10th Annual International Petroleum Environmental Conference

MONDAY, NOVEMBER 10, 2003

CONFERENCE REGISTRATION

I. WORKSHOPS

"Waste Minimization in Oil and Gas Exploration and Production" 9:00 am - 4:30 pm

Bart Sims, Texas Railroad Commission

"Microbial Forensics: Application of Molecular Methods for Understanding Microbial Processes in Systems Operation and Remediation" 1:00 pm - 5:00 pm

Greg Davis, Microbial Insights, Inc.
Aaron Peacock, University of Tennessee, Center for Biomarker Analysis

TUESDAY, NOVEMBER 11, 2003

CONFERENCE REGISTRATION 7:00 am - 7:00 pm

I. PLENARY SESSION 8:00 am - 11:15 am

WELCOME AND OPENING REMARKS 8:00 am - 8:15 am

Kerry L. Sublette, Conference Chair

PLENARY SPEAKERS:

John Veil, Argonne National Laboratory, Washington, DC
Zdravko Spiric, INA-Naftaplin, Croatia 8:15 am - 8:45 am

"Options for Water Management in the Oil and Gas Industry"

J. Daniel Arthur ALL Consulting, Tulsa, OK 8:45 am - 9:15 am

"Analysis of Water Management Alternatives and Beneficial Uses of Coal Bed Methane Produced Water"

James K. Otton USGS, Lakewood, CO 9:15 am - 9:45 am

"The Osage-Skiatook Petroleum Environmental Research (OSPER) Project - Insights into Oil Production Impacts and Implications for Remediation"

Aston Hinds ChemPro International, LLC, Houston, TX 9:45 am - 10:15 am

"Global Exploration and Production Companies Pick up the Gauntlet on Corporate Social Responsibility"

David Pierce Washburn University, Topeka School of Law, Topeka, KS 10:15 am - 10:45 am

"Reviewing a Decade of Environmental Regulation of Upstream Oil and Gas Operations"

Dan Gurney NPTO/NETL, U.S. Dept. of Energy. Tulsa, OK 10:45 am - 11:15 am

"DOE Environmental Activities in the Oil and Gas Programs"

II. VIEWING OF EXHIBITS 11:15 am - 12:15 pm

LUNCH

Speaker: **Rachel Pappworth** Sound Environmental Solutions, Houston, TX 12:15 pm - 1:30 pm

"Things My Mother Never Taught Me, But It Would Have Been Nice to Know!"

III. CONCURRENT TECHNICAL SESSIONS 1:30 pm - 6:00 pm

1. **Environmental Impacts of Petroleum Production: Recent Results from the USGS OSPER Project, Osage County, Oklahoma**
2. **Pollution Prevention and Waste Minimization**
3. **Bioremediation I**
4. **Hydrocarbon Characterization and Risk Analysis**

IV. POSTER SESSION 5:30 pm - 7:00 pm

V. EXHIBITS OPEN 10:30 am - 7:00 pm

VI. EXHIBITOR RECEPTION 5:30 pm - 7:00 pm

VII. OPENING DINNER 7:00 pm - 10:00 pm
Western "Fun & Fixins"

WEDNESDAY, NOVEMBER 12, 2003

CONFERENCE REGISTRATION 7:30 am - 12:00 pm

I. EXHIBITS OPEN 7:30 am - 12:00 pm

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

1. **Drilling Waste Management and Treatment / Chlorinated Hydrocarbons**
2. **Produced Water Treatment**
3. **Phytoremediation / Bioremediation II**
4. **Sediment Control With Silt Fence On Pipeline Construction**

LUNCH 12:00 pm - 1:30 pm

Speaker: **Kerry L. Sublette**, University of Tulsa, Tulsa, OK

"Lessons Learned from Small Independent Oil & Gas Producers"

III. WORKSHOPS 1:30 pm - 5:30 pm

"Water and Waste Regulatory Issues and Management Options"

Instructed by: John Veil, Markus Puder, and Debbie Elcock
Argonne National Laboratory, Washington, D.C.

"Fundamentals of Bioremediation of Hydrocarbon-Contaminated Soils"

Instructed by: Kerry L. Sublette
University of Tulsa, Tulsa, OK

THURSDAY, NOVEMBER 13, 2003

CONFERENCE REGISTRATION 7:30 pm - 5:30 pm

I. CONCURRENT TECHNICAL SESSIONS 8:00 am - 12:00 pm

1. **10 Years of Oil-Spill Research in Louisiana - and Still Counting!**
2. **Bioremediation of Hydrocarbons and MTBE in Groundwater**
3. **Legal and Regulatory Issues in Exploration and Production of Oil and Gas**
4. **Characterization and Remediation of Brine Impacted Soils**

LUNCH 12:00 pm - 1:30 pm

Speaker: **John Candler**, MI Drilling Fluids, Houston, TX

"Climbing Out of the Dumpster to Discover Beneficial Re-Use Options"

II. CONCURRENT TECHNICAL SESSIONS 1:30 pm - 6:00 pm

1. **Environmental Issues in Exploration and Production of Natural Gas and Gas Condensates/Environmental Management**
2. **Technology Transfer/Air Emissions**
3. **Environmentally Acceptable Endpoints & Ecosystems Restoration/Remediation of Petroleum Hydrocarbons**
4. **Produced Water Treatment/NORM**

III. NETWORKING RECEPTION 5:45 pm - 6:45 pm

FRIDAY, NOVEMBER 14, 2003

SYMPOSIUM REGISTRATION 7:30 am - 8:00 am

I. SPECIAL SYMPOSIUM 8:00 am - 1:30 pm

"Water Issues in the Production of Coalbed Methane"

Technical Sessions

TUESDAY, NOVEMBER 11, 2003 - AFTERNOON

ENVIRONMENTAL IMPACTS OF PETROLEUM PRODUCTION: RECENT RESULTS FROM THE USGS OSPER PROJECT, OSAGE COUNTY, OKLAHOMA

Chair: Jim Otton, USGS, Denver Federal Center, Lakewood, CO

- **Topographic and Geologic Controls on the Distribution and Movement of Produced Water and Hydrocarbons at the Osage Skiatook Petroleum Environmental Research Site "A"** James K. Otton, USGS, Denver Federal Center, Lakewood, CO
- **The Chemical Composition and Distribution of Groundwater Impacted by Petroleum Production Operations: The OSPER "A" Site, Osage County, OK** Yousif K. Kharaka, Robert Zielinski, and Bruce Smith, USGS, Menlo Park, CA
- **Natural Remediation of Groundwater Impacted by Petroleum Production Operations: The OSPER "A" Site in Osage County, OK** James Thordsen, Yousif K. Kharaka, Evangelos Kakouros and Gil Ambats, USGS, Menlo Park, CA
- **Determining the Distribution of Subsurface Salt Contamination Using the Composition of**

Oak Leaves: A Case Study at an Oil Production site, Northeast Oklahoma Robert A. Zielinski, James Cathcart, Tammy Hannah, and John Bullock, Jr., USGS, Denver, CO

- **Effects of Produced Water and Hydrocarbon Releases on Vegetation at Site A of the Osage-Skiatook Petroleum Environmental Research Project, Osage County, Oklahoma** Bobby D. Keeland and John W. McCoy, USGS, Lafayette, LA
- **Topographic Mapping Using GPS Receivers and GIS Software at the Osage-Skiatook Petroleum Environmental Research Sites in Oklahoma** Marvin M. Abbott, USGS, Oklahoma City, OK
- **The Fate of Petroleum Releases from the Osage-Skiatook Petroleum Environmental Research (OSPER) Sites, Osage County, Oklahoma** Frances Hostettler, Yousif K. Kharaka, and Edward Godsy USGS, Menlo Park, CA
- **Electrical Geophysical Character of Areas of Shallow Brine Contamination, Osage County, Oklahoma** Bruce D. Smith and J.K. Otton, USGS, Lakewood, CO; Marvin M. Abbott, USGS, Oklahoma City, OK; Alan Whitten, University of Oklahoma, Norman, OK
- **Nearby Lake Sediment Quality and Seedling Tree Survival on Eroded Oily Waste/Brine Contaminated Soil** Don H. Kampbell, US EPA ORD/GWERD, Ada, OK; Marvin M. Abbott, USGS, Oklahoma City, OK; Matt Smith, East Central University, Ada, OK
- **Hydrology and Subsurface Transport of Oil-Field Brine at the Osage-Skiatook Petroleum Environmental Research (OSPER) "B" Site, Oklahoma** William N. Herkelrath and Y.K. Kharaka, USGS, Menlo Park, CA

POLLUTION PREVENTION AND WASTE MINIMIZATION

Chair: Debbie Elcock, Argonne National Laboratory, Washington, DC

- **Potential Environmental Impact from Mishandled Waxy Crude Oils** J.R. Becker, BJ Unichem Production Chemicals, Tomball, TX
- **Development of an Environmentally Friendly and Economical Process for Plugging Abandoned Wells (Phase II) - IPEC FUNDED PROJECT** Dr. Subhash Shah and Yeon-Tae Jeong, University of Oklahoma, Norman, OK
- **Step Change in Development of Environmentally Responsible Chemicals** Janine Killaars, John Hall, and Don Whitfill, Halliburton BV, The Netherlands
- **Using GIS to Streamline Section 404 Permitting Review Process** Ray Stevens, Devon Energy, Bridgeport, TX; Peter D. McKone and Eric Huff, Carter & Burgess, Fort Worth, TX; Bruce Hunter and Minhe Ji, University of North Texas, Denton, TX
- **Future Outlook for Downhole Oil/Water Separators** John Veil, Argonne National Laboratory, Washington, DC
- **The Effect of Regional Conflicts and Political Rivalries on the Release of Petroleum Hydrocarbons to the Environment** Farhad Nadim, J. Iranmahboob, G. Hoag, C. Perkins, and A. Dahmani, University of Connecticut, Storrs, CT

- **Estimative for Slick Trajectories to Oil Spill Provocated by Exploration and Production Activities Both Offshore the Coast of and Inland the State of Espirito Santo** Marcela Borges Barros and Robson Sarmento, Universidada Federal do Espirito Santo, BRASIL
- **Reducing Remediation & Long-Term Monitoring Costs Through Accurate Site Assessment** Andre Brown and Jay W. Hodny, W.L. Gore and Associates, San Francisco, CA
- **Positive Potential of Offshore Applications of Managed Pressure Drilling Technology** Don M. Hannegan, Weatherford UBS, Ft. Smith, AR; Bill Bland, Weatherford UBS, Houston, TX

BIOREMEDIATION I

Chair: Babu Fathepure, Oklahoma State University, Stillwater, OK

- **Biodegradation of Petroleum Hydrocarbons in a Soil Containing Polyacrylamide** Sameer Khaitan and L.E. Erickson, Kansas State University, Manhattan, KS
- **Bioventing of Gasoline-Contaminated Soil: Some Aspects for Optimization** Stella M.C. Bezerra and Richard G. Zytner, University of Guelph, Guelph, ON, Canada
- **A New Tool for Characterization of Microbial Activity in Contaminated Soils During Remediation and Restoration** Kerry L. Sublette, Chintan Mehta, Aditya Moralwar and Laura Ford, University of Tulsa, Tulsa, OK; Aaron Peacock and David White, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN; Kathleen Duncan, University of Oklahoma, Norman, OK; Greg Thoma, University of Arkansas, Fayetteville, AR
- **The Effect of Fertilizer Use During Bioremediation of Crude Oil Contaminated Soil on Subsequent Restoration of Soil Ecosystems - IPEC PROJECT** Chintan Mehta, Aditya Moralwar, Kerry L. Sublette, and Laura Ford, University of Tulsa, Tulsa, OK; Josh Brokaw, Oklahoma State University, Stillwater, OK; Kathleen Duncan, University of Oklahoma, Norman, OK; Greg Thoma, University of Arkansas, Fayetteville, AR
- **Landfarming on the Alaskan North Slope - Historical Development and Recent Applications** James R. Chatham, BP Group, Anchorage, AK
- **Aerobic Biodegradation of Benzene, Toluene, Ethylbenzene, and Xylenes by Halophilic and Halotolerant Bacteria - IPEC-FUNDED PROJECT** Babu Fathepure and Carla Nicholson, Oklahoma State University, Stillwater, OK
- **Bioremediation of Soil Contaminated with Alkyllead Compounds - Laboratory Investigations and Field Trials** Claudia Gallert and Josef Winter, University of Karlsruhe, Karlsruhe, Germany
- **Restoring Sites Using Green Remediation Strategies** Dennis Beckmann, Group Environmental Mamnagement Company (A BP Affiliated Company), Tulsa, OK; Kurt Alloway, The RETEC Group, Inc., Salt Lake City, UT, and David Friday, The RETEC Group, Inc., Austin, TX
- **Microbial Activity in Soil During Gasoline-Ethanol Degradation** Patricia Osterreicher-Cunha and J. Guimaraes, Federal University of Rio de Janeiro - UFRJ, Rio de Janeiro, Brazil; E. Vargas, Jr. and M. Silva, Pontifical Catholic University of Rio de Janeiro, Brazil

HYDROCARBON CHARACTERIZATION AND RISK ANALYSIS

Chair: Sara McMillen, ChevronTexaco Energy Research and Technology Company, Richmond, CA

- **Impact of Weathering Processes on TPH Risk-Based Screening Levels** Sara J. McMillen, Nishi Nijhawan, and Kirk T. O'Reilly, ChevronTexaco, Richmond, CA
- **Realistic Soil Cleanup Standards With Dual Equilibrium Desorption** Mason B. Tomson, A. T. Kan, X. Cheng, and W. Chen, Rice University, Houston, TX
- **Characterizing Risks to Livestock from Petroleum Hydrocarbon Exposure** Mala Pattanayek and Bridgette DeShields, BBI, Inc., Petaluma, CA
- **Carbon Fractionation Approach to Clean-up Standards for Soils Contaminated with Hydrocarbons** Rafael G. Rivera, L. Benitez, C. Travis, and D. Miller, Alta Technical Services, Inc, Oak Ridge, TN
- **Probabilistic Reliability Modeling for E&P Facilities in the Tallgrass Prairie Preserve - IPEC PROJECT** L. Zambrano, G. Thoma, University of Arkansas, Fayetteville, AR; K.L. Sublette, University of Tulsa, Tulsa, OK; K. Duncan, University of Oklahoma, Norman, OK
- **Health Risk Analysis Carried Out in an Oil Storage and Distribution Station in Eastern Central Mexico to Determine Required Cleaning Levels** Rosario Iturbe, Rosa Ma Flores, Carlos Flores, and Luis G. Torres, Universidad Nacional Autonoma de Mexico, Mexico D.F., Mexico
- **Soil Clean-Up Levels for Residential and Industrial Land Use in Mexico: A Case Study Applying RBCA on a Site Contaminated by Hydrocarbons** Rosa Maria Flores-Serrano, Universidad Nacional Autonoma de Mexico, Mexico D.F., Mexico
- **Light, Medium and Heavy Mexican Crude Oils Characterization** Luis G. Torres, Guadalupe Urquiza, and Rosario Iturbe, Instituto de Ingenieria, UNAM, Mexico, D.F. Mexico; Beatriz Castro, Instituto Mexicano del Petroleo, Mexico, D.F. Mexico
- **A Model to Rank the Risk of Environmental Impact on the Biodiversity Around Pollution Systems** Kingsley E. Abhulimen, University of Lagos, Nigeria

POSTER SESSION

Chair: Brandy Fidler, University of Tulsa, Tulsa, OK

- **Identification of the Bioremediation Limiting Factors of a Clay Bearing Soil contaminated with Crude Oil** A.C.L. Rizzo, C.D. Cunha, R.S. Raimundo, M.H. Magalhaes, J.L.S. Lemos, V.S. Millioli and R.L.C. Santos, CETEM/MCT, Rio de Janeiro, Brazil; S.G.F. Leite, Federal University of Rio de Janeiro, Brazil; A.U. Soriano, CENPES, Rio de Janeiro, Brazil
- **Bioremediation: Assessing the Addition of Biosurfactants in the Presence of Fungi on Biodegradation of Clay Soil Impacted by Petroleum** Judith L.S. Lemos, V. Millioli, L. Santos, A. Rizzo, C. Cunha, and R. Santos, CETEM/MCT, Rio de Janeiro, Brazil; S.G.F. Leite, Federal

University of Rio de Janeiro, Brazil; A.U. Soriano, CENPES, Rio de Janeiro, Brazil

- **Biodegradation of Synthetic Base Fluids in Gulf of Mexico Sediments** David Herman and D. J. Roberts, University of Houston, Houston, TX
- **Conducting Refinery Audits for Benzene Waste Operations - NESHAP Compliance** Calvin Niss and David Wolfe, TriHydro Corporation, Laramie, WY; Cindy Mueller, ConocoPhillips, Houston, TX
- **Nematode Population Changes During Phytoremediation of a Crude Oil-Contaminated Soil - IPEC-FUNDED PROJECT** Mary Savin, S. Ziegler, G. Thoma, K. Greer, P. Tomlinson, and D. Wolf, University of Arkansas, Fayetteville, AR
- **Looking for the Signature of the Intrinsic Bioremediation of BTEX in Subsurface Microbial Ecology Using Bio-Sep® Bug Traps - IPEC-FUNDED PROJECT** Majorie Boone, Kerry L. Sublette, and Laura Ford, University of Tulsa, Tulsa, OK; Anita Biernacki, Aaron Peacock and David White, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN
- **Looking for the Signature of the Intrinsic Bioremediation of MTBE in Subsurface Microbial Ecology Using Bio-Sep® Bug Traps - IPEC-FUNDED PROJECT** Anita Biernacki, Aaron Peacock and David White, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN; Marjorie Boone, Kerry L. Sublette, and Laura Ford, University of Tulsa, Tulsa, OK; Ravi Kolhatkar, BP Group Environmental Mgmt Co., LaPalma, CA
- **Slow Release Properties of Bio-Sep® Beads; Baiting Bug Traps** Thomas Mathew, Kerry L. Sublette, and William Redman, University of Tulsa, Tulsa, OK; Aaron Peacock and David White, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN
- **Estimating the Aerial Extent of Spilled Fluids on Soil Surface with GIS Based Physical Model** C.Y Wong, G.Thoma, University of Arkansas, Fayetteville, AR; K.L. Sublette and L. Ford, University of Tulsa, Tulsa, OK; K. Duncan, University of Oklahoma, Norman, OK
- **Revegetation: A Comparison of Treated Contaminated Soil and Displaced Soil Following Bioremediation of a Crude Oil Spill in the Tallgrass Prairie Preserve - IPEC PROJECT** Chintan Mehta, Kerry L. Sublette, and Laura Ford, University of Tulsa, Tulsa, OK; Kathleen Duncan, University of Oklahoma, Norman, OK; Joshua Brokaw, Oklahoma State University, Stillwater, OK; Greg Thoma, University of Arkansas, Fayetteville, AR
- **The Impacts of Seismic Lines on Breeding Migratory Birds in the Kendall Island Migratory Bird Sanctuary (Canadian Arctic)** Amber R. Ashenhurst, Dr. Susan J. Hannon, University of Alberta, Edmonton, Alberta, Canada
- **Rock/Cement Permeability Under Conditions Relevant to Subsurface Disposal of Carbon Dioxide** Andrew J. Dugid, Robert G. Bruant, Jr., Mileva Radonjic, George W. Scherer and Michael A. Celia, Princeton University, Princeton, NJ; Charles A. Christopher, BP America, Inc., Houston, TX
- **Brine Impact Assessment in the Tallgrass Prairie** Alison Galatian, Bryan Tapp, University of Tulsa, Tulsa, OK

- **Status of Soil Nutrients Following Bioremediation of Petroleum Contaminated Tallgrass Prairie Soils** Joshua Brokaw, Oklahoma State University, Stillwater, OK; Kerry L. Sublette, Chintan Mehta, and Laura Ford, University of Tulsa, Tulsa, OK; G. Thoma, University of Arkansas, Fayetteville, AR; Kathleen Duncan, University of Oklahoma, Norman, OK
- **The Other and Original Produced Water Issue** Kerry Sublette, University of Tulsa, Tulsa, OK; J. Berton Fisher, Exponent, Inc., Tulsa, OK
- **Monitoring the Effectiveness of the Sulfate Amendment of a BTEX-Contaminated Aquifer Using Bio-Sep® Bug Traps** Kerry L. Sublette, Chintan Mehta, and Thomas Mathew University of Tulsa, Tulsa, OK; Ravi Kolhatkar, BP Group Environmental Mgmt Co., LaPalma, CA; Aaron Peacock and David White, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN; Dennis Beckmann, BP Group Environmental Mgmt Co., Tulsa, OK; David Cook, GeoEngineers, Seattle, WA
- **Remediation of Brine Spills With Hay, Continued - IPEC FUNDED PROJECT** Shailendra Singh, Laura Ford, Kimberly Carter, and Kerry L. Sublette, University of Tulsa, Tulsa, OK; Kathleen Duncan, University of Oklahoma, Norman, OK

WEDNESDAY, NOVEMBER 12, 2003 - MORNING

DRILLING WASTE MANAGEMENT AND TREATMENT / CHLORINATED HYDROCARBONS

Chair: John Veil, Argonne National Labs, Washington, DC

DRILLING WASTES

- **New Innovative Reclamation Procedures to Cap Drilling Waste Reserve Pits in the Permafrost Environmental of North Slope, Alaska** Judd Peterson, Alaska Department of Environmental Conservation, Anchorage, AK; Jim Chatham, BP Exploration (Alaska), Inc., Anchorage, AK
- **Drilling Fluid Chemicals and Earthworm Toxicity** Karen McCosh and Jonathan Getliff, MI Drilling Fluids, West Tullos, Aberdeen, UK
- **Chemical Method for Cleanup of Produced Oil-Coated Solids from Oil Well Operations** B. R. Reddy, Ian Robb, Tom Dealy, and Don Whitfill, Halliburton Energy Services, Duncan, OK
- **Onshore Drilling Waste Management: Beneficial Reuse of Cuttings** Mark L. Susich, Marathon Oil Company - Alaska, Anchorage, AK; Max Schwenne, VP OASIS Environmental, Anchorage, AK
- **Biodegradation of Synthetic Drilling Mud Base Fluids in Gulf of Mexico Deep-Sea Sediments** D. J. Roberts, D. Herman, D. Gangumalla, and V. Demir, University of Houston, Houston, TX
- **Slurry Injection of Drilling Wastes - Regulatory Requirements and Practices** Markus Puder, John Veil, and William Bryson, Argonne National Laboratory, Washington, DC
- **Probabilistic Approach to Modeling and Risk Assessment of Cuttings Re-Injection Operations** Quanxin Guo and Thomas Geehan, M-I Swaco, Houston, TX

CHLORINATED HYDROCARBONS

- **Natural Attenuation of Chlorinated Solvents in Groundwater** Monica P. Suarez, Tricia Rittaler, Hanadi Rifai, and Sarah Hausmen, University of Houston, Houston, TX

PRODUCED WATER TREATMENT

Chair: G. Dale Wesson, FAMU-FSU College of Engineering, Tallahassee, FL

- **Long-term Effectiveness of Surfactant-Modified Zeolite for Removal of BTEX from Produced Waters** J. Michael Ranck and Robert S. Bowman, New Mexico Tech, Socorro, NM; Brian Carrico and Lynn Katz, University of Texas, Austin, TX; Enid Sullivan, Los Alamos National Lab, Los Alamos, NM
- **Effect of Temperature and Salinity on BTEX Removal Using Surfactant-Modified Zeolite** Lynn E. Katz and Guifang Tan, University of Texas at Austin, Austin TX; Robert Bowman, New Mexico Tech, Socorro, NM; Enid Sullivan, Los Alamos National Labs, Los Alamos, NM
- **Cost Factors Associated with Managing Produced Water at CBM Properties in the Rocky Mountain Region** Deidre Boysen and Jessica Boysen, BC Technologies, Ltd, Laramie, WY
- **Small Diameter Hydrocyclone Separation Efficiency Estimation Computational Fluid Dynamics** Shannon Grady, G. Dale Wesson, Makola Abdullah and Egwu Kalu, FAMU-FSU College of Engineering, Tallahassee, FL
- **Final Evaluation of Pilot Wetlands for Produced-Water Treatment at Naval Petroleum Reserve No. 3** L.M. Jackson, U.S. DOE, Rocky Mountain Oilfield Testing Center, Casper, WY; J.E. Myers, Chevron Texaco, Bellaire, TX
- **Issues Related to Oil/Water/Solids Separation at a Commercial Produced Water Treatment Facility Operating in South Central Wyoming** John E. Boysen, Tim J. Larson and Robert E. Boysen, BC Technologies, Ltd, Laramie, WY
- **Flotation Pump Proves Successful for the Treatment of Produced Water** Paul Broussard, Monosep Corporation, Lafayette, LA

