic benefits throughout the West. However, such dramatic growth and exploration has resulted in numerous stakeholder concerns. In many areas, concerns over adverse environmental impacts, the regulation of development by local governments, and conflicts between surface owners and gas companies have all contributed to increased uncertainty and acrimony. Counties have sued state oil and gas regulatory bodies over who has responsibility for regulating the impacts of CBNG development. Companies have fought with counties over zoning and land use plans. Local community groups have sued federal and state agencies over water quality concerns. Environmental and recreation stakeholders increasingly clash with traditional oil and gas exploration and development stakeholders over handling, treatment and disposal/re-use of produced water.

Concentrate Management – An Economic Solution

Based on the high degree of complexity of produced water chemistry, produced water treatment technologies are generally not in wide use. Those that are have historically been applied only to lesser challenged produced waters (such as certain CBNG produced water), and they have largely been developed by oil and gas operators on a case-by-case approach. In those applications where the CBNG produced water is treated, large streams of concentrate brine (tail water) are generated as reject water. Depending on the quality of the influent, cut rates can range from 90% to under 50%. The resulting tail water is highly concentrated and is unable to effectively and economically be treated by membrane based systems. Such tail water has historically been trucked and related inland concentrate brine is traditionally disposed of via underground reinjection wells. The cost of such disposal is often prohibitive to the operator. Oil and gas companies must pay for disposal trucking companies to visit the site multiple times per week, pump the

produced water concentrate out of large storage tanks or evaporative ponds and transport the waste to commercial underground reinjection sites. These disposal trucks must often travel great distances to the reinjection sites. When these trucks are unavailable or during periods of poor weather, many sites must be shut down due to the inability to store and/or dispose of the concentrated brine on-site.

Concentrate management has been identified has a key water management area of focus. In 2001, Congress directed the United States Bureau of Reclamation (BOR) to partner with Sandia National Laboratories (SNL) to develop a desalination technology research plan for the nation. BOR and SNL formed a multi-disciplinary committee made up of experts from academia and the public, private, and non-profit sectors to develop the desalination technology research plan. As a result, The Desalination and Water Purification Technology Roadmap: A Report of the Executive Committee (Roadmap) was published in January 2003. The Roadmap presents a summary of the water supply challenges facing our nation through 2020, and suggests areas of R&D that may lead to technological solutions to these challenges. The guiding vision for the Roadmap provides that "…By 2020, desalination and water purification technologies will contribute significantly to ensuring a safe, sustainable, affordable, and adequate water supply for our nation". Concentrate management technologies that address the disposal and/or beneficial use of desalination waste streams were identified as central to the roadmap.

Altela's patented AltelaRain™ technology is such a concentrate management technology. The technology uniquely cleans oil and gas industry concentrated brine. The technology removes the salts, residual oils and other contaminants from the concentrate stream in a single treatment pass - allowing the clean water to be used on-site rather than requiring disposal in costly reinjection wells or evaporation ponds. In the arid western United States, purified concentrated brine represents a new water supply and very desirable asset. Altela-cleaned water is attractive to ranch and farm landowners leasing their mineral rights to oilfield producers. In addition, drilling operators need clean water for fractionation and tertiary recovery operations. Following treatment, the purified AltelaRain water meets water quality standards acceptable for irrigation, livestock watering, power plant cooling, or dust suppression.

Technology Process Description

The basic Altela technology is a simple and elegant process based on thermal distillation, which desalinates and decontaminates salty and polluted water in a fundamentally different way than the more familiar reverse osmosis and other membrane-based desalination technologies. In simple terms, the technology mimics nature's process of making pure rain water from seawater. What positions it as the first, truly new and disruptive water desalination/decontamination technology in over 50 years, however, is a scientifically complex, but inexpensively implemented, internal heat transfer process that allows the re-use of the latent heat of condensation over and over again to greatly offset the total latent heat of evaporation required in conventional thermal distillation. This internal heat transfer technology recaptures the energy used to evaporate water, thus yielding approximately 4 times the amount of distilled water per energy input as traditional distillation/evaporation techniques. Consequently, the AltelaRain™ technology yields energy costs that are approximately only 25% of comparable distillation/evaporation processes.

The water vapor from the evaporation chamber is transferred to the condensation chamber by a carrier gas, with the ability to absorb and desorb pure water from the produced water several times over, resulting in extremely high energy efficiencies, Figure 1. Ambient air is brought into the bottom of the tower on the evaporation side of a heat transfer wall. The wall is wetted by saline feed water, which is fed into the evaporation side at the top of the tower. As the air moves from the bottom to the top of the tower, low-temperature heat is transferred into the evaporation side through the heat transfer wall, allowing the air to rise in temperature and evaporate water from the wet saline liquid which coats the heat transfer wall. Water concentrated in contaminates leaves from the bottom of the tower and warm saturated air rises to the

top of the tower. Heat is added to this hot air by an external heat source (low grade, atmospheric pressure steam). This hotter saturated air is then sent back down through the tower on the condensation side of the heat transfer wall. The evaporation side of the tower, being slightly cooler than the condensation side, allows the air to cool and transfer the latent heat condensation from the condensation side to the evaporation side. Pure distilled water condensate leaves the condensation side of the tower at the bottom of the tower.

Individual AltelaRain™ towers are approximately the size of a residential water heater and are capable of processing approximately 330 gallons per day (8 BPD) of water with salt concentration in excess of 150,000 ppm. The AltelaRain™ System can reduce effluent disposal volumes by as much as 90%. Since the treated water stream is distilled water, the quality of water from the AltelaRain™ System is extremely high. In summary, the key advantages of the AltelaRain™ technology include:

- Extremely high quality of treated water
- Relatively low cost
- High thermal efficiency
- Unattended operation
- No fouling
- No scaling
- No membranes to replace
- Near ambient temperature operation
- Operates at ambient pressure
- Uses waste heat to operate
- No pre-treatment
- No post-treatment

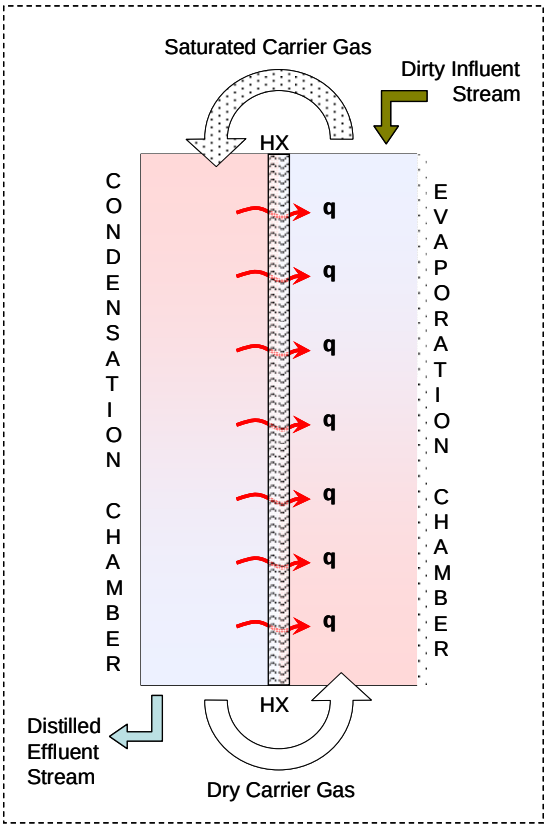

Figure 1: AltelaRain™ Process

The AltelaRain™ System is highly scalable in size and can be produced in a variety of configurations to fit individual on-site needs. A smaller capacity system can be built and installed in a single 8 by 40 foot container. For higher volume applications, larger 180 to 250 BPD systems can be joined together to double or triple production capacity. Scaling up the volume of the system in this manner yields some cost savings on a per-barrel cost basis. The AltelaRain™ System is designed to minimize maintenance and operation costs. The use of plastics minimizes or eliminates many of the maintenance issues related to scaling, fouling or corrosion of metal systems. The moving parts in the system are few, and consist of proven, robust, off-the-shelf components, such as low pressure water pumps and air blowers. The system operates at ambient pressures and modest temperatures, and as such, has few mechanical failures in plumbing and related systems. The ability to remotely monitor the system allows field operators to detect system problems early and take remedial action before major failures take place.

Summary of Field Results

A beta pilot test using real oil-field produced water was conducted by Altela, Inc. employing the AltelaRain™ System for a conventional oil well located in southeastern New Mexico in early 2006.

Coincident with this, Altela received from the New Mexico environmental regulatory authorities the first-ever permit issued for the surface discharge, on site, of clean water extracted from the highly brackish and contaminated produced water pumped from an oil or gas wellhead. The water quality test results received from an independent water quality lab demonstrate the very high quality of treated water obtained from this simple technology for the treatment of highly challenged produced water. Total dissolved solids were reduced from 41,700 mg/L to 106 mg/L. Chloride was reduced from 25,300 mg/L to 59 mg/L. Similarly, benzene levels were reduced from 450 ug/L to non-detectable following AltelaRain™ treatment. Detailed water quality data following AltelaRain™ treatment is outlined below in Table 1.

Table 1: AltelaRain™ Produced Water Pilot Test

	Water Contaminant (Analyte)	**Symbol**	**Before Altela (mg/L)** *except for Radium 226 and 228 which is in pCi/L	**After Altela (mg/L)** *except for Radium 226 and 228 which is in pCi/L
	Salts:			
1	Total Dissolved Solids	TDS	41,700	106
2	Chloride	Cl	25,300	59
3	Sulfate	SO4	81	0
	Metals:			
4	Arsenic	As	0.036	0
5	Barium	Ba	19.1	0
6	Cadmium	Cd	0	0
7	Chromium	Cr	0	0
8	Cyanide	CN	0	0
9	Fluoride	F	0.6	0
10	Lead	Pb	0	0
11	Total Mercury	Hg	0	0
12	Nitrate	NO3 as N	0	0
13	Selenium	Se	0.096	0.001
14	Silver	Ag	0	0
15	Uranium	U	0	0
16	Copper	Cu	0.02	0
17	Iron	Fe	38.1	0
18	Manganese	Mn	0.72	0
19	Zinc	Zn	0.01	0.03
20	Aluminum	A	0	0.3
21	Boron	Ba	44.8	0.2
22	Cobalt	Co	0	0
23	Molybdenum	Mo	0	0
24	Nickel	Ni	0	0
25	**BTEX:**			
26	Benzene		0.45	0

27	Toluene		0.45	0.0078
28	Ethylbenzene		0	0
29	Total Xylenes		0.76	0
	Radialogical:			
30	Radium 226		423	1.1
31	Radium 228		587	1.1
	Other:			
32	pH	pH	7.17	8.74

Upcoming Testing & Installations

Two additional well sites have been identified where the AltelaRain™ System will be employed to demonstrate its unique ability to purify highly challenged produced water, including concentrate brine "tail water. The first well site is located in the San Juan Basin of New Mexico inside the city limits of Farmington, San Juan County, NM. This State of NM sponsored project is anticipated to begin in late 2006 and finish in early 2007. Total dissolved solids at this site are 32,600 mg/L; chlorides are 20,200 mg/L, barium is 66.5 mg/L, Radium 226 is 68.3 and boron is 3.3 mg/L. The second well site is located in the Green River Basin of Wyoming. An AltelaRain™ System will be linked to a membrane treatment train to treat the concentrated "tail water" effluent from the membrane system. The tail water concentration is approximately 49,650 TDS, with the majority being sodium chloride.

Conclusion

Oil and gas companies need lower cost methods for handling and disposing of produced water concentrate, including tail water streams from CBNG production. The application of new proprietary technology to treat produced water concentrate on-site will yield major returns, both economically and environmentally.

AltelaRain™ represents a simple solution to removing all produced water contaminants, even in highly-challenged and extremely high-TDS conditions found in concentrated brine. Another major advantage of AltelaRain™ is its inherent flexibility and modularity. The low cost, scale-resistant materials used to fabricate AltelaRain™ towers enable treatment systems to be built that are modular and mobile, easily maintained, and capable of processing water with highly variable influent compositions. The modular design of an AltelaRain™ System enables installers to customize each treatment n with little or no additional cost to oil and gas companies. For example, an AltelaRain™ System can be installed to

minimize the effluent brine reject stream simply by re-configuring the physical layout of the primary system towers into differing series/parallel configurations. Like other thermal processes, AltelaRain™ is simple, easy to maintain, and can operate unattended for long periods of time. However, unlike other desalination methods the primary treatment components are fabricated entirely from plastic. This eliminates the need for costly influent pretreatment components (such as filters, flocculants, and anti-scalant additives) with respect to concentrated brine treatment.

The AltelaRainTM technology provides Altela several distinct competitive advantages in the concentrate brine treatment market. These include:

- Cost: The cost structure associated with building, installing, maintaining and servicing the system is significantly lower than the escalating costs associated with traditional concentrate brine hauling and reinjection.

- Energy Use: Altela's technology allows it to desalinate/decontaminate concentrate brine using less than 25% of the energy of competitive distillation/concentration technologies. As an essentially passive system operating at ambient pressures and comparatively low temperatures, Altela's System has little of the energy loss associated with powering high pressure electrical pumps and other machinery typical in other membrane technologies.

- On-Site Treatment: By treating directly on-site, Altela eliminates the cost and uncertainty of concentrate hauling, and assures continuous 24/7 production to the well operator.

- Universal Applicability: The AltelaRain™ technology can treat concentrate brine of varying chemistry and contaminate concentrations. Competing membrane technologies have great difficulty treating concentrate brine with TDS concentrations above 40,000, and require site specific pre- and post-treatment of brine streams. The AltelaRain™ technology is able to treat high TDS effluent streams and does not require pre- or post treatment.

- Environmental and Infrastructure Impact: Because the Altela treatment is done on-site, and the treated concentrate brine is converted into extremely pure water that can be surface discharged (or be put to use wherever clean water is needed), Altela's service significantly mitigates the damage to transportation infrastructure from water hauling and potential environmental problems from spills and improper reinjection.

- Water: The AltelaRain™ technology creates pure water from the concentrated brine stream that could be used at the well site for irrigation, stock watering, drilling "frac" water or other clean water uses. The AltelaRain™ System can easily and inexpensively be installed onsite, can treat concentrate brine, regardless of TDS concentration, and can be scaled according to treatment demand.

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[1] 40 C.F.R. §§ 435.41(bb), 435.11(bb)), in addition, s*ee generally* Northern Plains Resource Council v. Fidelity Exploration and Development Co., 325 F.3d 1155 (9th Cir.) cert. denied, 124 S. Ct. 434 (2003).
[2] Gregory C. Bank, Vello A. Kuuskraa, The Economics of Powder River Basin Coalbed Methane Development, U.S. Department of Energy, January 2006.

Toxicity Assessment of Produced Water and Monitoring to Detect its Potential Intrusion into an Oklahoma Reservoir

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ABSTRACT

This study investigated the toxicity of produced water and potential groundwater effects associated with its occasional surface overflow and possible groundwater transport along the shore of Skiatook Lake, Oklahoma. We monitored basic chemistry and acute toxicity of the water to the cladocerans, *Daphnia pulex* and *Daphnia magna,* and chronic toxicity to *Ceriodaphnia dubia* and fathead minnow, *Pimephales promelas*. *D. pulex* bioassays were also used to monitor water samples from groundwater wells near a produced water evaporation pond and injection well. Both the produced water and unconfined groundwater samples affected survival and sub-lethal endpoints in laboratory bioassays. Groundwater exhibited median lethal concentrations (LC_{50}s) ranging from 3.9% near the injection well to greater than 100% elsewhere at the impact site. Groundwater toxicity decreased somewhat with distance from impact source, but effects were still observed in sample wells located within the conservation pool of Skiatook Lake. Fathead minnows were less sensitive to produced water in bioassays than the three cladocerans tested. Toxicity Identification and Evaluation (TIE) procedures combined with predictions from the Ion Toxicity Model revealed that elevated salinity resulted in effects on fathead minnows, while cladocerans responded to salinity and other mixture contaminants, possibly hydrocarbons. Toxicity evaluations such as these can provide important data for produced water management, including regulation of disposal and potential beneficial re-use.

INTRODUCTION

Produced water is water co-produced with crude oil. It can be either naturally co-occurring in the same geologic formation with petroleum or artificially introduced to improve production. Both intentional and unintentional releases of produced water have been associated with oil production. For example, during the decade from 1993 to 2002, 12,863 fluid releases related to oil exploration and production were reported to the Oklahoma Corporation Commission. Of those releases, 76.1% involved oil or brine (produced water) and had median release volumes of 10 bbl (barrels; 1590 liters) and 40 bbl (6359 liters) respectively for a total of 1.46 million barrels (232 million liters) of brine released in Oklahoma (1).

Produced water typically contains contaminants such as hydrocarbons, salts, heavy metals, radionucleotides, and ammonia (2), and these releases are often associated with environmental impacts. Laboratory bioassays indicate that both produced waters (3, 4) and inland receiving waters (5) cause toxicity in the tests organisms *Ceriodaphnia dubia* and fathead minnow, *Pimephales promelas*, due to major inorganic ions and hydrocarbons. O'Neil et al. (6) reported declines in both diversity and density of stream benthic communities in systems that had received oil brines or coalbed methane waters with chloride concentrations greater than 565 mg/L. Communities exposed to less chloride than the 565 mg/L threshold experienced no significant community structure changes. Despite these potential environmental effects from inland produced water releases, few studies have investigated the effects of these discharges on resident communities.

The present study was conducted at Skiatook Lake, a 10,500-acre impoundment in Osage County, Oklahoma. Osage County ranks among the top oil and gas producing areas in the state, with some 38,000 oil wells. The Skiatook Lake watershed (about 820 km^2) contains 13,000 of those wells. Wells frequently occur within a few tens of meters from the lake shoreline or the banks of streams that feed into the system. The produced waters derived from these wells are typically reinjected into underlying formations for disposal. However, inadvertent spills, leaks, and accidents, have lead to both historic and present release of produced water in the riparian zone and into the lake.

An on-going study of these releases at two field sites on Skiatook Lake have been undertaken as part of the U.S. Geological Survey's Osage-Skiatook Petroleum Environmental Research (OSPER) Project (http://ok.water.usgs.gov/skiatook/). Persistent, unvegetated salt scars and generally elevated sodium chloride concentrations were reported in the soil at both the OSPER B (7) and OSPER A (8) field sites . Additionally, at the A Site, where oil production ceased in 1981, Blackjack oaks, *Quercus marilandica*, growing next to the salt scar exhibited elevated leaf chloride levels, indicative of salt contamination. A large groundwater plume about 3 ha in area contaminated with excess salts (electrical conductance of 44,000 µS/cm or 30,000 mg/L total dissolved solids) and soluble petroleum by-products was found beneath this site and extended under the lake bed (9).

This study investigates the environmental effects of produced water releases by an active oil production operation at the OSPER Site B. Oil production and unintentional produced water releases at this site has resulted in noticeable salt scars and potentially contaminated groundwater. Understanding the potential for effects on aquatic systems is an important consideration, especially given the proximity of contamination to Skiatook Lake, and is the basis for the present study. Toxicity evaluations can provide important data for produced water management, including regulation of disposal and potential beneficial re-use. Here, we present data characterizing produced water constituents and the toxicity of the produced water and receiving groundwater.

METHODS

Site Description

This study was conducted at the OSPER site B, a study area that is part of the U.S. Geological Survey's Osage-Skiatook Petroleum Environmental Research (OSPER) Project, along the shore of Skiatook Lake, a reservoir in Osage County, OK. Oil production at this site began in 1938, which predates lake impoundment in 1984. A produced water evaporation pond and an injection well overflow pool are located near the shoreline. Salt scars, characterized by bare soil and salt crystals on exposed rocks are apparent between these ponds and the lake, and run from both of these ponds to the lake. The site also includes a number of groundwater test wells that were drilled as part of the U.S. Geological Survey research project (Figure 1).

Sampling

Produced water and groundwater were sampled bimonthly starting in January 2006 and September 2005, respectively. Produced water was collected from onsite storage tanks in one-liter amber bottles with Teflon coated lids, filled from the bottom with a hose to reduce volatile chemical loss and minimize headspace, and held at 4°C. Groundwater samples were stored in clear glass bottles, held at 4°C, and filtered with glass microfiber filters (Whatman GF/A) to remove sediment before testing.

Chemical Analyses

Produced water and groundwater samples were analyzed for pH (Fisher Scientific Accumet AP62 portable pH meter), conductivity (Fisher Scientific Accumet AP65 portable conductivity meter), alkalinity (US EPA method 310.1) and, hardness (US EPA method D1126-96) at the Oklahoma State University Ecotoxicology and Water Quality Research Laboratory. Additionally, produced water was analyzed for total ammonia (Fisher Scientific Accumet AR25 dual channel pH/Ion meter), major ions (sodium, calcium, magnesium, potassium, nitrate, chloride, sulfate, boron, and bicarbonate; inductively coupled plasma emission spectroscopy by the Soil, Water, and Forage Analytical Laboratory at Oklahoma State University) and hydrocarbons (BTEX, Gasoline Range Organics, and Diesel Range Organics; US EPA method 8015B by Accurate Labs Inc., Stillwater, OK.).

Laboratory Bioassays

Static renewal acute (48h) and chronic (7d) toxicity testing of produced water samples was conducted in addition to chemical analyses. Acute tests utilized the test organisms *Daphnia pulex* and *D. magna* to generate median lethal concentrations (LC_{50}), though acute results were also generated from chronic toxicity tests (10). Chronic tests used *C. dubia* and the fathead minnow, *Pimephales promelas*, to respectively generate reproduction and growth endpoints (median effective concentrations-EC_{50}), in addition to survival results (11).

Toxicity Identification Evaluation (TIE, 12), a standardized method of identifying mixture constituents that contribute to toxicity, was conducted with produced water samples in February 2006. Results from each TIE manipulation were compared with baseline or unmodified sample toxicity results. Toxicity results and predictions from the Ion Toxicity Model, a statistical model to predict median effects levels based on empirically collected data from laboratory toxicity tests, were compared during each sampling period as a temporal measure of mixture constituent toxicity (13; but see 4).

Static renewal acute toxicity testing (48h) with *D. pulex* was also conducted on samples from selected groundwater wells (see Figure 1) on a bimonthly basis in conjunction with produced water tests.

Wells were selected to capture potential gradients in groundwater quality from produced water sources (evaporation pond and injection well) to the lakeshore. Groundwater wells were organized into three psuedo-transects. The first transect incorporated a groundwater well (BE53) near the injection well and a well on a salt scar near the lake (BE18), down-gradient from the injection well. Intermediate wells consistently produced insufficient water for toxicity testing. The second transect was located in an unvegetated salt scar and started near the evaporation pond (BE11), and ran down the evaporation pond salt scar to just above the lake conservation pool elevation (BE08) and then into the lake (BE07). The third transect was located in living vegetation and started near the evaporation pond (BE59), continued to just above lake conservation pool elevation (BE 61), and ended down gradient below the traditional water line (BE16).

Statistical Analyses

Statistical analyses on toxicity data were conducted using the Comprehensive Environmental Toxicity Information System (CETIS) version 1.1.2 (Tidepool Scientific Software, McKinleyville, CA). Logistic regression or the trimmed Spearman-Karber method, when data failed to meet regression assumptions, was used to derive toxicity endpoints and 95% confidence intervals. TIE results were compared with baseline toxicity using logistic regression (PROC GENMOD) in SAS version 9.1 (The SAS Institute, Cary, NC).

RESULTS

Produced Water

Comparison of models generated using logistic regression of produced water TIE results revealed three manipulations that significantly ($P<0.05$) differed from unmodified samples as potential sources of mixture toxicity (Table 1). Chelation by ethylenediaminetetraacetic acid (EDTA), filtration at pH 11, and aeration at pH 10 all significantly reduced measured toxicity when compared to baseline or unmodified produced water toxicity. When produced water pH was raised to at least 8, water color changed from yellow tinted clear to opaque green. Subsequent filtration removed all noticeable color from the water and significantly reduced toxicity.

The produced water had a relatively consistent composition through the course of monitoring, with respect to the specific ions and organics that were measured (Table 2). The mixture had high levels of sodium and chloride, though concentrations of calcium and magnesium ions were elevated as well. Overall ion content and mixture pH decreased during monitoring. Hydrocarbons fluctuated between 1.45 and 1.96 mg/L BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes) and between 6.3 and 8.0 mg/L TPH (Total Petroleum Hydrocarbons).

Acute toxicity test results for the four test organisms were similar within species over the period monitored (Figure 2). Similar survival responses (48-h LC_{50}'s) were observed for the cladocerans *D. pulex* (1.33 to 4.13%), *D. magna* (2.68 to 5.36%), and *C. dubia* (2.06 to 3.12%), while produced water had less of an effect on fathead minnow acute survival (7.71 to 8.54%).

Chronic toxicity test results appeared more consistent than acute results (Figure 3). Produced water had a greater effect at 7 days on *C. dubia* survival (LC_{50}: 1.78 to 2.54%) and reproduction (EC_{50}: 1.00 to 1.57%) than on fathead minnow survival (LC_{50}: 3.67 to 5.07%) or growth (EC_{50}: 3.22 to 5.33%).

Results comparing observed acute survival and predicted survival from the Ion Toxicity Model differed depending on test organism (Figure 4). Fathead minnow endpoints and confidence intervals either contained the predicted endpoint values or were slightly less than predicted values. Acute endpoints and confidence intervals for both *D. magna* and *C. dubia* were distinctly less than the corresponding predicted responses derived from the Ion Toxicity Model.

Groundwater

Some chemical parameters were not determined on all sampling dates because some groundwater wells were dry or had too little water available for collection. Samples from groundwater wells were intermediate in measured water quality parameters between produced water and lake water. Groundwater typically had a lower pH (Table 3), greater conductivity (Table 4), increased alkalinity (unless pH was below 5, Table 5), and greater hardness (Table 6) when compared to Skiatook Lake water.

Water collected from near the injection well had the greatest consistent effect (BE53, 48-h LC_{50}: 2.1 to 4.1%) on *D. pulex* during acute toxicity testing (Figure 5). There was less of an effect further away from the injection well (BE 18, 48-h LC_{50}: 13.5 to 36.8%). In contrast, toxicity appeared to increase with distance from the north side of the evaporation pond. The effect on *D. pulex* survival from water taken from wells BE11 (48-h LC_{50}: 5.8 to 35.4%) and, BE08 (48-h LC_{50}: 12.0 to 31.4%) was similar, while water from BE07 (48-h LC_{50}: 3.0 to 14.3%), the well farthest from the evaporation pond, had the greatest effect. Wells not located in a visible salt scar had the least effect on test organisms. The well closest to the evaporation pond along the south transect (BE59, 48-h LC_{50}: 48.1 to >100%) had the lowest recorded toxicity of all wells and included two months (March and May) when an LC_{50} could not be calculated at all. The other wells along the vegetated transect (BE61, 48-h LC_{50}: 11.7 to 38.2%; BE16, 48-h LC_{50}: 9.25 to 36.00%) had similar effects during bioassays.

DISCUSSION

Produced Water

Both sample manipulation with EDTA that reduced toxicity and predicted ion toxicity responses that were close to observed responses relative to the overall mixture toxicity suggest dissolved ions were a primary source of toxicity in produced water. Based on predictions from the Ion Toxicity Model, fathead minnows are likely responding to the high salt content and not other contaminants due to the similarity of observed toxicity and those predicted for major ions alone. The two cladocerans tested and modeled responded to major ion excesses but were also affected by other contaminants in the mixture. Both volatile (BTEX) and semi-volatile (GRO) hydrocarbons likely contributed to toxicity effects, though it is unclear from the TIE whether contaminants removed at pH 10 by aeration were removed via sparging, sublation or oxidation (12). The TIE bioassays and chemical analyses did not reveal why this effect was only seen at elevated pH or what toxicants had less effects on the test organism due to filtration at elevated pH.

Salts and hydrocarbons, among other contaminants, are frequently found in produced water (2), and Kharaka et al. (9) found produced water and groundwaters with high concentrations of sodium chloride salts and BTEX present at another site on Skiatook Lake. Produced waters vary depending on geographic location and no single contaminant has been found to consistently contribute to mixture toxicity, though major ion salts and hydrocarbons are the most common toxicants (3, 14, 15). The Ion

Toxicity Model has been successfully used in conjunction with Phase I TIE procedures to evaluate produced water toxic constituents. Produced waters where observed toxicity did not match model predictions were subjected to TIE procedures and found to be nonpolar organic compounds in one case and unidentifiable in another produced water sample (4).

Toxicity responses to produced water remained relatively stable during monitoring for both acute and chronic tests. Fathead minnows were consistently less affected by produced water toxicants for all endpoints, compared to the three cladocerans tested. Observed produced water toxicity decreased slightly during March and July for the three cladocerans in acute bioassays and for the fathead minnow chronic endpoints. Total petroleum hydrocarbons decreased in concentration during those two months, compared to other months, and may have contributed to the changing response.

Fucik (3) also found that fathead minnows were less sensitive to produced water effluents than *C. dubia*, unless high levels of hydrogen sulfide were present. The cladoceran was found to be more sensitive to the salinity of produced water than fathead minnows (3, 5).

Groundwater

Laboratory bioassays have been used to assess groundwater quality in response to potential contamination from sources including landfill leachate (16), lithium (17), and urban sources (18), but not for oil field brines. Groundwater toxicity was greatest near the injection well and decreased with distance from that well. No decrease in toxicity with distance occurred in relation to the evaporation pit. Instead, the opposite appeared to occur. Groundwater toxicities and visible salt scarring indicate a plume of contaminants originating from the evaporation pond, traveling to the lake, and also expanding down-gradient outside of the visible salt scar. Groundwater modeling of the OSPER B site (19) supports this conclusion by predicting that groundwater flow might follow a path to the lake that veered south from the visible salt scar.

Conclusions

Produced water from the study site is a complex mixture of potential toxicants including salts and hydrocarbons. The produced water has changed little over time in regards to measured effects on organisms during standardized bioassays. Patterns in groundwater toxicity are consistent with produced water contamination that may be originating from two sources: an injection well and an evaporation pit. Some measured toxicity decreased with distance from contaminant source, but test organisms were still affected by groundwater collected from wells located within the conservation pool of Skiatook Lake.

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Table 1. Effects of TIE manipulations on produced water toxicity to *D. pulex* expressed as 48-h LC_{50}'s for each manipulation and significance of difference from baseline toxicity.