PHYTOREMEDIATION / BIOREMEDIATION II

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

PHYTOREMEDIATION

- **Influence of Plants on Soil Community Dynamics in a Petroleum-Contaminated Soil - IPEC-FUNDED PROJECT** S.E. Ziegler, G. Thoma, K. Greer, and D. Wolf, University of Arkansas, Fayetteville, AR
- **Mathematical Modeling of Phytoremediation of Crude Oil Contaminated Soils - IPEC**

FUNDED PROJECT Greg Thoma, Duane Wolf, and Susan Ziegler, University of Arkansas, Fayetteville, AR

- **Phytoremediation of Petroleum Hydrocarbon Contaminated Soil: Results from the RTDF Cooperative Field Tests** P.A. Kulakow, B.A. Leven, and L. Erickson, Kansas State University, Manhattan, KS
- **Phytoremediation Potential of Amaranthus sp. for Heavy Metals Contaminated Soil of Oil Production Territory** A.B. Bigaliev, K.K. Boguspaev, and E.T. Zhanburshin, Kazakh National University, Almaty, Kazakstan
- **A Combined Use of Plants and Plant Growth Promoting Pseudomonas for Oil Spill Bioremediation** Alexander M. Boronin, I. Kosheleva, V. Kochetkov, and A. Filonov, Institute of Biochemistry and Physiology of Microorganisms, Pushchino, Russia; V. Dmitrieva, Center for Ecological Research and BioResources Development, Pushchino, Russia

BIOREMEDIATION II

- **Long-Term Composition Changes of Oil Residues in Patagonian Soils** N.S. Nudelman, Universidad de Buenos Aires, Buenos Aires, Argentina; Stella Maris Rios, Universidad Nacional de la Patagonia San Juan Bosco, Chubut, Argentina
- **Co-Composting of PAH-Contaminated Soil With Poultry Manure** Harrison I. Atagana, Technikon Mangouthu, Jacobs, Durban, South Africa
- **Bioremediation of Soil from Tengiz Oil and Gas Field** A.B. Bigaliev, A. Zhubanova, D. Dzhusupova, and A. Baktygaly, Kazakh National University, Almaty, Kazakstan

SEDIMENT CONTROL WITH SILT FENCE ON PIPELINE CONSTRUCTION

Chair: Bill Barfield, Khaled Gasem, Oklahoma State University, Stillwater, OK

- **Current Silt Fence Technology, Problems and Prospects** B.J. Barfield, Oklahoma State University, Stillwater, OK; J.C. Hayes, Clemson University, Clemson, SC
- Marty Matlock and R.A. Morgan, University of Arkansas, Fayetteville, AR
- **Monitoring Data on Effectiveness of Sediment Control Techniques** Mike Barrett, University of Texas, Austin, TX
- **Current Research to Find Proposed Solutions to Silt Fence Problems** Bill Barfield, Ellen Stevens, and Khaled Gasem, Oklahoma State University, Stillwater, OK
- **Silt Fence - Problems and Prospects from the Industry Viewpoint** Discussion led by Khaled Gasem, Oklahoma State University, Stillwater, OK

THURSDAY, NOVEMBER 13, 2003 - MORNING

10 YEARS OF OIL SPILL RESEARCH IN LOUISIANA - AND STILL COUNTING!

Chair: Don Davis, Louisiana State University, Baton Rouge, LA

- **A Pipeline GIS for Ouachita Parish, Louisiana** Michael A. Camille, The University of Louisiana at Monroe, Monroe, LA
- **Dispersant as an Oil Spill Countermeasure: Toxicity Evaluation and Oil Remediation in Wetland Environments** Quianxin Lin and Irving A. Mendelssohn, Louisiana State University, Baton Rouge, LA
- **Contingency Plans for Lousiana Coastal Waterways** Ehab Meselhe and Emad Habib, University of Louisiana at Lafayette, Lafayette, LA
- **Pipeline Mapping in Louisiana** John Snead, Louisiana State University, Baton Rouge, LA
- **Ocean Observing System for Oil Spill Contingency, Louisiana, USA** Gregory W. Stone, Louisiana State University, Baton Rouge, LA
- **Use of Oblique Aerial Video Imagery as a Resource for Coastal Issues** Karen Westphal, Louisiana State University, Baton Rouge, LA; Shea Penland, University of New Orleans, New Orleans, LA
- **An Oil Spill Data CD Program** George Wooddell, Robert Gramling, and Craig Forsyth, University of Louisiana at Lafayette, Lafayette, LA

BIOREMEDIATION OF HYDROCARBONS AND MTBE IN GROUNDWATER

Chair: Glenn White, Haley & Aldrich, Inc., Rochester, NY

- **Technology Sequencing to Reduce Groundwater Remediation Cost** Richard L. Sloan, Chickadee Remediation Company, Crosby, TX; Richard E. Woodward, Sierra Environmental Services, Inc., Houston, TX
- **Misconceptions Concerning the Behavior, Fate and Transport of the Fuel Oxygenates TBA and MTBE** Richard E. Woodward, Sierra Environmental Services, Inc., Houston, TX; Richard L. Sloan, Lyondell Chemical Company, Channelview, TX
- **Decision Support Software for Designing Groundwater Monitoring Plans** Meng Ling and Hanadi Rifai, University of Houston, Houston, TX; Julia Aziz and Charles Newell, Groundwater Services, Inc., Houston, TX; Jim Gonzales and Javier Santillan, Air Force Center for Environmental Excellence, Brooks AFB, TX
- **Monitoring the Effectiveness of the Sulfate Amendment of a BTEX-Contaminated Aquifer Using Bio-Sep® Bug Traps** Kerry L. Sublette, Chintan Mehta, and Thomas Mathew University of Tulsa, Tulsa, OK; Ravi Kolhatkar, BP Group Environmental Mgmt Co., LaPalma, CA; Aaron Peacock and David White, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN; Dennis Beckmann, BP Group Environmental Mgmt Co., Tulsa, OK; David Cook, GeoEngineers, Seattle, WA
- **Analysis of Microbial Communities Involved in the Remediation of BTEX in an Anaerobic Aquifer Using ^{13}C-labeled Compounds, Bio-Sep® Beads and In-Situ Microcosms** Roland Geyer, A. Peacock, D.C. White, The University of Tennessee, Knoxville, TN; K.L. Sublette,

University of Tulsa, Tulsa, OK; H.H. Richnow and M. Kastner, Center for Environmental Research UFZ, Leipzig, Germany

- **Proving the Viability of a Large Scale Bioremedy on an MTBE-Impacted Drinking-Water Aquifer in Southern California** Paul Tornatore and Glenn White, Haley & Aldrich, Inc., Rochester, NY; Kate Scow, University of California, Davis, CA; Jeff Baker, Tesoro Petroleum Companies, Seattle, WA; Aaron D. Peacock, University of Tennessee, Knoxville, TN
- **Source Zone Natural Attenuation Investigations at a Former Oil Field** Paul D. Lundegard, Unocal Corporation, Brea, CA; Paul C. Johnson, Arizona State University, Tempe, AZ
- **Oxygen Release Characteristics of ORC** Ashish Bagga, Hanadi Rifai, William Rixey, University of Houston, Houston, TX
- **Anaerobic Bio-Oxidation of MTBE and 1,2-DCA** David B. Vance, ARCADIS G&M, Inc., Midland, TX; Mark Lupo, ARCADIS G&M, Inc., Houston, TX; David Liles, ARCADIS G&M, Durham, NC; Neal McHugh, Kinder Morgan Liquid Terminals LLC, Carteret, NJ

LEGAL AND REGULATORY ISSUES IN EXPLORATION AND PRODUCTION OF OIL AND GAS

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

- **Results of the Inventory Required by the Energy Policy and Conservation Act (EPCA) Amendments of 2000** Richard L. Watson, Bureau of Land Management, Washington, DC
- **Using Fixed-Price 3rd Party Liability Transfer to Manage Petroleum Industry Related Environmental Liability** Nathan Block and Mike Holder, TRC Environmental Corporation, Austin, TX
- **Overfiling - A Closer Look at the Federal Enforcement Tool** Markus Puder and John Veil, Argonne National Laboratory, Washington, DC
- **Establishing Appropriate Numerical Water Quality Criteria For Salinity Minerals in Watersheds in Oklahoma** Patricia Billingsley, Oklahoma Corporation Commission, Oklahoma City, OK
- **Texas EMS Program Requirements with Respect to ISO 14001: 1996 and Responsible Care** Yoram Arnoni, Humble, TX; Bob Gifford and E. Susan Roothaan, Texas Commission on Environmental Excellence, Austin, TX
- **North Slope of Alaska Underground Injection Control Operations** Jim Regg and Bob Crandall, Alaska Oil and Gas Conservation Commission, Anchorage, AK
- **Best Management Practices (BMPs) - A New Way of Managing Oil and Gas Development on the Public Lands** Jim Perry and Tom Hare, Bureau of Land Management (BLM), Washington, DC
- **Oil and Gas Royalties Applications and Life Quality in the Communities of the Main Production Zone: Cases of Rio de Janeiro and Espirito Santo - Brazil** V.M.C. Ribeiro, Instituto de Apoio a Pesquisa e al Desenvolvimento do Estado do Espirito Santo, Vitoria, Brasil; J.F. Souza and R. Sarmento, Universidade Federal do Espirito Santo (UFES), Vitoria, Brasil

- **Introduction to the Voluntary Cleanup Program and Brownfields State Response Program, Railroad Commission of Texas** Aimee Beveridge, Railroad Commission of Texas, Austin, TX

CHARACTERIZATION AND REMEDIATION OF BRINE IMPACTED SOILS

Chair: Dennis Beckmann, BP Group Environmental Mgmt Co., Tulsa, OK

- **Remediation of Brine Spills With Hay, Continued - IPEC FUNDED PROJECT** Laura Ford, Shailendra Singh, Kimberly Carter, and Kerry L. Sublette, University of Tulsa, Tulsa, OK; Kathleen Duncan, University of Oklahoma, Norman, OK
- **Tallgrass Prairie Preserve: Recent Successes in Restoring A Historic Brine Scar** Dennis Beckmann, Kevin Heaton, and David Tsao, BP Group Environmental Mgmt Co., Tulsa, OK; Walter Zverina, RETEC, Austin, TX
- **The Use of a Hydroseeder to Revegetate Oil Brine Spill Sites** Milan C. Vavrek, Wes Colgan, III, and Jeffrey Monroe, Louisiana Tech University, Ruston, LA
- **Oil and Saltwater Releases from E&P Operations in Oklahoma, 1993-2003** Kerry L. Sublette, University of Tulsa, Tulsa, OK; J. Berton Fisher, Exponent, Tulsa, Oklahoma; Mike Schmidt, Oklahoma City, OK, Greg Thoma, University of Arkansas, Fayetteville, AR
- **Symbiotic Fungi and Plant Performance in Oil Brine Contaminated Soil** Wes Colgan III and Milan Vavrek, Louisiana Tech University, Ruston, LA
- **Molecular Methods to Describe Rhizosphere Fungal Communities from Oil Brine Contaminated Soils** D. Ross Patrick, Wes Colgan III, and Milan Vavrek, Louisiana Tech University, Ruston, LA
- **Halophyte Technology Mitigates Landowner-Driven Oilfield Saltwater and Petroleum Hydrocarbon Surface Impact Litigation** D.J. Carty, GreenBridge EarthWorks, Eldorado, AR; C.R. Nestrud, Chisenhall, Nestrud & Julian, Little Rock, AR; L.E. Deuel, Soil Analytical Services, Inc., College Station, TX ; N.P. Yensen, NyPa-International, Tucson, AZ
- **Restoration of Produced Water Release to East Texas Forest Land** Gay Gutierrez, The RETEC Group, Inc., Austin, TX; Kevin Heaton, Group Environmental Management Company (A BP Affiliated Company), Houston, TX; Michael Sitton, BP America Production, Longview, TX

THURSDAY, NOVEMBER 13, 2003 - AFTERNOON

ENVIRONMENTAL ISSUES IN EXPLORATION AND PRODUCTION OF NATURAL GAS & GAS CONDENSATES / ENVIRONMENTAL MANAGEMENT

Chair: Omar Barkat, McNeese State University, Lake Charles, LA

NATURAL GAS

- **Solving the Next Impediment to Coal Bed Methane Development in the Powder River Basin** Jim B. States, Rocky Mountain Oilfield Testing Center, Casper, WY; Terry Brown, Western Research Institute, Laramie, WY; Mickey Steward, Coal Bed Methane Coordination Coalition, Buffalo, WY
- **Design Enhancements to Decrease Sump Recrystalization in a Non-Regenerative Desiccant Dryer** Lori Acor, NATCO Group, Inc., Houston, TX
- **Environmental and Other Issues Respecting Exploration for and Development of Sour Natural Gas in Alberta, Canada and Means to Address the Issues** J.D. Dilay, Alberta Energy and Utilities Board, Calgary, Alberta, Canada
- **Pipeline Safety Regulations to Protect Human Health and the Environment** Deborah Elcock, Argonne National Laboratory, Washington, DC
- **BTEX Emissions in Natural Gas Plants** Omar Barkat and Muralidhar Ganji, Mcneese State University, Lake Charles, LA
- **Bioregenerable Selective Sorbents for Hydrogen Sulfide Removal From Natural Gas** Brandy R. Fidler and Kerry L. Sublette, University of Tulsa, Tulsa, OK; Gary Jenneman, ConocoPhillips, Bartlesville, OK; Greg Bala, INEEL, Idaho Falls, ID

ENVIRONMENTAL MANAGEMENT

- **Development of a Title V Permit Compliance System** Leigh G. McDaniel and Jeffrey A. Smith, ConocoPhillips Alaska, Inc., Anchorage, AK
- **Environmental Performance Evaluation of Upstream Activities for Oil and Gas Industry** J. F. de Souza, R. Sarmento, and V.M.C. Ribeiro, Universidade Federal do Espirito Santo (UFES), Vitoria, Brazil
- **Environmental Management Systems After Sarbanes-Oxley** Ann R. Barker, TRC Environmental Corporation, Austin, TX

TECHNOLOGY TRANSFER / AIR EMISSIONS

Chair: Phil Spurlin, BEACON Environmental Assistance Corp., Edmond, OK

TECHNOLOGY TRANSFER

- **Technology Transfer to Independent Oil Producers in Pennsylvania and New York for Restoration of Small Crude Oil-Contaminated Sites** James L. Brown, Lockheed Martin/ REAC, Edison, New Jersey; Harry Allen, U.S. EPA, Edison, NJ; Vincent Zenone, U.S. EPA, Philadelphia, PA
- **The Oklahoma Energy Resources Board - A Report on the First Ten Years of the Environmental Program** G. Phil Spurlin, BEACON Environmental Assistance Corporation, Edmond, OK
- **Hands on Audience Participation in Using IPEC Salt Soil Analysis Kit** G. Phil Spurlin, BEACON Environmental Assistance Corporation, Edmond, OK; George Collington, Oklahoma State University, Stillwater, OK

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

AIR EMISSIONS

- **A Stock Tank Emissions Model Based on Gas Solubility - IPEC FUNDED PROJECT** Jorge Plaza and R.E. Babcock, University of Arkansas, Fayetteville, AR
- **Identifying Fugitive Emisisions with Optical Imaging** Donald R. Robinson and R. Luke-Boone, ICF Consulting, Fairfax, VA
- **ICF Consulting GHG "Emissions Management System" (GEMS™)** Donald R. Robinson, R. Luke-Boone, V. Aggarwal, and Brian Gillis, ICF Consulting, Fairfax, VA
- **Emission Inventory for Offshore Oil Production at Campeche, Mexico** I. Schifter, C. Gonzalez-Macias, R. Villasenor, S. Gutierrez, A. Miranda, and E. Lopez-Salinas, Instituto Mexicano del Petroleo, Mexico, D.F., Mexico

ENVIRONMENTALLY ACCEPTABLE ENDPOINTS AND ECOSYSTEMS RESTORATION / REMEDIATION OF PETROLEUM HYDROCARBONS

Chair: Kathleen Duncan, University of Oklahoma, Norman, OK

EAE AND ECOSYSTEM RESTORATION

- **The Beaver (Castor fiber L.) in "Zutica" Oil Field Area, R. of Croatia** Zdravko Spiric, INA-Naftaplin, Zagreb, Croatia
- **Microbial Indicators of Soil Ecosystem Restoration Following Bioremediation of Oil and Brine Spills - IPEC PROJECT** Kathleen Duncan, E. Charles, B. Roe, D. Kupfer, and F. Najar, University of Oklahoma, Norman, OK; K.L. Sublette, C. Mehta, A. Moralwar, and L. Ford, University of Tulsa, Tulsa, OK; Joshua Brokaw, Oklahoma State University, Stillwater, OK; Tim Todd, Kansas State University, Manhattan, KS; Greg Thoma, University of Arkansas, Fayetteville, AR
- **Nematodes as an Indicator of the Restoration of Soil Ecology Following Oil and Brine Spills - IPEC PROJECT** Kerry L. Sublette, Chintan Mehta, Aditya Moralwar, and Laura Ford, University of Tulsa, Tulsa, OK; Josh Brokaw, Oklahoma State University, Stillwater, OK; Kathleen Duncan, University of Oklahoma, Norman, OK; Tim Todd, Kansas State University, Manhattan, KS; Greg Thoma, University of Arkansas, Fayetteville, AR
- **Comparing the Microbial Ecology of Oil and Brine-Impacted Soils Under Remediation - IPEC PROJECT** Aditya Moralwar, Chintan Mehta, Kerry L. Sublette, and Laura Ford, University of Tulsa, Tulsa, OK; Josh Brokaw, Oklahoma State University, Stillwater, OK; Kathleen Duncan, University of Oklahoma, Norman, OK; Tim Todd, Kansas State University, Manhattan, KS; Greg Thoma, University of Arkansas, Fayetteville, AR
- **Complicating Factors in the Use of Soil Microbial Ecological Indicators to Assess Soil Ecosystem Recovery - IPEC PROJECT** Kerry L. Sublette, Chintan Mehta, Aditya Moralwar, and Laura Ford, University of Tulsa, Tulsa, OK; Josh Brokaw, Oklahoma State University,

Stillwater, OK; Kathleen Duncan, University of Oklahoma, Norman, OK; Tim Todd, Kansas State University, Manhattan, KS; Greg Thoma, University of Arkansas, Fayetteville, AR

REMEDIATION OF PETROLEUM HYDROCARBONS

- **Modeling of Infinite-Dilution Activity Coefficients of Aqueous Systems** Brian J. Neely, S.S. Godavarthy, R.L. Robinson, and K. Gasem, Oklahoma State University, Stillwater, OK
- **Evidence of the Proliferation of Native Petroleum Reducing Bacteria Subsequent to the Application of Controlled In-Situ Chemical Oxidation** Thomas Douglas, Advanced Environmental Technologies, Pensacola, FL; William Lundy, BMS, Tinley Park, IL; H. Eric Nuttall, University of New Mexico, Albuquerque, NM
- **Remediation of TPH/PAH Contaminated Soil Using Soil Washing** Rosario Iturbe, Carlos Flores, Claudia Chavez, Guadalupe Bautista, and Luis G. Torres, Universidad Nacional Autonoma de Mexico, Mexico D.F., Mexico
- **Treating Petroleum Contaminated Soil and Sludges Using Plasma** R.N. Szente, Cidade Universitaria, Sao Paulo, Brazil; L. B. Souza, H. Pasquini, TSL Environmental Corp., Sao Paulo, Brazil
- **Optimization of Technological Cleaning Systems of Underground Water from Oil-Production in the Fergana Valley (Uzbekistan)** Mavlyanov N. Ganievich, B.D. Abdullaev, and J. Jamoljon, Institute of Hydrogeology and Engineering Geology, Tashkent, Republic of Uzbekistan

PRODUCED WATER TREATMENT / NORM

Chair: Mason Tomson, Rice University, Houston, TX

PRODUCED WATER TREATMENT

- **When Oilfields Become Water Fields, The Saga of Small Producers in California** Iraj Ershaghi, University of Southern California, Los Angeles, CA; Don Duttlinger, PTTC, Houston, TX; Lance Cole, PTTC, Sand Springs, OK
- **Water Clarifier Improves Throughput, Oil Quality, and Overboard Water All** Paul Hart, James Towner, and Joseph Cheng, Baker Petrolite Corporation, Sugar Land, TX
- **Online Monitoring for Wastewater Effluent Compliance in the Chinese Petrochemical Industry** John A. Satterfield, II, C.H. Guernsey and Associates, Oklahoma City, OK; Du Weidong, Petrochina Company Ltd, Hebei, China

NORM

- **NORM Scale Formation, Control, and Relation to Gas Hydrate Control** Mason B. Tomson, Amy Kan, G. Fu, and M. Al-Thubaiti, Rice University, Houston, TX
- **Association of NORM with Mississippi Hydrocarbon Production: Project Overview** Charles T. Swann, Joel Kuszmaul, Clayton McKay, and John Matthews, University of MS, University, MS; Rick Ericksen, MS State Board of Registered Professional Geologists, Jackson, MS

- **Chemical and Radiological Analyses of Mississippi Hydrocarbon Production Brines, Scales and Sludges** John C. Matthews, Charles T. Swann, Joel Kuszmaul, and Clayton McKay, University of Mississippi, University, MS; Rick Ericksen, MS State Board of Registered Professional Geologists, Jackson, MS
- **Radioecological Monitoring and Decontamination Technology of NORM Sludge from Vuctyl Oil and Gas Field** Vladimir Nekoutchaev and Eugenue Krapivski, Ukhta State University, Ukhta, Russia; Victor Ryzhakov, Vuctyl Company, Vuctyl, Russia

SPECIAL SYMPOSIUM

FRIDAY, NOVEMBER 14, 2003 - MORNING

WATER ISSUES IN THE PRODUCTION OF COALBED METHANE

Chairs: J. Daniel Arthur, ALL Consulting, Tulsa, OK
Kerry L. Sublette, University of Tulsa, Tulsa, OK

- **Analysis, Preparation and Review of Project Planning and Environmental Documents Pertaining to Coal Bed Methane Development** J. Daniel Arthur and Bruce G. Langhus, ALL Consulting, Tulsa, OK
- **Beneficial Uses of CBM Produced Water - Responsible Uses of a Critical Resource** Matthew Janowiak, BLM, Durango Colorado Field Office, Durango, CO; J. Daniel Arthur, ALL Consulting, Tulsa, OK
- **Hydraulic Fracturing of Coalbed Methane Reservoirs and Related Environmental Issues** Mike Paque, Ground Water Protection Council, Oklahoma City, OK; Lori Wrotenberry, NM Department of Energy, Minerals & Natural Resources, Oil Conservation Division, Santa Fe, NM
- **Designing and Implementing a Coalbed Methane Regulatory Program for Montana** Tom Richmond, Montana Board of Oil and Gas Conservation, Billings, MT
- **Industry Challenges in Coalbed Natural Gas Produced Water Management** Jeffrey Cline, Environment, Health and Safety, Anadarko Petroleum Company, The Woodlands, TX
- **CBM: The Canadian Experience - Canada's Regulatory Environment** Bill Gourley, Nexen, Inc., Calgary, AB, Canada
- **CBM: The Canadian Experience - A Technical View of CBM in Western Canada** Mike Simpson, Nexen, Inc., Calgary AB, Canada
- **Potential Habitat Loss and Population Bottlenecks Created by Increased Flows from CBM Operations** James Gore, Columbus State University, Columbus, GA
- **Limits on Produced Water Management Resulting from the Composition of Coalbed Methane Produced Water: The Powder River Basin** Cyndi Rice, USGS, Denver, CO; Yousif Kharaka, USGS, Menlo Park, CA; J. Berton Fisher, Exponent, Tulsa, OK

- **Dissolved Organics in Coal-Associated Waters: Implications for Human and Ecosystem Health** J. Berton Fisher, Exponent, Tulsa, OK; Annette Santamaria, Exponent, Houston, TX

OPTIONS FOR WATER MANAGEMENT IN THE OIL AND GAS INDUSTRY

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Water is nearly always produced along with oil and gas. The water is generally not clean enough to be used directly and therefore has traditionally been considered as a waste. The cost of managing produced water can be substantial and often plays a role in determining the economic viability of a well. There are multiple approaches to managing produced water, although not all are technically applicable or acceptable under existing regulatory guidelines. This paper discusses the range of produced water management options, including underground injection for disposal, injection for enhanced recovery, discharge, beneficial reuse, and others. The paper includes estimates of the volume of produced water generated each year, the range of costs associated with produced water management, and the U.S. regulatory requirements associated with produced water management. There is also a discussion of the responsibility of the petroleum industry (with a focus on Croatia's INA-Naftaplin) to ensure that produced water is managed in an environmentally safe and responsible manner and to share scientific knowledge about underground water quantity and quality developed through the oil and gas exploration and production process.

THE FATE OF PETROLEUM RELEASES FROM THE OSAGE-SKIATOOK PETROLEUM ENVIRONMENTAL RESEARCH (OSPER) SITES, OSAGE COUNTY, OKLAHOMA

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We are involved in a multidisciplinary investigation to study the transport, fate, natural attenuation and impacts of hydrocarbons, inorganic salts, trace metals, and radionuclides present in petroleum and produced-water releases at the OSPER A and B sites, located adjacent to the 4250-hectare Skiatook Lake, that provides drinking water to local communities and is a recreational fishery. More than one hectare of land at each site is affected by salt scarring, soil salinization and brine and petroleum contamination. Petroleum wells at the A site are inactive; the bulk of the hydrocarbon (now degraded and weathered oil) and produced water releases occurred 65-90 years ago. The B site includes an active production tank battery and adjacent brine and oil pit, an inactive tank battery and an injection well with a small brine pit. For this study, oil, soil, gas and/or water samples were obtained from several oil wells located at and adjoining the sites, from active pits at the B site, from inactive pits and surface accumulations at the A site and from several of the 60 boreholes, that are 1-71 m deep. Characterization of the resident microbial populations was completed for a number of these samples.

Results show that the local source oils are paraffinic-naphthenic light crude, containing n-alkanes as the dominant components. These oils, though obtained from shallow (300-600 m depth) sandstones, are not significantly impacted by biodegradation, probably because of the high salinity (~150,000 mg/L total dissolved solids) of the associated brine. The oils at the inactive A site are similar to each other although they do vary widely in stages of biodegradation. Some nearby oils at the active B site do not correlate with other site B oils, suggesting that there is not significant subsurface transport of the spilled oils. Microbial populations at both sites are degrading the water-soluble crude oil compounds. Concentrations of organic species, Fe, Mn, SO_4, and other geochemical evidence, and make-up of the microbial populations at both sites indicate that the systems are slightly different but based on free energy yields, are both poised at the level of iron reduction.

PIPELINE SAFETY REGULATIONS TO PROTECT HUMAN HEALTH AND THE ENVIRONMENT

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In November 2002, the President signed into law the Pipeline Safety Improvement Act of 2002. This law requires the U.S. Department of Transportation (DOT) to promulgate "integrity management" regulations for natural gas transmission pipelines to ensure their structural integrity and thereby protect public health and safety. In January 2003, DOT issued its proposed rule and since then has conducted several public meetings and entertained alternative proposals. The department is now working to meet the mandated promulgation date of December 2003. The rule has been described as the most significant regulation ever issued by DOT's Office of Pipeline Safety. It has also been described as one of the most confusing and potentially costly regulations facing the pipeline industry. Although this particular rule is for gas transmission lines, DOT is also writing additional environmental, health, and safety rules that could affect gathering lines used by oil and gas producers. This paper examines issues surrounding the proposed rule that producers may wish to consider as they prepare for similar rulemakings.

BTEX EMISSIONS IN NATURAL GAS PLANTS

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Over the past several years, concerns about hydrocarbon emissions from the regenerator vent in glycol dehydration units have become a significant issue. Clean air act amendments changed the way gas processors viewed their plants. Aromatic compounds including benzene, toluene, ethyl-benzene, and xylene (collectively known as BTEX) emitted from glycol units were included in a list of 189 hazardous air pollutants.

Process conditions such as glycol circulation rate, temperature and pressures are crucial factors in controlling the BTEX emissions from glycol dehydration units in natural gas plants. The approach in this study is to use the HYSYS integrated simulation environment as a potential incentive tool to study the performance of the glycol dehydration unit. The objective of this work is to observe the effect of stated process conditions without affecting the unit performance in terms of water removal from the water-rich glycol.

Results have shown interesting findings. Optimum conditions to minimize BTEX emissions were also investigated. The simulation study showed that diethylene glycol does the best job when it comes to removal of emissions. Various ways of removing BTEX from the sour water stream vented off the regenerator top were also investigated and will be discussed in this paper.

BIOREGENERABLE SELECTIVE SORBENTS FOR HYDROGEN SULFIDE REMOVAL FROM NATURAL GAS

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Millions of people depend on natural gas to heat their homes and businesses, cook their food, and even fuel some cars. However, natural gas contains impurities such as hydrogen sulfide ($H_2$2S) which must be reduced to acceptable levels before the gas is suitable for use. Sulfides present problems such as human health risk, environmental compliance, corrosion, reduced efficiency of fluid handling equipment, reduced well production, offensive odor, reduced product value, and increased operation costs. Conventional treatment methods present problems such as high energy usage, disposal of hazardous waste materials, high capital costs, and may require multiple processes to remove and subsequently destroy the H_2S.

Many new technologies have been investigated to improve the economics and safety of the gas desulfurization process. Biological oxidation of H_2S has several potential advantages including removal and elimination of H_2S in one process, low energy requirements, and minimal disposal products. The goal of this research is to produce an economically viable bioreactor for H_2S removal through the use of a sulfide-sorbing, bioregenerable support matrix. Bio-Sep® was chosen as the support matrix for this study. Bio-Sep® beads are spherical, approximately 2 to 3 mm in diameter, and are composed of Nomex® and powdered activated carbon. An improved version of the support matrix was created to immobilize the sulfide-oxidizing bacterium .ft I Thiobacillus denitrificans. The new version, Bio-Sep®S, was successfully created with the addition of a sulfide-selective sorbent and .ft I T. denitrificans has been grown using thiosulfate. Initial studies have shown that the culture will remove H_2S at a rate of

72 mg/h and a phospholipid fatty acid analysis (PLFA) has shown that the percentage of the total microbial population within the sulfide-sorbing beads has increased to 79%, up remarkably from 52% in previous studies using the original beads. This research is ongoing and trials are currently being conducted to increase the rate of H_2S removal.

ENVIRONMENTAL PERFORMANCE EVALUATION OF UPSTREAM ACTIVITIES FOR OIL AND GAS INDUSTRY

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The oil and gas industry in Brazil, after the flexibility of the union monopoly, lives deeply in a moment where great oil companies start to act side by side cooperating and competing, adjusting themselves to the requirements of a new market that is day by day getting more aware of the environmental issues. Facing this scene of competitiveness and challenges, the Environmental Management System, prevailed by the standard of the ISO 14.000 series, is distinguished as integral part of strategic planning, with the purpose to balance environmental protection and prevent pollution with the socio-economic necessities.

These workplace instruments for the environmental performance evaluation of the upstream activities of the oil and gas industry are becoming a necessary tool that will add value, assisting the decision makers on environmental, administrative, and political issues.

On the basis of ISO 14031, the result of this study consists of a methodology that makes possible the integration of the environmental data and the analysis of the activity performance, supplying concise information about the mass stream of the process, the management system, and the environmental condition.

TECHNOLOGY TRANSFER TO INDEPENDENT OIL PRODUCERS IN PENNSYLVANIA AND NEW YORK FOR RESTORATION OF SMALL CRUDE OIL-CONTAMINATED SITES

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A technology transfer program for managing oil spill cleanups is being developed for small independent oil producers in Pennsylvania and New York. The technology transfer program is based on the model developed by the Integrated Petroleum Environmental Consortium (IPEC). Treatment will utilize a phased bioremediation/phytoremediation approach developed by the U.S. Environmental Protection Agency's Environmental Response Team (U.S. EPA/ERT). It will also include successful oil spill cleanup methods implemented by the U.S. EPA in Region III during federal removal response activities in northwestern Pennsylvania, in consultation with the U.S. Department of Energy's (U.S. DOE) National Energy Technology Laboratory and Pennsylvania's Oil and Gas Management Program.

The IPEC model will require adaptation for humid region soils of Pennsylvania and New York. Soil limitations affecting treatment in Pennsylvania well fields typically include fine texture and poor drainage. Soil quality improvement will be required for successful treatment. Site restoration will include an option for revegetation with native plants.

The technology transfer program is currently being developed by the U.S. EPA/ERT for evaluation by the U.S. EPA in Regions II and III. Once this evaluation is complete, the program will be presented to selected independent oil producers in Pennsylvania and New York. The goal is to implement simple, effective, low-cost bioremediation/phytoremediation methods for small oil producers. The technology transfer program will require review and approval by state regulatory agencies before implementation.

THE OKLAHOMA ENERGY RESOURCES BOARD: A REPORT ON THE FIRST TEN YEARS OF THE ENVIRONMENTAL PROGRAM

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The Oklahoma Energy Resources Board (OERB), a State of Oklahoma board, is charged by statute with two primary objectives. These objectives include an educational program and an environmental program. The education component relates to informing the public in regard to the significance and viability of the petroleum industry in the State of Oklahoma in the future, as well as the present. The environmental component relates to restoration of orphaned and abandoned sites associated with exploration and production activities. As the OERB celebrates its ten-year anniversary, a report of the environmental program will be given.

The OERB's environmental program was initiated in August 1994 with two projects located in southeastern Oklahoma. From that humble beginning the program has cleaned up over 5,000 sites in 57 of Oklahoma's 77 counties. Having spent almost $22,000,000 over the past ten years, the environmental program is recognized throughout oil and gas producing states as the first successful voluntary clean-up program in the United States. Projects are initiated by the Oklahoma Corporation Commission and can involve working with other state agencies as well as federal agencies such as the United States Environmental Protection Agency. One example of such a project involved the OCC and the USEPA on a large-scale project near Lake Oologah, which will be briefly reviewed.

A progress report will be given on the current status of the program with up-to-date figures from the November 2003 board report. The presentation will include results from a recent survey of landowners that have had projects and sites cleaned up on their farms and ranches. This survey, undertaken by the OERB to confirm the effectiveness of the environmental program and its perception by those most affected, reveals a great deal about the nature of the program. The survey will show landowner responses to a number of questions relating to the overall environmental program.

ELECTRICAL GEOPHYSICAL CHARACTER OF AREAS OF SHALLOW BRINE CONTAMINATION, OSAGE CO. OKLAHOMA

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Ground electrical geophysical surveys of areas where surface salt contamination has taken place indicate specific subsurface areas of very high electrical conductivity. These areas in part correspond to surface salt scars. Subsurface water and geochemical sampling indicates saline waters occur in a much wider area than indicated by surface scarring. Electromagnetic (EM) subsurface images help refine the areas of contamination and possible subsurface controls for distribution of saline waters. Shallow borehole natural gamma and electrical induction logs help constrain the interpretation of the ground EM surveys.

HANDS-ON AUDIENCE PARTICIPATION IN USING THE IPEC SALT SOIL ANALYSIS KIT

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The Integrated Petroleum Environmental Consortium (IPEC) has developed a workshop dealing with cost effective soil remediation of crude oil and produced water brine spills. The workshop has been presented throughout Oklahoma and Arkansas in 2003. The purpose is to provide oil and natural gas producers with tools to empower them to clean up releases of produced fluids to surface soil. Applicable to recent small spills, information is also provided that enables the producer to respond to larger spills as well as historical issues dealing with soil impact and erosion. The emphasis is on providing how-to guidelines and supporting material to small "Mom and Pop" producers, but the workshop and materials are applicable to operations regardless of the company's size.

One of the products in particular that was developed and is provided in the workshop as a self-help tool is the Soil Salt Analysis Test Kit.

A demonstration of using this kit will be presented. Slides from the workshop will be presented while a hands-on demonstration using a salt- impacted soil composite sample collected from an actual site in Oklahoma will be performed during the presentation. Details will be given on how to define specific areas within a spill boundary for sampling. Actual sample collection will also be covered. As the salinity becomes known from the sample, the data will be related to reference cards found in the Kit to determine possible grasses and forage that will be tolerant of the salinity found in the sample soil.

Following this presentation, Soil Salt Analysis Test Kits will be available for your pick up, as well as information on how to order other no-cost IPEC products for oil and natural gas operators.

A STOCK TANK EMISSIONS MODEL BASED ON GAS SOLUBILITY

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Hydrocarbon emissions from petroleum field stock tanks provide a nuisance because of smell and in rare cases, even in the absence of hydrogen sulfide, actually create an identifiable health hazard. The June 17, 1999 regulations issued by EPA call for control systems to reduce emissions by 95% on stock tanks containing API gravity oil greater than 40° and having a gas-oil ratio (GOR) greater than 1750 SCF/STB. Emission control is desirable on stock tanks fluids with less volatility than those that fall under the promulgated national standards because of odor and loss of saleable product. Vapor recovery units (VRUs) are now available from vendors for capturing 95% of the emissions from stock tanks, but close tolerance on the design of such units is required to be cost effective. Cost driven recovery is preferable to being regulation driven. This in turn requires accurate prediction of cumulative salable emissions based on routine stock tank oil physical properties for VRU sizing.

This paper presents a model for predicting yearly cumulative emissions based on temperature driven gas solubility and an integrated form of degree days. The model uses the Scatchard Hildebrand solubility equation combined with the Prausnitz/Shair fugacity chart for fugacities of gases well above their critical temperature. The only stock tank oil parameters required are a ASTM D-86 boiling point distribution curve and API gravity. The specific details of the model will be presented and discussed as well as field testing of the model on sites in Oklahoma and Arkansas.

EMISSION INVENTORY FOR OFFSHORE OIL PRODUCTION AT CAMPECHE, MEXICO

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Meteorological, geographical, and air emission data for offshore oil platforms, gas and oil processing installations and the contribution of marine activities at the Sonda de Campeche, located at the Gulf of Mexico, were compiled and integrated to facilitate the study of long-range transport of pollutants into the region. From this important region, roughly 76% of the total Mexican oil and gas production is obtained. The data were specifically designed to contain information needed for the CALMET/ CALPUFF modeling system to estimate the amounts of sulfur dioxide emitted by stationary sources. It was therefore estimated that the total air emissions of all contaminants are approximately 658,000 tons per year. The hydrocarbons are the largest pollutant with 276,000 tons per year and SOx in second place with 181,000 tons per year. Marine and aviation activities contribute, with 2% of total emissions. Mass of pollutants emitted per barrel of petroleum produced calculated in this work are in the range reported by similar oil companies.

The modeling of dispersion of sulfur dioxide for February 3, 2000 (the most representative of at least four months per year) shows that the greater impact of emissions over the coast of the Gulf takes place in the morning and during the last hours of the day. Emissions from the platforms reach concentrations that are below the standard of 0.21 ppm once they reach the coast, but those emerging from inland facilities are greater than the environmental standard.

THE BEAVER (CASTOR FIBER L.) IN "ZUTICA" OIL FIELD AREA, R. OF CROATIA

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After their complete extinction, the Project of Beaver Repopulation in Croatian Ecosystems is currently under way. Based on research conducted by both local and foreign scientists, it was necessary to identify suitable habitats, meeting--among others--highly stringent environmental criteria where the beavers, donated to the Republic of Croatia by the German Federal State of Bavaria, could be released into nature. The forest of Zutica near Ivanic Grad has been identified as one of the suitable locations. It is in this area that INA-Naftaplin has been exploiting oil for over forty years now, it being one among the oldest and largest oil reservoirs in the Republic of Croatia. Over 20% of the total generated oil from local sources originates from the "Zutica" oil field. The selection of this very location for implementing the Project of Beaver Repopulation constitutes at the same time the best evaluation, as well as a direct indicator of INA-Naftaplin experts' most responsible relation, not only to the conservation, but also to the considerable advancement of both the environment and nature in general.

During work on the Project, we have collected much useful information that will help in the preservation and permanent survival of the newly populated species. The results obtained so far point to the need for strengthening the role of science and introducing a multidisciplinary approach to the programmes of environmental protection. Nature conservation and environmental management in the petroleum industry will in the future require an active, informed and more creative management as well as decision making processes based on scientific, ethic and sustainable development principles.

This paper presents research results obtained during Project implementation, for the purpose of monitoring the beaver population on the territory of the "Zutica" oil field. While considering the results, one should pay particular attention to the growing number and distribution directions of the beavers in the nearby areas in relation to complex natural (geological, hydrological, botanical and zoological), as well as anthropogenic properties of the area under research. The results and experience obtained on the "Zutica" oil and gas exploration and production field may serve as the model for (possible) future similar undertakings.

MICROBIAL INDICATORS OF SOIL ECOSYSTEM RESTORATION FOLLOWING BIOREMEDIATION OF OIL AND BRINE SPILLS

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The Tallgrass Prairie Preserve (Nature Conservancy, located in Pawhuska, OK) has historically been the site of oil production. Spills of produced fluids have on occasion occurred due to aging equipment. The sites of two such spills in 1999, one of dewatered crude oil alone, the other of oil plus brine, have been the subject of research aimed at assessing restoration of this highly biodiverse ecosystem. Although a number of possible ecological indicators of restoration have been evaluated, this presentation will focus on changes in eubacterial species diversity, particularly bacteria involved in nitrogen-cycling. Spills of crude oil and subsequent bioremediation procedures involving the addition of nitrogenous compounds to

the spill site to enhance the rate of hydrocarbon removal are expected to affect both the numbers and species composition of nitrogen-cycling bacteria. Disruption of nitrogen-cycling will affect the restoration of the plant community, which is frequently nitrogen-limited. Changes in species diversity of the dominant eubacteria at the sites will be assessed by PCR amplification using primers specific for 16S rRNA of DNA extracted from the sites, followed by the separation of the PCR products by DGGE (denaturing gradient gel electrophoresis). Ammonium-oxidizing bacteria (AOB), which perform the first step in nitrification (oxidization of ammonium to nitrite), will be detected by cloning and sequencing a portion of the gene coding for the first enzyme in the nitrification pathway, ammonium monooxygenase (amoA).

NEMATODES AS AN INDICATOR OF THE RESTORATION OF SOIL ECOSYSTEMS FOLLOWING OIL AND BRINE SPILLS

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The Integrated Petroleum Environmental Consortium (IPEC) is studying the effects of original contamination and the remediation process on grasslands soil ecology for spills of crude oil and brine. This work will provide guidance on performing ecological risk assessments for crude oil contaminated site by helping to define appropriate endpoints for remediation and developing appropriate indicators for these endpoints. An understanding of potential ecological impacts will be part of any risk-based decision making process for management of accidental spills of produced fluids and make for better use of limited resources.

This study uses two spills sites located in The Nature Conservancy's Tallgrass Prairie Preserve, Osage County, Oklahoma. One site is a spill of crude oil only, while the second site is a spill of oil and brine. Both spills occurred in 1999 and both have been remediated and are presently under restoration. Soil

microbiology at these two sites has been monitored using phospholipid fatty acid analysis (PLFA) and nematode analysis. Our experience indicates that although both types of analyses can be used to monitor soil ecosystem restoration following bioremediation of a crude oil spill or remediation of a brine spill, nematode numbers and trophic diversity appear to be the ecological indicators of choice based on sensitivity and cost. Nematode analysis of soil samples can be obtained from many land-grant university extension services for about $50 per sample. This analysis typically gives nematode numbers, trophic group counts and family-level identification.

COMPARING THE MICROBIAL ECOLOGY OF OIL- AND BRINE-IMPACTED SOILS UNDER REMEDIATION AND RESTORATION

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Once the spill of produced fluids has taken place it must be remediated or "cleaned" in order to restore the economic and/or aesthetic value of the impacted land as well as preventing further contamination of soil, groundwater, and surface waters by transport of contaminants off site. But how clean is clean? One view is that the soil ecosystem is "clean" when the ecosystem is sufficiently restored to support its previous use or an acceptable alternate use. The Integrated Petroleum Environmental Consortium (IPEC) is studying the effects of original contamination and the remediation process on grasslands soil ecology for spills of crude oil and brine. This work will provide guidance on performing ecological risk assessments for crude oil contaminated sites by helping to define appropriate endpoints for remediation and developing appropriate indicators for these endpoints. An understanding of potential ecological impacts will be part of any risk-based decision making process for management of accidental spills of produced fluids and make for better use of limited resources.

This study uses two spill sites located in The Nature Conservancy's Tallgrass Prairie Preserve, Osage County, Oklahoma. At the J6 site contamination resulted from a pipeline break on January 6, 1999 releasing about 70 barrels of dewatered crude oil. Immediately downslope of the pipeline it contaminated an area of about 10,000 ft^2 (J6N). The initial total petroleum hydrocarbon (TPH) concentration at J6N was about 33,500 mg/kg. For the purpose of treatment comparison, J6N was divided into fertilized and non-fertilized sections and remediation initiated in May 1999. Further, for comparison, two types of controls have been used--one is unimpacted prairie disturbed by tilling and the other is unimpacted and undisturbed prairie. The Gibbs #5 site resulted from a break in a gathering line in fall 1999 spilling both crude oil and produced water brine ([NaCl] about 130,000 mg/L). About 10 times as much brine as oil was spilled. Remediation of a portion of this site (N) began in June 2000 using tilling with hay and fertilizer.

Both J6N and Gibbs #5 N have been remediated by similar methods. This paper compares the rates of restoration of the soil ecosystems of these two sites in terms of ecological indicators such as phospholipid fatty acids (PLFA), nematode populations, nutrient cycling and revegetation. Although the brine spill at Gibbs #5 did not "sterilize the soil" as brine spills have been characterized, these ecological indicators do show that brine-impacted sites are slower to restore in terms of soil ecology than oil-impacted sites.

MODELING OF INFINITE-DILUTION ACTIVITY COEFFICIENTS OF AQUEOUS SYSTEMS

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Phase equilibrium data are essential for the proper design, operation, and simulation of many chemical processes. When experimental data are unavailable, thermodynamic models, such as group contribution methods, are used to predict phase equilibrium. The accuracy of these models in predicting infinite-dilution activity coefficients (g¥) of aqueous systems is questionable. Moreover, model development is hampered by a lack of (a) g¥ data at temperatures above 300 K, and (b) g¥ data for water in hydrocarbon systems. Using quantitative structure-property relationships (QSPR), mathematical models are developed relating the structure of a diverse set of organic molecules to g¥ values for hydrocarbons in water and water in hydrocarbons.

Multiple linear regression (MLR) and artificial neural networks (ANNs) are applied to a diverse database of infinite-dilution activity coefficients of aqueous systems. The database contains a total of 1469 data points at temperatures ranging from 283.2 to 373.2 K. The data include both direct and indirect measurements for a variety of hydrocarbons, including alkanes, alkenes, aromatics, halogenates, alcohols, phenols, aldehydes, ketones, acids, esters, ethers, amines, amides, nitriles, nitro compounds, and sulfur compounds. A suitable set of molecular descriptors is selected from a pool of approximately 700 descriptors, including constitutional, topological, geometrical, electrostatic, quantum chemical, and thermodynamic descriptors. Accounting for the significance of each descriptor provides for a statistical means to reduce the number of descriptors. A back propagation network is the primary neural network architecture employed.

The results obtained indicate that useful QSPR models may be developed for infinite-dilution activity coefficients of binary aqueous systems involving diverse hydrocarbons. Predictions within twice the experimental uncertainties have been realized. In addition, the descriptors used in the QSPR models provide insight for the effect of various structures on the non-ideality of water/hydrocarbon systems as expressed by g¥.