TIE Manipulation	LC50 (%)	*P*-value
Baseline	2.73	1.0000
pH 7	2.93	0.6027
pH 8	3.39	0.1181
EDTA	3.76	0.0176
Oxidant Reduction	3.41	0.1357
pH 3	2.07	0.1186
pH 11	2.90	0.8612
Filtration	3.51	0.1953
pH 3 filtration	1.56	0.0759
pH 11 filtration	3.77	0.0313
Aeration	2.56	0.6316
pH 3 aeration	2.81	0.8612
pH 11 aeration	4.07	0.0095
SPE	2.35	0.3610
pH 3 SPE	2.07	0.1186
pH 9 SPE	3.22	0.4052

Table 2. Produced water ions (mg/L), organics (mg/L) and physical/chemical data.

	2005	2006					
	Dec	Jan	Mar	May	Jun	Jul	Aug
Na	38928	38681	27063	24551	25804	24386	23782
Ca	6130	6366	3839	3648	3473	3605	3379
Mg	1458	1449	908	950	871	944	863
K	225	176	130	101	96	84	86
NO_3	0	0	0	0	0	0	0
Cl	67459	68274	50181	43634	40455	45313	44793
SO_4	212	214	122	153	183	137	115
B	1.81	2.03	0.80	0.92	1.24	0.92	1.3
HCO_3	61	83	2	0	0	0	12
Benzene			0.640	0.780	0.670	0.290	0.690
Toluene			0.300	0.290	0.380	0.300	0.260
Ethylbenzene			0.062	0.000	0.000	0.060	0.045
Xylene			0.740	0.590	0.910	0.800	0.640
BTEX			1.742	1.660	1.960	1.450	1.635
GRO			3.0	4.0	4.1	3.1	3.4
DRO			3.4	4.7	3.9	3.2	4.5
TPH			6.4	8.7	8.0	6.3	7.9
pH	6.9	6.9	5.0	4.0	3.7	4.0	5.2
Condcutivity (µS/cm)	148600	149500	112900	106700	106000	107800	106800
Hardness (mg/L $CaCO_3$)	21292	21843	13313	13009	12249	12878	11981
Alkalinity (mg/L $CaCO_3$)	50	68	2	0	0	0	10
Ammonia (mg/L)		63.60	27.70	52.72	54.36	54.85	41.60

Table 3. Sample pH from groundwater wells. Dashes (-) indicate no data.

	2005			2006			
Well	Aug	Sep	Nov	Jan	Mar	May	Jul
Lake	8.32	7.92	8.01	8.04	7.93	7.95	7.96
01	7.71	7.32	7.31	7.59	7.61	7.50	7.48
03	-	-	-	-	-	6.73	6.67
04	-	-	-	-	5.50	-	-
05	-	-	-	-	-	-	-
06	7.90	7.77	7.40	6.36	6.43	7.72	8.24
07		6.45	5.88	6.35	6.31	6.36	7.55
08	7.41	7.23	7.41	7.04	6.88	7.69	7.64
10	7.23	6.92	6.63	7.34	6.01	7.55	6.95
11	6.98	6.86	7.48	7.12	6.78	7.10	7.15
13	7.35	-	7.53	7.51	7.25	5.85	7.54
15	7.20	7.41	7.16	7.44	6.51	7.42	7.95
16	7.14	7.21	7.20	7.78	7.08	7.84	7.34
17	7.55	7.39	7.54	7.60	7.49	7.48	7.41
18	7.01	7.31	7.41	7.44	6.65	7.24	7.72
19	6.95	7.34	7.54	-	6.26	8.02	-
51	7.56	7.63	7.64	-	-	7.75	8.03
52	6.97	6.97	7.07	7.45	6.88	6.88	6.85
53	5.08	4.61	5.07	5.06	4.12	4.04	4.56
54	6.08	6.28	5.73	5.83	5.80	6.03	6.49
55	6.77	7.83	6.67	7.18	6.82	7.01	6.78
56	6.86	-	6.88	7.38	6.22	7.02	7.08
57	7.41	7,53	7.57	7.86	6.92	7.61	7.48
58	7.48	7.71	7.67	-	7.81	7.49	7.65
59	7.68	7.66	7.35	7.78	7.34	7.65	7.91
60	7.46	6.67	7.54	-	6.22	7.07	6.98
61	7.40	7.22	7.03	7.73	6.94	7.87	7.57
62	-	6.66	6.59	6.84	-	7.16	6.57

Table 4. Sample conductivity (µS/cm) from groundwater wells. Dashes (-) indicate no data.

	2005			2006			
Well	Aug	Sep	Nov	Jan	Mar	May	Jul
Lake	293	278	264	376	419	301	333
01	8006	9527	7986	10560	10530	7861	9777
03	-	-	-	-	-	10780	12910
04	-	-	-	-	18220	-	-
05	-	-	-	-	-	-	-
06	5574	7472	5742	3923	2964	7638	7236
07	-	14930	25170	28650	16080	17150	18340
08	12670	14780	14880	17000	15810	12830	11080
10	14150	22100	18410	16670	21260	12500	14910
11	19430	21910	22940	22050	16490	14160	16570
13	14620	-	15540	22670	15040	14240	14780
15	9298	7965	9694	7631	5903	7263	10080
16	11320	16390	14260	19760	13400	10230	11220
17	11150	13630	10150	16280	12650	9958	11900
18	17460	20650	22840	18190	13180	17100	16720
19	8013	7555	8270	-	5563	4728	-
51	12570	13130	13390	-	-	8784	11930
52	1599	16130	18490	14120	15780	11280	15650
53	25260	34780	30990	20540	33150	23580	20590
54	15030	17040	41310	24750	20350	13570	16810
55	26820	22810	25760	23400	22830	15880	20740
56	34380	-	36080	26520	21910	16280	23990
57	15020	15260	15910	11730	8118	9506	14560
58	11440	12170	10540	-	12560	9625	13040
59	11030	9041	7430	14490	6851	4831	9784
60	11500	14010	11230	-	13530	9451	14080
61	12950	17650	13500	20130	10990	9416	11550
62	-	16830	13630	20860	-	11540	13810

Table 5. Sample alkalinity (mg/L $CaCO_3$) from groundwater wells. Dashes (-) indicate no data.

	2005			2006			
Well	Aug	Sep	Nov	Jan	Mar	May	Jul
Lake	76	70	100	78	76	76	74
01	640	752	790	744	620	750	784
03	-	-	-	-	-	36	56
04	-	-	-	-	24	-	-
05	-	-	-	-	-	-	-
06	273	226	210	42	58	252	
07		166	178	152	122	224	428
08	596	826	702	532	260	764	822
10	424	152	96	128	56	88	222
11	210	202	200	100	84	154	124
13	558		574	830	898	34	760
15	382	278	302	166	140	264	446
16	440	636	760	838	660	670	460
17	862	876	944	992	960	954	912
18	544	692	540	570	316	630	644
19	290	148	170	-	36	232	-
51	960	912	670	-	-	764	622
52	480	542	524	498	334	260	428
53	8	4	0	2	0	0	0
54	60	82	60	54	58	62	40
55	564	440	314	566	194	334	458
56	480	-	392	412	84	222	362
57	550	508	472	282	160	326	482
58	592	568	378	-	416	434	604
59	334	-	-	328	-	158	330
60	506	276	94	-	38	144	150
61	54	1178	1092	1060	692	780	1076
62	-	414	570	524	-	482	428

Table 6. Sample hardness (mg/L $CaCO_3$) from groundwater wells. Dashes (-) indicate no data.

	2005			2006			
Well	Aug	Sep	Nov	Jan	Mar	May	Jul
Lake	84	86	86	90	90	94	96
01	4380	5480	5520	5520	5020	5860	5720
03	-	-	-	-	-	2860	2660
04	-	-	-	-	3400	-	-
05	-	-	-	-	-	-	-
06	2700	2000	7440	780	500	3300	2600
07	-	3400	5280	4700	3240	4620	8900
08	4840	7480	8220	6980	5100	6620	7540
10	8180	5740	5400	5020	5520	4260	5560
11	3760	4560	5680	3600	2640	2800	4280
13	6960	-	6480	8160	7820	2120	7060
15	4220	2900	3400	1760	1120	2620	4500
16	3090	8100	8600	8220	7720	7060	8460
17	8360	7960	7160	7660	7220	6840	6860
18	3520	9260	9420	9620	4400	7880	11060
19	1240	1380	1600	-	680	1160	-
51	8440	7980	9260	-	-	6080	6120
52	6600	8580	9960	7760	6680	3860	8340
53	20000	8000	9040	8760	10800	7700	9780
54	2720	2120	9560	6460	3320	3280	3500
55	12000	8600	9700	12920	7040	8060	11160
56	10260	-	40000	11180	2380	6700	12220
57	4560	5060	6340	3300	1860	3000	5780
58	3840	6560	5080	-	5100	5180	7960
59	2890	-	-	3580	-	1000	3200
60	4920	3300	2340	-	2060	4060	3080
61	5110	8140	8740	8380	5060	5600	8160
62	-	4600	6060	5040	-	4720	4940

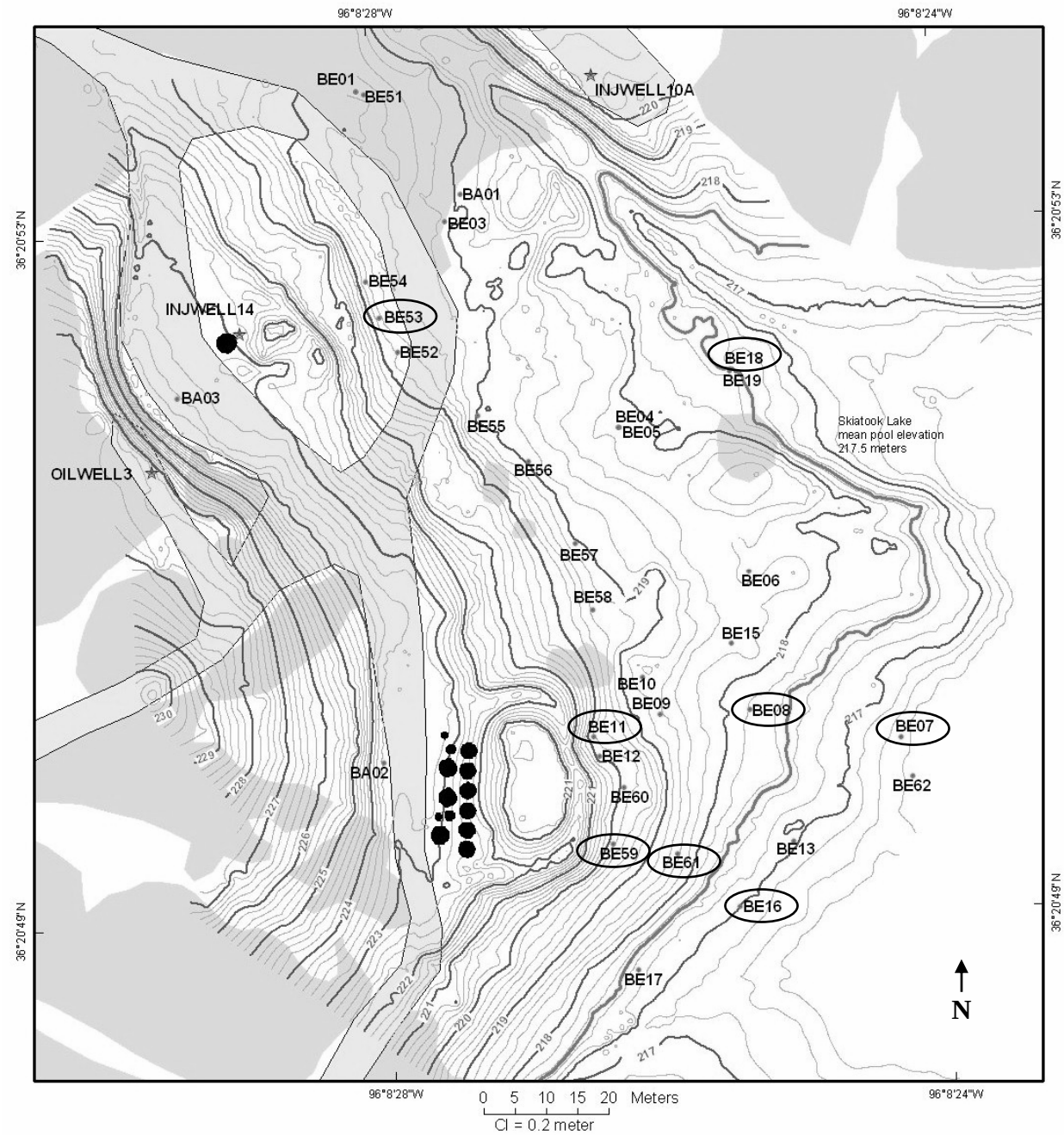

Figure 1. Topographic map of the study site. Points indicate groundwater wells and labels prefixed with "BE." Water samples from circled wells were subjected to toxicity testing in addition to routine water quality analyses. Image courtesy of the US Geological Survey.

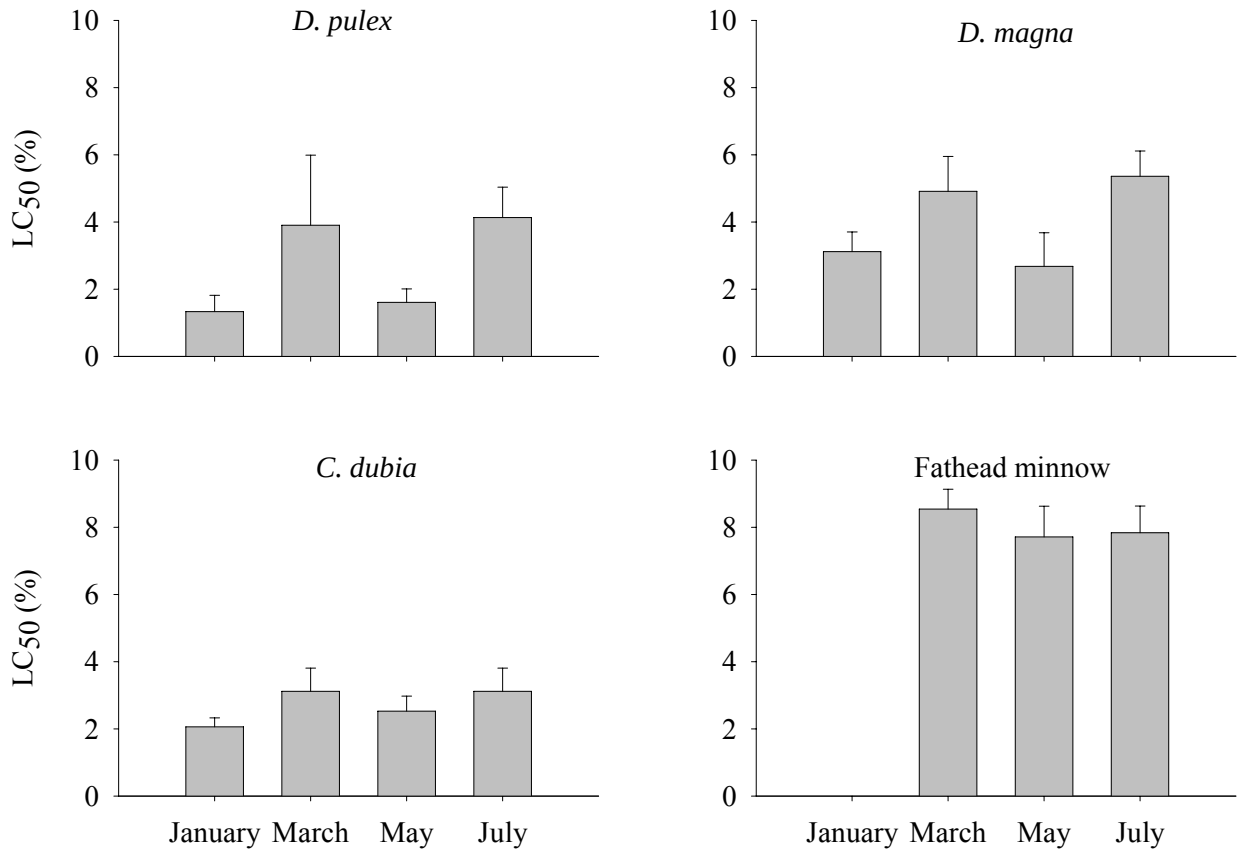

Figure 2. Acute toxicity expressed as 48 h LC50's of produced water for *D. pulex*, *D. magna*, *C. dubia*, and fathead minnows. Values are expressed as percent produced water. Error bars are 95% confidence intervals.

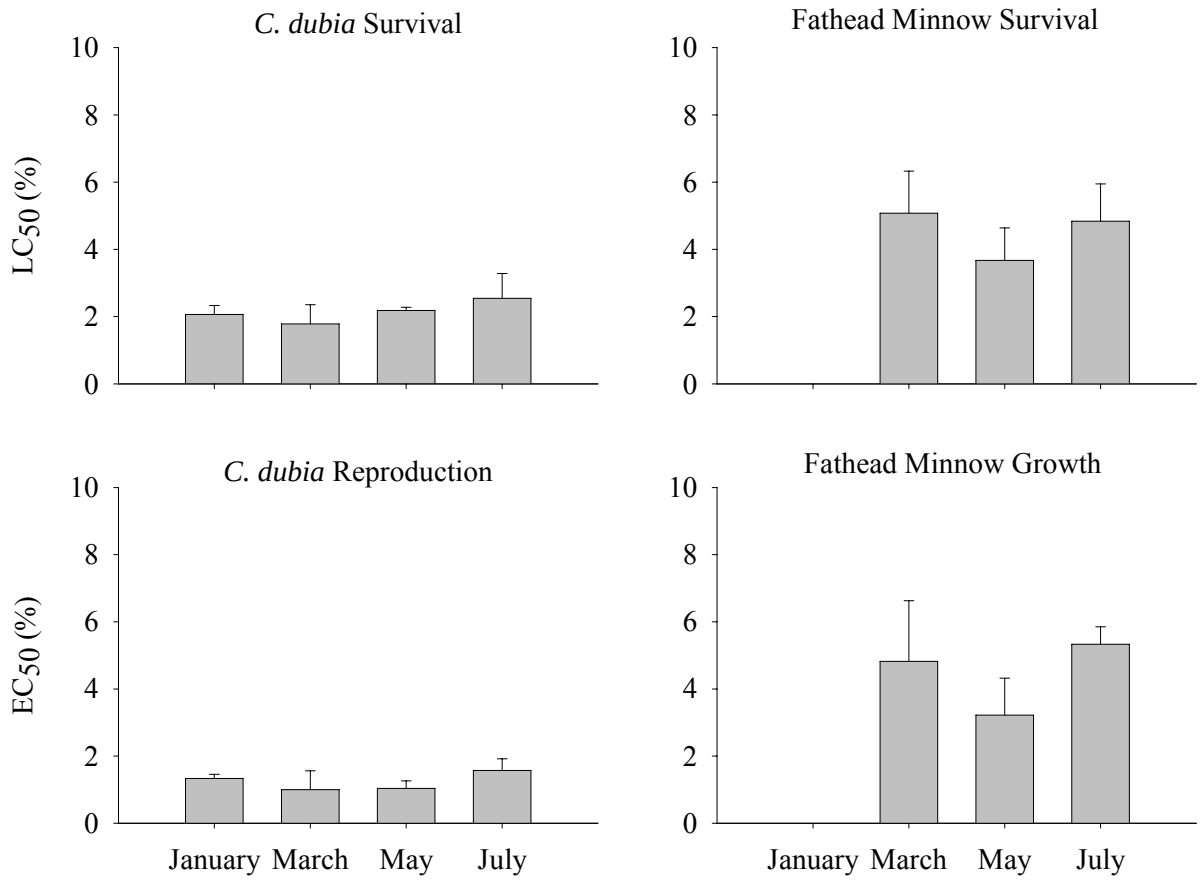

Figure 3. Chronic (7 d) toxicity expressed as LC50 values for survival endpoints and EC50 values for sublethal endpoints (reproduction and growth) of produced water to *C. dubia* and fathead minnows. Values expressed as percent produced water. Error bars are 95% confidence intervals.

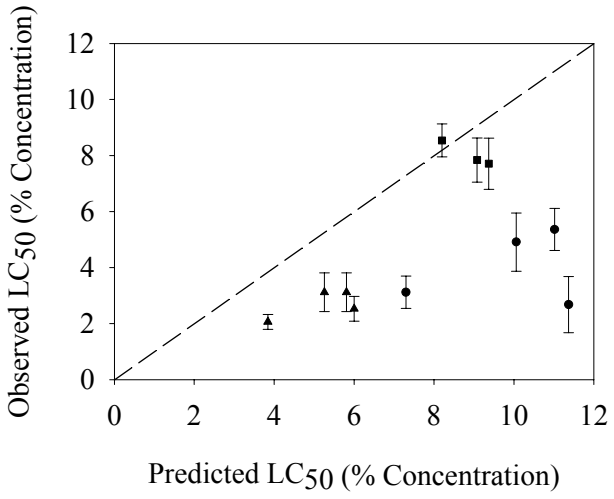

Figure 4. Observed produced water 48 h LC50 values (y-axis) plotted against LC50's predicted by the Ion Toxicity Model (x-axis) for *C. dubia* (▲), *D. magna* (●), and fathead minnows (■). The dashed line has a slope of 1 indicating agreement between observed and predicted endpoints. Error bars are 95% confidence intervals.

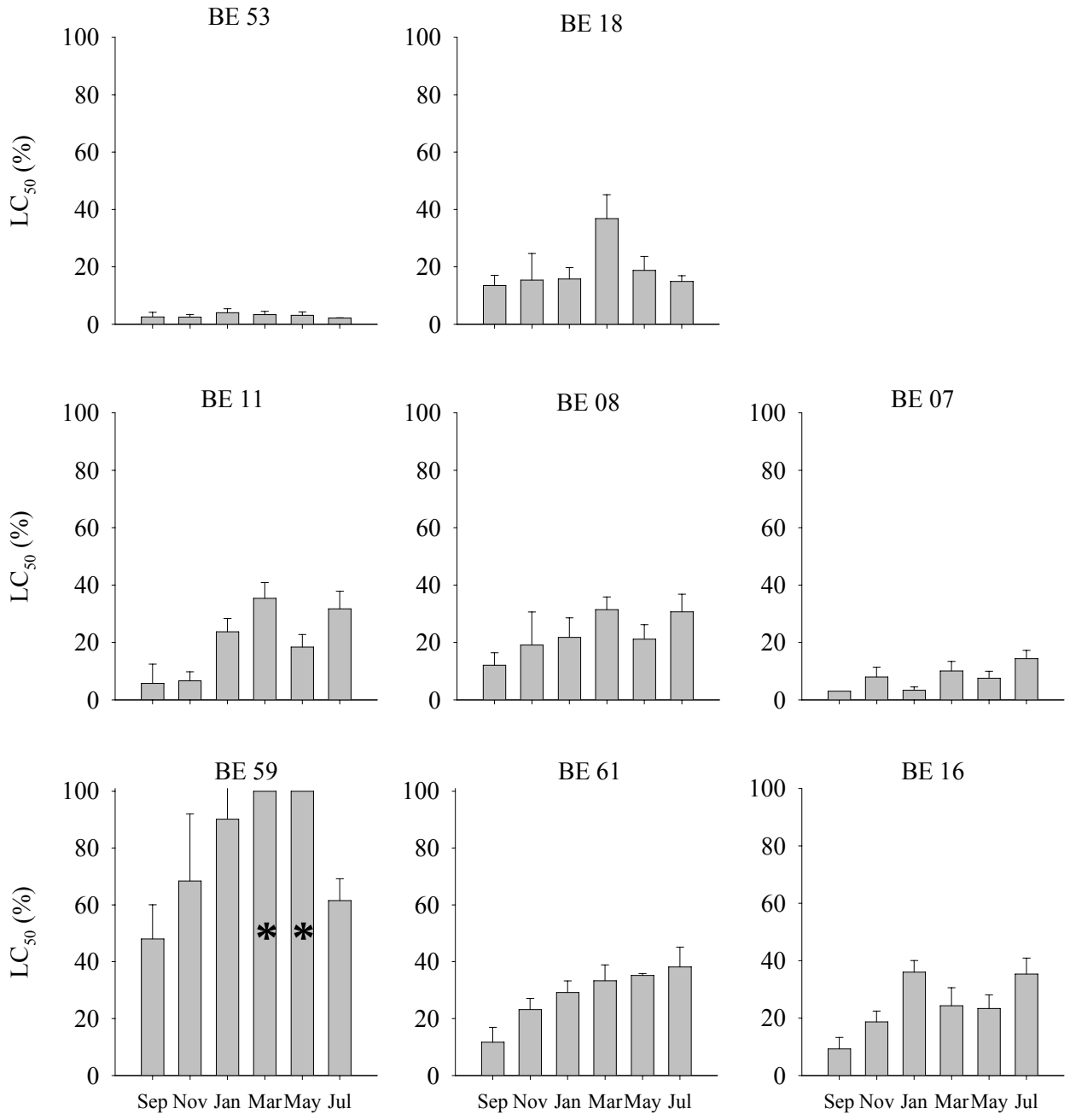

Figure 5. Acute toxicity of groundwater from selected wells to *D. pulex* expressed as 48 h LC50 values and 95% confidence intervals. An asterisk indicates insufficient toxicity to calculate an LC_{50}.

Advances in In-Situ Bioremediation of Chlorinated Solvents

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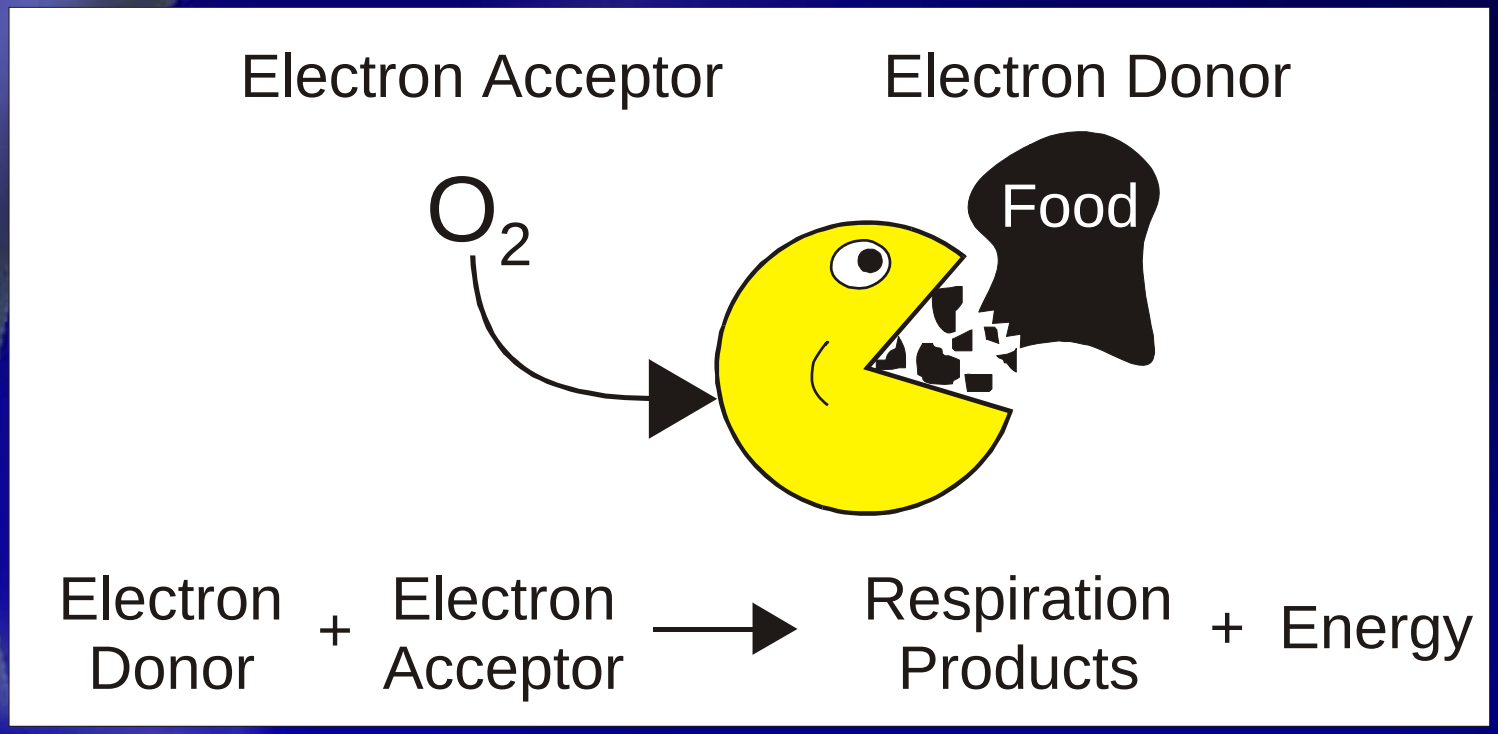
Tamzen W. Macbeth