EVIDENCE OF THE PROLIFERATION OF NATIVE PETROLEUM REDUCING BACTERIA SUBSEQUENT TO APPLICATION OF CONTROLLED IN-SITU CHEMICAL OXIDATION

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Rapid remediation of petroleum contaminated soil and groundwater at a gasoline station in Florida occurred following treatment using a controlled in-situ chemical oxidation (CISCO) process. Two main processes were thought to be responsible for the rapid and substantial decreases in petroleum contaminant mass in both soil and groundwater at this site in Bonifay, Florida. Soil and groundwater sampling confirmed a significant increase in petroleum reducing bacteria following the injection of a controlled in-situ chemical oxidation process. Soil and groundwater contaminants had impacted significant areas on the site owner's property and areas beneath an adjacent highway where underground fiber optic, water, and storm sewer utilities existed. A remedial strategy had to be selected which would assure that these utilities would be protected from physical and corrosive damage during any remediation process. One chemical oxidation process that could rapidly reduce/oxidize petroleum contaminants (BTEX, MTBE and PAHs), that would not adversely effect utilities or undermine sidewalk or roadway structures, and that could enhance biologic degradation of residual contaminants was discovered. This process (the BIOX® process - a controlled in-situ chemical oxidation "CISCO" process) already had an FDEP Underground Injection Control variance for use at petroleum sites in Florida. Time and cost limitations eliminated consideration of other conventional and innovative technologies. Post-injection soil and groundwater analytical results confirm that soil contaminants were reduced below the FDEP's CTLs and that dissolved groundwater contaminants were reduced below the FDEP's Natural Attenuation default CTLs rapidly in most wells. Ringed petroleum contaminants (BTEX, PAHs) and MTBE concentrations decreased and long-chained hydrocarbons (TRPHs) remained following injection of the BIOX® reagent. An environment rich in organic material and dissolved oxygen with a neutral pH was then present (well suited for biologic reduction). Laboratory data confirmed that substantial and sustained increases in population of native petroleum-reducing bacteria had occurred. These bacterial results have been documented at a second petroleum cleanup site and

similar results can be anticipated where similar CISCO treatment is being performed.

OPTIMIZATION OF TECHNOLOGICAL CLEANING SYSTEMS OF UNDERGROUND WATER FROM OIL-PRODUCTS IN THE FERGANA VALLEY (UZBEKISTAN)

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The Fergana (Uzbekistan) oil refining factory was founded at the beginning of 1960s on the northern extremity of the Qirguli hills. The long-term functioning (more than 40 years) of Fergana oil refining factory gradually resulted into an outflow and loss of raw material that led to the strong contamination of underground waters by minerals in surrounding territories, especially in the Tishlak area. Products after oil-extraction were fixed both in the surface and subsoil waters, as well as dissolved components in the subsoil waters. The contamination of subsoil water by oil products in the Tashlak area was first revealed in 1976. The area of distribution of oil-forms of these products (according to a 1998 survey), makes about 4.5 km^2 with a volume of 300,000 m^3 and a weight of about 280,000 tons.

Our institute and Fergana Expeditions carried out multiple-year, complex research on the elaboration of hydro-geological conditions of this site, specification of spatial borders of pollution, studying of features of development of processes of migration of mineral oil and a hydro-geological substantiation. Based on this, a two-turn intercepting system has been proposed. Results of these researches have brought in essential specifications to existing representations about the extension of pollution.

WHEN OILFIELDS BECOME WATER FIELDS, THE SAGA OF SMALL PRODUCERS IN CALIFORNIA

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California oilfields now operate on the average at a water oil ratio of 7:1 producing about 2.1 billion barrels of oil annually. Many of the fields previously operated by major oil companies have now become challenging operations for small producers. Pumping units and surface operations originally designed to handle primarily oil and some water are now producing primarily water and traces of oil. Economics of oil production in many cases look dismal even at occasional high prices. Added on top of that the environmental concerns about substantial produced water have brought many of California operations to the verge of extinction. Substantial resources of small producers are wasted through power cost to lift, process and dispose of voluminous amounts of water. This paper documents geologic- and completion-related causes of high water production in some of these geriatric oilfields and projects the type of investments needed to rescue these fields from premature abandonment.

ONLINE MONITORING FOR WASTEWATER EFFLUENT COMPLIANCE IN THE CHINESE PETROCHEMICAL INDUSTRY

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The People's Republic of China (PRC) is increasing trade with other countries and, in conjunction with this, sees good environmental stewardship as an important part in their development. In this regard, China has been developing and implementing regulatory initiatives addressing air emissions and wastewater effluent quality. The application of online monitoring is seen as an important tool in enabling them to regulate compliance.

In most nations, including the USA, online monitoring is generally used as a monitoring tool to assist in the operation of wastewater plants; but in few cases is it used by regulators to ensure that the discharge is within discharge limits. The Sino Environmental Protection Administration (SEPA) has taken the unusual but forward-thinking approach of specifying that online monitoring must be used by dischargers to show that their effluent meets their treatment standards. In the petrochemical industry, companies are required to monitor Chemical Oxygen Demand (COD), oil in water and, in some cases, ammonia-nitrogen, and all using online monitors.

The largest oil and gas company in China is PetroChina, with a production of over 880 million barrels-of-oil equivalent in 1998 and a Net income of RMB 55.231 billion (US $6.7 billion) in 2000. It is the fourth-largest Oil Company in the World. PetroChina is committed to investing in its environmental protection program [RMB 1.2 billion yuan (US $450 million) in 2001].

As part of its commitment to improved environmental performance, RIPED-Lanfang/EMCand C.H. Guernsey and Associates have partnered to investigate the best approach to online effluent monitoring for compliance. This project is partially funded by the US Trade and Development Agency (USTDA).

The project is evaluating the present use of online monitoring systems in the PRC and the availability and use of online monitors throughout the World. This evaluation is being performed to select the most suitable units for a 3-month pilot demonstration. This paper discusses the selection process and the findings of the first phases of the study. This includes technical and financial considerations in the selection of the instruments. Over 30 instruments were considered for the pilot and these were reduced to just 9 using a qualitative selection technique.

This paper will also present the approach taken in designing the online monitoring system and how it

will be implemented in the pilot study. Important implementation issues include the need for a good sample preparation system and an adequate maintenance schedule.

HYDROLOGY AND SUBSURFACE TRANSPORT OF OIL-FIELD BRINE AT THE OSAGE-SKIATOOK PETROLEUM ENVIRONMENTAL RESEARCH (OSPER B) SITE, OKLAHOMA

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As a part of a multidisciplinary study of the impact of oil wells and oil production on the environment, we are investigating the hydrology of the OSPER B site, which is located at Skiatook Lake in Osage County, Oklahoma. Salt and crude oil from oil well brine pits and accidental releases from oil-tank batteries have contaminated soil, ground water, and surface water at this site. Coring near a brine pit at the site showed that low permeability shale underlies 0.5-2 meters of surficial deposits (fill, soil, colluvium, and alluvium). The land slopes down from the pit at about a 1:10 slope to the lake, which is located about 20 meters from the pit. More than 40 shallow wells were installed at site B in order to enable periodic ground-water sampling for chemical analysis, to monitor water table elevations, and to delineate the subsurface contamination plume at the site. Five wells were instrumented with pressure transducers in order to continuously monitor water table elevation. Dielectric probes were installed to monitor soil water content. Probes were installed in the brine pit in order to continuously monitor pit water depth and electrical conductivity. A tracer test was carried out in order to estimate travel time from the pit to nearby observation wells. Results of computer simulations and field measurements indicate that subsurface brine flows slowly from the pit to the lake in a shallow saturated zone above the shale layer. Little brine has penetrated into the shale. In response to rainfall, the water table rises rapidly to the soil surface and runoff begins. Soil moisture content is very high at all times; there is little capacity to absorb rainfall, and recharge and mixing of rainwater with subsurface brine is limited. Breakthrough of tracer to observation wells was not observed, apparently because of very slow recharge through the pit bottom and high adsorption of rhodamine and fluorescein tracer in the surficial deposits.

RADIOECOLOGICAL MONITORING AND DECONTAMINATION TECHNOLOGY OF NORM SLUDGE FROM VUCTYL OIL AND GAS FIELD

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The present paper deals with the investigation of naturally occurring radioactive material (NORM) contamination at one of the largest oil and gas-condensate fields in the north of Russia - Vuctyl field.

The main sources of radioactive contamination from this field are radium 226, radium 228 and radon decay products. The main sources of radiation danger from oil and gas production facilities are sludges of produced water, deposits of radioactive salts on the equipment, and previously buried sludges and scale. The natural gas may contain considerable concentrations of radon.

The theoretical and methodical bases of the control for the processes of NORM sludge decontamination have been developed. At laboratory and industrial conditions the influence of the processes of leaching, sorption, dissolution, deemanation, thermal, chemical and high temperature processing on the decontamination of the large volumes of sludges with elevated radioactivity have been investigated. The way of transformation of insoluble radium minerals into the soluble forms has been developed.

The industrial installation and technology for NORM sludge decontamination have been created. To the best of the authors' knowledge the technology has no Russian analogues. It has been proved, that as a result of decontamination of sludge with a specific activity about 100 kBk/kg the solid insoluble final product may have specific activity no more than 1.5 kBk/kg, and liquid final product - less than 1 Bq/l.

FUTURE OUTLOOK FOR DOWNHOLE OIL/WATER SEPARATORS

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The oil and gas industry is interested in technologies that can bring oil to the surface at a lower cost or with less environmental impact. Technologies that can accomplish both of these goals are particularly attractive. Downhole oil/water separators (DOWS) have the potential to reduce operating costs while providing a greater degree of environmental protection. DOWS technology reduces the quantity of produced water that is handled at the surface by separating it from the oil downhole and simultaneously injecting it underground. A DOWS system includes many components, but the two primary ones are an oil/water separation system and at least one pump to lift oil to the surface and inject the water. Two basic types of DOWS have been developed; one type using hydrocyclones to mechanically separate oil and water and one relying on gravity separation that takes place in the well bore.

In 1998, the U.S. Department of Energy (DOE) provided funding to Argonne National Laboratory to conduct an independent evaluation of the technical feasibility, economic viability, and regulatory applicability of the DOWS technology. The results of that investigation were published in January 1999 and represent the most complete publicly available reference material on DOWS technology. Since 1999, DOWS have been used sparsely, although several new designs have been tested. This paper describes DOWS technology, how it has been used in the past, and what types of DOWS and related technology are currently being used by the industry. The paper also discusses some of the reasons why DOWS have not been more widely used, the future outlook for DOWS technology, and the steps that DOWS developers, producers, and government must follow to expand the usage of DOWS systems.

ANALYSIS OF WATER MANAGEMENT ALTERNATIVES AND BENEFICIAL USES OF COAL BED METHANE PRODUCED WATER

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A summary of work conducted to analyze coal bed methane produced water management and beneficial use alternatives in various basins throughout the western United States will be presented. Emphasis areas include the Powder River Basin and the San Juan Basin, but incorporate basins in other western states. Summary information to be presented will include technical and regulatory feasibility and preliminary conceptual engineering options of feasible alternatives. Case studies of produced water management practices will also be presented.

Research being presented is part of a project being funded through grants provided to the Ground Water Protection Research Foundation (GWPRF) by the Department of Energy's National Petroleum Technology Office (NPTO) - part of the National Energy Technology Laboratory (NETL) and the Bureau of Land Management. The U.S. Forest Service, more than a dozen CBM producers, several states, and other organizations are providing additional in-kind funding. Lead researchers for the project are ALL Consulting and Ft. Lewis College.

ESTIMATIVE FOR SLICK TRAJECTORIES TO OIL SPILL PROVOCATED BY EXPLORATION AND PRODUCTION ACTIVITIES BOTH OFFSHORE THE COAST OF AND INLAND THE STATE OF ESPIRITO SANTO

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Oil and gas exploration and production activities both offshore the coast of and inland the State of Espirito Santo promise to heat up the state's economy, thus bringing investments, creating jobs and generating income.

Inherent to this kind of activity there is the possibility of accidents occurring in spite of the complex safety systems installed on offshore facilities, such as equipment to prevent blowouts, bursting of pipes, structural defects in the platforms, as well as ship collisions.

If the oil spill reaches the coastline, damages would be catastrophic. This would be so not only because this area is home to major ecological systems but also due to the fact that a significant part of the population lives along the coastline, which is used for such activities as fishing, leisure and port installations.

Being thus, this research has the objective of making available information that contributes to elaboration of a contingency plan for the activities of exploration offshore of the ES, esteeming the time response for a possible accident happening in the Capixaba coast, originating from the facilities offshore, considering the force of the wind as the only force acting on the oil spot. This estimate was accomplished through a model of trajectory of oil spill.

POSITIVE POTENTIAL OF OFFSHORE APPLICATIONS OF MANAGED PRESSURE DRILLING TECHNOLOGY

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Approximately one-half of all known offshore resources of oil and gas (gas hydrates excluded) are economically undrillable with conventional overbalanced drilling methods and equipment. In deeper water where the hydrostatic head pressure caused by a long column of drilling fluid and cuttings in marine risers exceeds the wellbore fracture pressure limit, prospects that are economically drillable are much greater. Such gross overbalance overcomes all but the most robost of production zones and results in underground blowouts and a litany of drilling related obstacles such as loss circulation, differentially stuck drill pipe and associated well control issues.

Unlocking the economic viability of many of these offshore prospects today is a rapidly growing application of Managed Pressure Drilling (MPD) technology. MPD is based upon tools and methods developed for the safe practice of underbalanced drilling. However, in MPD the intent is not to invite hydrocarbon influx into the wellbore and to the surface as in true underbalanced drilling, but to more precisely manage/control/contain annulus fluids downhole and at the surface when drilling overbalanced. MPD applies to near-balanced, balanced, three variations of dual gradient deep water drilling and a zero discharge method of riserless drilling of top holes.

Because MPD relies upon a closed and pressurizable mud returns system and does not intend to produce hydrocarbons when drilling ahead, the technique offers a very positive influence upon environmental considerations and well control in general.

This paper discusses the MPD methods currently underway that are a major step towards zero discharge offshore drilling and specifically identifies the positive environmental ramifications of several MPD applications.

A NEW TOOL FOR CHARACTERIZATION OF MICROBIAL ACTIVITY IN CONTAMINATED SOILS DURING REMEDIATION AND RESTORATION

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Bio-traps containing autoclavable Bio-Sep® polymer beads have been shown to induce endogenous pelagic bacteria to form biofilms in solvent-resistant, autoclavable, polyfluorylalkoxy perforated tubes when deployed in aqueous environments. Bio-Sep® consists of 3-4 mm diameter spherical beads engineered from a composite of 25% aramid polymer (Nomex) and 75% powdered activated carbon (PAC). The bulk density is about 0.16 g/cm^3 with a porosity of 74%. Beads are surrounded by an ultrafiltration-like membrane with pores of 1-10 microns. The Nomex membrane resists formation of a surface biofilm with immobilization occurring through entrapment that concentrates extant microbes in internal biofilms providing biomarkers for viable biomass, redox environment, microbial community composition, and the nutritional status for correlation with attenuation effectiveness.

Bio-traps containing Bio-Sep® beads have now been used to monitor subsurface microbial communities in soil where crude oil was remediated with and without fertilizer addition and in associated tilled and undisturbed prairie controls. Beads were deployed at three depths (1, 3, and 5 inches) in each plot in triplicate in mesh bags or five weeks in May and June, 2003. The soil surrounding the beads was also retrieved. Triplicates (soil and beads) were then composite and analyzed for biomarkers including phospholipids fatty acids and 16S rDNA.

The microbial communities in the beads were found to be enriched in C_{16} fatty acids relative to the soil communities, were more aerobic in character, and exhibited faster growth rates. Bead communities were less diverse than soil communities and dominant bacteria in the soil were not necessarily dominant in the beads.

Lastly, differences could be seen in beads communities within the same plot at different depths which was not the case for soils. Bio-Sep® beads appear to offer potential advantages over soil analysis in the sampling of soil microbial communities in terms of selection of the more active community members and detection of subtle differences with depth.

THE EFFECT OF FERTILIZER USE DURING BIOREMEDIATION OF CRUDE OIL CONTAMINATED SOIL ON SUBSEQUENT RESTORATION OF SOIL ECOSYSTEMS

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Once the spill of produced fluids has taken place it must be remediated or "cleaned" in order to restore the economic and/or aesthetic value of the impacted land as well as preventing further contamination of soil, groundwater, and surface waters by transport of contaminants off site. But how clean is clean? One view is that the soil ecosystem is "clean" when the ecosystem is sufficiently restored to support its previous use or an acceptable alternate use. The Integrated Petroleum Environmental Consortium (IPEC) is studying the effects of original contamination and the remediation process on grasslands soil ecology for spills of crude oil and brine. This work will provide guidance on performing ecological risk assessments for crude oil contaminated sites by helping to define appropriate endpoints for remediation and developing appropriate indicators for these endpoints. An understanding of potential ecological impacts will be part of any risk-based decision making process for management of accidental spills of produced fluids and make for better use of limited resources.

The J6 crude oil spill site is located in The Nature Conservancy's Tallgrass Prairie Preserve, Osage County, Oklahoma. Contamination resulted from a pipeline break on January 6, 1999 releasing about 70 barrels of dewatered crude oil. Immediately downslope of the pipeline it contaminated an area of about 10,000 ft^2 (J6N). The crude oil then flowed down a gully in a lease road and contaminated another area of the prairie (about 4,800 ft^2, J6S). The initial total petroleum hydrocarbon (TPH) concentration in J6N was about 33,500 mg/kg and in J6S, 4,800 mg/kg. For the purpose of treatment comparison, each of these sites was divided into fertilized and non-fertilized sections. Further, for comparison, two types of controls have been used--one is unimpacted prairie disturbed by tilling and the other is unimpacted and undisturbed prairie.

This paper discusses the effect of managed bioremediation by fertilizer addition on the restoration of the soil ecosystems of the different test plots following remediation in terms of ecological indicators such as phospholipid fatty acids (PLFA), nematode populations, nutrient cycling and revegetation. Both the J6N and J6S sites experienced similar decreases in TPH concentrations with and without fertilizer addition. However at the higher TPH concentration (J6N) ecological indicators show that the rate of restoration of the soil ecosystem is increased by using fertilizer addition during remediation.

AEROBIC BIODEGRADATION OF BENZENE, TOLUENE, ETHYLBENZENE, AND XYLENES BY HALOPHILIC AND HALOTOLERANT BACTERIA

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Since conventional microbiological treatment processes do not function at high salt concentrations, bioremediation of oilfield brine can only be accomplished by stimulating either indigenous bacteria or through bioaugmentation of halophiles capable of degrading fuel hydrocarbons. Microcosms were established with brine soil obtained from different oilfields and other salterns in Oklahoma. Our preliminary studies showed that 14C-benzene was mineralized to 14CO2 under both aerobic and anaerobic conditions. We have obtained highly enriched microbial consortia from brine soil by repeated feeding with benzene and transferring sediment-free cultures to fresh mineral salts medium. Molecular characterization of the enrichment culture using denaturing gradient gel electrophoresis (DGGE) and 16S rDNA revealed that the Marinobacter sp. was the dominant organism. These enrichments rapidly degraded BTEX in the presence of high concentrations of NaCl and little degradation occurred when no salt was added. Attempts to enhance rate of benzene degradation through the addition of organic stimulants have met with little success. The impact of salt on microbial diversity of the benzene degrading enrichment was assessed by DGGE. The analysis shows that different organisms dominate at different salt concentrations and the organisms at high salt, 3 or 4 M NaCl showed low sequence match to the known organisms in the RDP (Ribosomal Database Project).

THE OSAGE-SKIATOOK PETROLEUM ENVIRONMENTAL RESEARCH PROJECT

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The Osage-Skiatook petroleum environmental research (OSPER) project is examining the impacts of oil production at two long-term research sites (A and B) adjacent to Skiatook Lake in Osage County, Oklahoma. About 1.5 and 1.0 hectare of land at the A site (an inactive oil lease) and the B site (an active oil lease), respectively, are affected by salt scarring, tree kills, soil salinization, and brine and petroleum contamination resulting from the leakage of produced water and associated hydrocarbons from brine pits and accidental releases from active and inactive pipes and tank batteries. To date, the studies have included aerial-photo interpretation and highly accurate GPS mapping of site features and topography, organic and inorganic geochemistry of ground waters, tracer test and long-term water-level monitoring, hydrologic modeling, surficial and bedrock geologic mapping, surface soil and bedrock geochemistry and mineralogy, microbial population and hydrocarbon degradation characterization, plant vegetation surveys, oak-tree-ring dating, and biogeochemistry of oak-tree leaves. In a collaborative effort, EPA scientists have characterized soil total petroleum hydrocarbon (TPH), nutrients, and salinity, and have planted remedial plots comprised of trees and grasses, and sampled lake bottom sediments for contaminants. Both sites are in a dissected area of modest relief underlain by interbedded shale, siltstone, and sandstone. Thicker resistant sandstone units typically form the hillcrests. Shale, mudstone, siltstone, and thin sandstone beds underlie hillslopes. A layer of eolian sand of varying thickness blankets much of the terrane. Oak forests cover the hillslopes and mixed grasslands and oak forests cover ridge crests. The following findings might provide insights for assessment and remediation of similar sites elsewhere: 1) 3-dimensional plumes of high-salinity water (as much as about 30,000 mg/L TDS) with chemical and isotopic characteristics similar to those of the produced-water source have been mapped at both sites. Currently, the depth and boundaries of these plumes are not well defined, because all completed wells, regardless of depth, show variable impacts of produced water and/or associated hydrocarbons; 2) highly saline produced waters (150,000 mg/L TDS) have been diluted by precipitation and ground water mixing, and are modified geochemically by interaction with bacteria and bedrock; 3) a surface layer of fine, permeable sand about 50 cm or more thick provides protection to the root zone of oaks, grasses, and forbs from salts in the underlying strata--the fine sand inhibits wicking of salt up to the root zone; 4) reducing, chloride- and organic-rich waters mobilize iron as Fe^{2+} which causes distinctive bleaching and iron staining of sandstone outcrops; 5) the altered physical and chemical features of an impacted area retard colonization by oaks, however, selected parts of an impacted area can

become colonized for reasons not yet understood; 6) hydrocarbons at and near the ground surface degrade readily to asphaltic residues with iron- reducing bacteria playing a significant role, but locally, BTEX compounds can persist in the subsurface; the abundant soluble iron present at the sites is acting as the terminal electron acceptor for the bacteria; 7) nitrogen levels are low in local soils, natural and impacted; 8) a chloride to conductivity ratio of 1:10 is diagnostic of local background waters or leachates of bedrock whereas a 1:4 ratio is diagnostic of produced-water-salt impacts; the chloride to bromide ratios are also distinctively different; 9) sodium found in salt-impacted soils and bedrock at the two sites is present both in soluble form and on exchangeable sites on clays; 10) large amounts of salts and organic compounds remain in the local groundwater at A site after more than 65 years of natural attenuation; 11) erosion developed early in the 70+ year history of the A site salt scar but also stabilized early probably because the channel eroded down to hard sandstone bedrock layers; and 12) oak trees near the A site salt scar are taking in chloride from produced-water salts through their roots in the shallow subsurface as much as 45 m from its margin, confirming the presence of such salts as indicated by electromagnetic geophysical signatures, shallow coring, and ultimately drilling.

RESTORING SITES USING GREEN REMEDIATION STRATEGIES

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The Group Environmental Management Company is piloting the use of remediation systems powered by renewable energy sources in various environmental restoration projects. This approach is often both a business and economic strategy, consistent with corporate sustainability values. The paper will review several projects featuring "green" remediation elements, highlighting successes and lessons learned. Business benefits include energy and resource efficiencies, reduced capital expenditures and OM&M costs, expedited construction, and enhancement of corporate reputation. Government agencies may have financial incentives to use renewable energy sources, which can further reduce the cost of implementing them and increase the level of positive interest by governmental agencies.

IMPACT OF WEATHERING PROCESSES ON TPH RISK-BASED SCREENING LEVELS

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In 1997, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) published a methodology for analyzing and assessing the potential risk of hydrocarbons in soil and groundwater to human health. In risk assessment, the first step is to calculate risk-based screening levels (RBSLs) for soil or water using very conservative, generic exposure, fate and transport assumptions. The TPHCWG approach to calculating screening levels for petroleum mixtures using an analytical method that quantifies 13 fractions of hydrocarbons has been adopted by several states. Some states have published "Tier 1" RBSLs for specific, fresh petroleum mixtures such as mineral oil, diesel, and crude oils. The impacts of weathering processes in soil, such as volatilization and biodegradation, on hydrocarbon RBSLs are not well defined. In this paper, the compositional changes that occur in petroleum in soil over time due to weathering processes have been quantified for both laboratory and field collected samples. Risk-based screening levels are then calculated for fresh petroleum mixtures and their weathered/ biodegraded counterparts. A discussion of how various weathering events can influence TPH RBSLs is presented along with the implications for establishing site closure criteria for bioremediation technologies, such as landfarming.

CARBON FRACTIONATION APPROACH TO CLEAN-UP STANDARDS FOR SOILS CONTAMINATED WITH HYDROCARBONS

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This paper outlines the methodology for the development of risk-based cleanup criteria that were proposed as the basis for the new clean up standards for the restoration of petroleum contaminated soils in Mexico. The study applies a carbon fractionation methodology to derive a risk-based cleanup criteria for soils contaminated with hydrocarbons for a limited set of land-use categories. The methodology was applied to four different regions of Mexico and recommendations on limits were based on the most restrictive levels defined. The calculation methods were based on standardized risk assessment algorithms. In general, the fractionation methodologies separate petroleum into several fractions (based on molecular weight) that exhibit similar environmental transport characteristics. Available toxicity data (individual compounds and mixtures) are used to evaluate the non-carcinogenic toxicity of each petroleum fraction, and these toxicity values are used to develop different cleanup criteria for each fraction.

PROBABILISTIC RELIABILITY MODELING FOR E & P FACILITIES IN THE TALLGRASS PRAIRIE

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In the area of risk assessment and equipment failure rate estimation, there has been a large amount of work and a number of models developed for many industries. However, there is not a model directly applicable to oil E&P facilities. Reliability theory and common hazard analysis techniques such as failure modes and effects analysis, fault tree analysis and event tree analysis were used to develop a model to estimate the failure probability of the equipment (including pipelines) typically used at production leases in the Tallgrass Prairie Preserve. We present the results of Monte-Carlo simulations of the failure probability due to the combination of the most significant failure modes of each lease component. Factors associated with a high risk of accidental release of produced fluids (oil, brine) can be identified. The failure probabilities can be coupled with the estimation of site specific consequences (ecosystem damage, cleanup costs, and fines) to create a risk index that can be used to schedule lease maintenance to reduce accidental fluid releases.

LIGHT, MEDIUM AND HEAVY MEXICAN CRUDE OILS CHARACTERIZATION

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Soil and water contamination due to hydrocarbon spills is a frequent problem worldwide. For the case of Mexico, even with programs oriented to the diminution of these undesirable events in progress, in year 2000 a total of 1,518 hydrocarbon spills were reported. The total amount of spilled hydrocarbons was around 6,250 tons. The main petroleum industry areas when those spills occurred were crude exploration and production, with 1,428 spills (1,097 tons), and crude refining, with 90 spills (5,155 tons). The main spills were in the refineries, pipelines and marine terminals.

Three Mexican crudes from El Batab (light), Paredón (medium) and El Carrizo (heavy) perforation wells were characterized with two different purposes: a) as an initial characterization of the complex mixture to be treated by physical-chemical or biological process, e.g., soil washing, biopiles, soil vapor venting, and b) with environmental forensic goals.

Gas chromatography using flame ionization (FID) and sulfur chemiluminiscence detectors (SCD) were used to visualize hydrocarbon patterns. Total petroleum hydrocarbons, diesel and gasoline fractions were estimated using the techniques suggested by EPA. In the case of the gasoline fraction, the analysis of the contribution of $<C_5$, $>C_5>C_{10}$, $>C_{10}<C_{15}$, and $>C_{15}$ (volatiles) as well as $>C_{15}<C_{20}$, $>C_{20}<C_{25}$, and $>C_{10}<C_{15}$ chains was performed. Besides, benzene, toluene, ethyl-benzene and xylenes measurements were carried out. The 16 PAHs suggested as priority by USEPA were measured too. An extensive quantification of metals was carried out and total sulfur was estimated for all crudes.

TOPOGRAPHIC AND GEOLOGIC CONTROLS ON THE DISTRIBUTION AND MOVEMENT OF PRODUCED WATER AND HYDROCARBONS AT THE OSAGE SKIATOOK PETROLEUM ENVIRONMENTAL RESEARCH SITE "A"

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Topography, surficial geology, and bedrock geology exert critical control on the distribution and movement of released produced water and hydrocarbons on the landscape at the research site "A". Major point sources for NaCl-bearing produced water and for hydrocarbons at the site appear to be two adjacent pits in which these fluids were stored separately. The two pits sit near the crest of a northwest-trending drainage divide. The northeast sector drains northward into the Cedar Creek arm of Skiatook Lake and the southwest sector drains northwest, west, and then south into the main trunk of the lake. Although it was a primary source for contaminants within the site, a small tank battery upslope and a manmade channel between it and the pits were minor sources of releases to the sector southwest of the drainage divide. Colluvium and bedrock contaminated by produced water salt (NaCl) are remarkably widespread on the site in positions that are topographically below the level of the two pits. The outlet of the produced water pit drained to the north; thus, most salt water was apparently released in that direction. Seepage through pit walls and overflow from the pit probably transported some lesser amounts of salt into the drainage southwest of the divide. Surficial sediments composed of a permeable eolian sand surface layer (20 to 120 cm thick), permeable sandstone-clast-rich slopewash, and clayey to conglomeratic colluvial deposits overlie weathered bedrock (sandstone, clayey sandstone, sandy claystone, and shale). Pathways for produced water movement include 1) topographic lows on the contact between the permeable surficial deposits and the underlying less permeable bedrock units; 2) permeable conglomeratic facies in the colluvial deposits; 3) laterally discontinuous, clean sandstone units in the bedrock; and 4) fractures in bedrock. Shale and dolomite-cemented sandstone might have acted as aquitards. On the outcrop scale, produced waters and hydrocarbons followed permeable zones caused by vertical burrows in bioturbated sandstone. The burrows commonly have a bleached halo around them caused by the dissolution and movement of iron. At one site beneath a pit, hydrocarbon fills an individual vertical burrow.

NEW INNOVATIVE RECLAMATION PROCEDURES TO CAP DRILLING WASTE RESERVE PITS IN THE PERMAFROST ENVIRONMENT OF NORTH SLOPE, ALASKA

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Capping of earthen drilling waste reserve pits has been conducted since the North Slope oil fields were discovered in the late 1960s. Recent abandoned site investigations have discovered that a significant percentage of these constructed caps have collapsed. The collapse generally results in the development of surface water impoundments on top of the drilling waste pit and chemical analyses often indicates conductivity of drilling waste contaminants into the surface ponds.

All backfilling activity in reserve pits on the North Slope is done in the winter when the pit contents are frozen and the material used as fill is frozen. After careful study, it was discovered that the caps collapse because the material used as backfill is ice-rich. During the short cool arctic summers, the entrained ice melts very slowly over a period of several years. The total amount of shrinkage is generally 25%. If the seasonal thaw penetrates to the depth of the covered drilling waste, the weight of the fill material presses the pore fluids from the drilling waste into the gravel cap. This leachate is the source of contaminants that end up in the water pools on top of the gravel cap.

Once it was determined how and why the ponds form in reserve pit caps and the source for the contaminants in the water, a new cap design was made that allows for the collapse of the cap. The end result is a cap that collapses exactly onto itself but remains above grade so surface water ponds do not form. Although simple to design and construct, this new innovative engineered design is a significant advance in the backfilling, reclamation and long term stability of North Slope drilling waste reserve pits.

BIODEGRADATION OF SYNTHETIC DRILLING MUD BASE FLUIDS IN GULF OF MEXICO DEEP-SEA SEDIMENTS

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Drilling of oil exploration wells beneath the sea floor requires a drilling mud that can lubricate the drill bit, carry rock cuttings to the surface, and control reservoir pressure. One component of drilling mud is synthetic base fluids (SBF), which are non-aqueous phase, olefin-based or ester-based liquids. After separation from the drilling mud, drill cuttings contaminated with residual SBF are discharged to the sea floor. We will present evidence of anaerobic biodegradation of surrogate SBF compounds in sediment collected from beneath drilling platforms in the Gulf of Mexico. Biodegradation experiments were performed under environmentally relevant conditions of low temperature (4°C) and high hydrostatic pressure (between 97 and 786 psi, depending on the depth of sampling). The ability to degrade the surrogate SBF was linked to prior exposure of the sediment to cuttings discharge. Microbial characterization of the sediment will also be presented. Experimental data will be used to complete a model which estimates the response and recovery of cuttings-impacted sediment based on microbial response, environmental conditions, and SBF chemical properties.

SLURRY INJECTION OF DRILLING WASTES - REGULATORY REQUIREMENTS AND PRACTICES

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Argonne National Laboratory (Argonne) has conducted a comprehensive feasibility evaluation of using slurry injection technology to dispose of drilling wastes for the U.S. Department of Energy. The regulatory portion of Argonne's evaluation is presented in the final report entitled Compendium of Regulatory Requirements Governing Underground Injection of Drilling Wastes (February 2003) (the Regulatory Compendium). This presentation describes the Regulatory Compendium, including the collection and organization of the pertinent information, and the findings and trends relative to the regulations and practices governing slurry injection in the United States. Drilling wastes are generally made up of used drilling fluids and drill cuttings. Slurry injection involves grinding solid or semisolid drilling wastes or otherwise reducing the particle size, mixing solid particles of suitable size with a fluid to create a slurry, and then injecting the slurry underground at a pressure high enough to fracture the receiving formation. When the pressure is reduced, the fluid bleeds off into the formation and the solids are trapped in place in the fractures. The use of the different forms of slurry injection has increased over the past decade, primarily in oil-producing areas such as the North Slope of Alaska and the Gulf of Mexico. In addition to slurry injection, the Regulatory Compendium surveys other injection technologies, including subfracture injection, annular injection, injection prior to plugging, disposal in abandoned salt caverns, and disposal in coal mines.

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PROBABILISTIC APPROACH TO MODELING AND RISK ASSESSMENT OF CUTTINGS RE-INJECTION OPERATIONS

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Many cuttings re-injection projects have been carried out worldwide. Operational experience has proved that cuttings injection through hydraulic fracturing is a cost-effective and environmentally friendly means of complying with environmental legislation because of its many advantages. However, the major issue with this technology is to ensure the safe containment of the disposed wastes and to manage the potential risks. Since it is not possible to have all the geological and operational information with total certainty, a probabilistic approach to modeling and risk assessment of cuttings re-injection operations may be more appropriate. For example, prediction of the injected waste extent or disposal capacity depends on whether a single fracture or multiple fractures are generated from the injection operations. When and where secondary fractures are generated may depend on factors such as initial in-situ stress magnitude and orientations, local stress change from cuttings injection operations, and others.

This paper will highlight a probabilistic approach to modeling of disposal capacity and risk assessment in cuttings re-injection operations. Storage mechanisms of multiple fractures are reviewed first and factors contributing to formations of secondary fractures are identified. A Monte Carlo approach is used to evaluate their impacts on disposal capacity and waste extent with associated uncertainties. Implications of the approach and results on cuttings re-injection engineering, operation and monitoring will be given.

NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER

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Natural attenuation of petroleum hydrocarbons has become an accepted remediation remedy and the application to chlorinated solvent sites has also emerged as a viable remediation alternative, including those sites affected due to drycleaning operations. Available data from a total of 137 drycleaning sites registered with the Texas Voluntary Cleanup Program were compiled and used to evaluate the efficacy of utilizing natural attenuation as a remediation strategy. An evaluation of the extent of soil and groundwater contamination and the relationships between maximum chlorinated solvent concentrations, daughter products, and site characteristics was conducted. Correlation analyses were completed between plume geometries, depth to water, seepage velocity, duration of facility operation, and maximum soil and source concentrations. Data gathered from the evaluation of plume stabilities, point and source decay rates, and bulk attenuation rates were also compiled to further evaluate the potential for application of natural attenuation at these sites.

LONG-TERM EFFECTIVENESS OF SURFACTANT-MODIFIED ZEOLITE FOR REMOVAL OF BTEX FROM PRODUCED WATERS

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Produced water contains high levels of various hazardous organic compounds including benzene, toluene, ethylbenzene, and xylenes (BTEX). Benzene concentrations can exceed the U.S. drinking water standard by a factor of more than 7000. Earlier we reported laboratory and field evidence that surfactant-modified zeolite (SMZ) effectively removes BTEX from produced waters, and that SMZ could be regenerated once without loss of sorption capacity. In the current study we report on the effectiveness of SMZ for BTEX removal after multiple sorption/regeneration cycles, and on changes of SMZ sorption characteristics over time. Preliminary results suggest SMZ's BTEX removal efficiency actually increases with use, apparently due to retention of low-volatility produced-water components that also serve as a sorption medium. A cost analysis indicates SMZ-based systems can be competitive with other produced-water treatment technologies.

THE CHEMICAL COMPOSITION AND DISTRIBUTION OF GROUNDWATER IMPACTED BY PETROLEUM PRODUCTION OPERATIONS: THE OSPER A SITE, OSAGE COUNTY, OK

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We are involved in a multidisciplinary investigation to study the transport, fate, natural attenuation and impacts of released petroleum compounds and inorganic salts in produced water at the Osage-Skiatook Petroleum Environmental Research (OSPER) A and B sites in Oklahoma. In this report, we summarize the impacts on the groundwater at the OSPER A site, where ~1.5 hectare of land has been affected by oil operations that started in 1913 and were largely terminated by 1937. Groundwater impacts are being investigated by repeated sampling of 35 wells (1-36 m deep), completed with slotted PVC tubing. The well locations were based on: (1) The presence of salt scars, excessive soil and rock erosion, brine and asphalt pits, degraded oil, dead trees and shrubs and other visible surface features; (2) results of electrical conductance, Cl, Br and SO_4 measurements on aqueous leachates from samples of shallow soil (0-15 cm), selected soil profiles (0.5-1.7 m) and core samples from prior drilled wells; and (3) results of shallow penetrating (<10 m) electromagnetic (EM) and deeper (30-60 m) DC resistivity surveys used to map the subsurface distribution of saline water, soil and bedrock.

Results of water analysis are in general agreement with those obtained from soil and core samples and the geophysical surveys. We are mapping a 3-D plume of high salinity water (5,000-30,000 mg/L TDS) with chemical and isotopic characteristics similar to those of the source produced water. The depth of this plume is not currently well defined; the one well that penetrates into a deeper aquifer has lower salinity (~2,000 mg/L TDS), but high Fe, Mn and dissolved organics. The horizontal plume boundaries are also not well delineated, since all wells deeper than 2 m at the site encounter the plume. A background well, drilled 0.6 km to the NW of the site has freshwater (450 mg/L TDS) and other characteristics of the pristine local groundwater, but also has relatively high dissolved organics, including BTEX. Results to date clearly show that large amounts of salts and organics remain in the local groundwater after more than 65 years of natural attenuation.

EFFECT OF TEMPERATURE AND SALINITY ON BTEX REMOVAL USING SURFACTANT-MODIFIED ZEOLITE

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The United States oil and gas industry generates more than three billion tons of produced water every year. In addition to oil and grease, produced waters contain a number of hazardous aromatic compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) as well as high salt concentrations varying from 100 ppm to 300,000 ppm. As part of our continuing evaluation of a surfactant-modified zeolite (SMZ) treatment process for produced water, batch and column sorption studies were conducted to evaluate the effects of temperature and salinity on BTEX sorption. Results from these experiments indicated that BTEX sorption increases with increasing temperature and salinity. Partitioning models consistent with these results were used to describe the results and predict performance in laboratory and pilot scale columns.

SMALL DIAMETER HYDROCYCLONE SEPARATION EFFICIENCY ESTIMATION USING COMPUTATIONAL FLUID DYNAMICS

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Although operation of a 10-mm hydrocyclone is simple, the turbulent, swirling flow field within a 10-mm hydrocyclone offers a unique challenge to computational fluid dynamics (CFD). In addition to the computational challenge, very few experimental measurements have been reported in the literature concerning the flow field of the mini-hydrocyclone for which to compare the CFD results. This research specifically addresses the modeling of the flow field of a volute entry, 10-mm (or mini-) hydrocyclone. The feed flow rate is 4.5 L/min yielding a Reynolds number (based on the hydrocyclone diameter) of 9,500 and a swirl number of 8.4.

Results indicate that the second order Reynolds-stress model predicts characteristics common to this type of confined swirling flow, i.e. a Rankine vortex structure and a long, narrow reverse flow core. Lack of availability of experimental measurements of the flow field in mini-hydrocyclones forces a comparison with similarly proportioned 76-mm hydrocyclone velocity field characteristics. In these comparisons, the forced vortex portion of the 10-mm hydrocyclone is much more pronounced than in the 76-mm hydrocyclone in accordance with a smaller cross-sectional area for swirl development. A deficit in the axial velocity profiles of 76-mm hydrocyclones observed in the literature is reproduced in the 10-mm simulations. Also, the speculation concerning high levels of centrifugal acceleration inside the mini-hydrocyclone is demonstrated, with accelerations as high as 10,000 times gravity being present. Finally, separation efficiencies generated by the simulations are compared to experimental hydrocyclone separation efficiencies to check consistency with the flow field predictions.

FINAL EVALUATION OF PILOT WETLANDS FOR PRODUCED-WATER TREATMENT AT NAVAL PETROLEUM RESERVE NO. 3

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This paper presents the design, construction, operation and data collection of free water surface (FWS) and subsurface flow (SSF) pilot wetlands from June 2001 through September 2003. Often the treatment performance of pilot wetlands ranges from poor to excellent, in part due to a lack of understanding of wetland treatment capabilities and of how to effectively conduct pilot wetland studies. This project was funded jointly through a three-year cooperative research and development agreement (CRADA) between the Department of Energy Rocky Mountain Oilfield Testing Center and ChevronTexaco Energy Research and Technology Company. The impetus for this three-year wetland pilot study is to build an operational knowledge of treatment wetlands and to obtain a data set that can be used to redesign a full-scale wetland for produced water treatment at Naval Petroleum Reserve No. 3 located approximately 32 miles north of Casper, Wyoming. The wetland pilot units are set up outdoors to test climatic influences on treatment and simulate real-time conditions. The discussion covers treatment performance of these pilot systems, maturation of plant and microbial populations, water quality, troubleshooting, lessons learned and pilot operations with summer students.

Flotation Pump Proves Successful for the Treatment of Produced Water

ABSTRACT

The treatment of produced water continues to be one of the biggest world wide economic and environmental concerns. Oil and Gas Producers are looking for economic ways to treat produced water from both onshore and offshore locations for disposal, reuse, or re-injection. The need for efficient equipment to treat produced water has led to much research and a variety of methods have been developed to treat this water. The produced water flow rate capacities can range from very low volumes to well over 500,000 BPD. Supplying the needs for such equipment has kept companies looking for new and creative ideas. One such idea developed by Monosep Corporation is our patented Dissolved Gas Flotation (DGF) technology, which includes a specially designed pump. This pump creates the micro-fine bubbles needed for flotation equipment to operate efficiently.

This paper will present an overview of the history and development of the DGF Technology that has occurred over the past several years. In addition, it will explain the advantages of the DGF Technology over other current available technologies along with specific data generated in the numerous applications it is currently being used in.

I. INTRODUCTION

In order to protect the environment we need efficient systems for cleaning the produced and processed water throughout the world. Flotation technology is one of the main systems used for removing contaminates from these waters. Oil and Gas Producers are always looking for new technology to accomplish this task for both onshore and offshore applications. Not only is there a need to increase the efficiency of these systems, there is also a necessity to reduce the size of the equipment, and to handle the pitch and roll of deep-water production facilities.

Monosep has developed and successfully applied new flotation systems to meet these needs. This technology is centered on a new type of pump that creates the micro-fine bubbles needed for flotation equipment. The pump can dissolve vapors into the produced water, which then breaks out as extremely small bubbles in the process equipment. The pump is called a Dissolved Gas Flotation (DGF) Pump. Monosep has installed over 75 DGF pump systems throughout the world with excellent results. Monosep owns the DGF pump patents for process systems and equipment for water treatment.

This paper will present the development and success of this technology. The background and importance of the flotation process will be discussed along with the variety of equipment it has been installed in. Next the mechanical aspects of the DGF pump will be explained, followed by the results of the shop testing and field results. The current installations and future applications will be presented. This paper will close with a brief summary and a projected outlook for the DGF Pump Technology.

II. FLOTATION PROCESS

Flotation systems are used for a variety of applications throughout the world. The process floats solids, oils and other contaminates to the surface of liquids. Once on the surface these contaminates are skimmed off and removed from the liquids. Oil and gas production facilities have used flotation systems to remove oil and solids from their produced and processed water for many years.

The keys to good separation are both gravity and the creation of millions of very small bubbles. Based on Stokes Law, the size of the oil droplet and density of the droplet will affect the rate of rise to the surface.

The larger and lighter the droplet the faster it will rise to the surface. By attaching a small gas bubble to an oil droplet it will decrease the density of the droplet, which will increase the rate at which it will rise to the surface. Therefore, the smaller the gas bubbles created the smaller the oil droplet floated to the surface. Efficient flotation systems need to create as many small bubbles as possible. The method in which the bubbles are introduced into the water stream

and retention time are also important factors. The average retention time for a vertical unit is typically 4 to 5 minutes and 5 to 6 minutes for a horizontal unit.

There are a few different types of flotation systems.

1. Dissolved Air Flotation (DAF) system: In this method the air is compressed and dissolved into the water stream. These bubbles are very small and give good results, but the system requires a compressor and a saturation tank. This system is not suited for offshore platforms due to space and maintenance requirements.

2. Induced Gas Flotation (IGF) systems: These IGF systems can be mechanical or hydraulic.

    a) The mechanical system uses a motor and paddle assembly to basically shear the gas out of the water. As the paddle spins in the water it agitates the cell with small bubbles. This system requires significant maintenance. The motors, bearing, and paddles need to be greased and oiled routinely.

    b) The hydraulic system uses a recirculation pump to drive an eductor, which induces fine gas bubbles into the water. Each flotation cell is filled with many micro-fine gas bubbles. The recirculation pump recycles from 25% to 125% depended on the equipment design.

3. Gas Sparging system: This system uses a porous SST tube to sparge small gas bubbles into the water. The gas bubbles are very small and provide good results. The sparging tubes however are prone to plugging with scale and/or hydrocarbons.

Figure 1. Comparison of mechanical and hydraulic systems.

These methods have been in the industry for many years. Monosep has introduced a new hydraulic method for flotation without the need of eductors. The recirculation pump used in this system dissolves the gas bubbles within the pump and associated piping.

III. NEW DGF PUMP CONCEPT

A. About the DGF Pump

The impeller in this DGF pump is designed with dual sides. One side is designed to drive the liquid like a normal centrifugal pump and the other side is designed to draw vapor into the pump and mix it with the liquid. In addition to the new impeller, a special seal was invented to extend the life of the pump. With these innovations the pump creates a sub-atmospheric pressure region within the pump's seal chamber. As the impeller draws in the vapor it is mixed with the liquid being pumped and compressed into micro-fine bubbles. Because of the close tolerance between the backvanes of the impeller and the backplate of the pump the vapor is sheared into fine bubbles and then they are compressed in the sub-atmospheric pressure region of the pump. These fine bubbles become dissolved into the liquid within the volute of the pump.

The result of this process provides similar size bubbles to the Dissolved Air Flotation system discussed above. The backpressure valve on the discharge piping can regulate the bubble size in this DGF Pump. The bubble size ranges from 50 to 1 micron or less. Video footage illustrating the range of the bubble size and some so small that the rise rate to the surface is very slow.

B. Flow and Pressure

The flow rate of the liquid in the discharge piping and the backpressure on the pump are key factors to creating different size bubbles. The way the pump is piped to the process equipment is very important. An optimum velocity of the pump piping should be 2 to 5 feet per second. Also a saturation time of five to ten seconds is needed in the discharge piping before the backpressure valve. An optimum backpressure on the pump varies per pump size but is generally between 35 and 65 PSI. To calculate the discharge piping size and length the follow formula can be used.

$Q = V * A$

Q = flow rate
V = velocity of fluid media
A = area of pipe

Multiply the Velocity by the desired saturation time (5 to 10 "seconds") to calculate the length of pipe needed before the backpressure valve.

Figure 2. Vessel and pump with discharge piping.