October 19, 2006

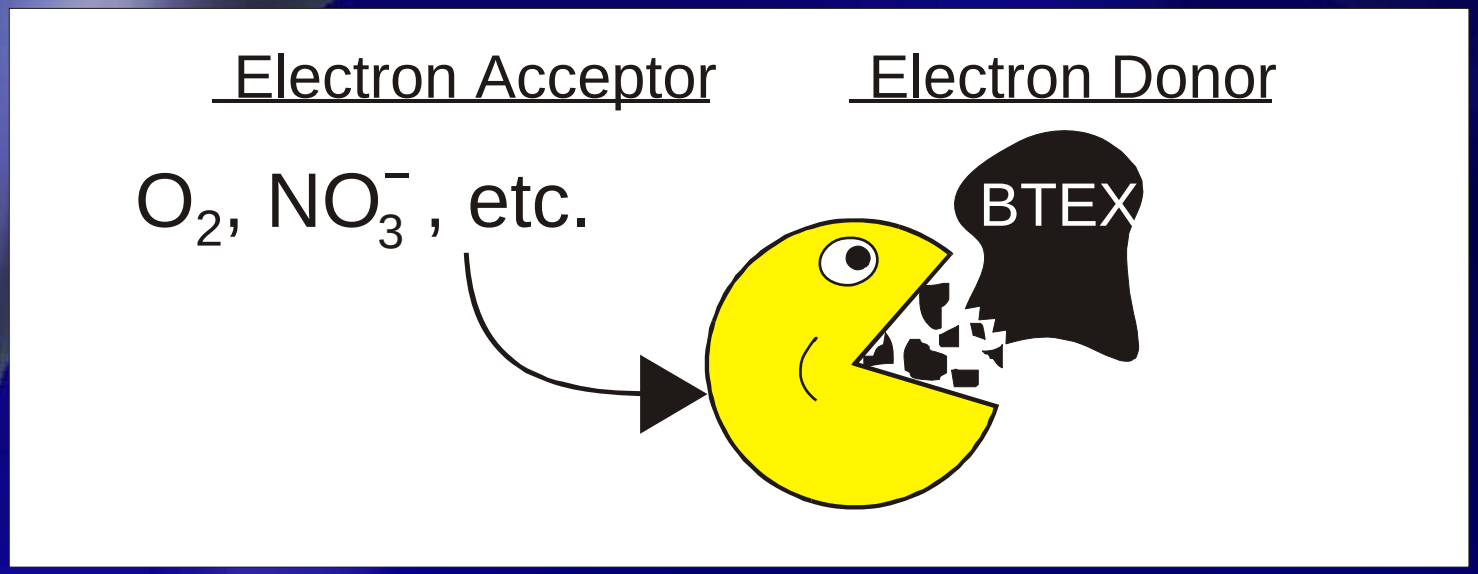
Presentation Outline

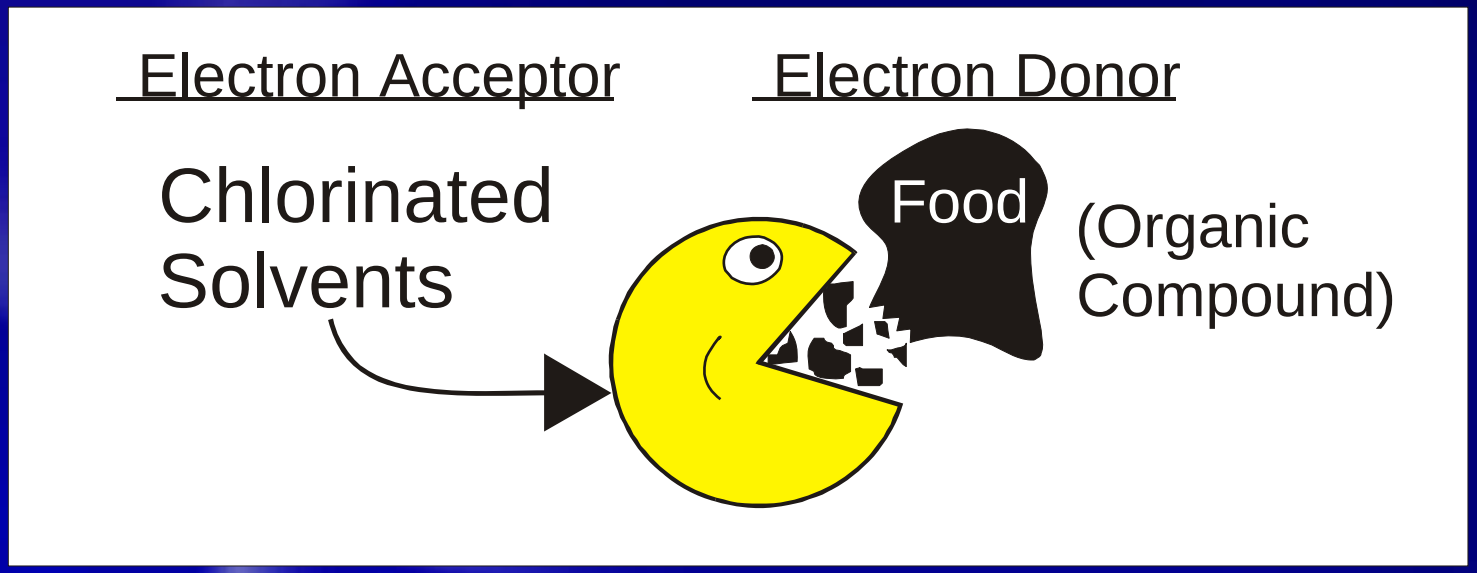
- Reductive dechlorination basics
- Bioremediation of source areas
  - Background
  - Case studies
- Bioaugmentation
  - Background
  - Case study
- Summary and conclusions

Microbial Metabolism

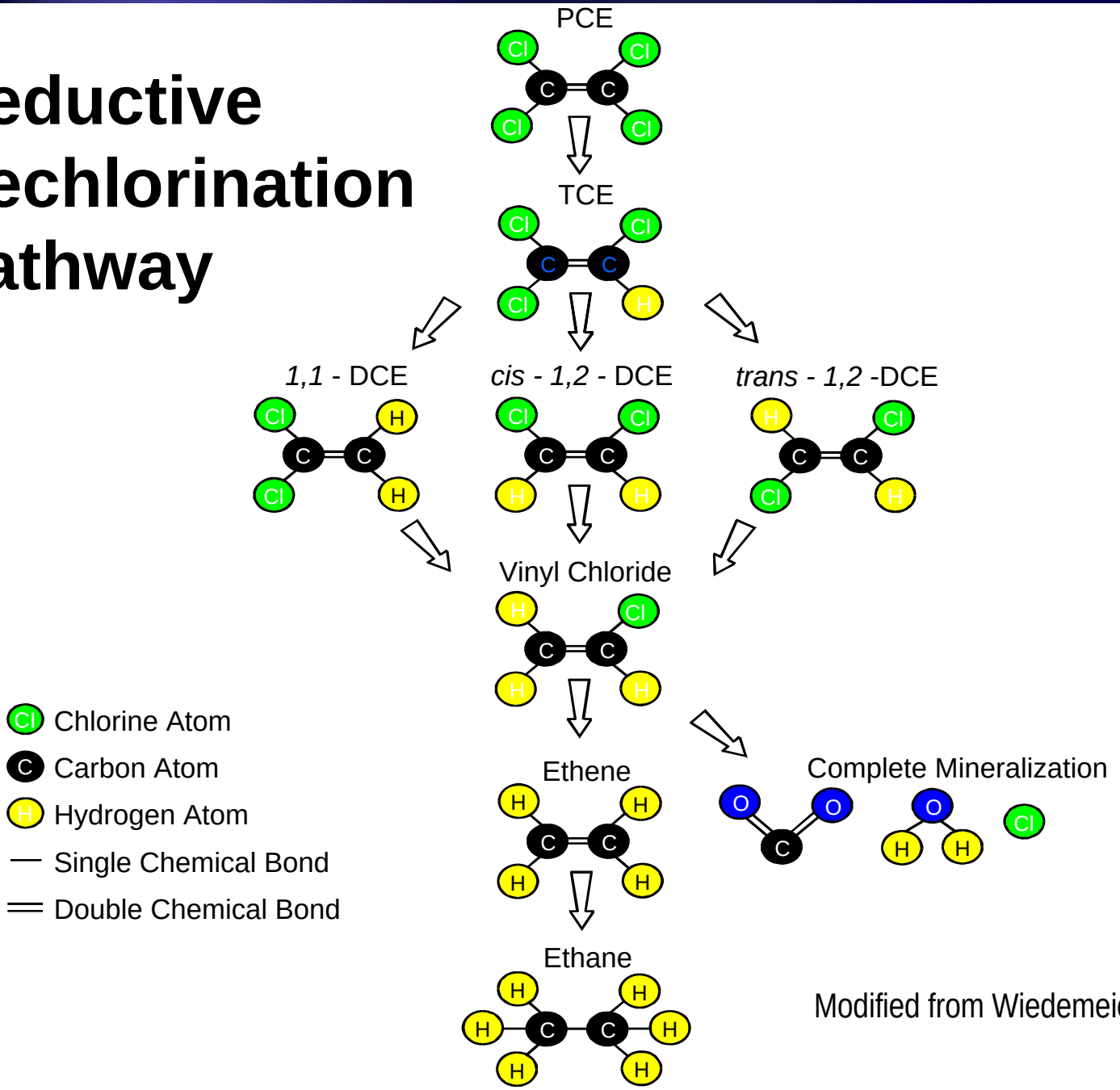


Bioremediation Metabolism



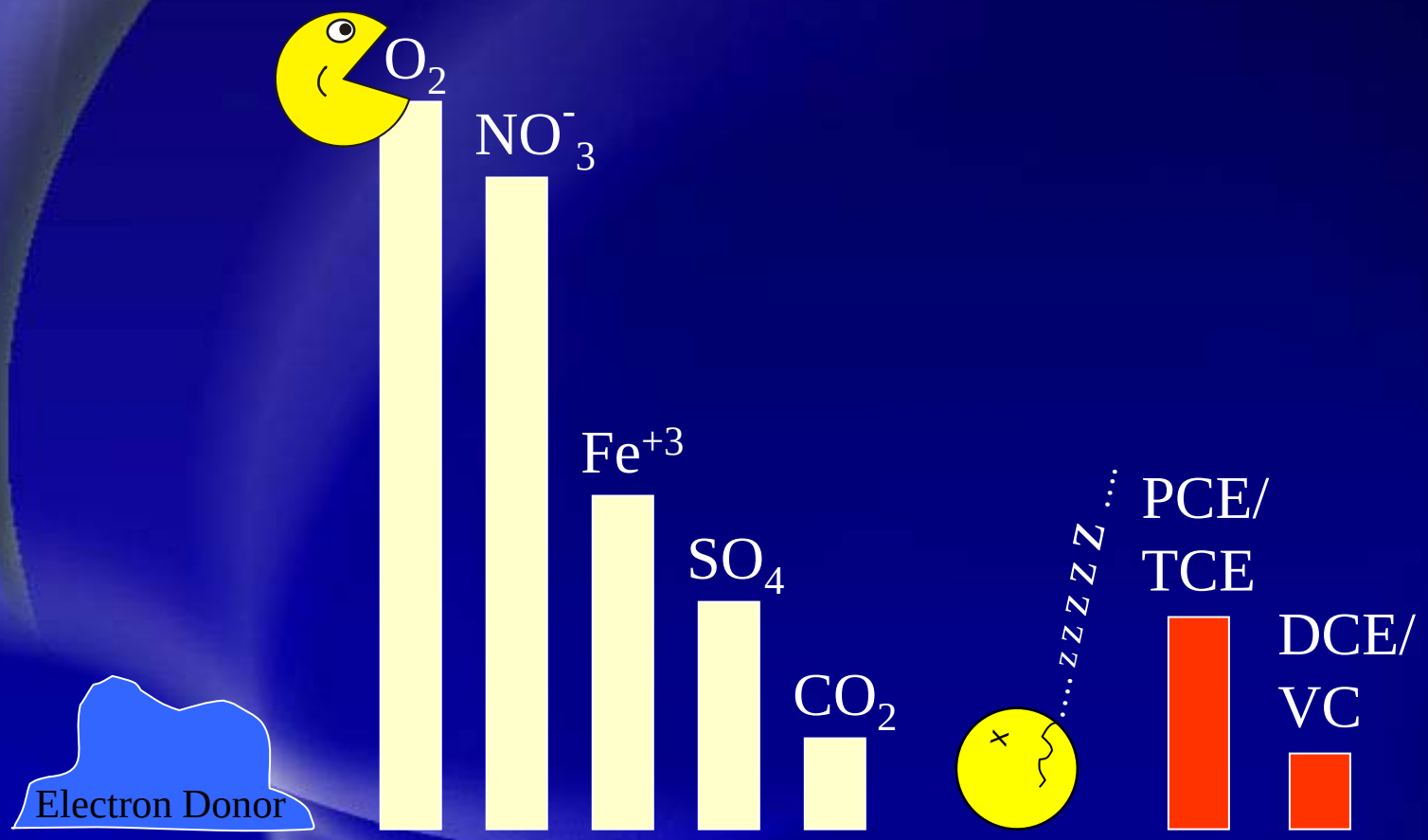


Reductive Dechlorination Pathway

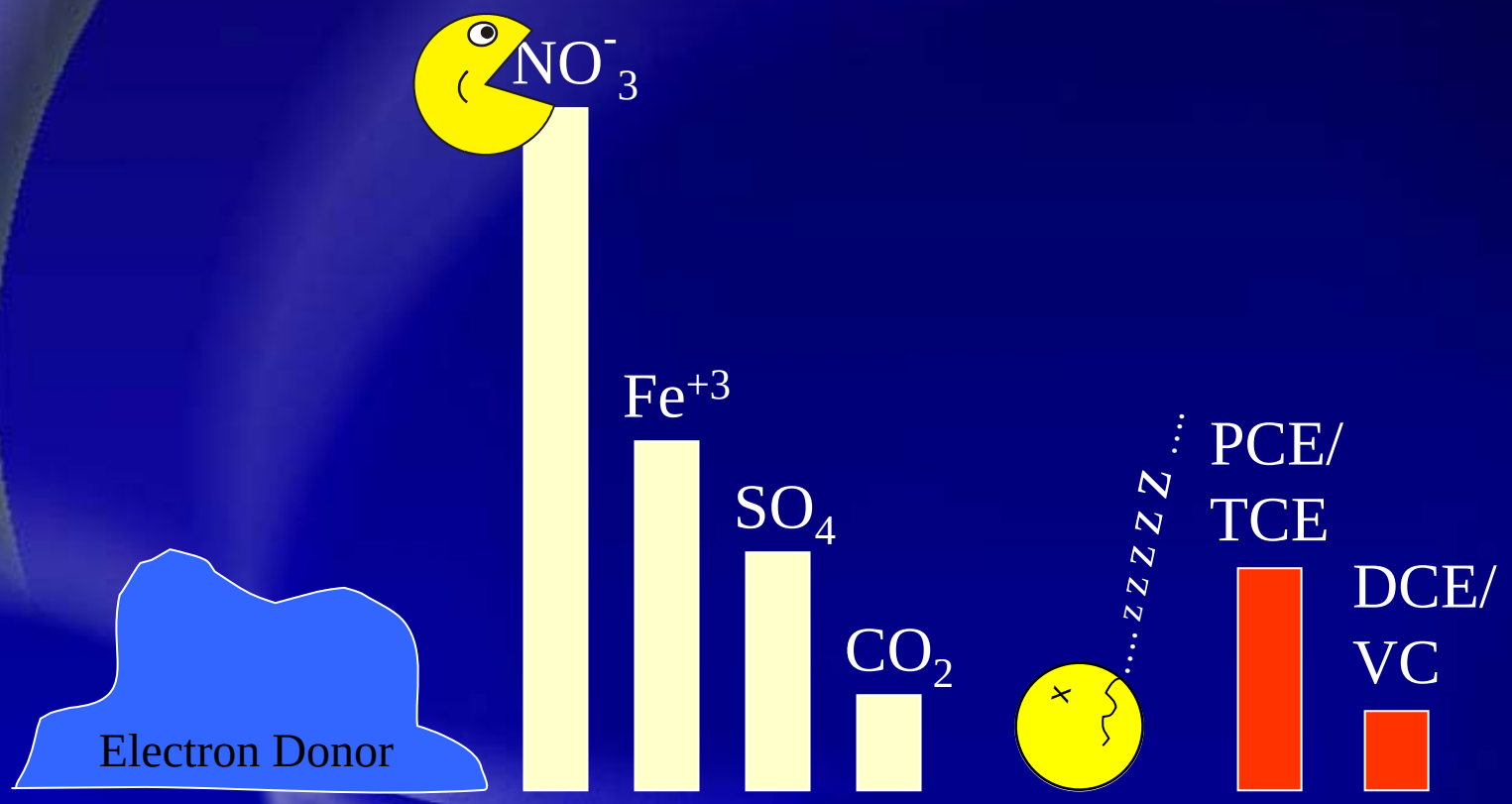


Modified from Wiedemeier et al., 1996

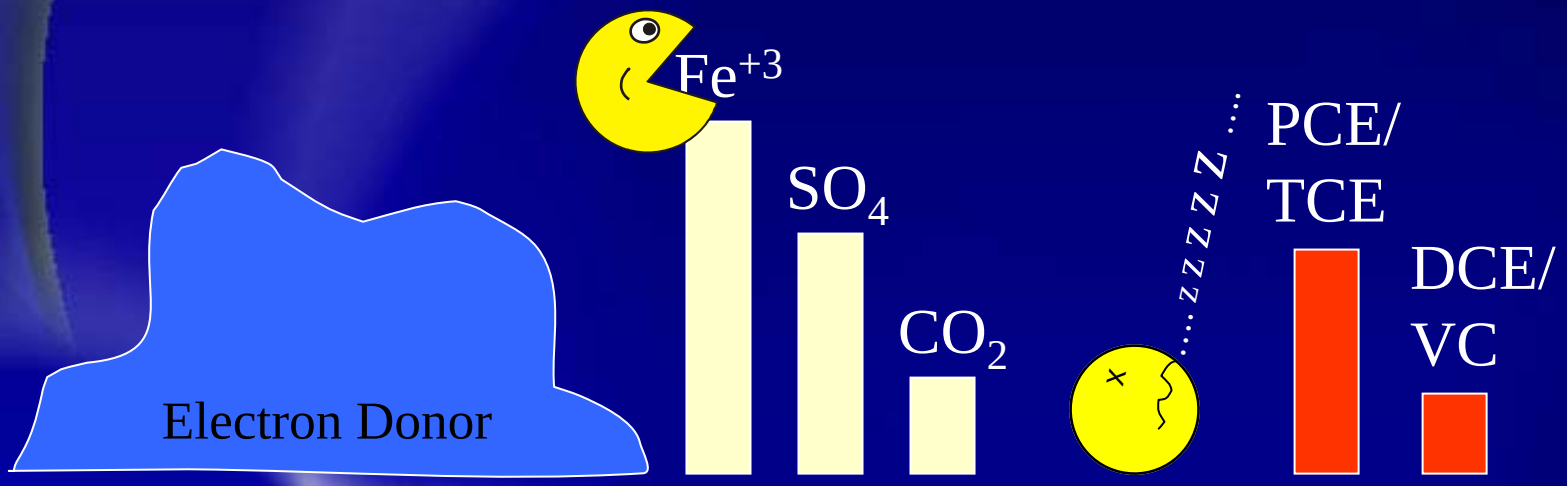
Electron Donor, Redox Conditions, and Dechlorination



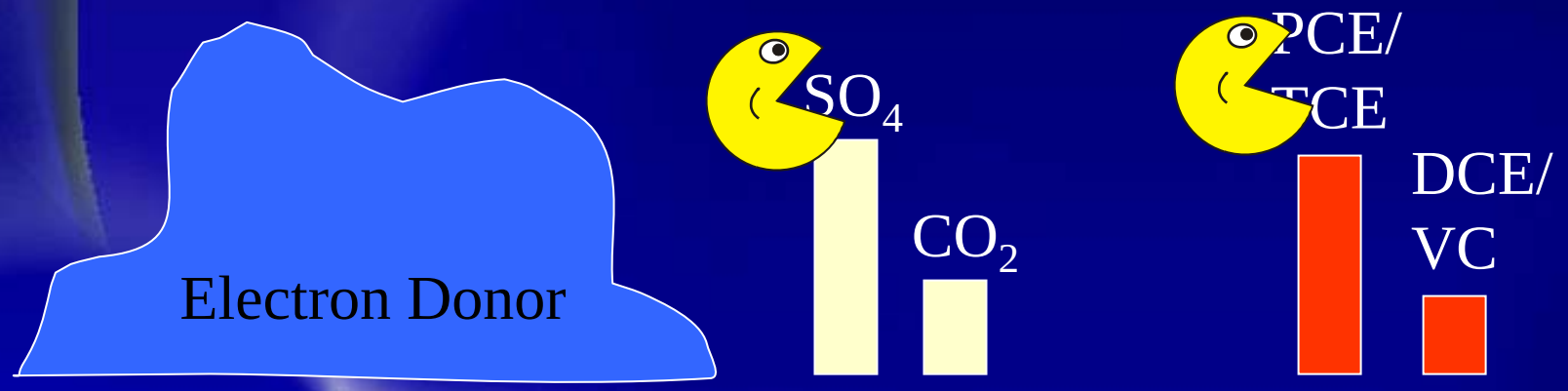
Electron Donor, Redox Conditions, and Dechlorination (continued)



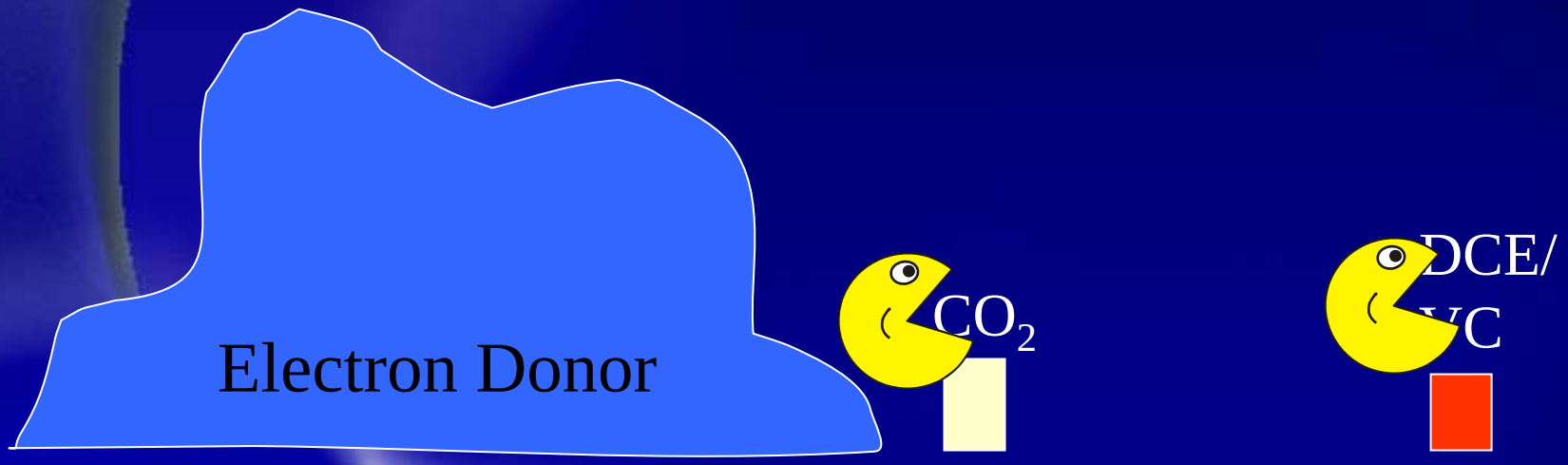
Electron Donor, Redox Conditions, and Dechlorination (continued)



Electron Donor, Redox Conditions, and Dechlorination (continued)



Electron Donor, Redox Conditions, and Dechlorination (continued)



A Paradigm Shift for Source Areas

- Conventional applications for *in situ* bioremediation limited to dissolved phase for two primary reasons:
  - Concerns about toxicity
  - Impact on nonaqueous sources thought to be no better than pump and treat
- New research reveals that *in situ* bioremediation may be extremely effective for chlorinated solvent source areas
- Key: Bioavailability Enhancement Technology™

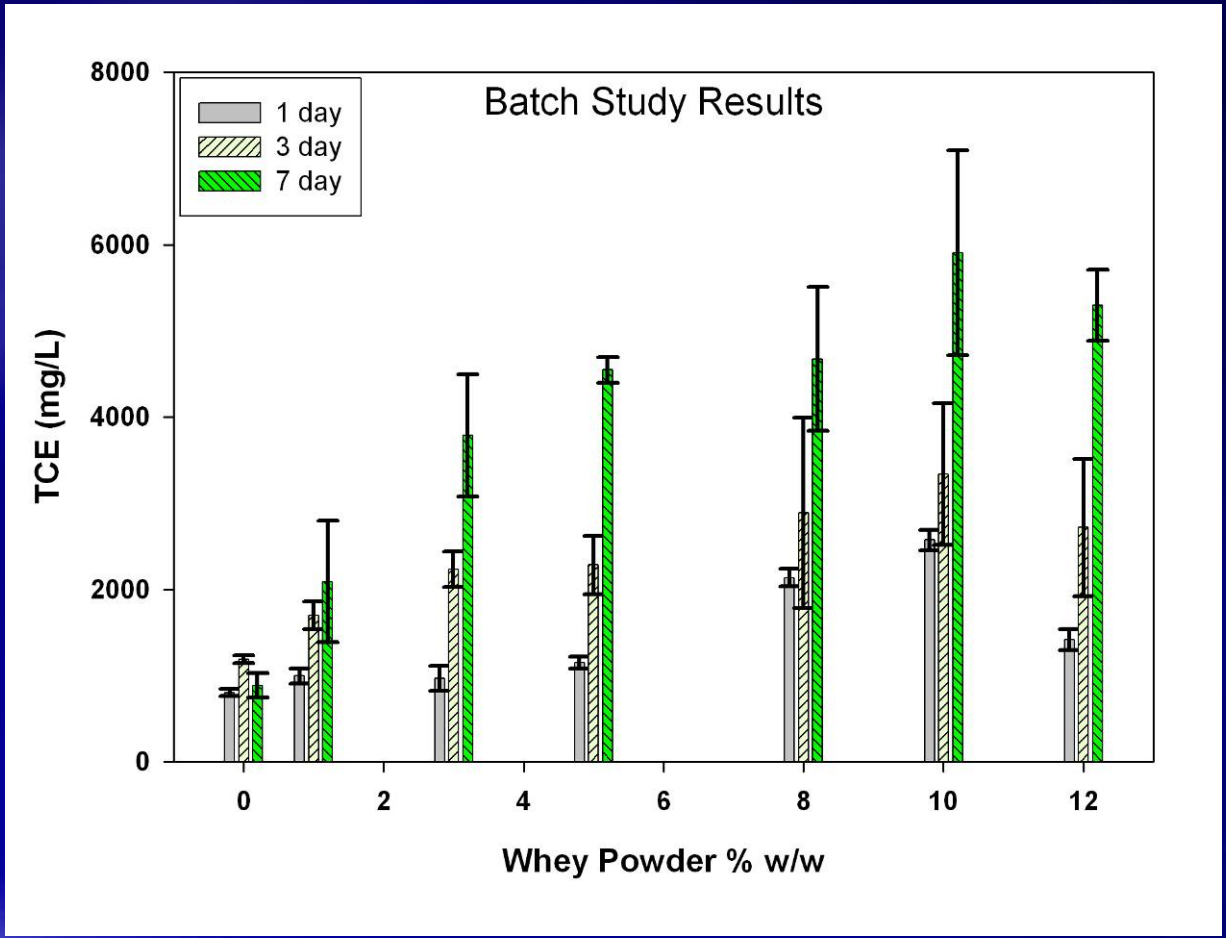
Mechanisms of Enhanced Mass Transfer

- Mechanisms for enhanced mass transfer:
  - Bioremediation removes contaminants from the aqueous phase, thereby increasing the driving force for mass transfer = $k(C_s-C)$ (Yang and McCarty, 2000; Carr et al., 2000; Cope and Hughes, 2001)
  - Increasing solubility and decreased hydrophobicity of degradation products greatly increases the aqueous contaminant loading (e.g., Carr et al., 2000)
  - The electron donor solution can be used to accelerate dissolution / desorption abiotically (e.g., Sorenson, 2002)

Mechanism 3 – Batch Study with Whey

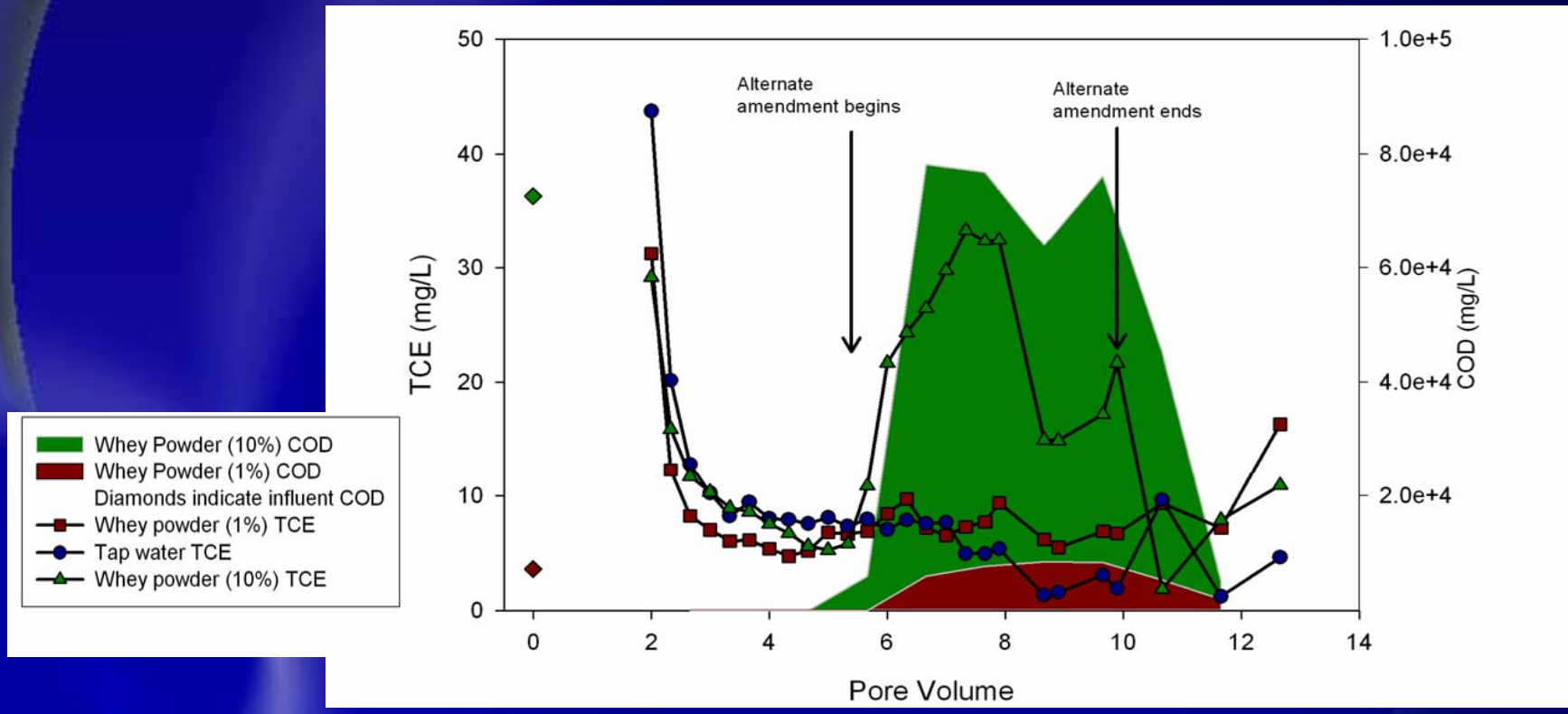
- **Whey enhanced DNAPL solubility greater than a factor of 5 at high concentrations**

  (Macbeth, T.W., L.O. Nelson, J.S. Rothermel, R.A. Wymore, and K.S. Sorenson, 2006. "Evaluation of Whey for Bioremediation of Trichloroethene Source Zones." Bioremediation Journal, in press.)



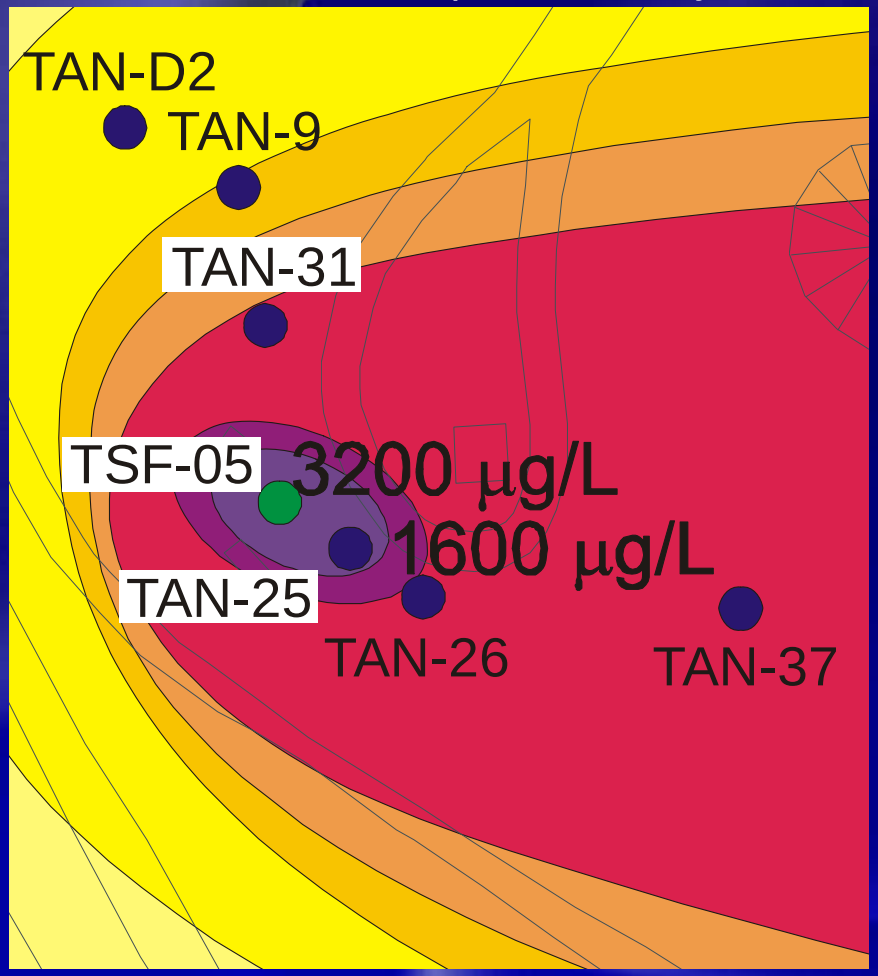
Mechanism 3 – Column Study with Whey

- **High concentrations of whey solution increased mass removal by factor of ~6** (Macbeth, T.W., L.O. Nelson, J.S. Rothermel, R.A. Wymore, and K.S. Sorenson, 2006. "Evaluation of Whey for Bioremediation of Trichloroethene Source Zones." *Bioremediation Journal*, in press.)

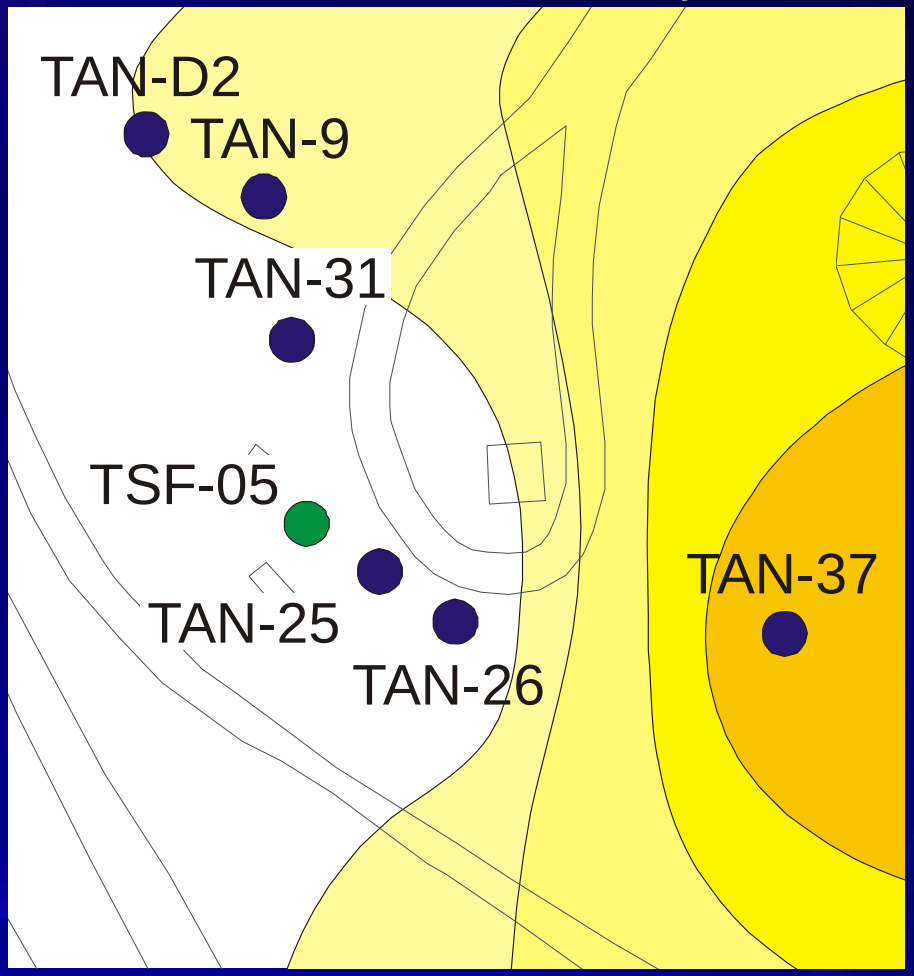


First Field Results: TCE Isopleth Contours in Residual Source Area Pre- and Post-Sodium Lactate Injection

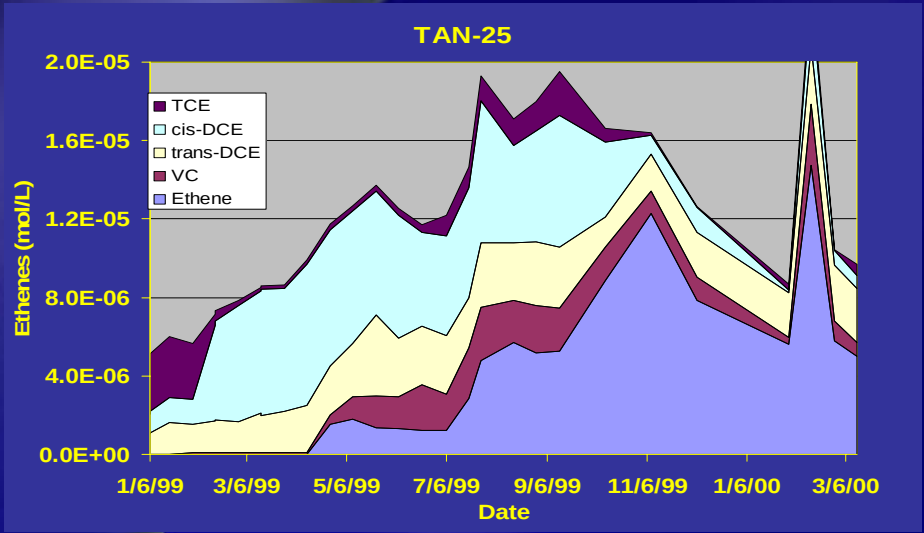
TCE Concentrations pre-lactate injection

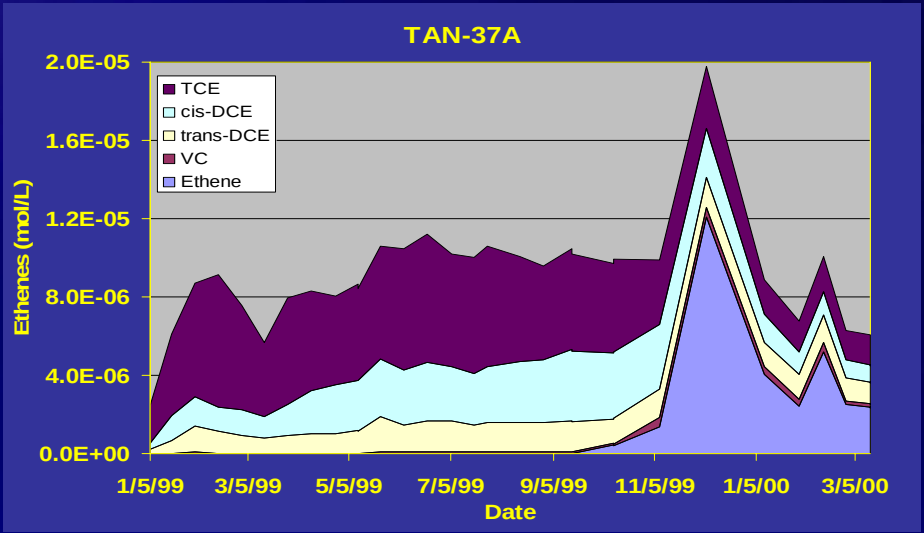


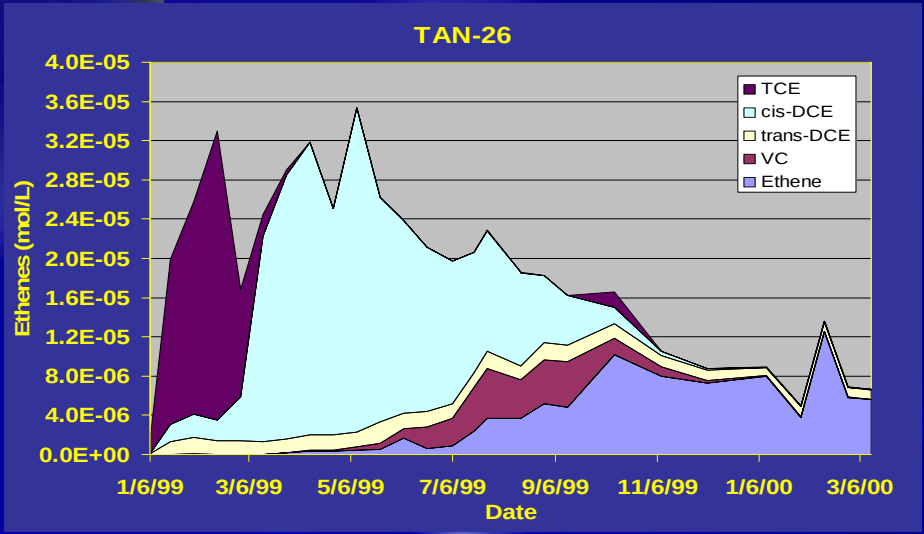
Effect of 21 months of lactate injections

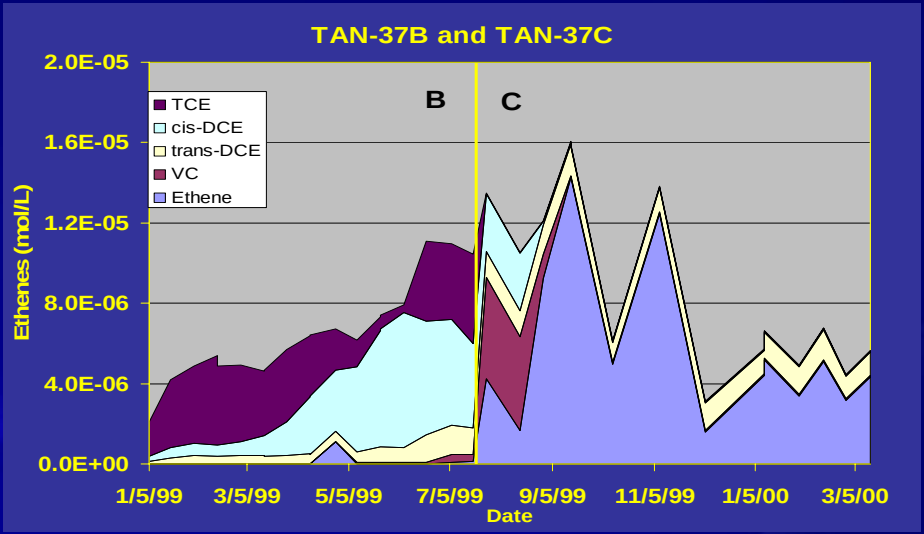


Long-Term Dechlorination



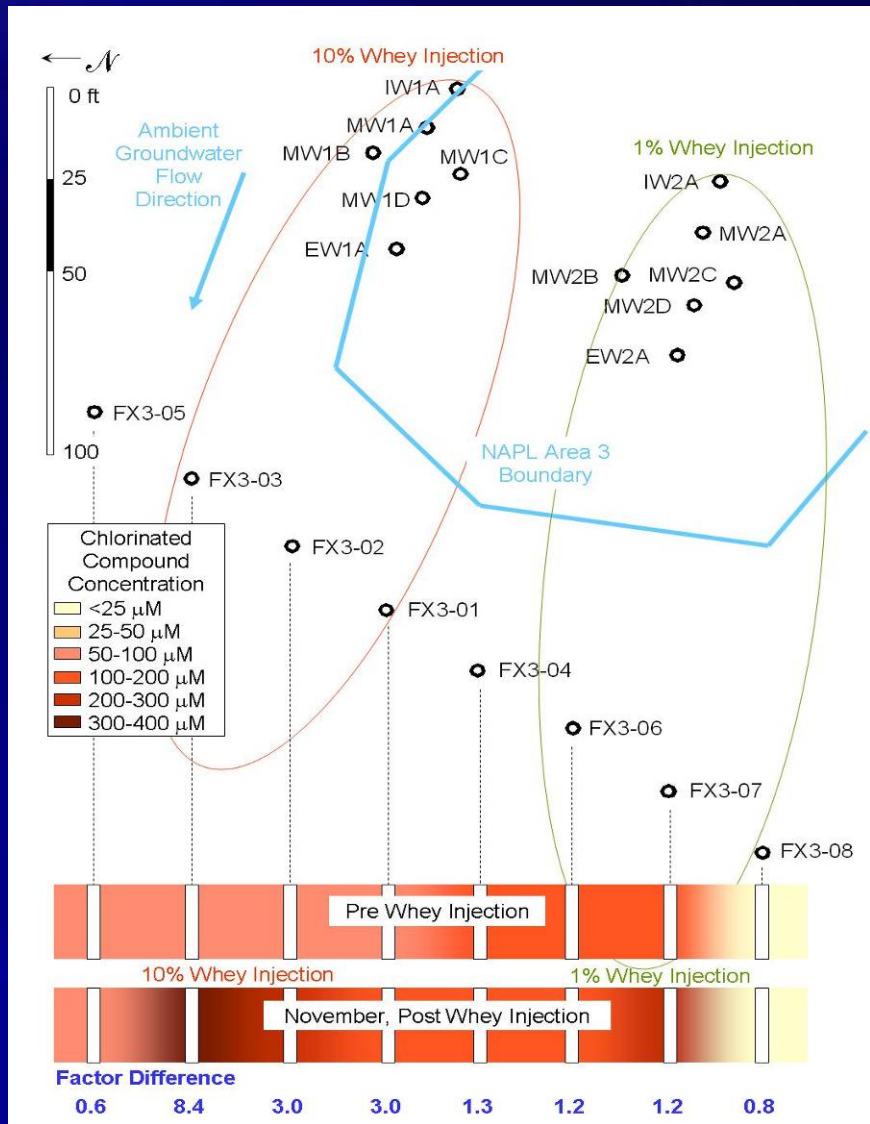






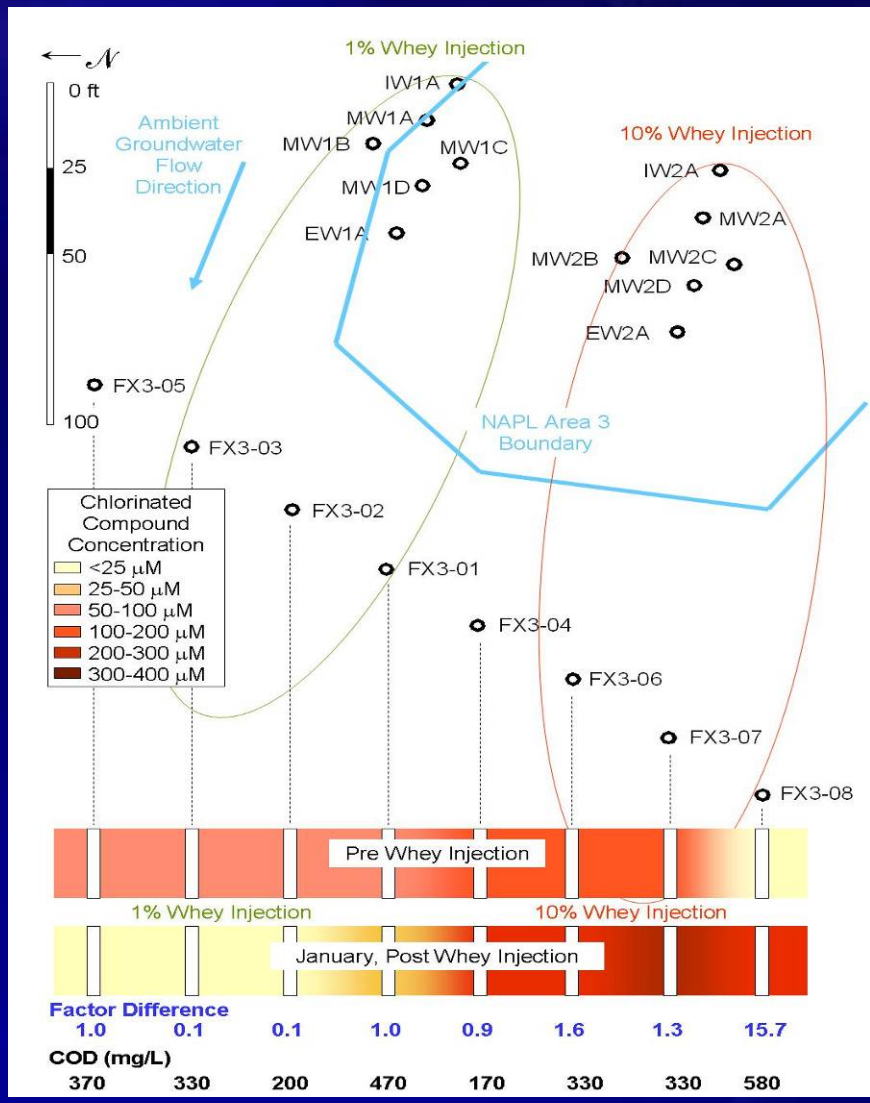
Ft. Lewis Demonstration: Downgradient Response

- 8 wells showed downgradient impact of whey injections
- Injection Strategy 1:
  - Wells downgradient of Cell 1 showed factor of 3-8 increase in CVOCs
  - Wells downgradient of Cell 2 showed essentially no change



Ft. Lewis Demonstration: Downgradient Response

- Injection Strategy 2:
  - Wells downgradient of Cell 1 decreased to as low as 10% of baseline
  - Wells downgradient of Cell 2 increased by a factor of 2 to 13 relative to previous month

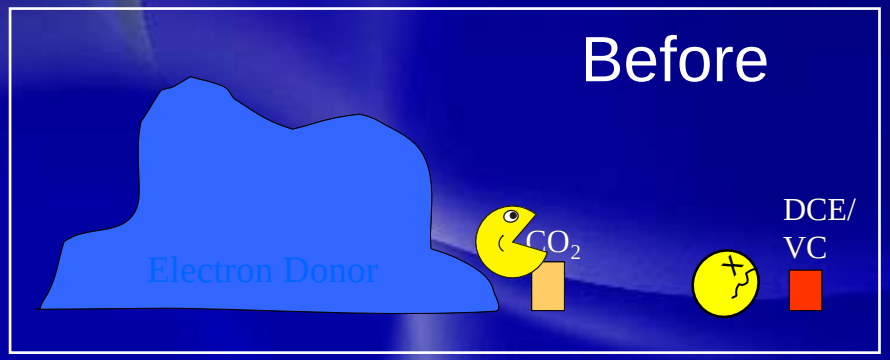


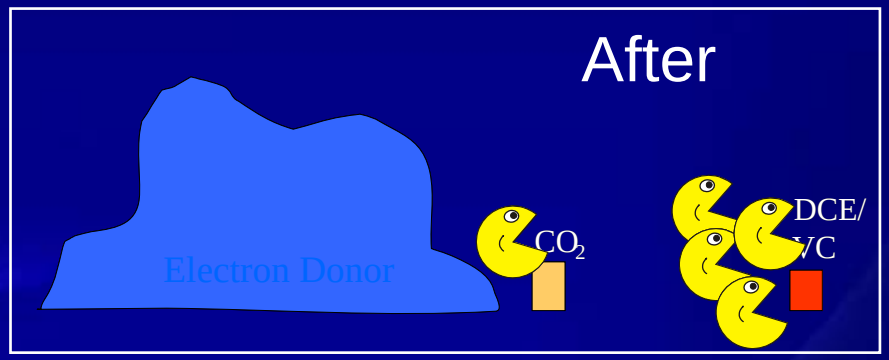
Bioaugmentation Background

- At some sites, dechlorination “stalls” at c-DCE rather than proceeding to ethene
- Only one species of bacteria has been identified that is capable of complete dechlorination of PCE or TCE to ethene in a pure culture: *Dehalococcoides ethenogenes*
- Characterization all over the world has revealed that *D. ethenogenes* is present in a wide variety of environments, but is not ubiquitous.
- A survey of dechlorinating sites in North America and Europe, *D. ethenogenes* was detected at all 21 sites with complete dechlorination, and none of the 3 sites with DCE stall.

Bioaugmentation Background (cont.)

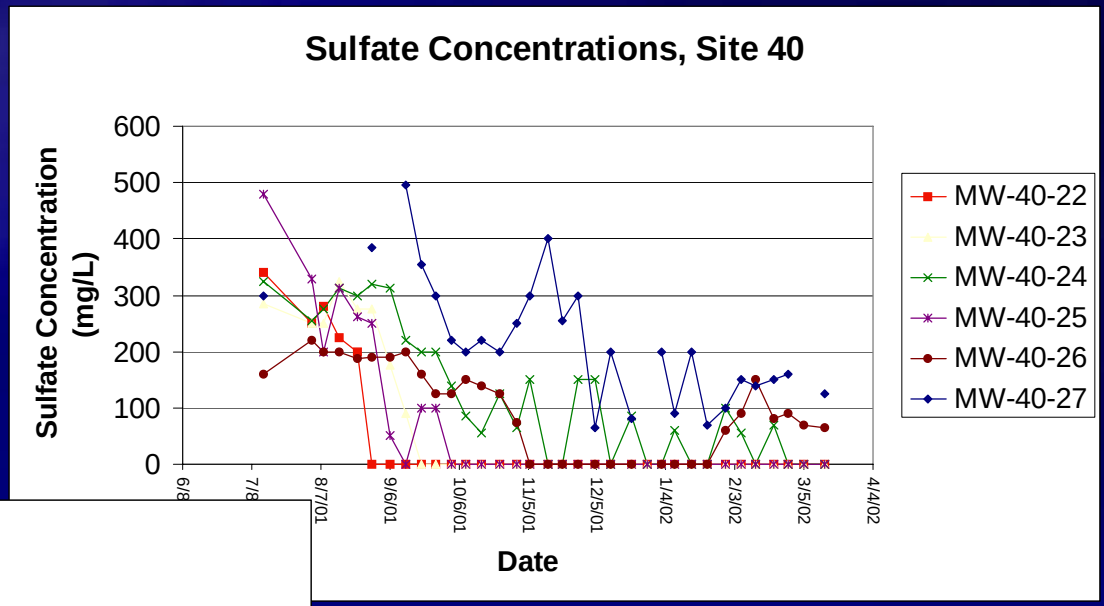
- Once it is determined a biological limitation exists at a site, bioaugmentation becomes a viable option
- This application involves the addition of a *D. ethenogenes*- containing microbial culture to site groundwater to facilitate complete dechlorination to ethene

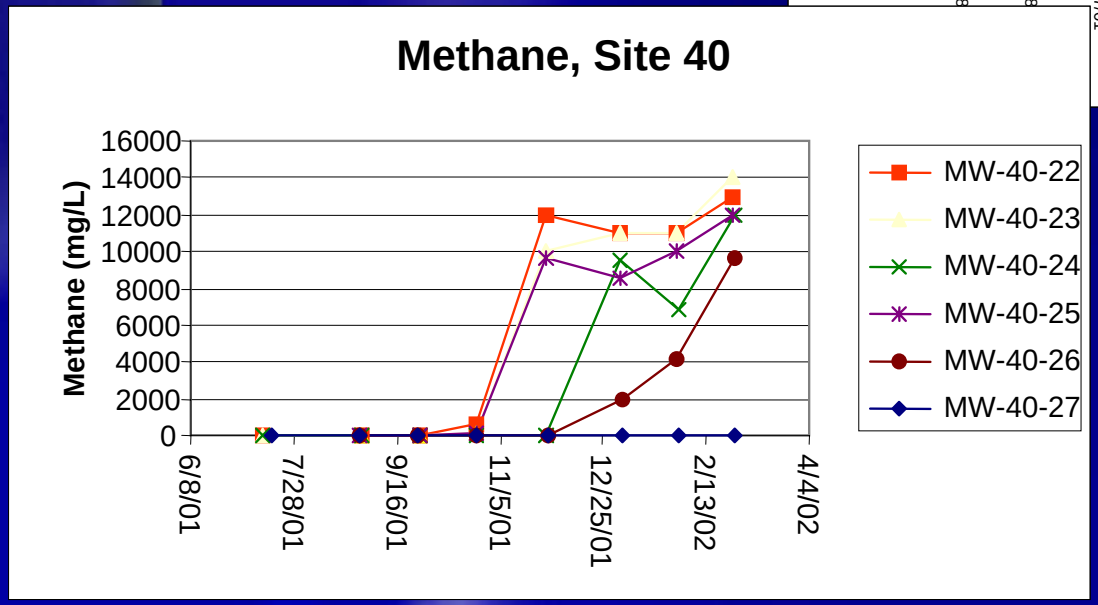




Bioaugmentation at Naval Weapons Station Seal Beach

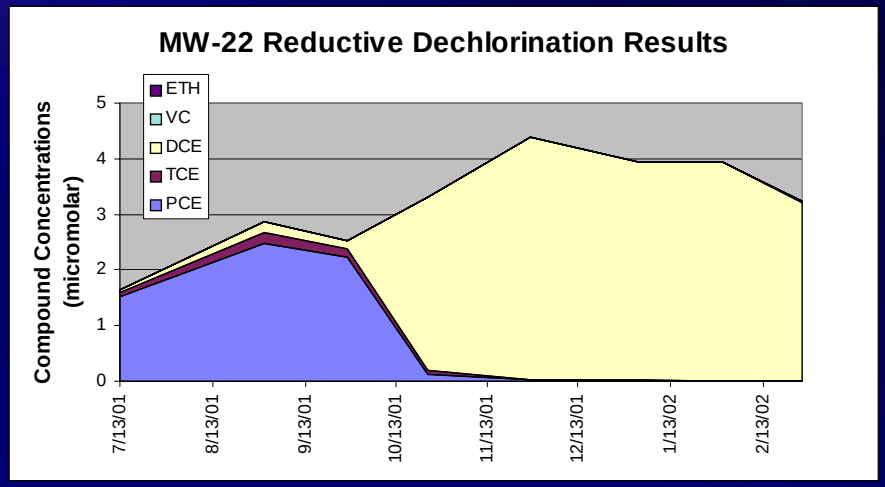
- Sodium lactate injections performed for 6 months
- Sulfate was depleted within 2 months and methanogenesis was significant within about 3 months

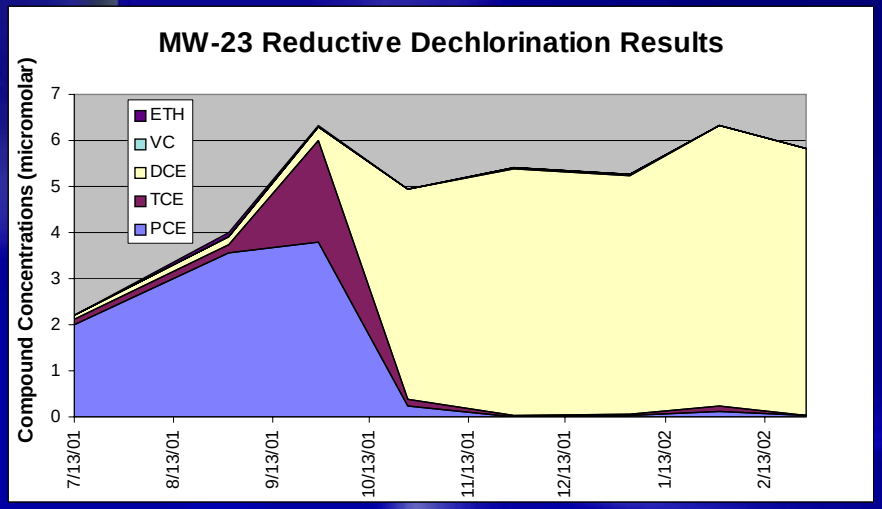


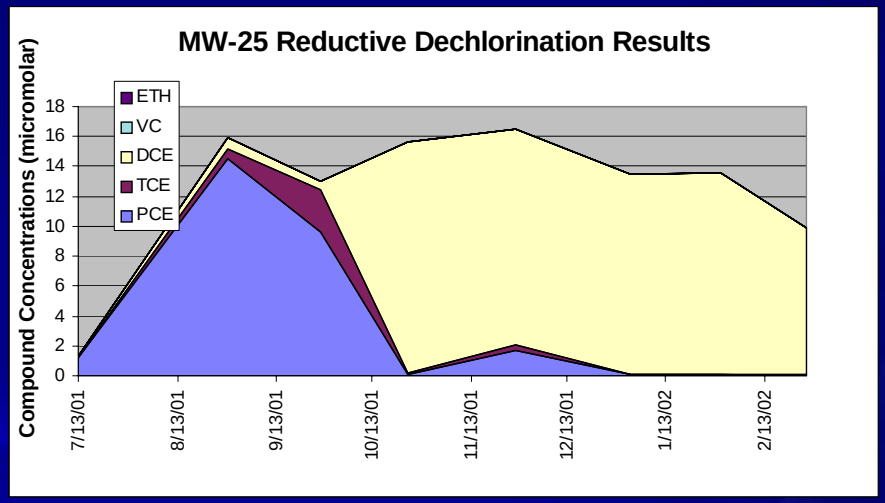


Naval Weapons Station Seal Beach (continued)