C. Applying the Pump

The DGF flotation pump has been applied to applications involving processing of produced water. The liquid driven by the pump is produced water; the vapor drawn into the pump to be dissolved into the produced water is produced gas. In the treatment of produced water the elimination of oxygen from the treatment system is essential. Therefore, produced gas is used for the flotation vapor. Gas vapor has more affinity to oil and will attach to an oil droplet easier than oxygen. Most importantly, oxygen will precipitate iron oxide into the produced water stream, which has a tendency to become oil wet and contaminate the discharge.

IV. SHOP AND FIELD TESTING

A. SHOP TESTING

Initially, Monosep tested the DGF Pump in an existing rental unit in 1997. A vertical gas sparging flotation unit was equipped with the new DGF Pump in the shop. The internal sparging tubes were removed and the existing external piping for the sparging system was utilized. The liquid used in the vessel was fresh water. The vapor inlet of the pump was open to the atmosphere for this test. The results were fantastic. The vessel was quickly filled with billions of micro-fine bubbles, which turned the water "milky white". The ½"piping for the sparging system provided the correct amount of backpressure on the pump to allow the air to dissolve into the water. These positive results lead to having a few more pumps built for further testing.

The next test was done on a horizontal unit. The existing eductor piping was used and the eductors were not removed. The results were poor because the backpressure on the pump was insufficient. The water traveled through the piping too fast for the air to dissolve into the water.

A small test unit was used for further testing. The unit was about 2-½ foot by 2-½ foot by 4 foot tall. This box was built on legs and had plexi glass sides so that the bubbles could be viewed. The pump suction came off the bottom and the pump discharge was piped down into the water from the top. After testing several size orifices, we found the correct size to provide the backpressure on the pump to create the micro-fine bubbles. However, it was decided that using a valve to control the backpressure would be more favorable during field operations.

Figure 3. Test system with four down comers.

The final shop test was conducted on a new vertical unit that was designed with two manways on opposite sides of the vessel. A plexi glass cover was made for both manways so that the bubbles could be observed and filmed.

Once the valves where pinched off to provide the correct backpressure, clouds of micro-fine bubbles filled the vessel. The clear water became milky white. A small red sign was placed in the water about 8" from the plexi glass. Before the pump was turned on the sign was clearly visible. Within a few moments after the pump is turned on the sign becomes hard to see due to the billions of fine bubbles clouding up the water. The bubbles became extremely small and suspended in the water rising very slowly to the surface. It was noted that rust particles and oils from the steel floated to the surface because of the very fine bubbles.

Figure 4. Monosep SPINSEP complete with DGF pump.

Upon confirmation of these great results, Monosep rented this test unit to an offshore client who achieved 8 to 12 PPM discharge verses 25 to 35 PPM on the previous unit. This test unit was then sold to another client after a subsequent successful trial test.

B FIELD TESTING

Before construction on the test unit began, a client agreed to retrofit an existing sparging unit offshore with the DGF Pump. The installation went as planned and the results were very good. The discharge water quality of the new DGF Pump was better and much more consistent than the previous sparging system.

Another client agreed to retrofit a sparging unit on an offshore platform. Again the results were very good. On these units, valves keeping the pressure around 40 to 50 psi controlled the backpressure on the pump.

Next, two new vertical units were built for the same company in the same field. One gave better results in the field with lower psi differential pressure (25 to 35 psi on the pump discharge vs. 35 to 45 psi). The reason is believed to be associated with the differences in the oil/water characteristics. Since the DGF pump is capable of actually varying the bubble size in the field, there is greater success treating the water.

Next, a new DGF horizontal unit was built. Due to the extremely small bubble size and having multiple chambers or cells for the bubbles to rise to the surface, performance was better than expected. It was also discovered that the bubble size in each cell could be controlled and varied from the next cell. In the first cell we created extremely small bubbles and in the next few cells created slightly larger bubbles. The flexibly to change the bubble sizes in each cell and have a combination of bubble sizes in the unit has increased the efficiency of the equipment.

Monosep also field-tested the DGF pump in other offshore vessels. DGF pump systems have been used to successfully improve the efficiency of existing skimmers. In all cases the performance of the equipment improved.

C Advantages of the DGF Pump

There are some important technical advantages of the DGF Pump system, which are highlighted in Table 1.

V. CURRENT INSTALLATIONS AND FUTURE APPLICATIONS

A Current Installations

Over the past few years numerous DGF pump systems have been built and installed. As of August 2003, Monosep has built 25 new vertical units, 18 new horizontal units, and refurbished/retrofitted over 40 existing units. In addition, we have added the DGF pump system to five existing skimmer vessels by piping the discharge of the pump through the bottom drains.

B Case Studies

The following are two case studies from major oil and gas producers in the Gulf of Mexico.

Case Study One

Company – Major Oil and Gas producer

Location – Brazos Area

Project Type – Produced Water Treatment
Client was using media to meet overboard discharge limits
Media was eliminated due to installation of MONOSEP SPINSEP Flotation Unit downstream of skimmer

Improvements/Savings

Elimination of Media: $30,000 per month
Elimination of Personnel: $15,000 per month
Chemical Savings: $300 per month
Total Annual Savings: $543,600 per year

Improved Water Quality by using DGF Technology Gravimetric Oil & Grease <10 ppm

Case Study Two

Company – Major Oil and Gas producer

Location – Vermillion Area

Project Type – Produced Water Treatment
Converted vertical sparge tower to DGF Pump system in order improve efficiency so that downstream media could be eliminated.

Improvements/Savings

Gas savings: 74 mcf x $3.00 per foot = $222 per/ft x 365 = $81,030
Solid sock filter savings: $442 x 365 = $161,330
Filter disposal 12 bins per year @ $2000 = $24,000
Labor savings = $12,288 per year
Chemical savings $36 x 365 = $13,140 (50% reduction)
Absorption Media: $76,000 per year

Total Annual Savings: $367,788 per year

Water quality improvement 32 ppm to 13 ppm

C Future Applications

Monosep is looking to test our DGF technology in various other water treatment applications such as steel mills and paper plants. The use of improved flotation technology to remove oils and solids will result in increased efficiency in these industries. Monosep anticipates testing this new technology in these and many other applications in the next few months.

Monosep is currently experimenting with a new media, that combined with the DGF system can improve the efficiency in present produced and process water applications. Initial results are extremely promising, which has led us to begin construction on the first full-scale unit. This unit will be installed in the Middle East and should be in operation by December of 2003.

VI. SUMMARY

Numerous horizontal and vertical units have been installed throughout the world using DGF Pump technology. It has been proven that the use of DGF technology can decrease chemical usage by up to 25% over conventional eductor style units. Monosep has also installed DGF technology on platforms that had mechanical flotation systems and the DGF system performed, on average, greater than 35 % more efficient.

The future of the Dissolved Gas Flotation Pump continues to look very promising. With over 75 units in operation providing excellent results, Monosep is moving forward by continuing to expand the supply and service of the DGF Pump Technology to our customers.

Advantages of the DGF Pump

TECHNICAL ISSUES	DGF Pump	EDUCTOR
RECYCLE RATE	15% to 25% of process capacity is recycled, thus resulting in a smaller recycle pump/motor. Decreased electrical consumption More retention time.	50% to 100% of process capacity is recycled. Larger pump/motor, larger footprint Increased electrical consumption. Less retention time.
MAINTENANCE	Monosep flotation equipped with standby DGF system. No downtime during maintenance of unit due to Backup DGF system. Simply reconfigure valve arrangement. No internal mechanical maintenance since all bubble size. Components are external to unit.	Single eductor does not allow duplicity. Unit will not have floatation during maintenance of eductor. May result in O&G exceedances.
PROCESS	Monosep flotation has multiple DGF discharge nozzles, which allows for greater distribution of flotation bubbles. The micron size of the bubbles can be varied for each specific nozzle external of the vessel. Bubble size is changed by simply adjusting the backpressure on the pump. The bubble size can be changed from one micron to several hundred microns. This results in better efficiency in terms of O&G removal. The ability to vary bubble size in "real time" results in a reduction in chemical usage.	Eductor technology is not as efficient as the DGF technology. It is set at one bubble size and cannot be adjusted without changing eductors. In addition, it will not produce as small a bubble as DGF. Some Eductor systems Typically only have one eductor per vessel, which is not sufficient to saturate the vessel volume with the appropriate bubble concentration.

Table 1. Technical Advantages

INFLUENCE OF PLANTS ON SOIL COMMUNITY DYNAMICS IN A PETROLEUM-CONTAMINATED SOIL

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Plant growth can influence the composition of the biological community ultimately responsible for the effectiveness of the phytoremediation of petroleum-contaminated soil. The study objective was to evaluate plant shoot and root growth and microbial community dynamics at an oil-spill site that had an initial total petroleum hydrocarbon (TPH) concentration (by GC/FID) of 9,175 mg/kg. Four replications of the following treatments were used: non-fertilized vegetation-free control; ryegrass - fescue mixture + fertilizer; or bermudagrass - fescue mixture + fertilizer. Chemical and biological properties were analyzed at 0, 6, 17, 21, 30, 37, and 42 months after initiation of the field study. Vegetation was successfully established at the site and vegetated fertilized plots had significantly greater reductions in TPH as compared to the non-vegetated non-fertilized control plots. Vegetation establishment and fertilizer addition resulted in increased bacterial and fungal numbers. The results of these studies demonstrate that plants alter the soil biological community and influence clean up of crude oil-contaminated sites.

MATHEMATICAL MODELING OF PHYTOREMEDIATION OF CRUDE OIL CONTAMINED SOILS - IPEC FUNDED PROJECT

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A mathematical model of phytoremediation based on exploration of contaminated soils by grass species root systems has been developed. Both temperature and soil moisture affect the degradation kinetics, and have been incorporated into the model. We will present a comparison of the model predictions driven by the site specific weather and rooting patterns to observed decreases in contaminant concentration at several of the national Remediation Technologies Development Forum sites. The effects of different treatments at on the fitted degradation rates will also be presented.

PHYTOREMEDIATION PETROLEUM HYDROCARBON CONTAMINATED SOIL: RESULTS FROM THE RTDF COOPERATIVE FIELD TESTS

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Cooperative field trials have been in progress since 1998 to test phytoremediation of weathered petroleum hydrocarbon contaminated soils as part of the Remediation Technologies Development Forum. Participants in the trials include United States Environmental Protection Agency, Environment Canada, United States Department of Defense, petroleum and utility corporations, universities, and environmental consultants. Thirteen test locations include refineries, former manufactured gas plants, spill sites, motor vehicle wastes, and oil production sites. The purpose of the trials is to determine if there is evidence that vegetation enhances progress toward meeting practical environmental management objectives for petroleum sites within a three-year period. A standardized experimental protocol with site-specific adjustments was developed, recognizing that changes in hydrocarbon concentrations are likely to be slow and subtle, contaminant distribution in the soil is variable, and monitoring will be needed for a long time. Most locations included three treatments: an unvegetated control, a cool-season grass/legume mixture, and a locally selected treatment of native plants or trees. Laboratory analyses included estimation of total petroleum hydrocarbons, polycyclic aromatic hydrocarbons, a hopane biomarker, and petroleum hydrocarbon fractions by the TPH criteria working group method. Eleven locations have completed the planned three-year trial period. Statistical analyses showed that observable effects of vegetation treatments on hydrocarbon concentrations varied among locations. Some locations showed strong positive effects of vegetation treatments while others did not show evidence of treatment differences. High variability, especially at refinery sites, decreased the ability to detect treatment differences. Conclusions and lessons learned will be discussed. Appropriate applications of phytoremediation for petroleum sites will depend on contaminant composition, local conditions, and site-specific environmental management objectives.

NATURAL REMEDIATION OF GROUNDWATER IMPACTED BY PETROLEUM PRODUCTION OPERATIONS: THE OSPER A SITE IN OSAGE COUNTY, OK

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The Osage-Skiatook Petroleum Environmental Research (OSPER) A site, located within the depleted Lester lease, has an area of about 1.5 hectare that is impacted by produced water and hydrocarbon releases that occurred primarily 65-90 years ago. In addition to groundwater contamination, impacts include salt scars, excessive soil and rock erosion, brine and asphalt pits, degraded oil, dead trees and shrubs and other visible surface features. Eventually, the bulk of inorganic salts and dissolved organic species will reach the adjacent Skiatook Lake, a 4250-hectare reservoir that provides drinking water to local communities and is a recreational fishery. Water samples from nearby oil wells indicate that the produced water source was a Na-Ca-Cl brine (~150,000 mg/L total dissolved solids), with relatively high concentrations of Mg, Sr, Fe, Mn and NH_4, but low concentrations of SO_4, H_2S and dissolved organics.

Results of detailed analysis of water samples, periodically obtained from 35 wells (1-36 m deep), were used to map a 3-D plume of high salinity groundwater (5,000-30,000 mg/L TDS) with chemical and isotopic characteristics that are similar to those of the produced water. These and future results will be used also to investigate the natural processes that modify the chemical composition of the plume-groundwater, including mixing with pristine groundwater and percolating water from precipitation, sorption, mineral precipitation/dissolution, evapotranspiration, volatilization and bacterially mediated oxidation/reduction reactions. The rate of salt removal from the site by surface runoff is being determined by measuring the volume and chemical composition of water flowing over a weir installed close to the Skiatook reservoir in a location that captures most of the surface and base flow from this site following precipitation. Results to date show that the natural salt-removal processes at this site are slow, thus providing a valid explanation for the fact that large amounts of salts from produced-water releases still remain in the groundwater plume after more than 65 years of natural attenuation.

A COMBINED USE OF PLANTS AND PLANT GROWTH PROMOTING PSEUDOMONAS FOR OIL SPILL BIOREMEDIATION

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One of the promising bioremediation approaches is the concurrent use of plants and rhizosphere microorganisms of the Pseudomonas genus known for their plant growth promotion ability (PGPRP). Many genetic systems responsible for degradation of oil hydrocarbons and resistance to toxic substances (e.g. heavy metals) are located on plasmids. It is possible, therefore, to modify PGPRP Pseudomonas to obtain variants with a wide range of necessary properties. Some new combinations of plasmids and host bacteria degrade polycyclic polyaromatic oil hydrocarbons more efficiently. The microorganisms, constructed using natural microbial isolates and plasmids via a horizontal transfer of genetic information (primarily by conjugation) inherent of living matter in nature, offer no threat to the environment. In all probability, the purposively created plant-PGPR Pseudomonas or plant-PGPRP-endomycorrhizae fungi combinations, can form the basis for further development of bioremedation technologies.

LONG-TERM COMPOSITION CHANGES OF OIL RESIDUES IN PATAGONIAN SOILS

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This paper examines the interdependence between the oil residue desorption fate and the shifts in the oil residual composition due to natural environmental processes. Experimental data of several parameters (nC_{17}/pristane, nC_{18}/phytane, content of the aliphatic, aromatic, polar and asphaltene fractions, etc.) determined for different regional field samples (spills), show that the changes in the chemical composition of the residues correlate better with exposure time in hydrophobic environments than with other variables such as the initial spill crude oil source or the soil composition. The results show an increase of the polar fraction during the first years and a continuous decrease in the nC_{17}/pristane, nC_{18}/phytane ratios when the environmental exposure time increases. An increase of the distribution coefficients (Kd) with age can be also observed. This could be attributed, not only to the loss of the more soluble components, but it also suggests that sequestration may be an important process. The influence of assistant degradation was also evaluated.

Key words: Oil spill, Polluted Patagonian soils, Distribution coefficients, Natural attenuation, Assistant degradation.

BIOREMEDIATION OF SOIL FROM TENGIZ OIL AND GAS FIELD

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Tengiz oil and gas field is located on the northern and eastern part of the Kazakhstan coast of the Caspian Sea Basin. We can consider Tengiz oil and gas field as one of the biggest oil and gas fields in the world discovered in last 15 years. By the experts' accounting, in the stock of the Tengiz field we have 23.6 billion barrels of oil. In last year, JV "Tengizchevroil" (TCO) produced 13 million tons of oil per year; therefore this appointment is one of the best in the Republic of Kazakhstan. Of course, this achievement is very closely connected with high potential activity on the field operation, especially on drilling and workover rig locations, because there are a lot of oil and drilling mud (oil base mud) spills on the soil of this territory. As we know, the oil impact to the microorganisms depends on its concentration. Also, in light concentration oil serves as a support system for several types of microorganisms. However, with a high concentration, oil has an acute toxic impact to all soil microorganisms. All soil samples were selected from oil fields, including drilling and workover rigs. These points were selected because five drilling and workover rigs of the Parker Drilling Company worked these wellheads. Sowing and accounting of the microorganism cells was conducted by the Kokh method on the five nourishing stamps. In the results of our work, we noticed very good activity of soil microorganisms from soil sample point T-116. The activity of microorganisms especially on this soil sample was attributed to selection of the samples on T-116 while the rig was down, which led to extra oil and drilling mud spills.

CURRENT SILT FENCE TECHNOLOGY, PROBLEMS AND PROSPECTS

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An overview of the use of silt fence in control of sediment from construction sites and pipeline construction is given, including the design principles, types of materials used, example locations, and a discussion of the associated problems. Typical standards are given along with an analysis of the likelihood of failure. A current EPA project investigating the success and failure of current silt fence technology is discussed and preliminary results are presented. Finally, an overview is given of the problems that need to be solved to make silt fence an effective sediment control technology for linear construction projects such as pipeline installation.

MONITORING DATA ON EFFECTIVENESS OF SEDIMENT CONTROL TECHNIQUES

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Silt fence is one of the most common BMPs implemented for sediment control at construction sites. Field evaluation of the efficiency of silt fences in removing sediment in highway construction runoff showed that sediment removal was not attributable to filtration by the fabric, but was the result of particle settling. Geotextile silt fences proved to be ineffective in reducing turbidity. The particles responsible for creating turbidity are mainly silt and clay size and are normally much smaller than the size of the openings in the fabric. The observed data indicated that silt and clay size particles comprised 92% of the total suspended solids. These particles also have very low settling velocities and consequently are not removed by sedimentation.

The field efficiency of silt fences appears to be dependent mainly on the detention time of the runoff behind the control. The detention time is controlled by the geometry of the upstream pond, hydraulic properties of the fabric, and maintenance of the control. Despite comments by project supervisors that little maintenance of controls was required, numerous installation and maintenance deficiencies were noted during the study.

High sediment removal efficiencies were achieved with silt fences in the flume studies. The geometry of the flume created a large ponded area behind the controls, resulting in long detention times and significant particle settling even with the fine-grained sediment used in the tests. Mean sediment removal efficiency in the flume ranged from 68 to 90% and was highly correlated with the detention time of the runoff. This indicates that silt fences should be sited in the field to maximize the ponded volume behind the fence.

A PIPELINE GIS FOR OUACHITA PARISH, LOUISIANA

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This paper presents the results of the first phase of a project intended to create a comprehensive Geographic Information System (GIS) of petrochemical transmission pipelines throughout Louisiana. Pipeline networks in all metropolitan areas within Louisiana will ultimately be surveyed; however, this paper focuses only on Ouachita Parish as a case study to illustrate the rationale, methodology, and expected results for the statewide project. Because of its past and present importance in petrochemical exploration and transmission, Ouachita Parish serves as an excellent model for the application of GIS technology to mapping existing and abandoned pipelines. Over the past 85 years, drilling in the large Monroe Gas Field led to the extensive development of pipelines throughout Ouachita Parish. Unfortunately, the development of the pipelines was far from systematic, with little control or planning in the process. Presently, maps with pipeline information are out-of-date, inaccurate, and/or too generalized to be useful.

DISPERSANT AS AN OIL SPILL COUNTERMEASURE: TOXICITY EVALUATION AND OIL REMEDIATION IN WETLAND ENVIRONMENTS

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The effect of dispersant on wetland plant and oil remediation was studied. The dose-response study indicated that the effect of the dispersant, per se, on marsh plant Sagittaria lancifolia was limited. In addition, toxicity of the dispersed diesel on the marsh plant was much greater than that of the dispersed crude oil, which did not detrimentally affect Sagittaria even at an oil dosage of 145,800 ppm. In the experiment simulating oil dispersed before entering the coastal marshes, the dispersant application greatly relieved the adverse effect of both diesel and crude on the vegetation. Without the dispersant, the oils significantly decreased plant photosynthetic rate and increased the mortality rate. With dispersant application, however, the oils did not significantly affect the marsh plant. In addition, dispersant application significantly reduced oil adsorption to the marsh sediment, thus minimizing the long-term impact of the oil in the sediments. The present study indicates the potential of using dispersants as an oil spill countermeasure in near shore environments for protecting marsh habitats.

CONTINGENCY PLANS FOR LOUISIANA COASTAL WATERWAYS

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Spill accidents are likely to occur within waterways with heavy oil traffic. Therefore it is important to develop contingency plans to evaluate threats that toxic contaminants pose to water intakes, fish, marine mammals, and other aquatic species, as well as their supporting habitats. It is crucial to assess the effects of contaminants on such environment, help develop cleanup plans, and coordinate projects to maintain such important and vital waterways.

Contingency plans have been developed for some water bodies along the Louisiana coast. The Trajectory Analysis Planner (TAP) computer model developed by National Oceanic and Atmospheric Administration (NOAA) was used to prepare these plans. This model assists oil spill contingency planners to investigate how spilled oil might move and spread. The model provides information regarding sensitive sites affected by a spill, and the time available to take remedial actions.

Implementing the TAP model for any given estuarine system includes three main steps: calibrating the hydrodynamic component of TAP, populating the TAP trajectory database with numerous simulations, and finally mapping potential spill sites.

Examples of water bodies for which contingency plans have been developed include the Calcasieu and Sabine Lakes. Effort is underway to develop a contingency plan for the Lower Mississippi River.

PIPELINE MAPPING IN LOUISIANA

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The current state of published pipeline maps in Louisiana is poor. The best paper maps are out of date and small-scale, while the newer digital maps are incomplete and inconsistent. Accurate, statewide pipeline mapping is a massive and complicated task, yet Louisiana is unique among oil and gas states in not having a dedicated pipeline mapping program. Years of cumulative cartographic errors exist in the currently available reference maps. The pipeline industry is volatile, with numerous mergers and acquisitions. Pieces of pipeline systems are bought and sold every day and systems are abandoned without fanfare. Field investigation with global positioning system (GPS) equipment is essential, as is digital compilation and maintenance of data in a geographic information system (GIS).

The prospects for obtaining the state funding needed to properly investigate and compile a GIS of the state pipelines are currently poor. Consequently, the LGS has successfully sought sponsored funding to continue pipeline mapping efforts. Funding for such projects has been obtained from state and federal government clients. Projects have addressed the field investigation of pipeline crossings of major Louisiana waterways, pipeline GISs of several state metropolitan areas, mapping of federal pipelines crossing the state coastal zone, and investigation of abandoned and undocumented pipelines in specific study areas.

OCEAN OBSERVING SYSTEM FOR OIL SPILL CONTINGENCY, LOUISIANA, USA

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An online oceanographic and meteorological observing system has been developed and is being implemented off the Louisiana coast to provide critical information during offshore emergencies, including oil spills. The program, WAVCIS (WAVe Current Information System), provides wave information (sea state) including wave height, period, direction of propagation, water level, surge, water column velocity profiles, and meteorological conditions on a near real time basis. Information of this sort did not previously exist for an area approximating 135,000 km^2 off Louisiana's coast. WAVCIS involves offshore deployment of instrumentation around the entire state in order to provide near real time information on a frequent basis (3 hours or less) describing sea state, current velocity, and meteorological conditions. Information from each station is transmitted via cellular satellite telephone to a base station at Louisiana State University where it undergoes quality control, post-processing and archiving in an online database. The information is then made available on the World Wide Web and is accessible to computers with an Internet connection and web browser. Various data displays are available for the near real time information as well as a specified time history for archived data. The program provides a highly unique online information database for multiple uses. Examples include (1) information necessary to provide an emergency response decision tool for agencies faced with decision making during storm threats in the Gulf of Mexico involving evacuation or early warning enhancement; (2) information necessary to assist in decision making during oil spill response coordination; (3) information useful for assisting operations support for offshore industries, commerce and trade; and (4) information critical for input boundary conditions in numerically modeling the behavior of surface and underwater oil, gas and oil/gas mixtures.