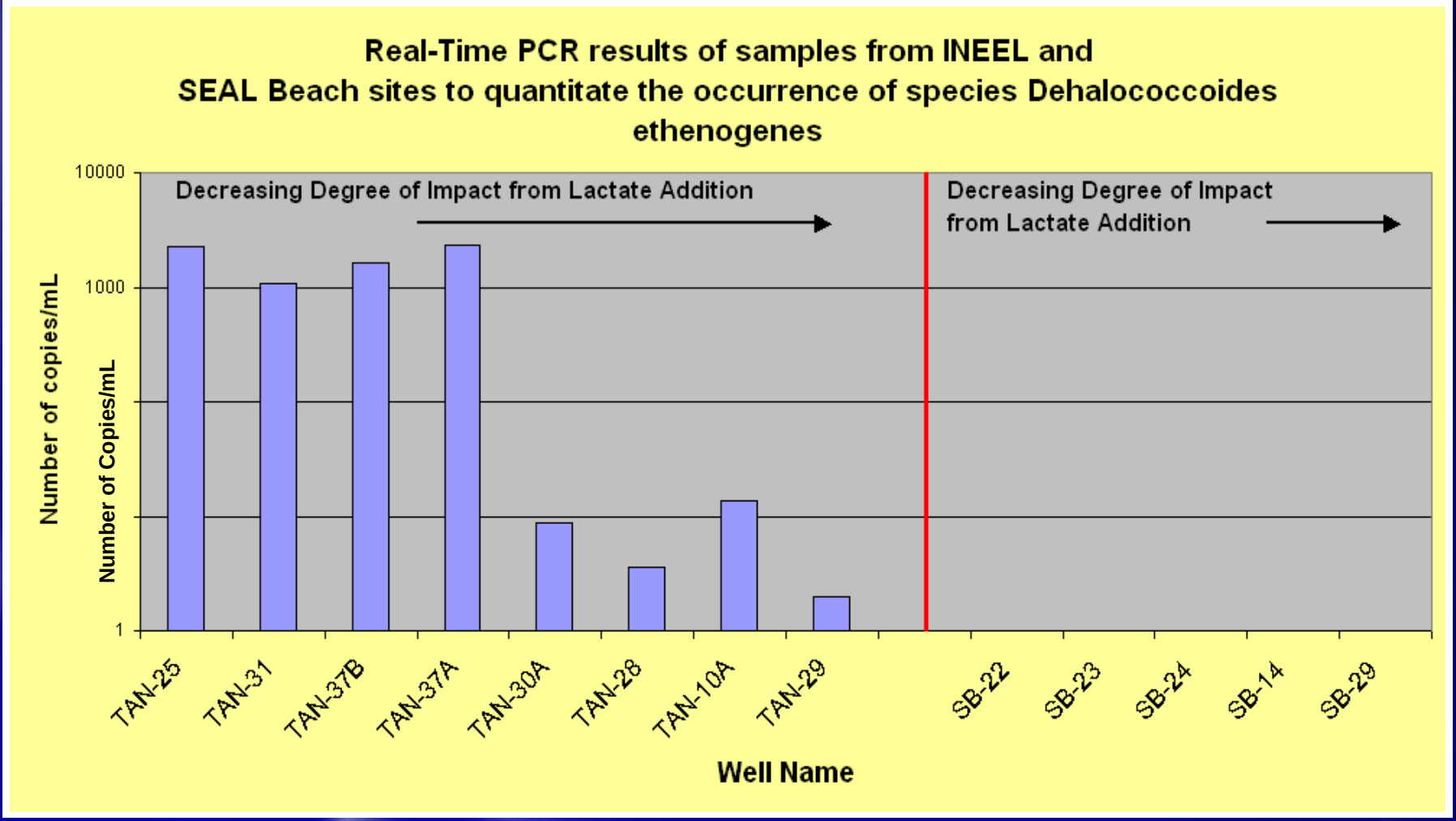
- **Dechlorination to *cis*-DCE in about 3 months, but stalled there**





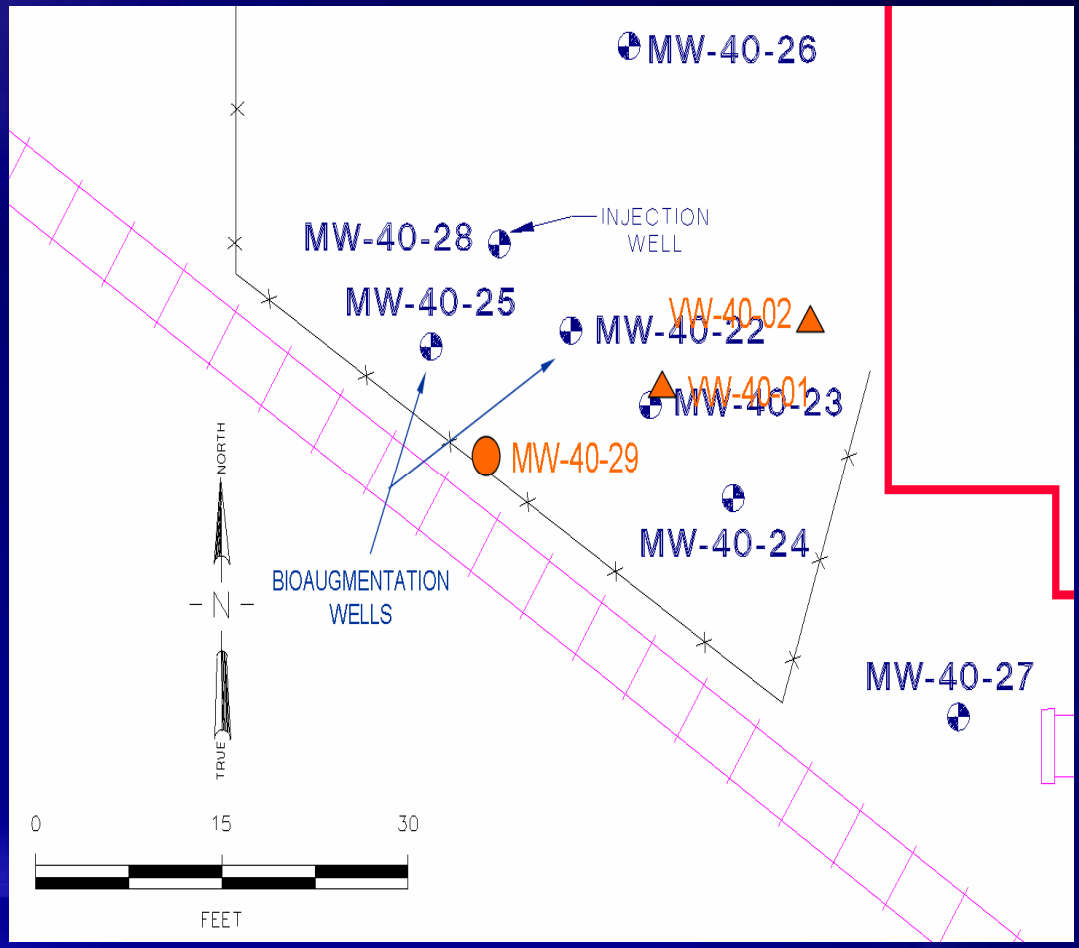


DNA Analysis for *Dehalococcoides spp.*



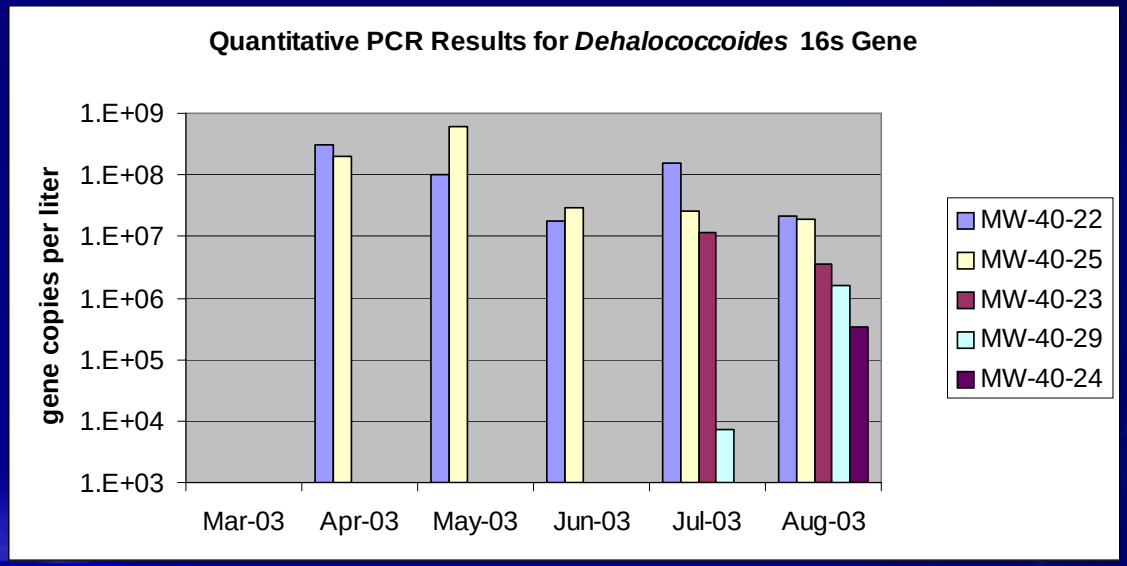
Bioaugmentation Pilot Test

- Bioaugmentation in April 2003 through addition of 20 L of *D. ethenogenes*-containing culture (KB-1) in each of two inoculation wells
- Some conversion of DCE to VC within 1 month of inoculation; complete degradation in about 6 months



Bioaugmentation – Naval Weapons Station Seal Beach (continued)

- DNA Analysis - Real-time polymerase chain reaction (PCR) to monitor survival and proliferation
- Dehalococcoides DNA detected:
  - 2.4 m downgradient after 3 months
  - 4.9 m downgradient and 8 ft upgradient in 4 months
  - 12 m downgradient in 11 months

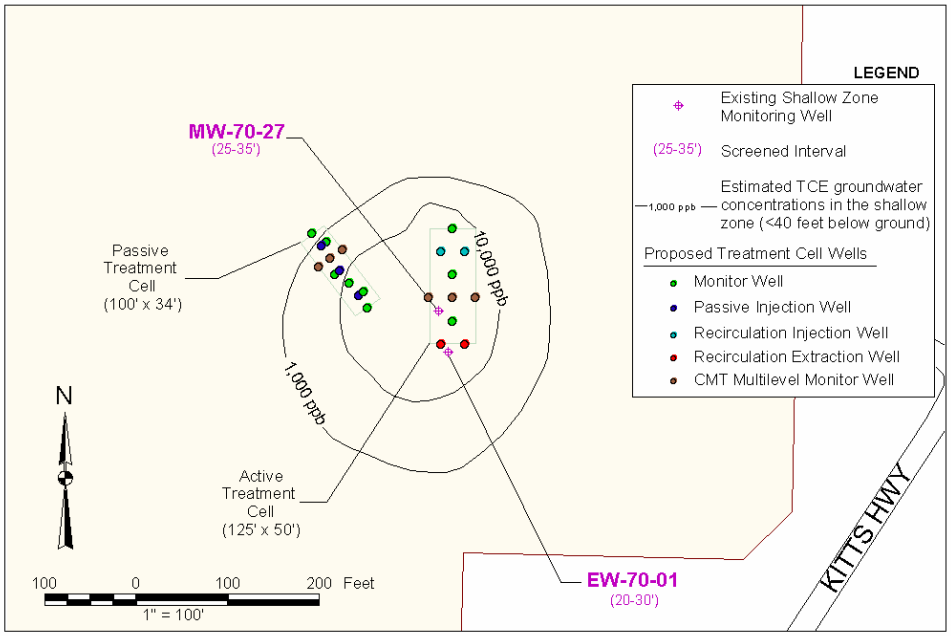


What About Scale-Up?

- Most demonstrations to date at a scale of tens of feet
- Scale-up will require either:
  - Long-times for natural bacterial distribution
  - Large volumes of inoculum at multiple points
- Can this be accomplished cost-effectively?

Potential Scale-up Strategies for Bioaugmentation

- Active recirculation
- Passive inject and drift
- One-time inundation
- Redistribution from one area of the site to another
- ESTCP project is underway to compare the first two approaches
- CDM has used the last approach at two industrial sites



* Note - Concentration contours from Geosyntec Consultants 2005 Draft Technical Memorandum. Contours are based on September 2005 permanent monitoring wells groundwater concentrations including MW-70-27 and EW-70-01.

Figure 3-4
Proposed Treatment Cell Locations
NAVWPSTA Seal Beach IR Site 70
Seal Beach, California

Summary

- Bioremediation shows significant promise for accelerating chlorinated solvent source removal under a variety of conditions
- ITRC's Bioremediation of DNAPLs team has published a technology overview document in 2005
- Bioaugmentation is a viable mitigation strategy for c-DCE stall
- Cost effective scale-up approaches are being developed and applied

CDM

Elucidation of Aerobic Cometabolism as an Important Intrinsic Degradation Mechanism for MNA of Chlorinated Ethene Hydrocarbons

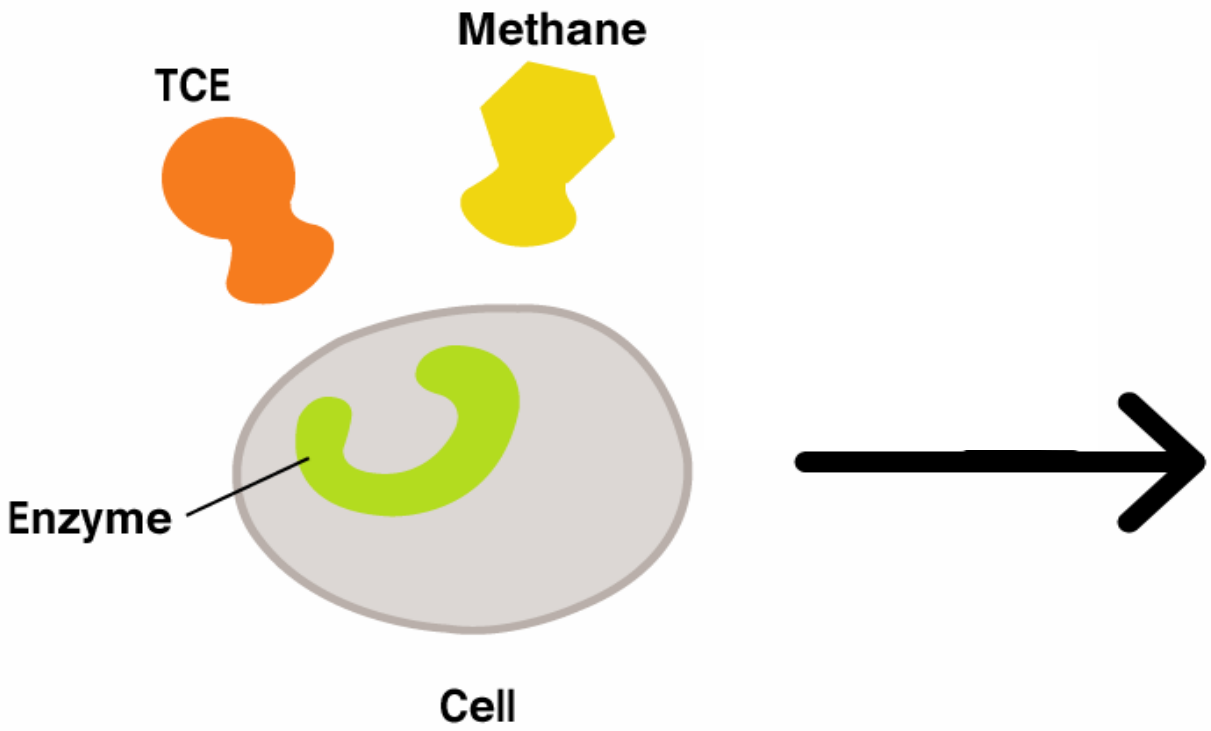
Ryan A. Wymore, P.E.
Kent S. Sorenson, Jr., Ph.D., P.E.
Hope Lee, Ph.D.

October 19, 2006

Cometabolism

- Bacterial enzymes have active sites that transform their primary substrates (e.g. methane)
- Some bacteria have enzymes that fortuitously transform chlorinated solvents under aerobic conditions
- The bacteria gain no carbon or energy from this process

Cometabolism



carbon dioxide,
water,
chloride
(from TCE)

Cometabolism – Field Applications

- Several field studies conducted in the late 1980's and early 1990's, (Semprini et al, 1990; Semprini et al, 1991; Hopkins and McCarty, 1995; McCarty et al, 1998)
- In all cases, amendments of the primary substrate and oxygen were required to stimulate cometabolism
- Since most intermediate byproducts are transient, the only means to assess performance is to monitor the disappearance of the contaminants themselves

Implementing MNA for Chlorinated Solvents

- The EPA developed the "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater," (EPA, 1998)
- The protocol provides a means for assessing site conditions and evaluating MNA through biodegradation as a remedy
- Reductive dechlorination is primary biodegradation process that should be considered for MNA
- The protocol gives no consideration to aerobic cometabolism as a significant mechanism for biodegradation

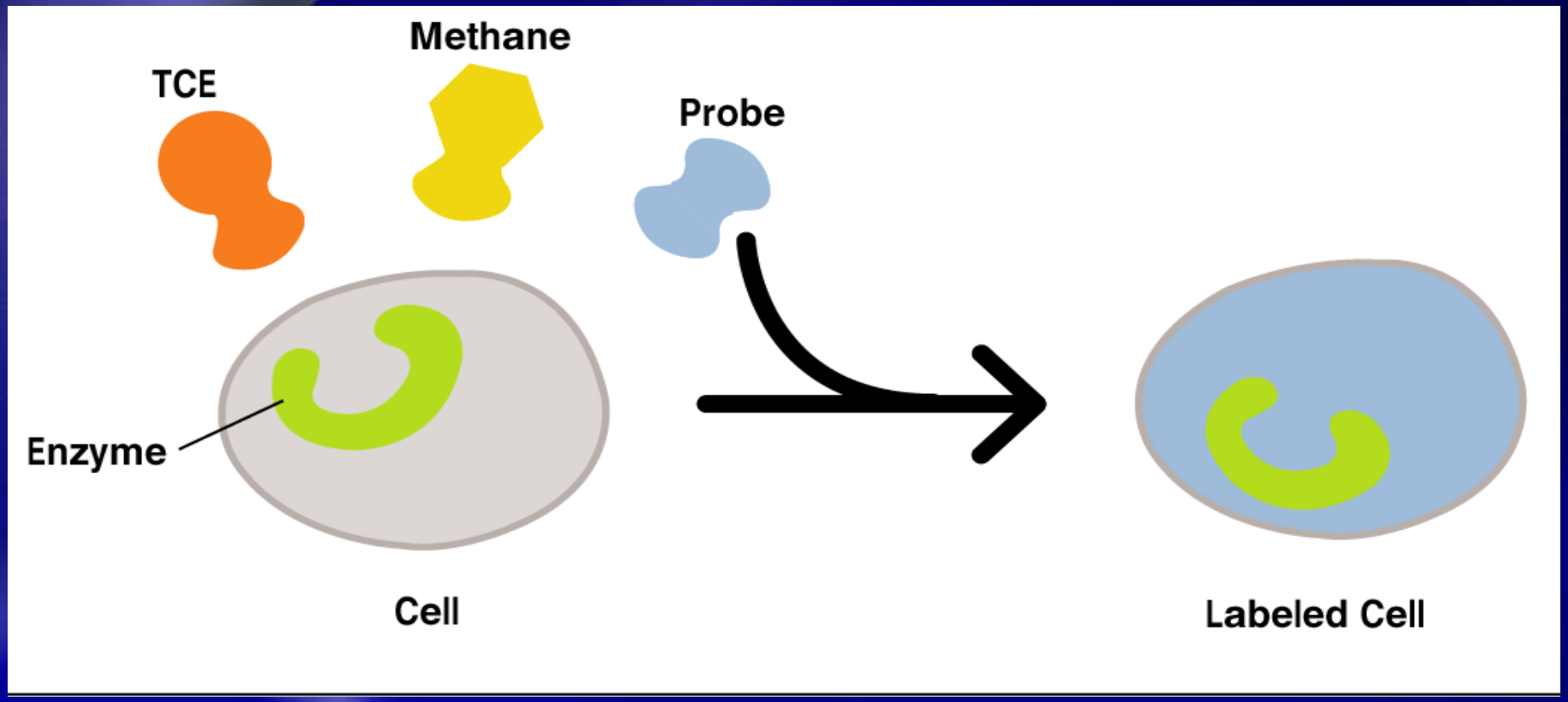
Implementing MNA for Chlorinated Solvents

- The protocol is a valuable tool for assessing MNA at most sites
- However, it is possible to select MNA as a remedy for a site that does not “score” well using the protocol
- Recent work has shown that aerobic biodegradation processes can be environmentally significant when compared to remedial timeframes
- An innovative suite of assays can be used to document intrinsic aerobic cometabolism

Activity-Dependent Enzyme Probes

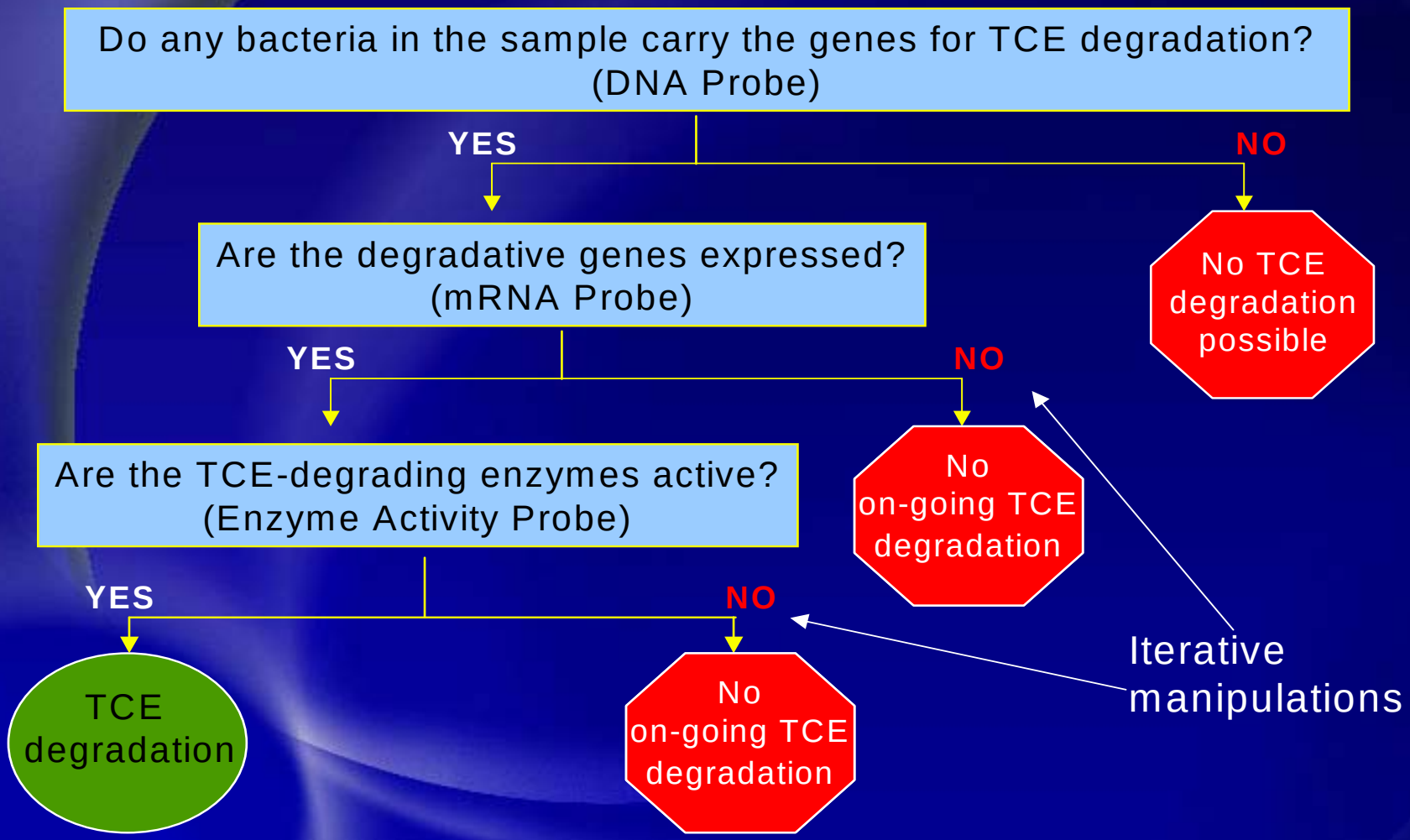
- Enzyme-activity probes provide direct evidence for enzyme presence and activity:
  - four separate toluene oxygenases
  - soluble methane monooxygenase (sMMO)
- Signal is detected only when the enzyme is present and active

Activity-Dependent Enzyme Probes



Other natural substrates that support TCE oxidation: toluene, ammonia, phenol

Activity-Dependent Enzyme Probes

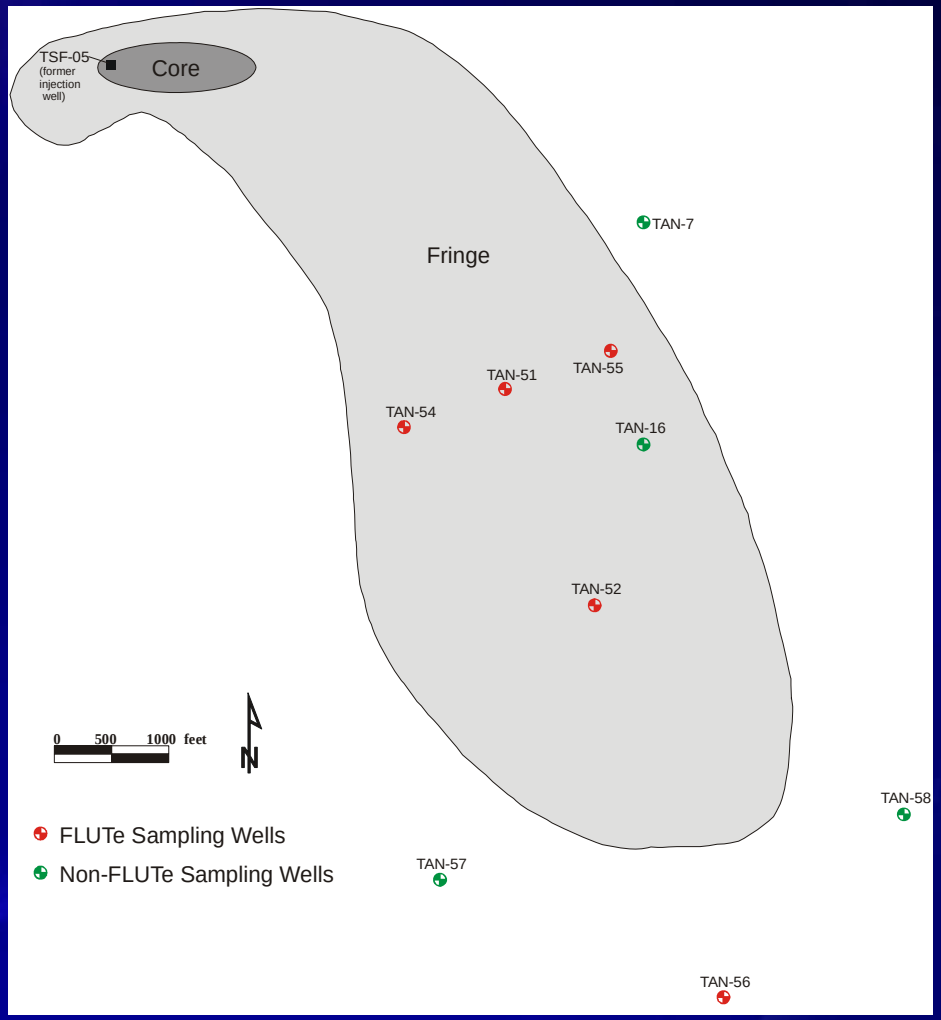


Molecular Techniques

- Molecular probes for toluene and methane-oxidizing microbial populations
- Used to provide context for the enzyme probes:
  - Detecting functional genes
  - Assessing levels of enzyme production

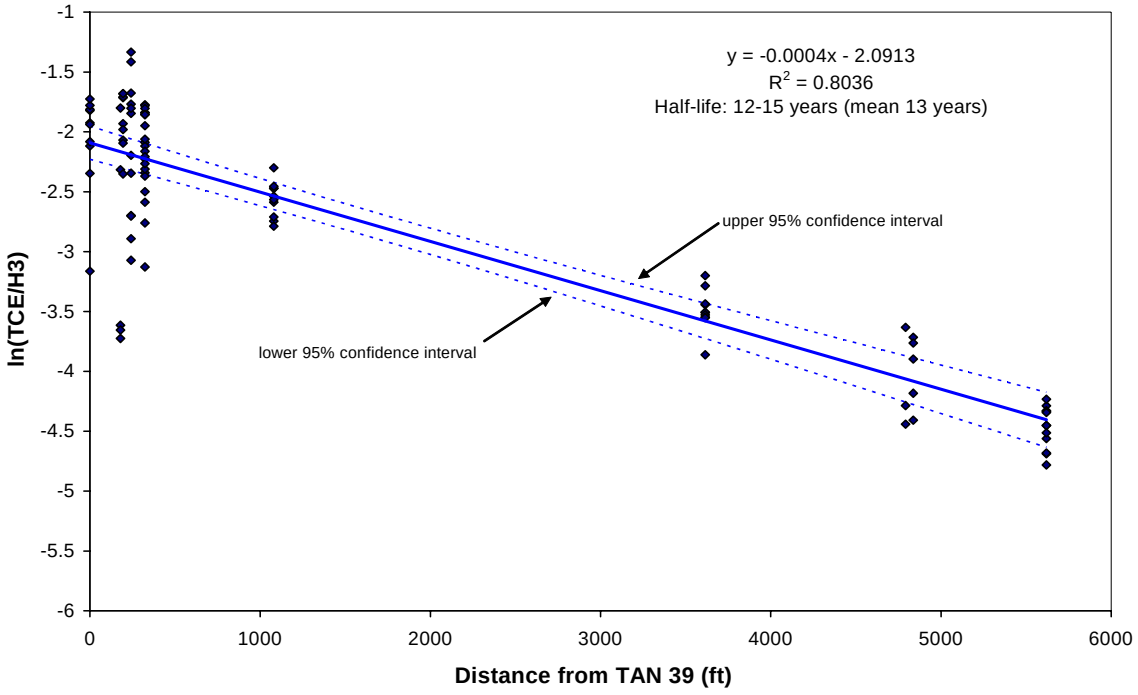
Case Study - Idaho National Laboratory Test Area North

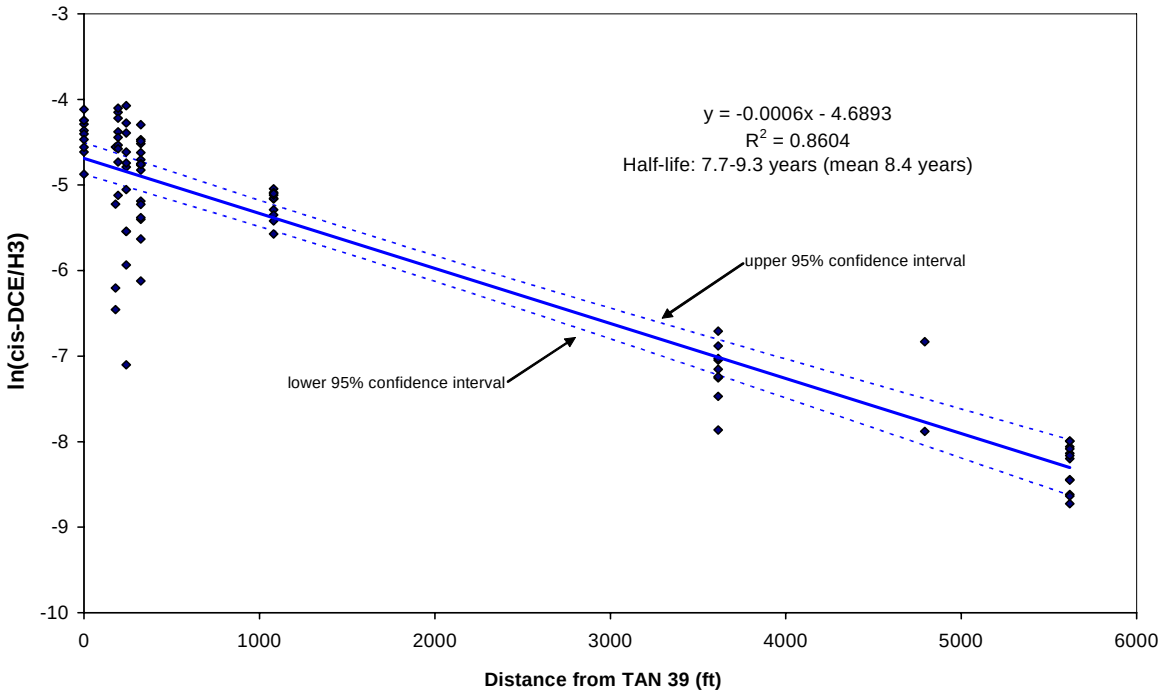
TAN TCE Plume



TAN MNA Field Evaluation

- Studied all attenuation mechanisms per EPA protocol
- Protocol scoring suggested MNA was not viable because reductive dechlorination was occurring only near the plume's source
- However, TCE and c-DCE were attenuating relative to two internal tracers, PCE and tritium, with a half-life of 13 and 8 years, respectively
- Field and lab data suggested that the mechanism was aerobic cometabolism
- Enzyme probes and molecular methods were applied during a two-year sampling program





(Wymore, R.A., M.H. Lee, W.K. Keener, F.S. Colwell, A.R. Miller, M.E. Watwood, and K.S. Sorenson, Jr., 2006. "Intrinsic Aerobic TCE Cometabolism by Methanotrophs Expressing sMMO," *Bioremediation Journal*, in preparation.)

TAN Enzyme Probe Results

- 1 - Each plus sign represents a positive response for one of four different toluene enzyme probes
- 2 - The number presented is Intensity / minute

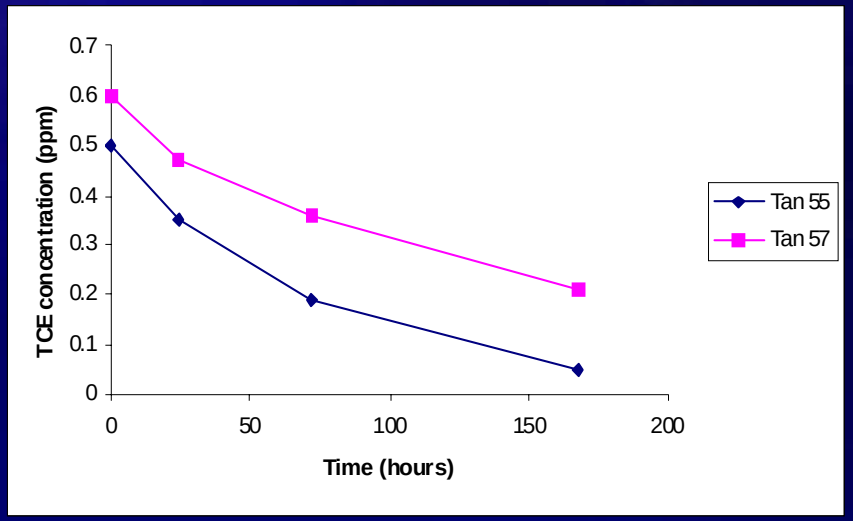
Well	Sample Location (ft below land surface)	Toluene Probes[1]	Methane Probes[2] (intensity/min)
TAN-51	240	++	+8
	263	++	+21
	322	+	+4
	342	+++	+18.5
	413	-	+9
	460	-	+17
TAN-55	317	++++	+19
	424	++++	NA
	461	++++	+20
TAN-52	242	+++	+6
	266	+	+19
	361	+++	+9
	373	+	NA
	438	++	+8
	456	+	+18.5
TAN-16	307	++	+23
TAN-56	242	-	+21
TAN-57	230	+	+12
	285	+	+7
	438	+	+10
TAN-58	295	++++	+10
TAN-7	300 (#1)	+++	+19
	300 (#2)	+++	+14
	300 (#3)	++++	+17.5

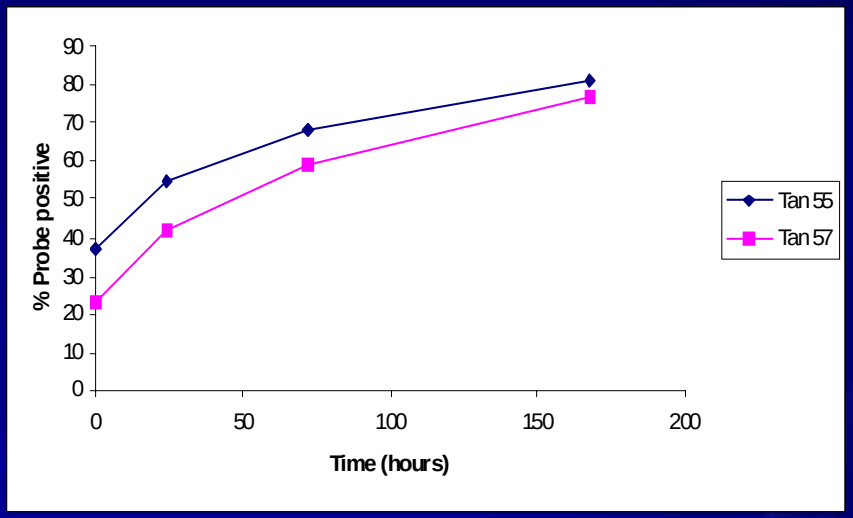
TAN Enzyme Probe Results

- sMMO active in all samples tested
- Methane oxidizers were successfully enriched from many samples
- sMMO genes present in 22 sampling locations
- Control studies implicated sMMO in enzyme probes transformation

TAN Enzyme Probe Results (cont.)

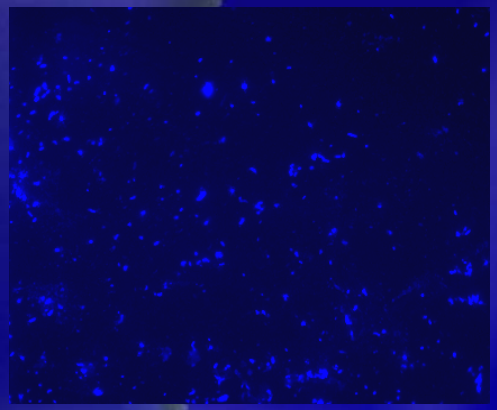
- Toluene oxidizers enriched from many samples
- Correlation between toluene consumption, TCE degradation, and enzyme probe response
- Toluene oxygenase enzymes active in 21 of 24 samples

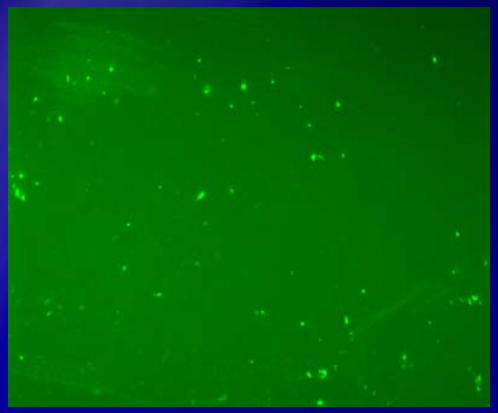




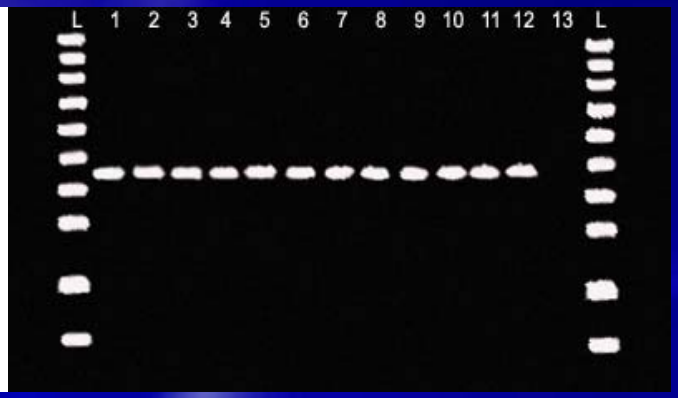
TAN Enzyme Probe Results Summary

All Wells Sampled Showed Positive Response to Enzyme Probes and Contained sMMO Genes

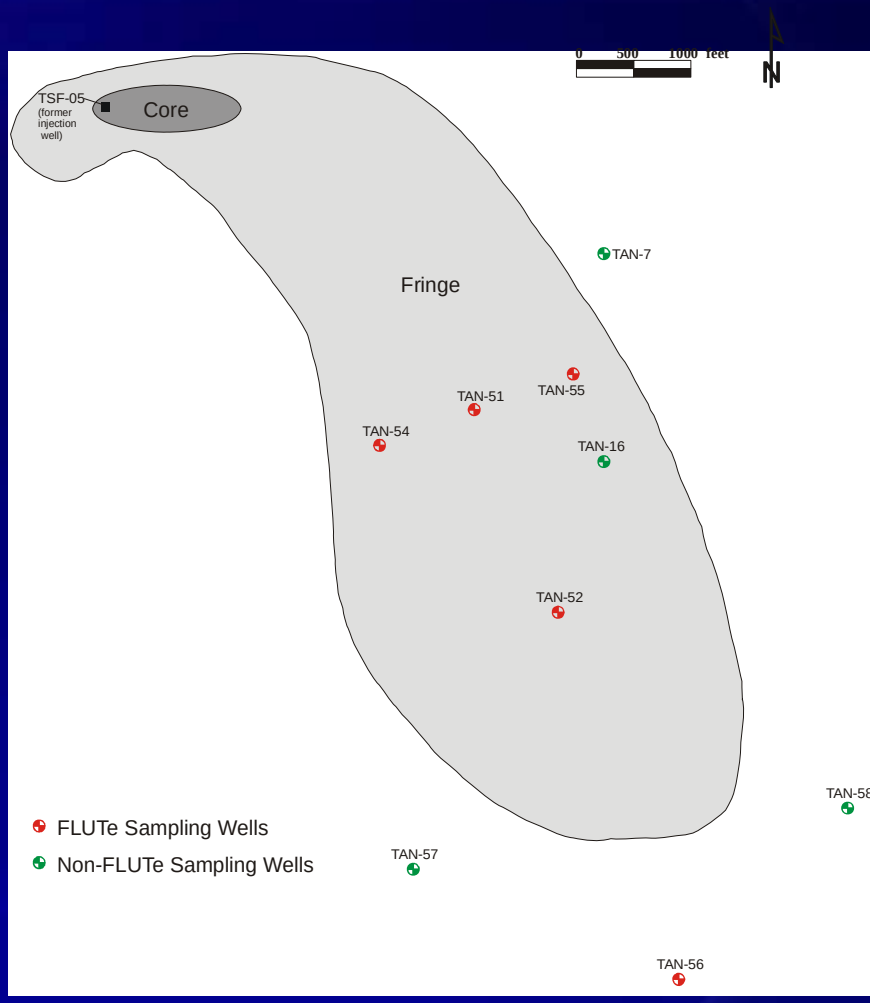




L- 100 bp ladder
1- 58, 295 ft
2- 16, 307 ft
3- 56, 242 ft
4- 52, 242 ft
5- 52, 361 ft
6- 52, 438 ft
7- 51, 240 ft
8- 51, 322 ft
9- 51, 413 ft
10- 57, 230 ft
11- 57, 285 ft
12- 57, 438 ft
13 negative control

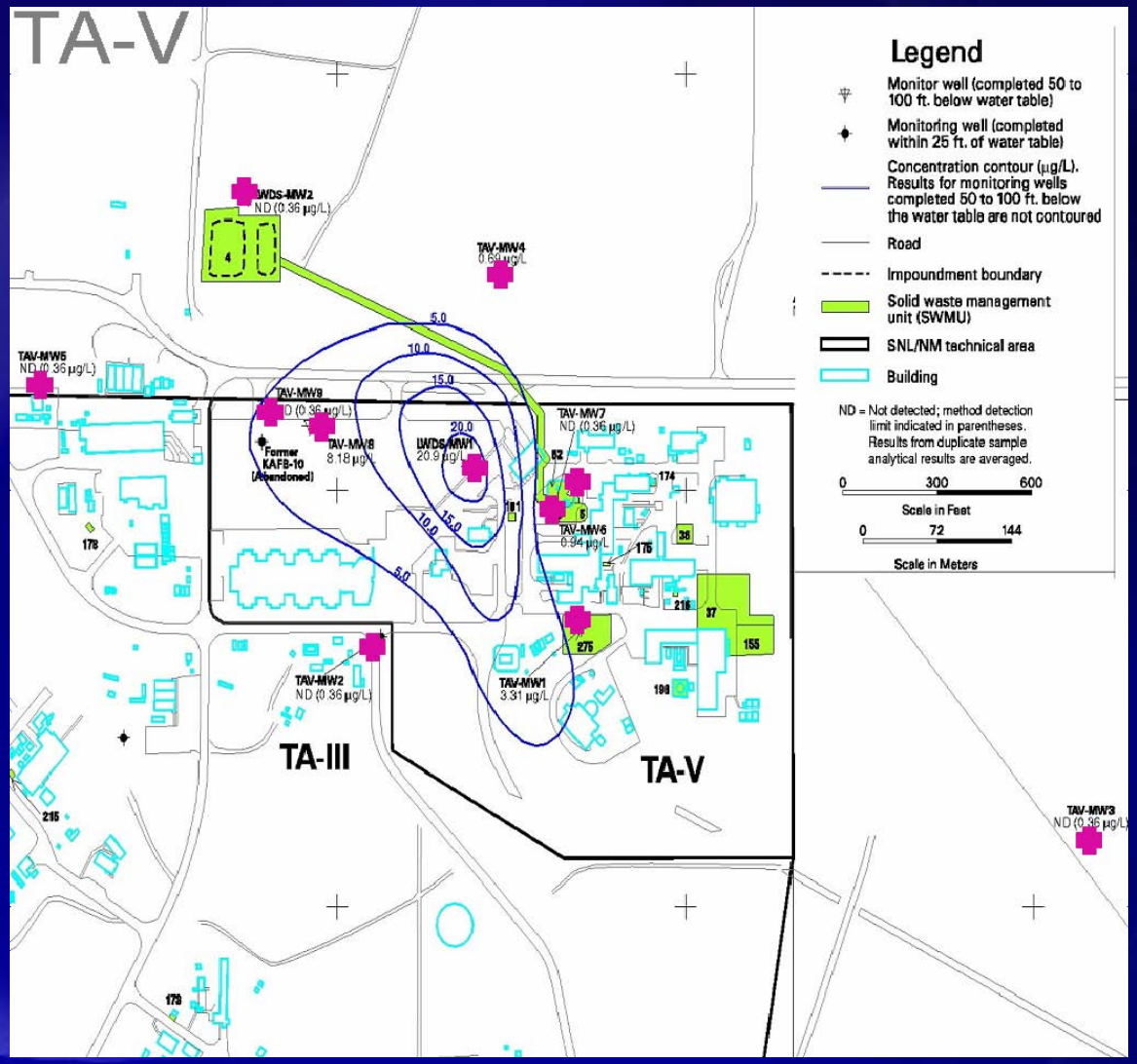


TAN TCE Plume



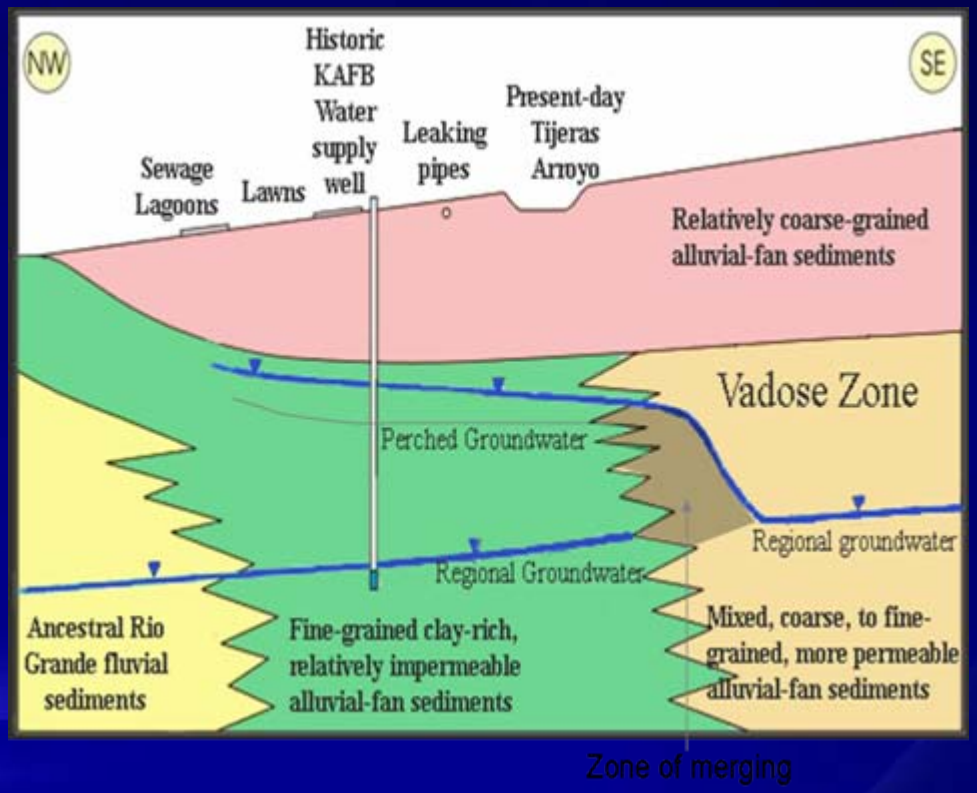
Case Study – Sandia National Laboratories

- SNL/NM is located on Kirtland Air Force Base (KAFB), in Albuquerque, NM
- Operate 5 Technical Areas (TAs)
- TA-V – began operating in 1960s as a research and testing area; covers approximately 35 acres
- Low levels (< 30 ppb) of TCE covering large area



Sandia National Laboratories – Tijeras Arroyo Groundwater (TAG)

- TAG encompasses approximately 40 square miles centered on the northwest corner of Kirtland Air Force Base (KAFB)
- Tijeras Arroyo is the most significant surface-water drainage feature
- TAG has both a perched and regional aquifer
- Low levels of TCE detected (<10 ppb) in perched aquifer



Sandia MNA Evaluations

- MNA assessment per EPA protocols for both sites showed that MNA was not viable
  - No reductive daughter products
  - Plume-wide aerobic conditions
- Enzyme probe and molecular assays were applied during a one-time sampling event at each site
- Numerical modeling was also used at TA-V to demonstrate the effects of dilution

Summary of Results with Enzyme Activity Probes

TA-V

- Coumarin (sMMO probe) indicated activity in all wells
- Toluene oxygenase probes showed activity in all wells
- sMMO and toluene oxygenase activity detected both inside and outside of contaminated areas

TAG

- Coumarin (sMMO probe) indicated activity in 50% wells
- Toluene oxygenase probes showed activity in all but one of the wells
- sMMO and toluene oxygenase activity detected both inside and outside of contaminated areas

- Based on probe results and numerical modeling for TA-V, regulatory agencies have agreed to MNA
- Based on enzyme probe results and the very low TCE concentrations at TAG, regulatory agencies have agreed to MNA

Summary and Conclusions

- Enzyme probes allow for assessment of the presence and activity of enzymes known to cometabolize chlorinated solvents
- Application involves a one-time sampling event
- Documentation of this mechanism can support selection of MNA at sites where it was previously not considered
- This can lead to significant life-cycle cost savings
  - At TAN, selection of MNA along with bioremediation for the source area led to a savings of $23M over pump and treat
  - At Sandia, active remedies would have involved significant expense because of large area and depth to groundwater

Argonne NATIONAL LABORATORY

... for a brighter future

Why Are Produced Water Discharge Standards Different throughout the World?

John A. Veil

Environmental Science Division

Argonne National Laboratory

13th IPEC

San Antonio, TX

October 19, 2006

U.S. Department of Energy

THE UNIVERSITY OF CHICAGO

A U.S. Department of Energy laboratory managed by The University of Chicago

Topics for Discussion

- What is produced water?
- What is in produced water?
- Approaches to minimize risk
  - U.S. approach
  - North Sea approach
- Why are there differences?

What is Produced Water?

- Water that comes to the surface with oil and gas
- Contains many chemical constituents
  - Salt content (salinity, total dissolved solids [TDS], electrical conductivity)
  - Oil and grease
    - *Composite of many hydrocarbons and other organic materials*
  - Toxicity from various natural inorganic and organic compounds or chemical additives
  - NORM
  - Some oxygen demanding materials

Produced Water Volume

- Largest volume waste stream from oil and gas production
  - Worldwide estimate – 77 billion bbl/year (2003 SPE paper)
  - U.S. offshore – >1 billion bbl/year
  - U.S. onshore (more than 850,000 wells)
    - *18 billion bbl/year (1995 API study)*
    - *14 billion bbl/year (2002 estimate from inquiries to states)*
      - Problems with missing data for many states
      - Does not account for gas and CBM wells

Ratio of Water to Oil

- Worldwide estimate – 2:1 to 3:1
- U.S. estimate – 7:1
- Many older U.S. wells have ratios > 50:1
  - This often determines profitability of well

Number of U.S. Producing Wells in 2002

Type of Well	Total
Onshore - low production (stripper wells)	648,033
Onshore - high production	247,019
Offshore	6,948
Total	902,000

Source: U.S. Department of Energy, Energy Information Administration and Interstate Oil and Gas Compact Commission

Approaches to Minimizing Risk from Produced Water Discharges to the Ocean

- U.S. approach
  - Gulf of Mexico
  - California
  - Alaska

- North Sea regional approach
  - Norwegian approach

U.S. Approach to Minimizing Produced Water Risk

- Emphasizes combined or holistic effect of the effluent when it is discharged
- Follows U.S. legal/regulatory framework
- Specific requirements vary between regions, but all:
  - Start with national oil and grease limits
  - Add effluent toxicity testing requirements for several species
  - Add other monitoring, studies, or operational controls to meet regional needs and interests

EPA Oil and Gas National Discharge Standards Effluent Limitations Guidelines [40 CFR 435]

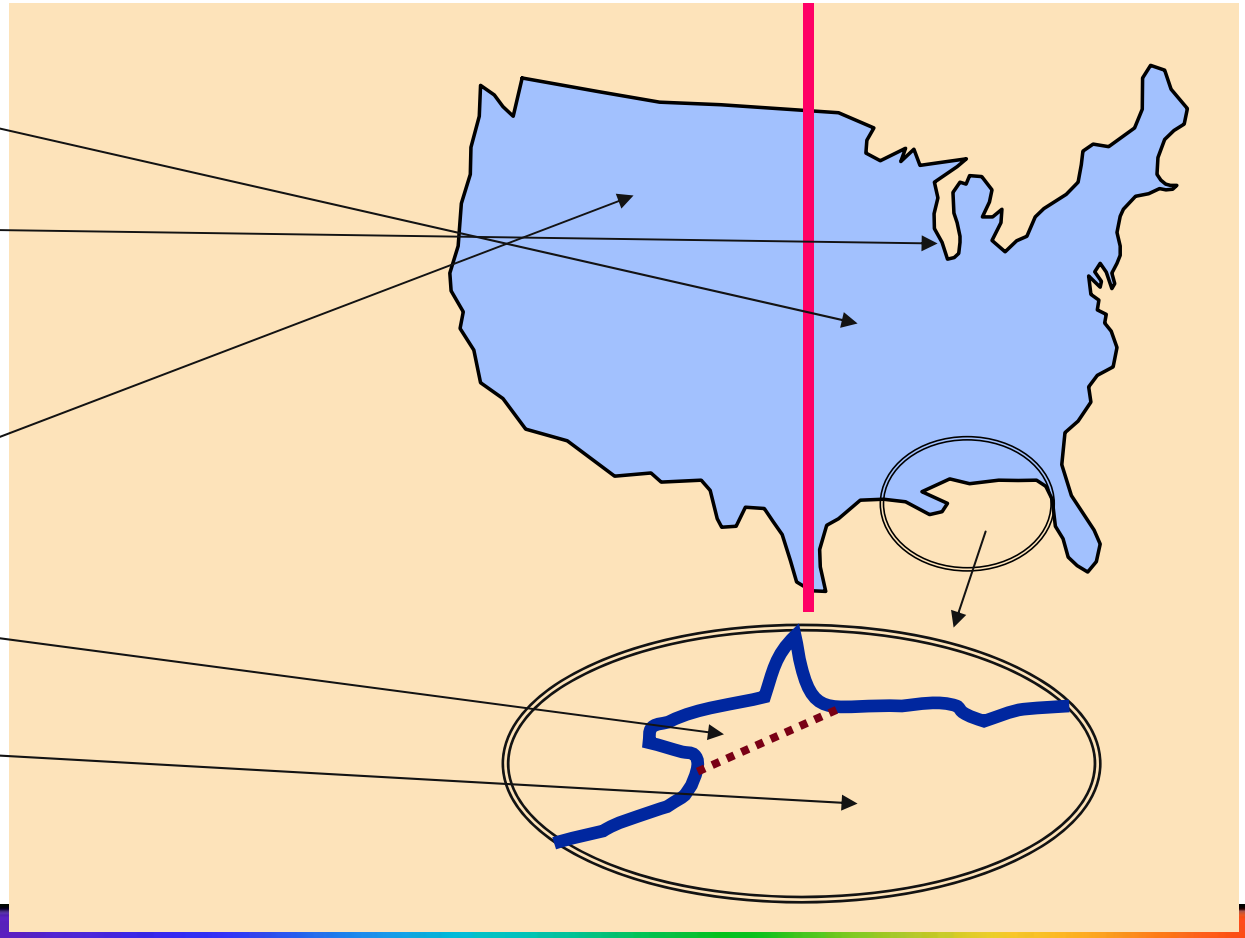
Onshore

Stripper (<10bbl/day)

Agricultural and wildlife use

Coastal

Offshore



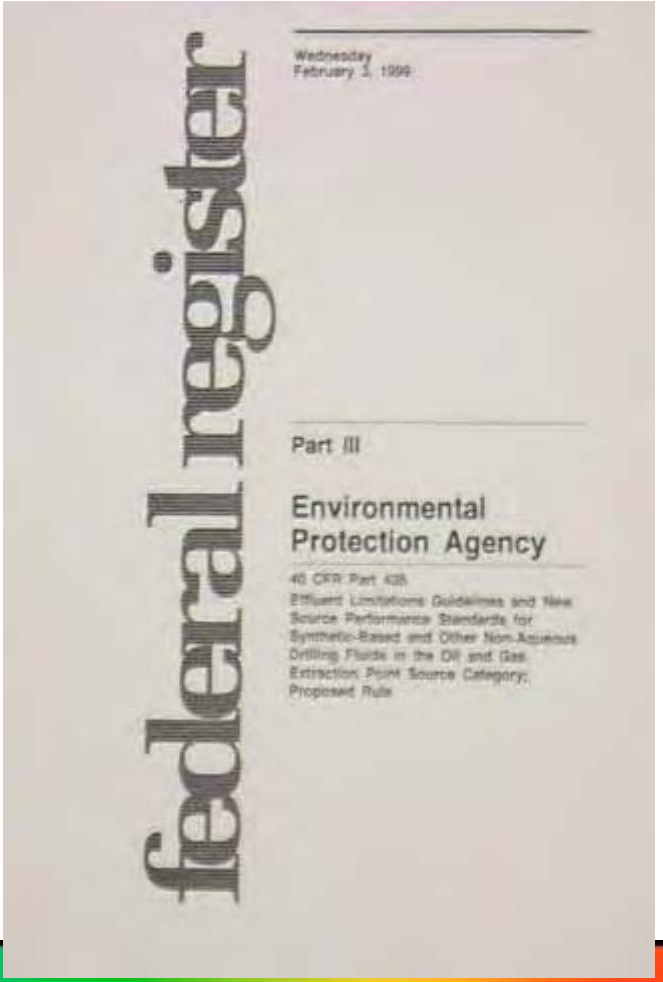
National Produced Water Discharge Standards for Wells Located Onshore