USE OF OBLIQUE AERIAL VIDEO IMAGERY AS A RESOURCE FOR COASTAL ISSUES

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The Aerial Video Survey Program at LSU has been acquiring oblique, low-altitude, video imagery of the rapidly changing Louisiana shoreline by helicopter since 1984, and of other parts of the US GOM since 1992. The video was originally used as a tool for studying shoreline change and hurricane effects, but with realtime GPS data on the imagery, video was recognized by many agencies as a valuable tool in other applications. Although many discount the value of oblique imagery as being non-quantitative, this opinion overlooks the vast qualitative value and the overall information it contains. It has been used for environmental sensitivity mapping in Texas and Mississippi; shoreline type mapping in Louisiana; for oil spill contingency planning and in oil spill response; and for coastal restoration pre-planning, evaluation and storm performance. Video of the Louisiana Gulf shoreline and the lower Mississippi River are now being converted to digital imagery that is indexed on DVDs through projects funded by the LA Applied Oil Spill Research & Development Program.

AN OIL SPILL DATA CD PROGRAM

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Decision makers in government and industry stand in need of fast access to the facts about oil spills. But, current databases of oil spill characteristics are huge and unwieldy. The Louisiana Oil Spill Coordinator's office wanted to rectify that situation. Thus, the current work is to present a simple, fast, self-contained, free CD database program for desktop computers, that makes accessible to non-technical users, massive amounts of information about actual oil spills. This paper describes the program, its use and its uses. The data are a modified version of those collected by the National Response Center.

TECHNOLOGY SEQUENCING TO REDUCE GROUNDWATER REMEDIATION COST

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Unintentional release of fuels and other organic chemicals has contaminated groundwater and in some cases threatened public health or the environment. The most cost-effective approach to remedial action, required to reduce the threat to acceptable levels, is a site-specific sequence of technologies starting with receptor protection and source control, continuing to free-phase recovery/treatment and to dissolved phase treatment, and ending with monitored natural attenuation. Technology selection and sequence depends on the properties of the Chemicals of Concern (COC), status of the nearest receptors and the groundwater pathway, status of the chemical source(s) and available facilities, utilities, and site space. The cost and efficiency optima of remediation technologies are a function of site conditions and the COC concentrations. A compilation of the cost/benefit decision framework, with emphasis on the level of detail needed to make effective technology sequencing decisions, used in several technology sequencing case studies will be discussed in detail.

DECISION SUPPORT SOFTWARE FOR DESIGNING GROUNDWATER MONITORING PLANS

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Groundwater monitoring at a large number of sites for long time periods represents a tremendous cost liability. Groundwater monitoring plans can be made more effective and efficient by: 1) conducting spatial and temporal data analysis to optimize sampling location and frequency, and 2) visualizing data using automated, updatable data visualization software that is integrated with a data management system. These features have been incorporated into the Monitoring and Remediation Optimization System (MAROS) Version 2.0, a public-domain database management, statistical analysis, and data visualization tool. MAROS 2.0 is designed to help site managers formulate cost-effective, scientifically based long-term groundwater monitoring programs. MAROS can be used for a variety of ground water contaminants (e.g., fuels, solvents, metals) and for continual modification of long-term monitoring plans as the plume or site conditions change over time. A case study at a site contaminated with petroleum hydrocarbons is presented to demonstrate the vigor and applicability.

MONITORING CHANGES IN MICROBIAL ECOLOGY DURING SULFATE AMENDMENT OF A BTEX-CONTAMINATED AQUIFER USING BIO-SEP® TRAPS

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A gasoline-contaminated aquifer in Washington state has been under remediation since 1999 using soil-vapor extraction and catalytic oxidation following a period of free product removal. By late 2002 the highest benzene concentrations in the plume were 0.8-4 mg/L. A field trial is currently underway to enhance natural attenuation of hydrocarbons at the site by amending the aquifer with sulfate, which is introduced into the aquifer using an infiltration trench in 1,000-gal batches.

Prior to initiation of the field trial five groundwater monitoring wells (one upgradient, three plume, and

one fringe) were investigated to predict the effect of the sulfate amendment on subsurface microbial ecology by incubating two types of Bio-Sep® traps in each well. In each well one trap contained non-baited Bio-Sep® beads. The second trap contained both non-baited beads and beads in which Na_2SO_4 had been incorporated during fabrication. The baited beads provided a source of slow-release sulfate in the trap to mimic the effect of sulfate amendment of the aquifer. After 30 days of incubation the trap biofilms were analyzed using phospholipid fatty acid (PLFA) analysis and analysis of PCR-amplified 16S rDNA. Biofilms from the sulfate-baited traps and the non-baited traps were shown to have distinctly different community structures. Sulfate-baited traps were more likely to contain lipid anaerobic biomarkers, biomarkers for sulfate-reducing bacteria, and specifically identified anaerobes like Geobacter sp.

The aquifer is currently being monitored using non-baited Bio-Sep® traps to determine whether the predicted shifts in the subsurface microbial ecology are observed as the sulfate amendment is introduced. Initial results have shown that the aquifer has become aerobic due to the inadvertent addition of oxygen during sulfate injection. Anaerobes are still present in the groundwater. However, since the initiation of sulfate injection they are not being found in the Bio-Sep® beads indicating that they are not actively growing under the current aquifer conditions.

ANALYSIS OF MICROBIAL COMMUNITIES INVOLVED IN THE REMEDIATION OF BTEX IN AN ANAEROBIC AQUIFER USING ^{13}C- LABELED COMPOUNDS, BIO-SEP® BEADS AND IN-SITU MICROCOSMS

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Groundwater at a former hydrogenation plant in Zeitz (Saxonia, Germany) is contaminated with benzene (up to 850mg L^{-1}) and toluene (50mg L^{-1}) significant biodegradation of toluene has been shown at this site by isotope fractionation analysis and evidence for the anaerobic biodegradation of benzene was found within the aquifer. However, clear evidence of biodegradation of benzene by microorganisms was elusive. Under sterile conditions, unique 'Bug Traps' containing Bio-Sep® beads, spiked with ^{13}C-labeled benzene and toluene, were suspended within existing groundwater monitoring wells. The Bio-Sep® beads facilitated enrichment of microorganisms that used the labeled benzene and toluene as a carbon source. Lipid biomarkers and DNA were extracted from the beads after 5 weeks exposure and analyzed with mass spectrometry and molecular biological methods. The isotopic ratio of remaining amounts of ^{13}C-labeled contaminants (20%) showed no alteration, indicating no exchange with aquifer hydrocarbons occurred. Isotopic ratio analysis of microbial fatty acids clearly verified benzene and toluene degradation by transformation into biomass and that 80% of the loaded substrates were degraded. Fatty acids patterns of total lipid extracts and polar lipid fatty acids (PLFAs), and their isotopic composition showed significant differences which can be used to follow the path of the labeled carbon within the developing microbial community. Due to the loading of the traps with i.e. ^{13}C-labeled benzene and toluene, these small-scale, easy-to-access systems are powerful tools for long-term monitoring programs in enhanced and natural attenuation approaches.

PROVING THE VIABILITY OF A LARGE SCALE BIOREMEDY ON AN MTBE-IMPACTED DRINKING-WATER AQUIFER IN SOUTHERN CALIFORNIA

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This paper discusses the first ever deployment of Bio-Traps and analysis of genetic markers to successfully demonstrate the viability of a large scale bio-remedy including treated groundwater re-injection on an MTBE plume in close proximity to municipal supply wells in the northern Los Angeles basin. Bio-Traps are recently developed down-well devices used to collect sample biofilms. DNA from biofilm samples was used for DGGE and Real Time TaqMan PCR analyses. Known MTBE degrader PM-1 was identified among other microorganisms commonly seen at sites where MTBE biodegradation has been documented. The evaluation also included an MPN test and Compound Specific Isotope Analysis, which both resulted in additional evidence of potential MTBE biodegradation.

The results of this study demonstrated the viability of a conceptual remedy that relies on plume hydrodynamic control and biostimulation using re-injection of oxygenated treated groundwater and the controlled circulation of oxygen enriched groundwater. The remedy has received preliminary approval from the Los Angeles Regional Water Quality Control Board (RWQCB) and intended to address the highest MTBE concentrations directly, slow migration, and provide tertiary treatment for low concentrations of MTBE that may remain in the aquifer after highest concentrations have been depleted. The RWQCB agreed that this conceptual remedy is indeed viable and presents a potential benchmark approach to characterization of other MTBE impacted sites in and around California.

OXYGEN RELEASE CHARACTERISTICS OF ORC

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An Oxygen Releasing Compound (ORC) was injected in a clean zone at an aquifer in Texas to understand oxygen release behavior in soils and groundwater. Mass flux estimates of dissolved oxygen indicated that less than 2 percent of the releasable oxygen (10% of its weight) was accounted for during the field experiment. Results from the field study suggest that the aquifer sediments exert a significant oxygen demand. Laboratory column experiments are underway to characterize the ORC behavior in a controlled setting in groundwater aquifers and to quantify the inorganic oxygen demand exerted by the sediments at the site. These experiments mainly focus on the physical-chemical characteristics of oxygen release from ORC. Data from the tracer studies are used to determine the fate and transport of the released oxygen in the column experiments.

Using Fixed-Price Environmental Liability Transfer

10th International Petroleum Conference

November 2003

Agenda

- ✓ Liability Transfer Overview
- ✓ Case Studies
- ✓ Environmental Insurance
- ✓ Implementation

TRC
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Liability Transfer Overview

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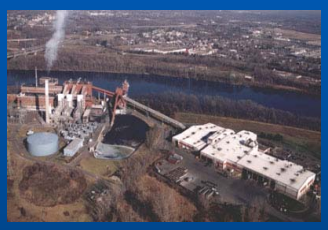
Approach



- ✓ Company Assumes Complete Liability and Responsibility at Fixed Price
  - Contractual
  - Legal
  - Environmental Remedy
- ✓ Financial Assurance and Insurance to Guarantee Performance
- ✓ Flexible Solution, Custom Designed for Each Customer Situation

TRC
Customer-Focused Solutions

Applications

- ✓ Mergers and Acquisitions
- ✓ Divestitures & Restructurings
- ✓ Discontinued Operations
- ✓ Multi-Party / Superfund Settlements
- ✓ Real Estate Transfers
- ✓ Brownfields Redevelopment
- ✓ Equity Offerings and Debt Financing
- ✓ Corporate Donations

TRC Customer-Focused Solutions

Typical Structure

- ✓ TRC, a publicly-traded (NYSE) and experienced cleanup company, becomes the sole responsible party for site remediation and post-closure OM&M for the known environmental liabilities
- ✓ **TRC Companies, Inc.** (**parent company**) provides Client with a contractual indemnity against future liability or costs for environmental remediation
  - **In perpetuity indemnity - NO term or dollar limit**

TRC Customer-Focused Solutions

Typical Structure (continued)

- ✓ TRC executes a consent decree or alternative agreement with the regulatory agencies that obligates TRC to complete work in lieu of Client
- ✓ A++ Insurance Company manages all funds under a finite policy that names Client as an insured, and pays funds out only as cleanup is performed
- ✓ Policy doubles as financial assurance to guarantee contractual performance and meets regulatory financial assurance requirements

TRC Customer-Focused Solutions

Benefits

Allows True "Walk-Away"

- ✓ Removes Environmental Risk Uncertainties
- ✓ Removes Multi-Party Interdependencies
- ✓ Provides Tax and Balance Sheet Benefits
- ✓ Reduces Administrative and Frictional Costs

TRC Customer-Focused Solutions

Exit Strategy Program ®
Case Studies

Mergers and Acquisitions
Discontinued Operations
Redevelopment Projects
Multi-Party Sites

TRC
Customer-Focused Solutions

Exit Strategy Statistics

- ✓ **46 Active Sites**
- ✓ **7 Sites Completed**
  - 25 M&A / Transaction Related
  - 14 Discontinued Operations
  - 10 Redevelopment
  - 4 Multi-Party
- ✓ **$2.3B in Assets**
- ✓ **$3.5B in Planned Development**
- ✓ **$360+ MM Remediation**
- ✓ **$1.1B in Insurance Coverage**

TRC
Customer-Focused Solutions

Energy Project Example

- ✓ $1.4 Billion Acquisition
- ✓ 18 Plants and 350 Ancillary Facilities Located in Six States
- ✓ Buyer and Seller were $100 Million Apart on Cleanup Cost Estimate
- ✓ Seller did not want Cleanup Liability

TRC Customer-Focused Solutions

Energy Project Risks

- ✓ Partial and Undefined Site Conditions
- ✓ Unclear Regulatory Standards
- ✓ Off-site Contamination and Property Damage
- ✓ Potential Impact to On-going Operations
- ✓ Limited Due Diligence Time

TRC Customer-Focused Solutions

Energy Project Solution

- ✓ TRC Assumed Responsibility and Liability for Fixed Price
- ✓ $150 Million Financial Assurance and Insurance Program Portfolio Established to Reduce Costs ($100 Million in Cleanup Protection; $50 Million for Third Party Liability)
- ✓ Buyer and Seller Released from Liability and Responsibility
- ✓ Site Restoration (without Operations Disruption) that Prevents Future Environmental Impacts

TRC Customer-Focused Solutions

Waste Oil Site Example

- ✓ Largest Uncontrolled, Hazardous Waste Site in Maine's "Superfund" Program
- ✓ 10-Acre Waste Oil Disposal Site: Four Oil Lagoons; Sludge Spreading Area; Oil, Solvent, PCB, and Lead Contaminants; Soil & Groundwater Contamination
- ✓ Remediation Stalled Due to Large Number of PRPs (over 2,900)

TRC Customer-Focused Solutions

Waste Oil Site Solution

- ✓ TRC signed Consent Decree as Single Work Defendant
- ✓ TRC Obtained State Release of PRPs from All Future Liability Associated with Remediation, Operation and NRDs
- ✓ TRC Provided Corporate Indemnification to Each Settling PRP; Backed by Insurance Policy
- ✓ TRC Performed Remedial Design, Remediation (now complete) and Long-Term Operation, Monitoring and Maintenance

TRC Customer-Focused Solutions

Waste Oil Site Benefits

- ✓ Allowed the PRPs to settle quickly with no litigation or other transaction or administrative costs
- ✓ Cashed out the PRPs at a cost that was 25% - 33% less than estimated for a traditional approach
- ✓ Achieved a full site cleanup in 19 months (plus O&M), despite remediating 30% more soil than had been estimated
- ✓ Provided the town with an opportunity for beneficial reuse of the property
- ✓ Prohibited any recalcitrant PRP from getting a better deal, consistent with EPA/State policy

TRC Customer-Focused Solutions

Pipeline Maintenance Facility Project

- ✓ Historic Use of Chlorinated Solvents Impacted Underlying Drinking Water Aquifer
- ✓ Former Owner Retained Significant Portion of Liability
- ✓ Former Owner was Being Acquired and Needed Risk Management Solution for Cleanup Liability - Purchaser Did NOT Want Liability ($1.8 Billion Transaction)
- ✓ Current Owner Wanted Solution to Mitigate Its Minority Interests In Cleanup Liability

TRC Customer-Focused Solutions

Pipeline Maintenance Facility Project Risks

- ✓ Potential Impact to Nearby City Water Supply Wells
- ✓ Remedy Selection / Implementation for Cleanup of Deep Groundwater Zone

TRC Customer-Focused Solutions

Pipeline Maintenance Facility Project Solution

- ✓ TRC Assumed Site Environmental Liability In Perpetuity for Fixed Price
- ✓ TRC Executed a Voluntary Agreement with the State for the Site Cleanup
- ✓ $20 MM Cleanup Cost Insurance Protection (30 Year Term)
- ✓ $30 MM Pollution Legal Liability Insurance (3rd Party Property Injury and Bodily Injury – 10 Year Term)

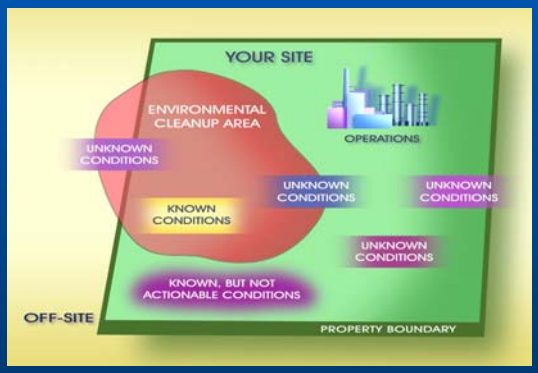
TRC Customer-Focused Solutions

Environmental Insurance Overview

TRC Customer-Focused Solutions

Combined CCC + PLL Insurance

- ✓ **All Risk Protection**
  - Provides Premium Savings When Compared to Purchase of Separate Coverages
- ✓ **Coverage**
  - First Party
- ✓ **Claims Approach**
  - Finite
  - Cost Cap + PLL



TRC Customer-Focused Solutions

How Finite Works

- ✓ Funds Equal to Net Present Value of Estimated Project Cost are Deposited into Policy
- ✓ Funds are Placed in Notional Commutation Account and Accrue Interest
- ✓ Project Costs are Drawn Down from Policy as Progress is Completed

TRC Customer-Focused Solutions

Approach Comparison

Pay As You Go

ADVANTAGES

- Less Up-Front Funding
- Provides Remediation Overrun Coverage for Smaller Projects

DRAWBACKS

- Each Claim can be Disputed
- Additional Financial Assurance Mechanism Required

Finite

ADVANTAGES

- Claim Disputes Minimized or Eliminated
- Provides Financial Assurance with Policy
  - Bond-Like Protection
- Environmental Liabilities Removed from Balance Sheet
- Accelerated Tax Deductions can be Captured
- Longer Term (Extending >30 Yrs)
- Insurer Provides Oversight

DRAWBACKS

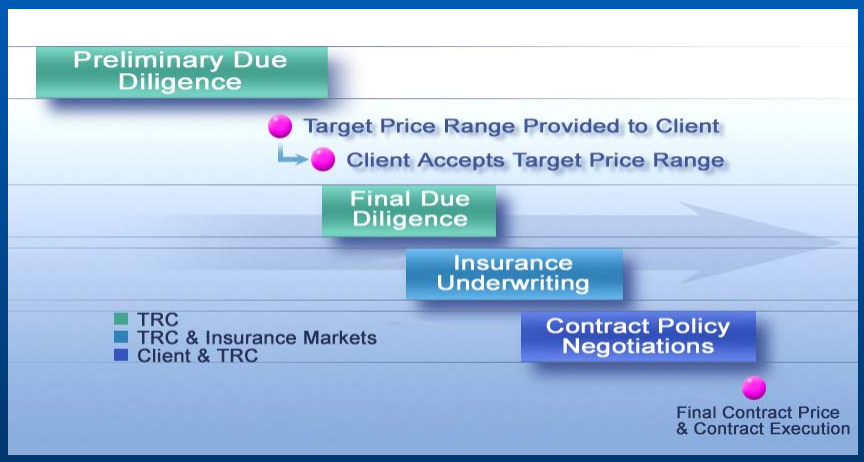
- Up-Front Funding Required

TRC Customer-Focused Solutions

Implementation

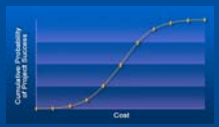
TRC Customer-Focused Solutions

Exit Strategy® Process



Due Diligence Goal

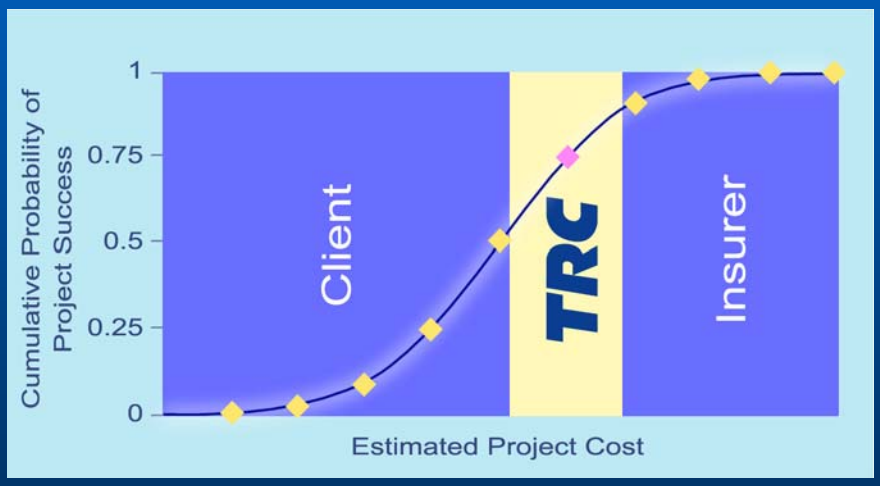
Evaluate an Uncertain Future to Achieve an Acceptable Balance Between Assumption of Risk & Full Liability Transfer at Minimum Cost



Primary Uncertainty Sources

- ✓ Remedy Selection - *Deterministic Outcomes Multiple Potential Alternatives - Decision Tree Analysis*
- ✓ Remedy Implementation - *Multiple Potential Outcomes for Deterministic Alternative - Monte Carlo Analysis*
- ✓ Aggregating Sites Moderates Uncertainty Impacts - *Portfolio Approach*

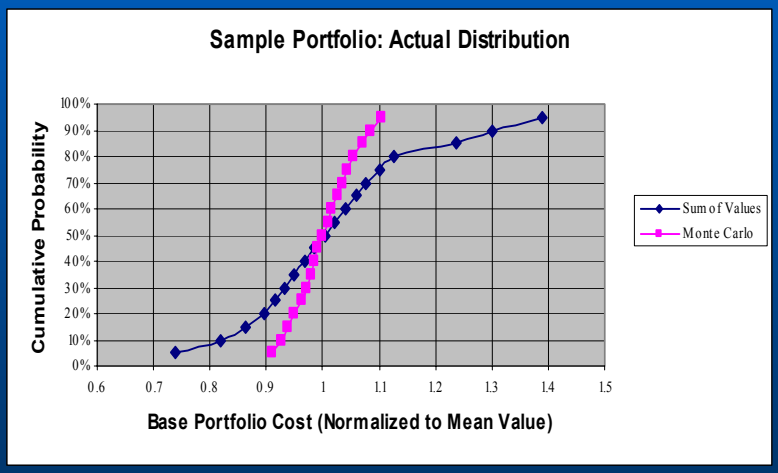
Balance of Expectations



Portfolio Approach

- ✓ Impacts of Uncertainties Are Moderated by Aggregating Sites
- ✓ Risk Is Shared Across Sites: Cost Increases or Surprises at One Site Balanced by Success or Cost Decreases at Another Site
- ✓ Requires Single Contract and Insurance Policy for Portfolio
- ✓ May Reduce Insurance Attachment Point and Lowers Insurance Pricing by Tightening Cumulative Probability vs. Cost Curve

Portfolio Analysis



Summary

- ✓ Establishes firm fixed cost to a highly variable liability in perpetuity *(cost cap and cashflow certainty)*
- ✓ Liquidates known and contingent environmental liabilities – eliminates from balance sheet
- ✓ Simplifies sales transaction by removing environmental remediation issue now and forever, which also avoids future disputes often associated with traditional contract indemnification and risk transfer provisions
- ✓ Potentially allows for acceleration of tax deduction of future costs
- ✓ Relieves burden of managing the cleanup, thereby reducing operational and administrative costs
- ✓ Minimizes or eliminates claims disputes
- ✓ Facilitates agreement on level of environmental risk
- ✓ Functions like a performance bond
- ✓ Provides for oversight by insurer

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TRC
Customer-Focused Solutions

OVERFILING - A CLOSER LOOK AT THE FEDERAL ENFORCEMENT TOOL

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Overfiling occurs with the initiation of a federal enforcement action, either administrative or civil, following state enforcement relative to violations that arise out of the same set of operative facts. This is the case when, after a state has settled with a polluter, the U.S. Environmental Protection Agency (EPA) finds the settlement inadequate and files a case against the same polluter based on the violation just settled between the state agency and the polluter. The debate over the EPA's authority to overfile falls into two interconnected rubrics - permissibility under the applicable statutory regime and preclusion under the res judicata principle (i.e., a valid and final judgment on a claim bars a second action on that claim or any part of it). This presentation discusses overfiling in light of recent litigation in two Circuit Courts of Appeal. In addition, case studies of two important cooperative federalism programs are conducted. Overfiling is examined from the perspective of the federal regulators, the primacy states, the regulated community, and other interested parties.