- Onshore subcategory
  - Zero discharge
- Stripper subcategory
  - No national requirements
  - Jurisdiction left to state or EPA region
- Agricultural and Wildlife Use subcategory
  - Produced water must have a use
    - *Water must be of good enough quality for wildlife, livestock, or other agricultural use*
    - *Produced water must actually be put to that use*
  - Oil and grease limit of 35 mg/l maximum

National Discharge Standards for Produced Water Discharges to Offshore and Coastal Waters

- Coastal wells
  - Zero discharge except in Cook Inlet, Alaska
  - Offshore limits required there

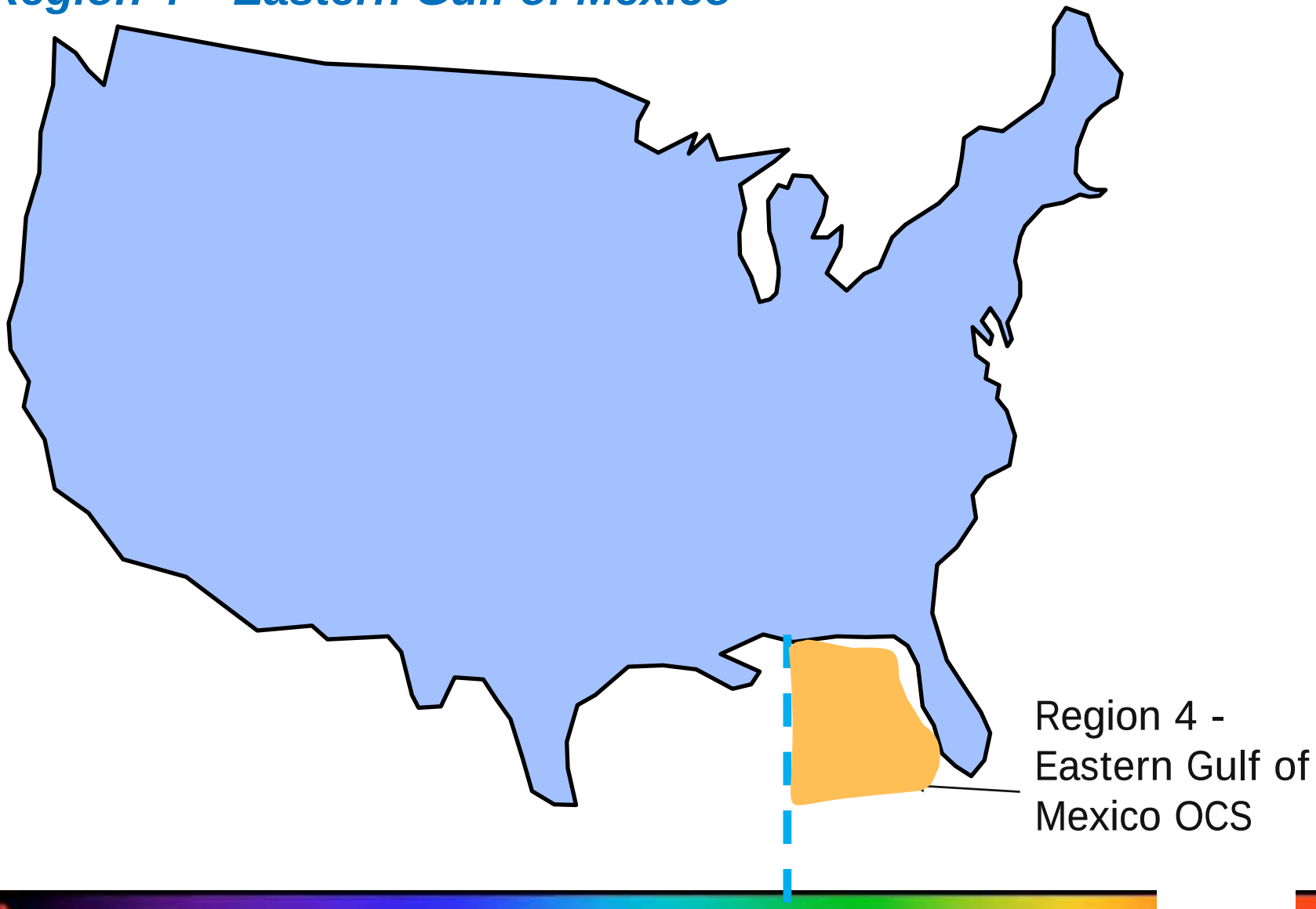
- Offshore wells
  - Oil and grease limits before discharge
    - *29 mg/l monthly average*
    - *42 mg/l daily maximum*
  - No other parameters are limited by national standards
  - Discharges are regulated through NPDES (National Pollutant Discharge Elimination System) general permits



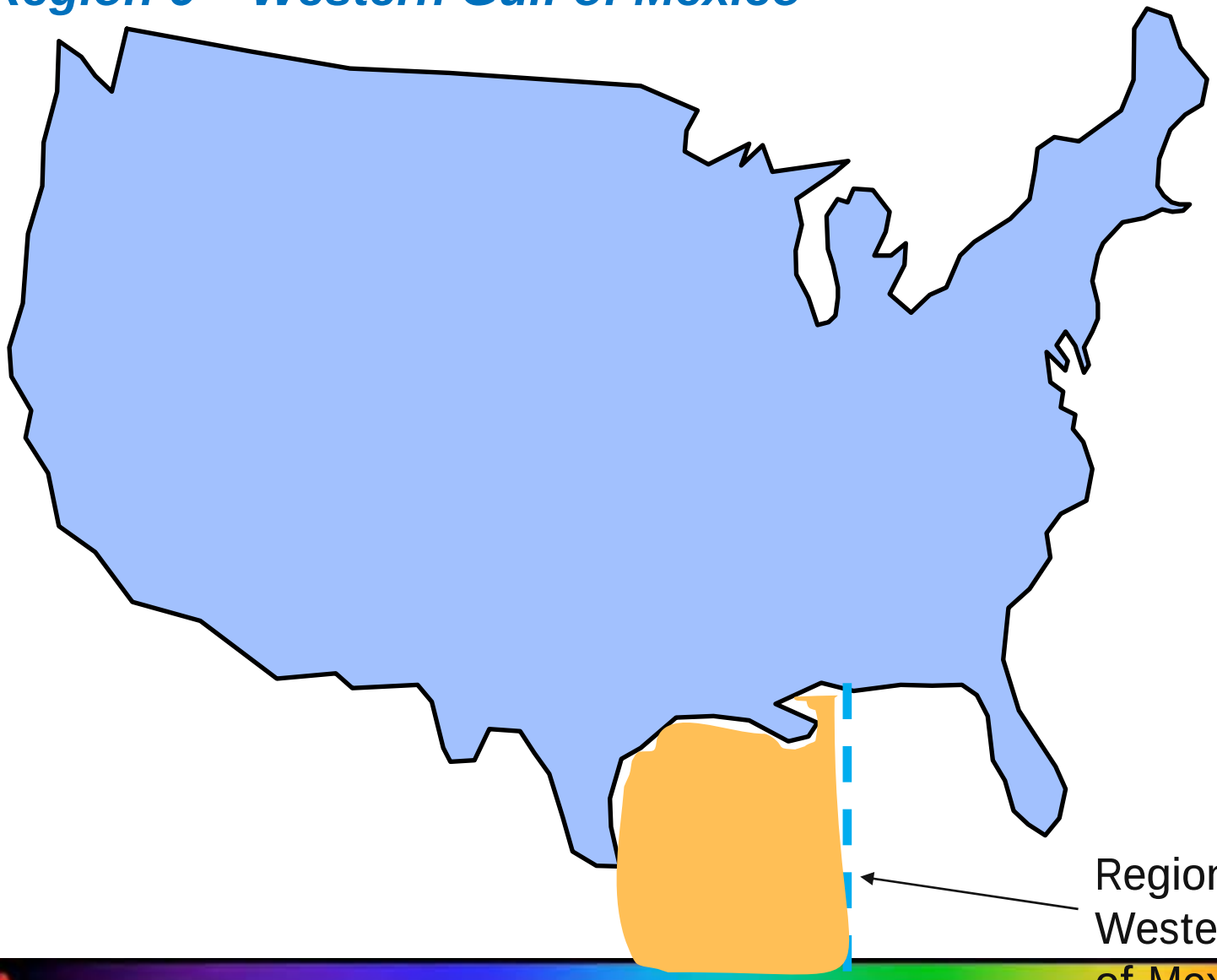
Basis for U.S. Offshore Produced Water Standards

- Oil and grease limit used as a "surrogate" for other pollutants
  - When oil and grease are controlled, other pollutants will also be controlled
- Limit is based on a statistical analysis of data from 60 U.S. platforms
  - Monthly average = 95th percentile = 29 mg/l
  - Daily maximum = 99th percentile = 42 mg/l

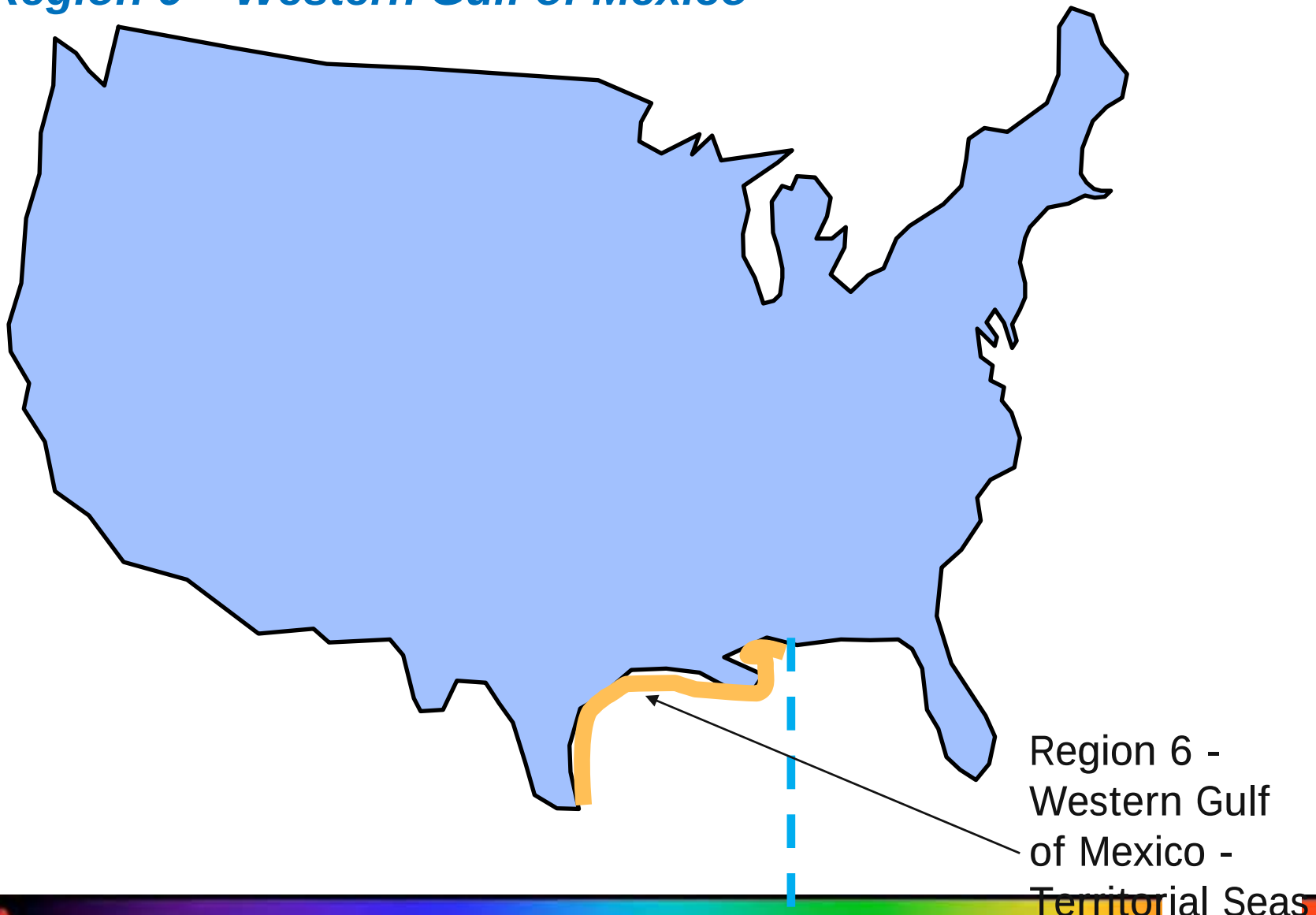
EPA Region 4 – Eastern Gulf of Mexico



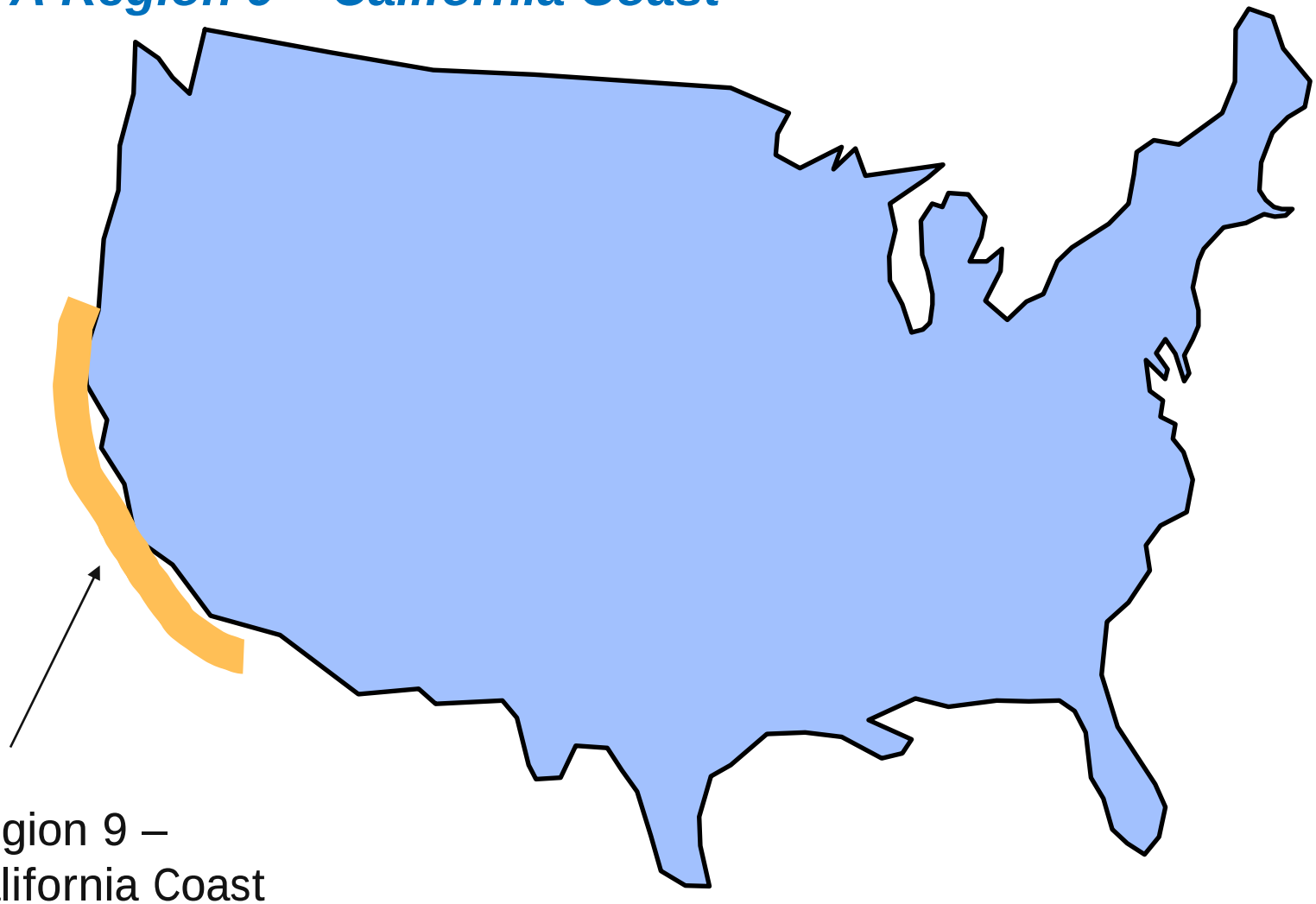
EPA Region 6 – Western Gulf of Mexico



EPA Region 6 – Western Gulf of Mexico



EPA Region 9 – California Coast



Region 9 –
California Coast

Produced Water Controls in EPA Permits

- Oil and grease limits
- Toxicity tests
  - Limits based on water quality modeling
- Limits on other pollutants
- Restrictions or prohibitions on discharge
- Studies

Comparison of Toxicity Requirements in EPA Permits

Permit	Date Issued	Type of Test	Species
Region 4,	12/04	Chronic	Mysid shrimp (*Mysidopsis bahia*) Inland silverside minnow (*Menidia beryllina*)
Region 6, OCS	9/04	Chronic	Mysid shrimp (*Mysidopsis bahia*) Inland silverside minnow (*Menidia beryllina*)
Region 6, Territorial Seas	8/05	Chronic plus 24-hour acute test using full-strength effluent	Mysid shrimp (*Mysidopsis bahia*) Inland silverside minnow (*Menidia beryllina*)
Region 9, California	12/04	Chronic	Red abalone (*Haliotis rufescens*) Giant kelp (*Macrocystis pyrifera*) Topsmelt fish (*Atherinops affinis*)
Region 10, – current permit	4/99	Chronic	Mysid shrimp (*Mysidopsis bahia*) Inland silverside minnow (*Menidia beryllina*) Mussel (*Mytilus* sp.) or Pacific oyster (*Crassostrea gigas*)
Region 10, – proposed new permit	3/06	Chronic	Topsmelt fish (*Atherinops affinis*) Mussel (*Mytilus* sp.) or Pacific oyster (*Crassostrea gigas*) Purple sea urchin (*Strongylocentrotus purpuratus*) or sand dollar (*Dendraster excentricus*)

Comparison of Other Produced Water Requirements

Permit	Discharge Prohibition	Other Limits	Other Requirements
Region 4	Within 1,000 m of Area of Biological Concern	NA	Notification before using new chemicals
Region 6, OCS	Within Area of Biological Concern or National Marine Sanctuary	NA	Conduct study of discharges to hypoxic zone
Region 6, Territorial Seas	Within 1,000 m of Area of Biological Concern	NA	NA
Region 9, California	NA	- Limits on 9 metals, cyanide, and phenols - Monitoring for 26 chemicals and toxicity	- Annual discharge volume limits are set for each platform - Conduct study of on-line oil-and-grease monitors - Companies must submit a study to the EPA to determine the feasibility of disposal of produced water by means other than discharge
Region 10, Cook Inlet, Alaska, current permit	- To shallow water or other sensitive areas - Within certain distance of coastal marsh, river mouth, parks, or wildlife areas	- Limits on various pollutants	N/A
Region 10, Cook Inlet, Alaska, proposed new permit (3/06)	- To shallow water or other sensitive areas - Within certain distance of coastal marsh, river mouth, parks, or wildlife areas	- Limits for each of the 9 platforms for 8 toxic pollutants and effluent toxicity	- Collection of water column and sediment samples at 50-m intervals over a grid - Samples must be analyzed for total aromatic hydrocarbons, total aqueous hydrocarbons, copper, manganese, lead, nickel, and zinc

North Sea Approach to Minimizing Produced Water Risk

- Emphasizes control of the chemical products used in the well and during treatment such that the combined impact will be acceptable
- Follows a more complicated framework of requirements
- Based on OSPAR Convention
  - Specific requirements vary between countries, but all meet certain baseline requirements

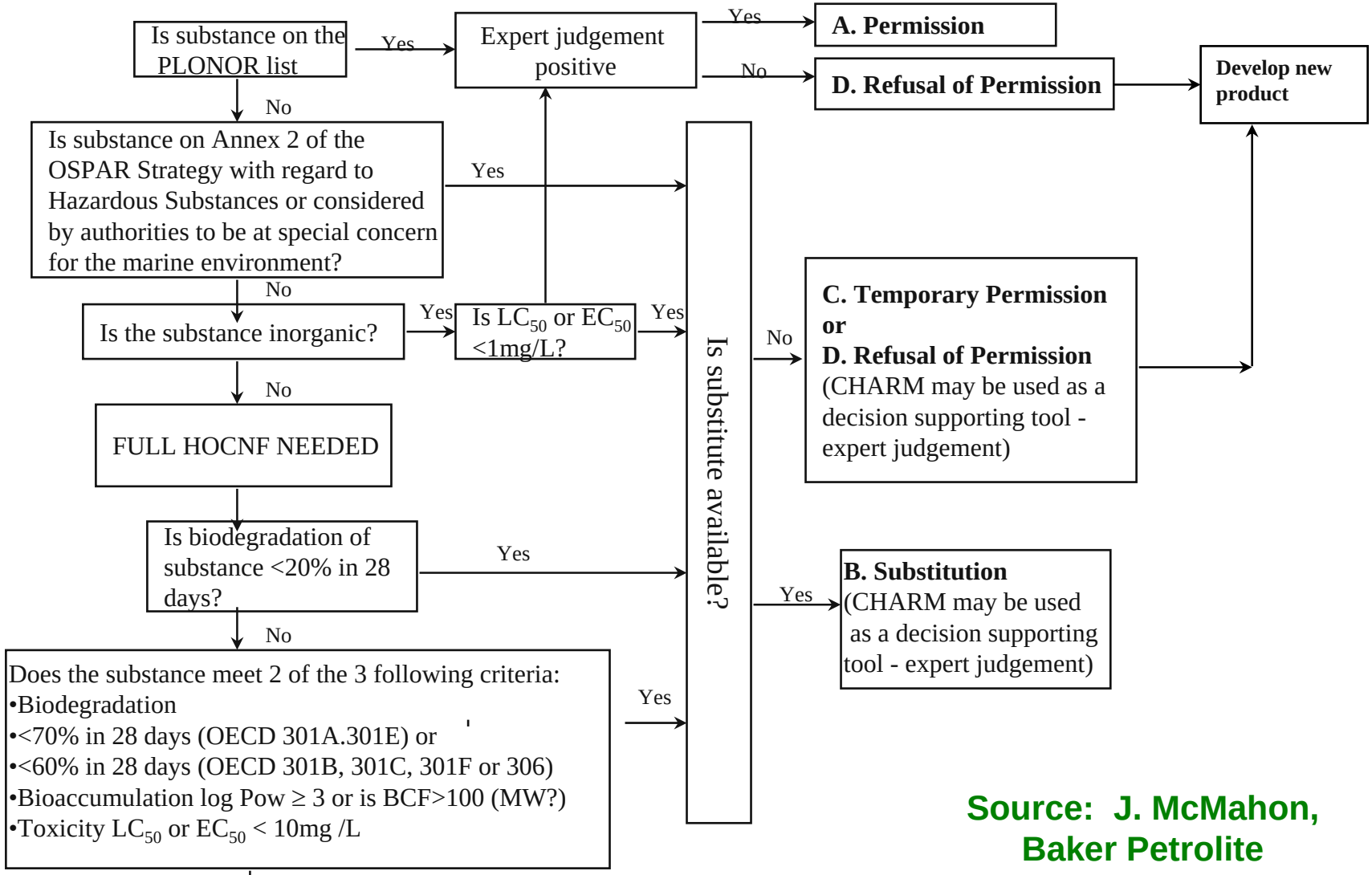
North Sea Regulatory Requirements

- Follow common philosophy:
  - Precautionary principle
  - Polluter pays principle
  - Use best available techniques
- Long-standing oil and grease limit of 40 mg/l
- Changes take effect in 2006
  - Oil and grease limit of 30 mg/l
  - Achieve 15% reduction in total oil loading compared to 2000 level

North Sea Approach Considers Impacts and Risks

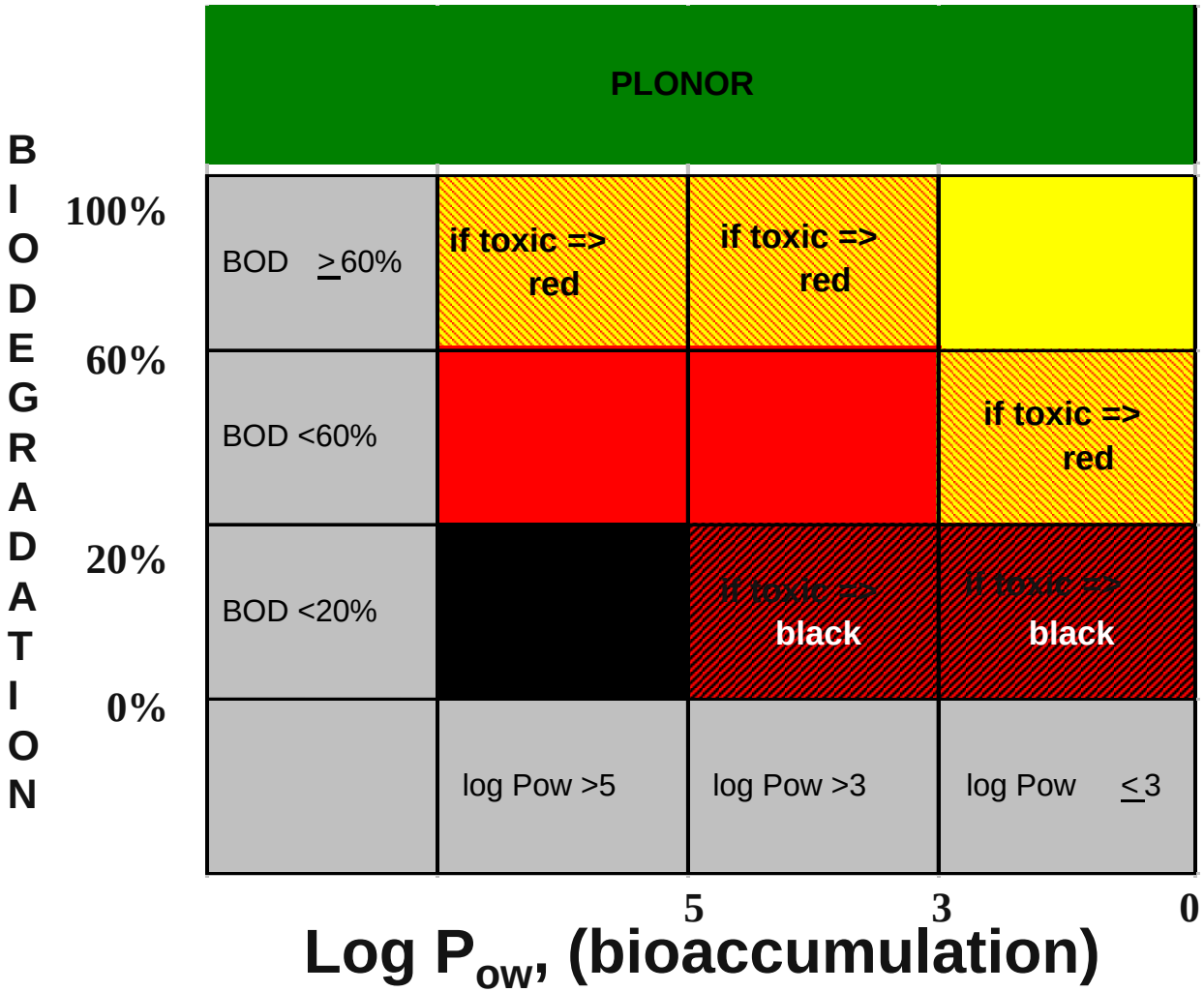
- Use risk assessment approach to authorize discharges
- OCNS (offshore chemical notification system)
  - Chemicals must be tested and pre-approved before they can be used
  - Must consider biodegradation, bioaccumulation, and toxicity
  - Chemicals on PLONOR (poses little or no risk) list can have reduced screening
- Evaluate whether predicted environmental concentration (PEC) exceeds predicted no effect concentration (PNEC)
  - PEC/PNEC should be <1

HMCS Pre-Screening Scheme



Source: J. McMahon, Baker Petrolite

Screening Criteria



Black = no discharge permitted
Red = to be substituted
Yellow = acceptable
Green = PLONOR and water

"If toxic" applies if measured toxicity by EC-50 or LC-50 is less than 10 mg/l.
Product toxicity should be used unless component toxicity is available.

Substances with less degradation than 20%, must be tested on:

- *Skeletonema*
- *Acartia*
- *Corophium*

Source:
J. McMahon,
Baker Petrolite

Norway Has Additional Controls

- CHARM model used to estimate PECs and PNECs

PNEC is determined from all available acute and chronic toxicity data for each compound group of the EIF:

✓One compound is selected as a representative for each group
✓All available data are evaluated (OECD quality criteria)
✓The highest toxicity value is selected as basis
✓PNEC is reached by dividing this by an assessment factor

The assessment factor compensates for the variable data quality, lab/field differences ++

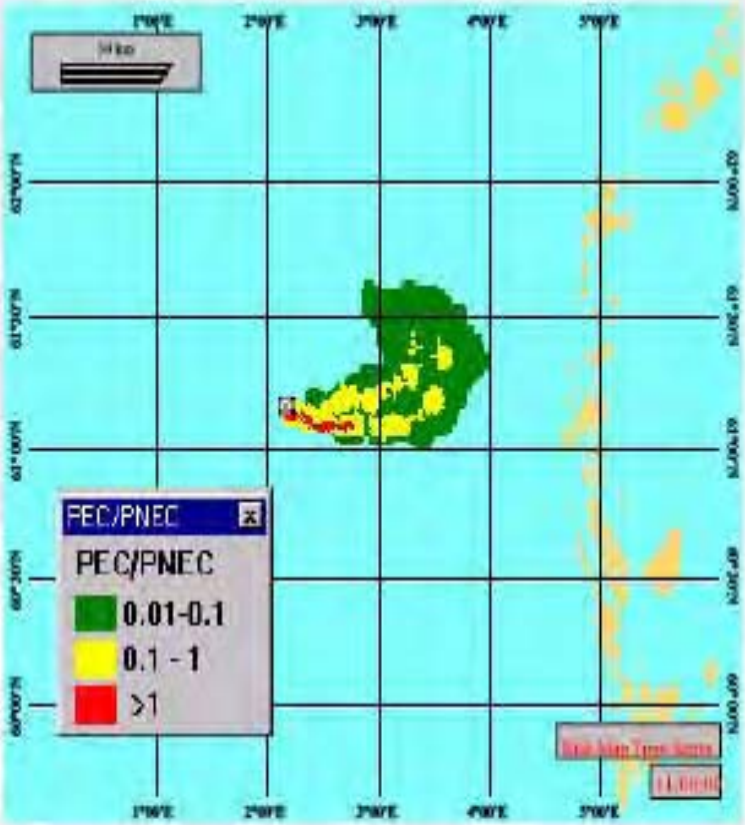
Assessment factor criteria	Assessment factor
Acute toxicity data only	1000
Chronic toxicity for one level (fish)	100
Chronic toxicity for two levels (fish and algae)	50
Chronic toxicity for fish, algae and zooplankton	10

Source:

S. Johnsen
Statoil, 2003

More on the Norwegian Approach

- Norwegian industry further developed the DREAM model
  - Used to calculate EIF (environmental impact factor) and the volume of water surrounding a platform that has PEC/PNEC > 1



Risk map showing area (volume) as function of the PEC/PNEC ratio

Source:

S. Johnsen
Statoil, 2003

Determining EIF

Group	Main groups	Volume m³/day	Conc. in water ppm	PNEC ppb	Contr. to risk %	Risk volume PEC/PNEC >1	Weights	Contr. to risk Weighted%
1	BTEX		7,9	17	1,2	0,8	1	0,8
2	Naphthalenes		1,2	2,1	3,4	2,4	1	2,4
3	PAH 2-3 ring		0,24	0,15	25,0	17,5	1	17,5
4	PAH 4 ring+		0,001	0,063	0,2	0,1	2	0,2
5	Phenol C_0-C_1		5,7	2,0	17,5	1,2	1	1,2
6	Alkyl-phenol C_2+		0,24	0,026	18,1	12,7	2	25,4
7	Aliphatic hydrocarons		29,0	40,4	11,4	7,9	2	15,8
8	Metals 1		0,3	2,4	0,1	0,3	1	0,3
9	Metals 2		0,01	0,34	0,1	0,2	1	0,2
10-n	Process chemicals		50,0	Calc.	23,3	26,9	Calc.	35,1
Total		41 550				70,0		98,9

Source: S. Johnsen Statoil, 2003

OSPAR and Other Regional Conventions

Convention	Oil in Water Limit	Other
OSPAR (North East Atlantic)	40 mg/l now; 30 mg/l by 2006	Pre-approval of chemical additives
HELCOM (Baltic Sea)	15 mg/l; up to 40 mg/l if BAT cannot achieve 15 mg/l	Pre-approval of chemical additives
Kuwait Convention and (Red Sea region)	40 mg/l ; 100 mg/l max.	
Barcelona Convention (Mediterranean)	40 mg/l; 100 mg/l max.	

Requirements for Other Countries

- The following tables are derived from a paper by Fredrick Jones, Arthur Leuterman, and Ian Still (2002)
  - "Discharge Practices and Standards for Offshore Operations around the World," presented at the 7th International Petroleum Environmental Conference, Albuquerque, New Mexico, USA, November 7-10, 2000
  - Practices and standards should be verified on a case-by-case basis
    - *Some revisions have been offered to reflect more recent OSPAR instruments*

Country	Legal Basis	Oil in Water Limit
Albania	Barcelona Convention[1]	40 mg/L 100 mg/L max
Algeria	Barcelona Convention[1]	40 mg/L 100 mg/L max
Angola		No Standard set
Argentina	Resolution No. 105/92	Case-by-case
Australia (Western)		30 mg/L 50 mg/L max
Azerbaijan		
Bahrain	KUWAIT Convention [2]	40 mg/L 100 mg/L max
Belgium	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Brazil		20 mg/L max.
Canada	Act RSC 1987	40 mg/L avg. 80 mg/L max
China	GB 4914-85	30-50 mg/L avg. 75 mg/L max.
Colombia	SEPC[6]	Removal of 80% of oil
Denmark (North Sea)	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Denmark (Baltic Sea)	HELCOM Convention[7]	15 mg/L max. 40 mg/L (Alternative)

Ecuador	SEPC[6]	
Egypt	Decree No. 338/95	15 mg/L max. 40 mg/L max. (Alternative)
Estonia	HELCOM Convention[7]	15 mg/L max. 40 mg/L (Alternative)
Finland (North Sea)	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Finland (Baltic Sea)	HELCOM Convention[7]	15 mg/L max. 40 mg/L (Alternative)
France (Mediterranean)	Barcelona Convention[1]	40 mg/L 100 mg/L max
France (North Sea)	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Germany (Baltic Sea)	HELCOM Convention[7]	15 mg/L max. 40 mg/L (Alternative)
Germany (North Sea)	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Greece	Barcelona Convention[1]	40 mg/L avg. 100 mg/L max
Indonesia	MD KEP 3/91; 42/97	75 mg/L avg.
Iran	KUWAIT Convention [2]	40 mg/L avg. 100 mg/L max
Iraq	KUWAIT Convention [2]	40 mg/L avg. 100 mg/L max
Ireland (North Sea)	Rules & Procedures for Offshore Petroleum Exploration Operations;	40 mg/L; 30 mg/L (2006)
Israel	OSPAR Convention[3] Barcelona Convention[1]	40 mg/L avg. 100 mg/L max
Italy	Dm of 28.7 1994	40 mg/L avg.

Kuwait	KUWAIT Convention[2]	40 mg/L avg. 100 mg/L max
Lebanon	Barcelona Convention[1]	40 mg/L 100 mg/L max
Libya	Barcelona Convention[1]	40 mg/L 100 mg/L max
Lithuania	HELCOM Convention[7]	15 mg/L max. 40 mg/L (Alternative)
Monaco	Barcelona Convention[1]	40 mg/L 100 mg/L max
Morocco	Barcelona Convention[1]	40 mg/L 100 mg/L max
Netherlands	Mining reg. 1996; Reg. 687/ 1224, 1987; OSPAR Convention[3]	40 mg/L avg. 100 mg/L max.
Nigeria	Act No. 34/68: Regs 1992	40 mg/L avg. 72 mg/L max.
Norway	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Poland	HELCOM Convention[7]	15 mg/L max. 40 mg/L (Alternative)
Portugal	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Qatar	KUWAIT Convention[2]	40 mg/L avg. 100 mg/L max.
Oman	Decree No. 10/82; KUWAIT Convention[2]	40 mg/L avg. 100 mg/L max.
Russia	Water Code 1995/ GOST 1977	0.05 mg/L MPC
Russia (Baltic Sea)	HELCOM Convention[7]	15 mg/L max. 40 mg/L (Alternative)
Saudi Arabia	KUWAIT Convention[2]	40 mg/L 100 mg/L max

Spain (Mediterranean)	Barcelona Convention[1]	40 mg/L 100 mg/L max
Spain (North Sea)	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Sweden (Baltic Sea)	HELCOM Convention[7]	15 mg/L max. 40 mg/L (Alternative)
Sweden (North Sea)	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
Syria	Barcelona Convention[1]	40 mg/L 100 mg/L max
Thailand	NEQA 1992: Gov. Reg. 20/90	100 mg/L max.
Trinidad		40 mg/L max.
Tunisia	Order of 1989	10 mg/L max.
Turkey (Mediterranean)	Barcelona Convention[1]	40 mg/L 100 mg/L max
United Arab Emirates	KUWAIT Convention[2]	40 mg/L avg. 100 mg/L max.
United Kingdom	OSPAR Convention[3]	40 mg/L; 30 mg/L (2006)
United States	40 CFR 435	29 mg/L 42 mg/L max
Venezuela	Decree No. 833/1995	20 mg/L
Vietnam	Decision No. 333/QB 1990	40 mg/L
Yugoslavia	Barcelona Convention[1]	40 mg/L 100 mg/L max

Why Are the Two Approaches Different?

- Number of offshore wells and discharges
- Length of time offshore production has occurred
- National/regional culture and politics
- Different analytical methods
- Human nature

Comparison of the Number of U.S. Offshore to North Sea Producing Wells

Country/Region	# Platforms /Offshore Fields	Producing Oil Wells (2004)
Denmark	19	225
Netherlands	12	69
Norway	40	801
UK	174	1,383
North Sea Total	245	2,478

Source: Oil & Gas Journal, December 19, 2005

Country/Region	# Platforms	Producing Oil & Gas Wells (2002)
U.S. Gulf of Mexico	3,895	6,948

Source: U.S. Department of Energy, Energy Information Administration, and U.S. Minerals Management Service

Effect of Number of Wells on Risk Management Approach

- U.S. has had thousands of offshore wells to regulate for several decades
- North Sea, and particularly Norway, has far fewer discharges to regulate
  - This allows for more platform-specific analyses and studies
- Parallel example can be seen by comparing strategies between EPA Regions
  - Region 6 (Gulf of Mexico) has thousands of platforms
  - Region 9 (California) has 22 platforms
  - Region 10 (Cook Inlet) has 9 platforms
- Region 6 permit requirements are general, while Region 9 and 10 permits allow for platform-specific requirements

Duration of Offshore Experience

- U.S. began in 1940s
  - Kerr-McGee drilled the first well from a fixed platform offshore out-of-sight of land in 1947.
  - By 1949, 11 fields were found in the Gulf of Mexico with 44 exploratory wells.
- North Sea
  - The first offshore hole in the North Sea was made by the drilling platform *Mr. Louie* in May 1964 thirty miles north of the island of Juist, in the German sector
  - The Drilling Barge *Sea Gem* was the first rig ever to find hydrocarbons in the British North Sea sector in September 1965
  - In May 1963, Norway asserted sovereign rights over natural resources in its sector of the North Sea. Exploration started in July 1966. First oil came in August 1969.

Effect of Duration of Experience on Risk Management Approach

- The U.S. had already drilled hundreds to thousands of offshore wells by the time the first North Sea wells were drilled
- Certain produced water management practices were already established
- Early U.S. platforms did not include space for extensive produced water treatment
  - Many were relatively small compared to the North Sea platforms
- When first round of U.S. offshore permits were being written in the 1980s, agencies needed to look at existing facilities and technologies
- North Sea started later and had larger facilities to work with

Culture/Political Differences

- European culture, law, and politics have developed over a much long time frame than U.S. culture
- European nations have had to live side-by-side with other nations for many centuries and have developed different ways of dealing with shared resources (i.e., North Sea water quality) than have North American countries
- Much of Europe leans toward “green” politics and policies

Effect of Culture/Politics on Risk Management Approach

- There is a wide range of politics and societal attitudes about oil and gas in different parts of the U.S.
  - Citizens and regulators in California and Florida do not strongly support offshore production
  - Texas and Louisiana do support offshore production
- Most U.S. offshore production is off the coast of Texas and Louisiana
  - Consequently, there has been less strong objection to produced water management practices there than in Europe or in California and Florida
- U.S. discharge policy is based on setting standards, then letting industry figure out how to do it most effectively and economically
  - EPA does not generally get involved in how the limits are met

Analytical Methods

- Measurement of oil and grease depends on the analytical method used
  - Oil and grease is not a single chemical substance
  - The test measures the sum of many different hydrocarbons and other organic substances that happen to be detected by the analytical method
- The U.S. oil and grease standards are based on statistical analysis of hundreds of samples measured using an analytical method that included Freon as the extraction solvent
- The phase-out of Freon caused EPA to change its approved analytical method to use hexane as an extraction solvent
  - The current compliance samples are being made using a different analytical method

Effect of Analytical Methods on Risk Managemen Approach

- The North Sea region uses still different analytical methods for oil and grease
- Conclusion: the U.S. and the North Sea are not measuring exactly the same commodity “oil and grease”
- Although oil and grease is a reasonable indicator of the hydrocarbon and other organic concentrations in the produced water, the effectiveness of regulatory controls based solely on oil and grease are not as precise as regulators may believe

Source: Turner Designs

Effect of Human Nature on Risk Management Approach

- Humans are stubborn and tend to show strong “pride of ownership” for their own ideas, systems, and procedures
- Even if one society sees parts of the other society’s system that look better or appear to be more effective, there will generally be strong resistance to dropping your own system and adding major features from the other system
- This “regulatory inertia” has contributed to development and maintenance of two distinct approaches to regulating and managing risk from produced water discharges

Conclusions

- Oil and grease is the baseline of produced water regulatory controls in most countries
  - Most jurisdictions use additional controls beyond oil and grease limits
- The two best-established systems (U.S. and North Sea) have followed dramatically different approaches to manage produced water risk
  - Both approaches successfully manage risk but place the management controls on opposite ends of the process
    - *North Sea emphasizes inputs*
    - *U.S. emphasizes outputs*

Conclusions (continued)

- The previous slides outline the details of both approaches and describe five sets of factors that can help to explain how and why the approaches are different
- Is one approach better than the other?
  - One may be more effective than the other in some situations
  - Conversely, one may be more constraining or restrictive than needed to ensure environmental protection

Produced Water Requirements for Discharges in Region 4 (Eastern Gulf of Mexico) - December 2004

- No discharge allowed within 1,000 meters of:
  - Area of Biological Concern
  - Ocean disposal site for dredged material
- Toxicity
  - 7-day NOEC (no observed effect concentration) must not exceed concentration determined by using critical dilutions
    - *Mysid shrimp (Mysidopsis bahia)*
    - *Inland silverside minnow (Menidia beryllina)*
  - Critical dilutions based on water depth, pipe diameter, and flow rate
  - Dilution calculated using CORMIX 2 model
  - Dilution can be increased by using a diffuser or adding seawater

Other Conditions Relating to Chemical Usage

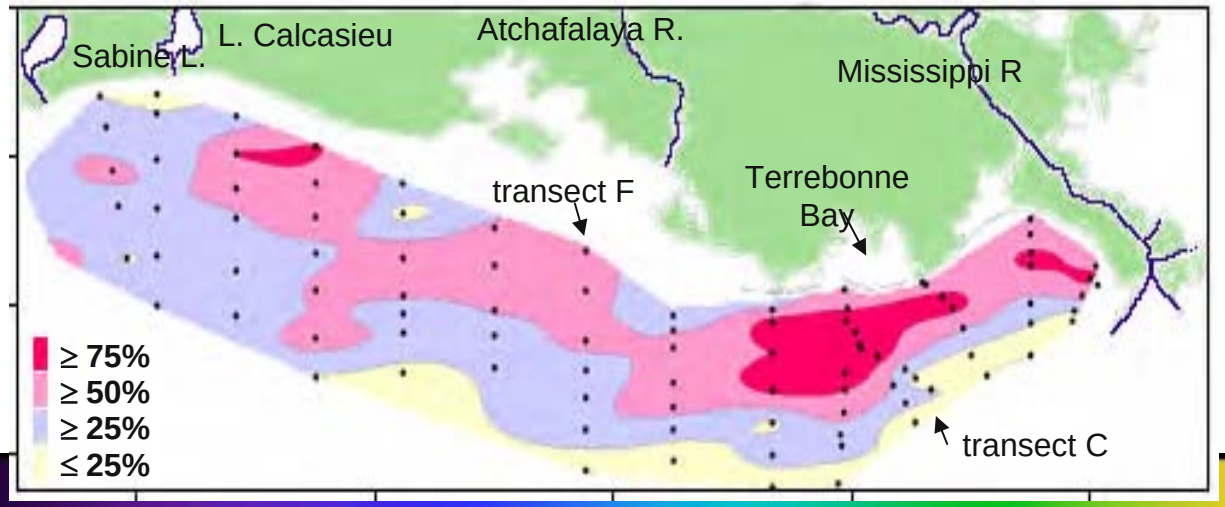
- The company must notify EPA prior to planned use and discharge of any chemical, other than chlorine or other products previously evaluated by EPA, that is to be used in subsea operations. Such notification shall include:
  - Name and general composition of the chemical,
  - Frequencies of use,
  - Quantities to be used,
  - Proposed discharge concentrations,
  - Any acute and chronic toxicity data

Produced Water Requirements for Discharges in Region 6 Western Gulf of Mexico – Outer Continental Shelf -September 2004

- No discharge within Area of Biological Concern or National Marine Sanctuaries
- Toxicity
  - 7-day NOEC must not exceed concentration determined by using critical dilutions
    - *Mysid shrimp (Mysidopsis bahia)*
    - *Inland silverside minnow (Menidia beryllina)*
  - Critical dilutions based on water depth, discharge depth, pipe diameter, and flow rate
  - Dilution calculated using CORMIX 2 model
  - Dilution can be increased by using a diffuser or adding seawater
  - Frequency of testing based on volume of discharge

Other Produced Water Requirements for Region 6 (Western Gulf of Mexico – Federal Waters – Outer Continental Shelf)

- Platforms located within the hypoxic zone must conduct sampling program for BOD, TOC, nitrogen, and phosphorus
- Argonne coordinated a 2005 joint industry study to sample 50 platforms and characterize oxygen demanding substances in produced water



Produced Water Requirements for Discharges in Region 6 - Western Gulf of Mexico – Territorial Seas (0-3 miles from shore) –August 2005

- No discharge allowed within 1,000 meters of Area of Biological Concern
- Toxicity
  - 7-day NOEC must not exceed concentration determined by using critical dilutions
    - *Mysid shrimp (Mysidopsis bahia)*
    - *Inland silverside minnow (Menidia beryllina)*
  - 24-hour test using full-strength produced water mus not kill more than 50% of the test animals
    - *Mysid shrimp (Mysidopsis bahia)*
    - *Inland silverside minnow (Menidia beryllina)*

Produced Water Requirements for Discharges in Region 9 – California –December 2004

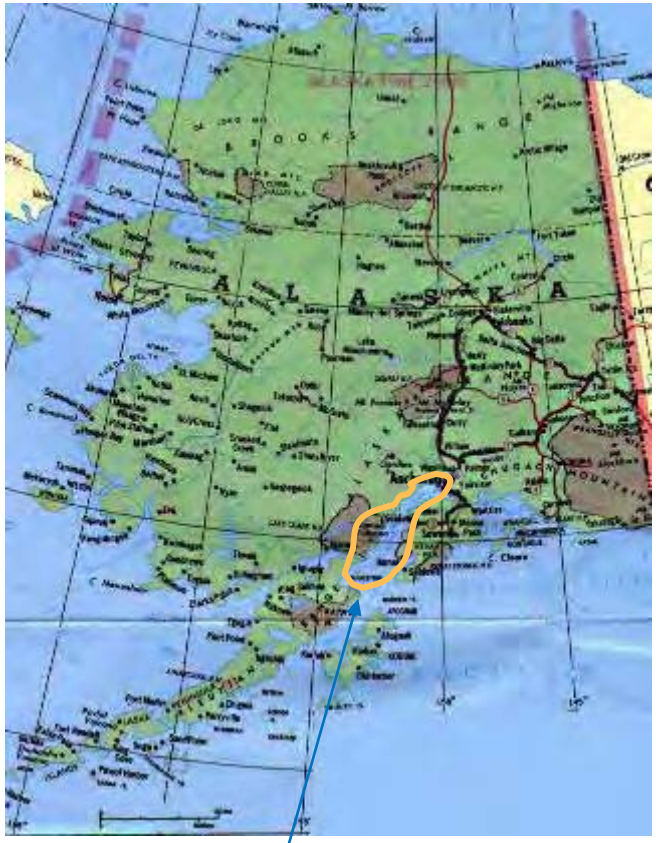
- Sample produced water for 26 chemicals and for effluent toxicity to determine if those substances are likely to cause a water quality problem
  - Determine available dilution using PLUMES model
    - *Dilution can be increased by using a diffuser or adding seawater*
  - Permit sets discharge limits on 9 metals, cyanide, and phenols
- Annual discharge volume limits are set for each platform
- Conduct study of on-line oil and grease monitors
- Companies must submit to EPA a study or studies to determine the feasibility of disposal of produced water by means other than discharge into ocean waters (e.g., reinjection and barging).

Region 9 – Produced Water Toxicity Requirements

- Monthly chronic testing with red abalone (Haliotis rufescens)
- Annual chronic testing with plant (giant kelp – Macrocystis pyrifera) and fish (topsmelt – Atherinops affinis)
- Separate NOEC triggers are set for each platform based on discharge volume and dilution
  - If limits are exceeded, must sample more frequently
  - If limits are still exceeded, must undertake a toxicity reduction evaluation (TRE)
    - *Identify sources of toxicity*
    - *Take actions to mitigate toxicity*
    - *Retest to confirm results*
- Study of impacts of produced water discharges on fish

Other Permit Requirements for Region 10 - Alaska

- Offshore general permit does not authorize produced water discharges in offshore areas of Alaska
- Cook Inlet general permit allows discharges of produced water
  - No discharge
    - *To shallow water (generally < 5 meters)*
    - *Within certain distance of coastal marsh, river mouth, parks, or wildlife areas*
    - *Other sensitive areas*
  - Separate numerical limits for each of the 9 platforms for 8 toxic pollutants and effluent toxicity
    - *Based on CORMIX model*



Region 10 – Cook Inlet, Alaska

Region 10 – Toxicity Requirements

- NOEC limits set for each platform
- *Current permit (issued 2001)*
  - Annual chronic testing using 3 species
    - *Inland silverside minnow (Menidia beryllina)*
    - *Mysid shrimp (Mysidopsis bahia)*
    - *Mussel (Mytilus sp.) or Pacific oyster (Crassostrea gigas)*
- *New draft permit (released March 2006)*
  - Annual chronic testing using 1 fish (topsmelt – Atherinops affinis), mollusc (either Pacific oyster or mussel), and 1 echinoderm (eithe purple sea urchin or sand dollar)
- If limits are exceeded, must sample more frequently
- If limits are still exceeded, must undertake a toxicity reduction evaluati (TRE)
  - Identify sources of toxicity
  - Take actions to mitigate toxicity
  - Retest to confirm results

Other Produced Water Requirements for Region 10 (in March 2006 draft permit)

- Companies discharging greater than 100,000 gallons per day of produced water must conduct a study of the potential impacts of the discharge
- The study must include collection of water column and sediment samples collected at 50 meter intervals over a grid extending a distance of 2,000 meters both north and south of the discharge point and 100 meters in width
- Samples must be analyzed for total aromatic hydrocarbons, total aqueous hydrocarbons, copper, manganese, lead, nickel, and zinc.

Example of Critical Dilutions for Toxicity

Table 1: Produced Water Critical Dilutions
Table 1-A: Critical Dilution (Percent Effluent) for Discharges with a Depth Difference Between the Discharge Pipe and the Sea Floor of Greater than 0 Meters to 4 Meters

Discharge Rate	Pipe Diameter (inches)					
(bbl/day)	>0" to 5"	>5" to 7"	>7" to 9"	>9" to 11"	>11" to 15"	>15"
0 to 500	0.05	0.05	0.05	0.05	0.05	0.05
501 to 1000	0.12	0.12	0.12	0.12	0.12	0.12
1001 to 2000	0.29	0.29	0.29	0.29	0.29	0.29
2001 to 3000	0.49	0.48	0.48	0.48	0.48	0.49
3001 to 4000	0.66	0.64	0.64	0.64	0.64	0.64
4001 to 5000	0.9	0.87	0.85	0.85	0.86	0.87
5001 to 6000	1.13	1.11	1.07	1.07	1.08	1.09
6001 to 7000	1.36	1.33	1.30	1.28	1.28	1.30
7001 to 8000	1.57	1.55	1.51	1.47	1.48	1.50
8001 to 9000	1.80	1.78	1.74	1.68	1.68	1.70
9001 to 10,000	2.02	2.00	1.95	1.89	1.88	1.90
10,001 to 15,000	3.09	3.17	3.08	3.02	2.92	2.88
15,001 to 20,000	3.90	4.26	4.15	4.07	3.95	3.77
20,001 to 25,000	4.60	5.26	5.25	5.10	5.00	4.60
25,001 to 35,000	5.68	6.92	7.28	7.00	6.86	6.30
35,001 to 50,000	6.83	8.80	9.67	9.80	9.35	8.74
50,001 to 75,000	8.23	11.1	12.8	13.9	14.2	13.1

Environmental Due Diligence in Oil & Gas Transactions

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Principal Concerns

- To what extent should environmental liabilities be factored into a transaction?
  - The parties to a transaction can generally account for known environmental risks.
  - Unquantifiable risks lead to uncertainty that can upset the deal.
  - Lenders often require a minimum level of due diligence.
- The primary objective of environmental due diligence is to reduce uncertainty by:
  - Identifying Risks
  - Quantifying Risks
  - Allocating Liabilities

Relevant Deal Points

- Stock versus Asset Purchase
- Price Negotiation
- Carve-outs
- Representations and Warranties
- Covenants
- Releases
- Indemnification
- “As Is” provisions
- Insurance
- Escrow
- Post Acquisition Integration
- Timing for Due Diligence
- Importance of environmental issues to overall scope of the deal.

The Players

- Seller
- Buyer
- Lenders/Passive Investors
- Deal Brokers (Investment Bankers)
- Attorneys
- Environmental Consultants
- Regulators

Seller

- Lay groundwork prior to selling:
  - Hire a reputable environmental consultant that is familiar with the industry to conduct Phase I ESAs and compliance audits.
  - Prepare cost estimates of issues.
  - Identify company representative that is knowledgeable of operational and environmental issues.
  - Package information with a cover memo and organized supporting documents.

Buyer

- Generally prefers to purchase assets rather than stock to avoid the assumption of liability.
- Wants to conduct a full review of environmental issues to identify potential liability:
  - Reduced asset value
  - Corporate stigma
  - Non-compliance (injunction, penalties)
  - Environmental harm (Remediation costs, Natural Resource Damage)
  - Human Exposure (OSHA, Toxic Torts)
  - Individual liability of officers and managers

The Environmental Review

- Site-specific
  - Soil, surface water, groundwater contamination
  - Recognized environmental conditions
- Offsite Disposal
- Operational/Regulatory Compliance
  - Emissions/discharge limitations
  - Environmental Management Systems
  - Reporting & record keeping
  - Environmental testing and monitoring data (historical Phase I ESAs)
  - Permitting
    - Are necessary permits in place?
    - Will the permits transfer to a new owner?
  - Health & Safety
  - Future Compliance Issues (New, Pending, & Proposed Requirements; Changes in operations)
- Public Disclosures
  - Press Releases
  - Website (voluntary sustainability reports)
  - Financial Statements/SEC Reporting (Environmental reserves/asset retirement obligations)
- Legal
  - Litigation: claims or threatened claims
  - Contractual: prior indemnification agreements, insurance policies
  - Governmental: orders and decrees, compliance history
- Legacy liability relating to divested properties or businesses for which Seller may retain liability.

Hiring a Consultant

- Independent consultants should provide objectivity -- Don't hire Seller's consultant.
- Reliance on consultant opinions is limited by the consulting contract
  - Reps/Warranties
  - Liability Limits / Insurance
  - Indemnities
  - Waste disposal costs
  - Confidentiality
  - Who will hire: Client or Attorney?
- The applicability of the ASTM standard may be limited depending on whether the CERCLA petroleum exclusion applies. In any event, the ASTM Standard doesn't require the following to be addressed:
  - Asbestos
  - Lead Based Paint
  - Drinking Water
  - Wetlands
  - Endangered Species
  - Mold
  - Radon Gas
  - Regulatory Compliance
  - Health & Safety
  - Cultural or historic sensitivities

Negotiation of Inspection Period Issues

- Ability to conduct sampling
- Who pays for waste disposal expenses
- Permission to talk to regulatory agencies
- “Free Look” Period
- Regulatory Reporting Requirements

Confidentiality/Privilege Issues

- Non-disclosure Agreement
  - Buyer may walk, leaving Seller with reporting obligations…
  - Control what or how Buyer can disclose information to Seller and 3rd parties (including governmental agencies).
- Attorney Client Privilege
  - Enables the client to avoid disclosure of confidential communication made between the client and his attorney for the purpose of obtaining legal advice. But, the privilege:
    - does not generally protect raw data;
    - can be waived;
    - does not shield the client from answering questions about the violation itself, and;
    - does not eliminate otherwise applicable reporting requirements.
- State Environmental Audit Privilege Statutes
  - Generally provides a shield against disclosure and offers limited immunity for violations that are detected, reported, and corrected.
  - The Party conducting the audit may need to provide notice of the audit to regulatory authorities before the audit begins.

Sources of Environmental Liability

- Federal Law
  - Clean Air Act, Clean Water Act, RCRA, OSPCCA
  - CERCLA petroleum exclusion
  - Federal Agencies: EPA, MMS, Corps of Engineers, Coast Guard, BLM, OSHA, SEC
- State Law
  - State environmental laws generally implement federal environmental programs but may be stricter than federal requirements.
  - Oil & gas statutes and regulations
  - Common Law
    - Torts (negligence, strict liability, nuisance, trespass)
    - Contracts
- Local/Municipal Laws
  - May enforce state programs and may be stricter than state or federal law.

Typical Oil & Gas Concerns

- Plugged Wells & Abandoned Wells
- Saltwater Seeps
- Urban Encroachment
  - Residential neighbors
  - Buyer may want to eventually decommission the field for development.
- Waste Management and Disposal
- Spills from Tank Systems and Pipelines
- Subsurface Injection Control
- Oilfield Remediation
- Endangered Species
- Hydrogen Sulfide
- NORM wastes
- PCBs & Mercury from pumping stations
- Air Permits

Methods of Shifting Risk

- Indemnity/Escrow
- Environmental Insurance
  - Remediation cost cap, Pollution legal liability
  - Requires a few weeks to get policy
  - Need a baseline of information (at least Phase I's)
  - Hard to insure known problems
  - Easier to insure a portfolio of properties
  - Counsel should assist negotiation and review of policy
- Fixed Cost Remediation Agreements
- No Further Action Letters
  - Generally not a release from liability
- Voluntary Clean Up Programs/State Oilfield Cleanup Funds
  - State may provide a release associated with past contamination
  - Standards for closure?
  - Who will do work?
- Brownfield Response Programs

Questions & Answers

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