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ESTABLISHING APPROPRIATE NUMERICAL WATER QUALITY CRITERIA FOR SALINITY MINERALS IN WATERSHEDS IN OKLAHOMA

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Oklahoma state water quality standards (OAC 785:45-5-13(e)) forbid allowing increased mineral levels that restrict ANY beneficial use. However, current state numerical salinity standards (OAC 785:45-5-13 Appendix F) were set only for total dissolved solids (TDS), chlorides, and sulfate, and only apply for the agricultural beneficial use. These standards were set for large basin segments containing many watersheds based on historic average concentrations found in major Oklahoma streams and rivers in sampling done during the 1980s, not on either actual levels found in streams arising within specific watersheds or on (beneficial) use attainability analysis (UAA) as per 40 CFR 131.10.

In many watersheds the standards were set based on rivers (e.g. the Salt Fork of the Arkansas, the Cimarron) that have naturally high salt concentrations, and not on the much fresher waters arising in local watersheds that flow into these rivers. Because of this, a stream can be salt polluted well above its background level from brine spills or CAFO (confined animal feeding operation) sources, yet still meet state salinity standards. Conversely, a stream could have purely natural high TDS and sulfate levels from flowing over gypsum deposits, yet violate state salinity standards based on standards set from lower TDS rivers (e.g. the Canadian) that it flows into.

To begin to resolve these standards problems, and to include other potentially harmful minerals such as sodium often dissolved in surface waters, the Oklahoma Corporation Commission, in partnership with the Oklahoma Conservation Commission, has undertaken a project to sample streams that arise in 20 historic oil producing watersheds in order to set watershed-specific numeric minerals criteria. We sampled streams for a suite of anions and cations including sodium, potassium, magnesium, calcium, chlorides, sulfate, bicarbonate, boron, and nitrate, plus evaluating the pH.

NORTH SLOPE OF ALASKA UNDERGROUND INJECTION CONTROL OPERATIONS

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The State of Alaska Oil and Gas Conservation Commission (AOGCC) has primacy for the underground injection control program wells designated as Class II. The Environmental Protection Agency maintains primacy for all other classes. This paper is designed to provide an overview of the UIC efforts in Alaska's North Slope oil and gas fields and discuss the unique aspects of Alaska and how they impact the UIC efforts.

Inherent to the discussions will be the relationship of the indigenous population to oil and gas-related UIC activities, the geologic setting and distribution of aquifers, engineering, permitting and inspection considerations for injection wells, and some representative performance data for injection wells involved in both waste disposal as well as enhanced oil recovery. The role of nonhazardous UIC Class I wells on the North Slope will also be discussed.

The intent of this paper is to demonstrate the high degree of safety, environmental protection, and wide range of injection operations afforded through the UIC program as implemented by the AOGCC.

BEST MANAGEMENT PRACTICES (BMPS) A NEW WAY OF MANAGING OIL AND GAS DEVELOPMENT ON THE PUBLIC LANDS

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As environmental awareness increases and oil and gas development on the public lands comes under increased public review, the Bureau of Land Management (BLM) has led the way in developing "Best Management Practices" to minimize environmental impacts. Federal law directs the BLM to manage and develop public oil and gas resources under the principles of multiple use and sustained yield. Increased resource use (including oil and gas development, recreation, etc.) has resulted in increased resource conflicts with new or potential listings of endangered species, wildlife habitat needs, and sensitive areas. To mitigate these conflicts and ensure the continued development of oil and gas resources, BLM has combined best technologies with the most effective environmental requirements to create a tool kit of best management practices. Where needed, these practices limit the total amount of surface disturbance, reduce the visual appearance of the development, employ improved reclamation techniques, and restore the landform. Applications of these practices are shown in examples from several States in the western United States, including coal bed natural gas developments.

OIL AND GAS ROYALTIES APPLICATIONS AND LIFE QUALITY IN THE COMMUNITIES OF THE MAIN PRODUCTION ZONE: CASES OF RIO DE JANEIRO AND ESPIRITO SANTO - BRAZIL

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This paper discusses two subjects related to the oil and gas industry's royalties in Brazil: the legal instruments of fiscalization and the social responsibility of the local governments on the performance of the indicators of life quality in the communities which take part of the main production zone of Rio de Janeiro and Espírito Santo. It concludes that there is no evidence that the use of royalties has improved the life quality in these communities; and finally that the legal instruments don't make possible an effective fiscalization.

TOPOGRAPHIC MAPPING USING GPS RECEIVERS AND GIS SOFTWARE AT THE OSAGE-SKIATOOK PETROLEUM ENVIRONMENTAL RESEARCH SITES IN OKLAHOMA

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Survey-grade Global Positioning System (GPS) receivers were used at the two Osage-Skiatook petroleum environmental research sites to obtain data for detailed topographic mapping. A real-time kinematic GPS method was used because it is stable, fast, and accurate (±1 centimeter horizontal, ±2 centimeters vertical).

The GPS antenna was mounted on a modified 2-meter measuring wheel because of its high mobility and to maintain a constant instrument height above the ground. The GPS receiver recorded data points every 1.5 meters along traverses of the sites. The traverses were initially spaced evenly across the sites. Traverses were then added where ground features, such as rapid slope changes, needed to be mapped. Approximately 8,600 data points were logged in 30 hours.

The data points were incorporated in a digital elevation model (DEM) using the ARC/INFO® GIS software. The software uses an interpolation method specifically designed for the creation of DEMs for comparatively small areas that have well defined elevation. The software assumes a surface drainage system model on the area. The software uses an iterative finite difference interpolation technique that has been modified to allow the fitted DEM to follow abrupt changes in terrain. This model of an assumed drainage condition produces more accurate surfaces with less input data. The program acts conservatively in removing closed low areas and will not impose the model of an assumed drainage in locations that would contradict the input elevation data.

The DEM grid-cell elevations were compared to known ground-level data across the sites for quality assurance and quality control. Sixty-nine grid cells were near control points. The mean difference between the grid cells and the control points was -2.4 centimeters and the interquartile range was -6.4 to +1.1 centimeters.

The DEMs were computed with a cell size of 0.6 meter. A smaller cell size did not illustrate closed depressions in the smaller pits at the B-site. The DEMs were used to produce topographic contour maps of the sites with a contour interval of 10 centimeters. These topographic maps will be used in contaminant-flow and sediment-erosion modeling at the research sites.

Operator Cleanup Program

- Approximately 500 complex operator cleanup sites managed by Site Remediation in Austin.
- Routine cleanups and emergency response managed by District Offices.
- Over 1,200 reportable releases and 1,000 complaints in 2003.

Voluntary Cleanup Program

- Provides incentive to lenders, developers, owners, and operators who did not cause or contribute contamination to cleanup up brownfields.
- Applies to waste cleanups under Railroad Commission jurisdiction.
- Provides a release of liability to the state
- A mechanism that allows for true market value of a property.

Voluntary Cleanup Program Structure

- Application w/ $1000 fee (retainer) – determine eligibility
- Execute VCP agreement that sets cleanup standards, cleanup schedule
- Conduct investigation and remediate site
- Certificate of Completion issued to property after cleanup is completed.

Brownfields Initiatives (Federal)

- Brownfields is general term used nationally to describe property whose redevelopment potential has been impaired due to real or perceived liability associated contamination.
- Traditionally liability tied to CERCLA contamination (non E&P sites)
- Regardless of legal separation, EPA recognizes need to extend federal Brownfields Initiatives to E&P sites

RRC Brownfields Response Program

Federal Legislation known as *Small Business Liability Relief and Brownfields Revitalization Act*, H.R. 2869, 2002

- Clarifies liability protections
- Offers funding tools to states, tribes, non-profits, local governments, and, in some cases, private sector

Terms and Conditions for EPA-RRC Cooperative Agreement

Petroleum only brownfields sites must meet the following:

(1) site is of relatively low risk

(2) there is no viable responsible party for the site; and

(3) the site will not be assessed, investigated, or cleaned up by a person that is potentially liable for cleaning up the site.

RRC Brownfields Response Program

- 2003-RRC received approval from EPA to offer Phase I & II ESAs at brownfields where support for redevelopment from the local community exists.

- RRC looking for partners for cleanups of former abandoned oil field sites. Please contact us if you are interested in the program.

What is a Risk Assessment Anyway?

RRC Cleanup Standards

- In general cleanups options fall into the following:
  - Cleanup to background
  - Rule 91 cleanup (limited applications)
  - Risk-Based Cleanup
    - **Assuming residential land usage, or**
    - **Assuming commercial land usage**
- Combinations of the above possible

Phase I Site Assessment

- Recognized O&G Environmental Conditions

Historical well Blowout.

Oil and Gas Phase I Assessment

- Aerial photographic review: look for lease roads, well heads, tank batteries and pits.
- Oil and gas well location maps available from RRC… http://www.rrc.state.tx.us/divisions/og/maps/mapinfo.html.
- Guidance on locating oil and gas wells available on RRC VCP web page.
- Pipeline locations available from the Pipeline Safety Division.
- Guidance on Phase I site assessments will be available in the near future.

Primary Production Facilities

Unplugged Oil and Gas Wells

Petroleum and Saltwater Storage Tanks

Pipelines and flowlines

Drilling Mud Pits

Historic Saltwater Storage Pits

Mercury meters

Transportation Pipelines

- In addition to pipelines consist of associated facilities such as meter stations and compressor stations used to maintain pipeline pressure.

Glycol Dehydrator at a Compressor Station possible Source of BTEX in soil

RRC Rules of Interest

www.rrc.state.tx.us/tac/16ch3.html

- § 3.8 Water Protection Rule
- § 3.14 Plugging Rule
- § 3.30 MOU Between RRC & TNRCC
- § 3.91 Cleanup of Soil Contaminated by a Crude Oil Spill
- § 3.94 Disposal of NORM Waste
- § 3.98 Standards for Management of Hazardous Oil & Gas Waste
- § 4.4 Voluntary Cleanup Program

Contact Us

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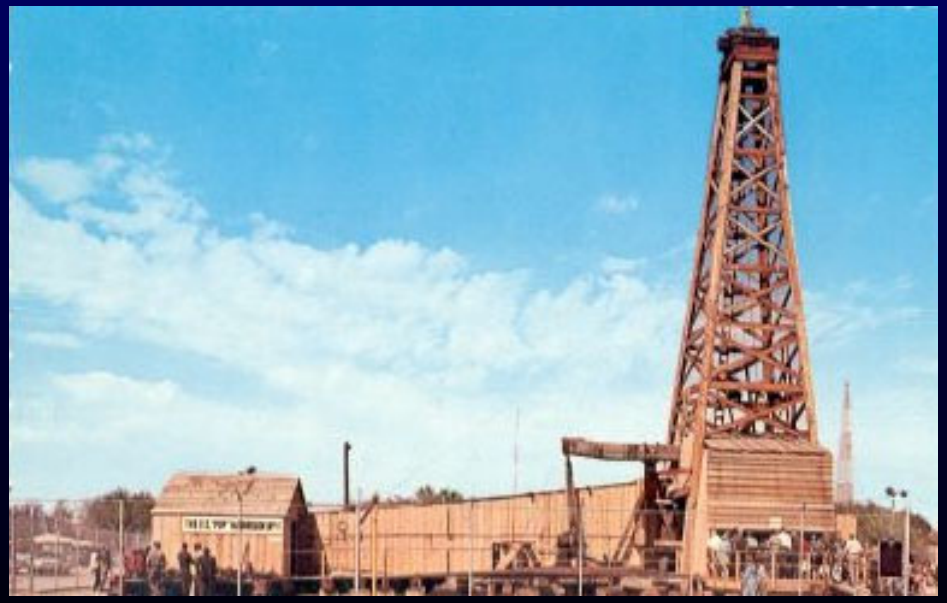
Links to Site Remediation Information

http://www.rrc.state.tx.us/divisions/og/environmental_protect.html



REMEDIATION OF BRINE SPILLS WITH HAY, YEAR 2

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The field demonstration of the IPEC project "Remediation of Brine Spills with Hay" has been running for two full years and a third summer. In the first year of this project, we set up a field demonstration to treat two produced fluids spill sites and a control site with four different soil amendments to determine the effectiveness of hay as a soil amendment for brine spills. Our four soil treatments are tilling, tilling with hay, tilling with fertilizer, and tilling with hay and fertilizer. Eight microcosms were built to treat contaminated soil with the same soil amendments and provide controlled watering and aeration. The microcosms were operated for only the first year. The field sites and microcosms were sampled regularly during the first year to track changes in concentrations of brine components, soil properties, and microbial populations to determine the mechanism(s) by which remediation occurs. First year results indicate that the first proposed mechanism is probably active: the hay provided physical openings in the soil and increased the hydraulic conductivity. The second proposed mechanism, increased cation exchange capacity from decay products of organic matter, does not appear to be active. Neither is the third proposed mechanism, increased wet aggregate stability from compounds formed during the decay of the hay. Microorganisms in sites and microcosms with hay were different from those without hay. Salt components decreased more in microcosms with hay than those without. Over the first year, salt components decreased most in the field sites with tilling and fertilizer, interestingly. Sampling was suspended in the field sites for the second year and started again in the third summer. The field sites were watered during the third summer to supplement natural rainfall (and correspondingly the remediation rate). Results to date for soil salt concentrations, soil properties, and microbial populations will be presented.

TALLGRASS PRAIRIE PRESERVE: RECENT SUCCESSES IN RESTORING AN HISTORIC BRINE SCAR

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The Tallgrass Prairie Preserve is a site where oil production and conservation exist side by side. However, the Preserve, which is owned by the Nature Conservancy, has several sites that have been impacted by oil production. One of these sites is a brine spill that appears to date back to the 1930s. BP chose this site to begin investigation of improved methods for remediating brine-impacted soil. BP did initial restoration work on this site in 2000 as part of a technology demonstration project. The technology demonstration looked at five different approaches to remediating the site: phytoremediation, mycorrhizal fungi, gypsum, and proprietary chemical amendments. The site is now showing definite improvement after being barren for nearly 70 years. This presentation will discuss the remediation approaches and which seem to have the greatest impact. The important findings so far have been the difficulty of getting seed to germinate but the ability of transplants of seedlings to survive and grow in the saline and sodic soil and the need for organic material to restore soil structure.

OIL AND SALTWATER RELEASES FROM E&P OPERATIONS IN OKLAHOMA, 1993-2002

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Since 1993 the Oklahoma Corporation Commission has maintained a complaint database of reported spills of oil and brine in Oklahoma. By 2003 this database contained over 15,000 records. Included in many of these records are the source and cause of the spill, an estimate of the volume of fluid spilled, and the impact of the spill. These records indicate that very large amounts of oil and saltwater are released each year. For example, from 1993-2002 a volume of saltwater was reported released in Oklahoma that is equivalent to four Exxon-Valdez-size spills. These spills released 28,000 tons of salt into the environment. The most common cause of spills of all types was corrosion of tanks and pipelines or in other words, aging infrastructure.

SYMBIOTIC FUNGI AND PLANT PERFORMANCE IN OIL BRINE CONTAMINATED SOIL

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The vast majority of land plants form symbiotic relationships with soil fungi. These fungi are an extension of the plant's root system, granting access to water and nutrients otherwise not available to the plant host. To better understand roles these fungi play in the revegetation of oil brine contaminated soils, a greenhouse experiment was established. Soils from naturally regenerating spill sites was collected and trap cultures were established to produce inoculum. Rye and Bermuda grass were inoculated and then grown in ebb and flow system with oil brine diluted to 16dS/m. Inoculation improved total biomass compared to control in the majority of treatments. Vaminoc G (a commercial AM fungal inoculant) and inoculum produced from soil samples from Ranger, Texas improved rye biomass significantly compared to controls. These data support the hypothesis that introducing symbiotic soil fungi to brine contaminated soils can improve plant performance.

MOLECULAR METHODS TO DESCRIBE RHIZOSPHERE FUNGAL COMMUNITIES FROM OIL BRINE CONTAMINATED SOILS

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Restoration of oil brine spill sites commonly involves re-vegetation. It has been shown that arbuscular mycorrhizal fungi can alleviate some of the stresses that plants may experience in an oil/brine situation. The aim of this project is to determine species and strains of AM fungi that improve plant performance in oil/brine contaminated soils. Tolerant plants were inoculated with rhizosphere fungi and grown under controlled conditions, after which, fungal DNA was extracted from the rhizosphere and amplified via PCR using fungal specific primers. The use of clone libraries and Temporal Temperature Gradient Gel Electrophoresis methods allowed for differentiation between species and strains. These methods for identification of beneficial fungal species will hopefully lead to a more complete understanding of the role of these organisms in the regeneration of oil brine contaminated sites.

HALOPHYTE TECHNOLOGY MITIGATES LANDOWNER-DRIVEN OILFIELD SALTWATER AND PETROLEUM HYDROCARBON SURFACE IMPACT LITIGATION

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Decades of historic standard-practice oilfield saltwater and petroleum hydrocarbon surface releases in Smackover oilfield (Arkansas) resulted in substantial loss of vegetation, soil erosion/re-deposition, and receiver stream impairment. Currently practiced state of the art reinjection of saltwater, improved retention of petroleum hydrocarbons, and remediation of the land surface, near-surface groundwater, and stormwater runoff using natural rainfall, natural revegetation, and halophyte remediation technology are facilitating low-cost restoration of impacted areas to native pine forest vegetation in this maturing oilfield. This presentation focuses on a recent case study which demonstrates the potential that implementation of halophyte (salt loving plants) technology has in resolving landowner property damage claims.

RESTORATION OF PRODUCED WATER RELEASE TO EAST TEXAS FOREST LAND

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A 2,000 barrel brine release in April 1999 resulted in damage to approximately five acres of forest and undergrowth at a site near Tatum, Texas. In June 1999, the surface soil was treated with chemicals to displace the sodium in soil with calcium. In order to accelerate subsurface soil remediation, chemicals were introduced through percolation ponds located adjacent to the release areas. A temporary French drain installed downgradient was used to capture the subsurface flow. In 2000, dead trees were cut to mitigate a potential overhead hazard and were used for erosion control. Rows of hay bales were placed across damaged areas to slow erosion and provide stable islands for re-growth. The impacted surface soil was retreated with a sodium replacement chemical. Re-vegetation of the impacted areas initially consisted of small clumps of growth (grasses and weeds) around hay bales and at the edges of the damaged areas. The areas of re-growth slowly expanded and pine seedlings were noted. Three years after the release, the site contained poorly vegetated areas surrounded by re-growth and the pine seedlings were approximately two feet tall. Currently, the site is 90 to 95 percent vegetated, and the pine seedlings are about 6 feet tall.

Chemical and radiological analyses of Mississippi hydrocarbon production brines, scales, and sludges

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ABSTRACT

Approximately 300 brine samples collected throughout Mississippi were analyzed for radium-226 and radium-228. TDS, pH, and chloride content were also measured for each sample. The majority of brine samples were found to have radium activities greater than 100 pCi/L, while 99% of these samples were also found to have chloride concentrations in excess of 20 g/L. While a strong correlation has been reported between radium-226 and radium-228 by other researchers, we found only a moderate correlation ($r = 0.74$). Mean concentrations of Cl^-, Ba^{+2}, and SO_4^{-2} vary significantly from one geologic formation to another, while radium-226 appears to show significant variation within each formation compared to variations between formations. Radioactive scales and sludges alone were found to be highly resistant to leaching of radioactive material. However, incubation of these materials with moist top soil greatly increased the solubility and leaching of radioactive material, primarily due to soil microorganisms.

Association of Naturally Occurring Radioactive Materials With Mississippi Hydrocarbon Production: A Project Overview

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ABSTRACT

Naturally occurring radioactive materials (NORM) has been documented from hydrocarbon production in Mississippi. The lack of compositional data regarding NORM concentrations in produced fluids, scales and sludges provided the stimulus to acquire such information in order to aid the hydrocarbon industry and governmental agencies. These scientifically-defensible data are now being utilized to construct elements of best practice and test NORM predictive models. The data base consists of a total of 329 samples, with 275 brine samples from 37 reservoirs and representing all major producing areas in Mississippi. The remaining samples represent samples of scale, soil, sludge, salt, and biological samples. This data base is perhaps the most extensive in the Southeastern U.S. that is available for public use.

NORM Scale Formation, Control, And Relation To Gas Hydrate Control

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ABSTRACT

Some oil field scales have the potential to contain regulated levels of naturally occurring radioactive materials (NORM). It is estimated that between 300,000 and 1,000,000 tons of NORM scale are produced each year. The most common NORM containing scale is $BaSO_4$, or barite. Research at the Brine Chemistry Consortium have studied the causes of barite scale formation and control techniques. Recent research have shown that NORM scale formation can be adversely affected by the presence of gas hydrate inhibitors, e.g., methanol or glycols. Chemical threshold scale inhibitors have proven to be most efficient to inhibit barite scale formation in production systems. A semi-empirical mathematical model has been developed to predict inhibitor efficiency for barium sulfate scale control in industrial processes. This model can be used for selecting effective inhibitors and determining the minimal effective concentration needed for a given system. The model prediction for barium sulfate scale control was in good agreement with laboratory observations and field experience.

Water Clarifier Improves Throughput, Oil Quality, and Overboard Water All

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ABSTRACT

In order to maintain produced water discharge quality while running far above its intended water handling capacity, a platform had been forced to permanently divert water through the test separator and put over 50% BS&W to the pipeline. Several efforts to use demulsifiers to drop more water from the oil failed. Increasing the water removed from the pipeline crude resulted in excessive oil being carried into the water discharged overboard. An investigation into the root cause of the problem found that the capacity limitation was due to an oil-in-water (reverse) emulsion in the primary production separator. Feeding an appropriate water clarifier to the production separator increased the water handling capacity by 80%. This dramatically reduced the BS&W to the pipeline and allowed reinstatement of the test separator to its intended purpose while maintaining consistent overboard water compliance.

TREATING PETROLEUM CONTAMINATED SOIL AND SLUDGES USING PLASMA

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Abstract

Traditional processes, such as incineration, cement kiln processing, centrifuging and others, used for treating soil contaminated with petroleum, oil, diesel, etc and or for treating oily sludges (generated from the exploration, production and refining of petroleum), present several environmental, technical and economical restrictions. A new process, based on the use of a plasma system, was developed for treating those materials, including petroleum contaminated soil and oily sludges. The process is based on the use of a plasma system, to transfer energy to the material being treated. The contaminated material is heated in a controlled ambient, without the presence of oxygen, up to 1,200 ^{0}C, using a plasma torch operating at temperatures around 15,000^{0}C. The organic compounds volatilize under those conditions and leave the reactor; the vapors are cooled in condensers, recovering the organic compounds in the form of a light oil. The oil can be readily reused. The soil after the treatment presents less than 0.01% in weight of hydrocarbons (legal limit for discarding it is 1%); similar results were obtained when treating sludges containing up to 90 % hydrocarbons. Nil or almost nil off gases are generated in process. A demonstration unit was built (200 kg/h capacity) and industrial units are being designed and constructed for treating up to 5,000 kg/h of those materials.

I. Introduction

Soils contaminated with petroleum or different types of oils, caused normally by accidental spills or during normal maintenance of oil transportation pipes, are commonly found materials, specially in areas located inside or close to petrochemical or refinery plants. It is common to find soil contaminated with more than 25 % in weight of petroleum or oil. The spilled petroleum or oils may cause serious treat to the environment, endangering different vegetal and animal species, including human beings. In the same category, it can be included soils, sludges and similar materials contaminated with other organic compounds, such as pesticides and insecticides. In this case the amount of contamination could vary from tens of ppm (parts per million) to few percents. In all contamination cases mentioned above there is a considerable risk to the environment if the toxic or hazardous organic compounds are not removed from the soil or sludge and then properly treated.

There are several possible manners to treat contaminated soils containing organic compounds. The most commonly used processes include incineration, the use of centrifuges and bioremediation. However, those processes present considerable drawbacks as shown below.

a) Incineration

In the incineration process, the contaminated soil is normally fed into a rotating furnace that contains proper lining. Gas or oil burners are used to maintain the temperature inside the furnace in the range of 500 to 1,000 ^{0}C; air is allowed inside the furnace. The combination of the oxygen from the air and the temperature inside the furnace result in the partial or complete combustion of the contaminating organic compounds. The result of the process is material that in principle would be free of organic toxic or hazardous compounds. The process is conducted in dedicated incineration units or in cement kilns.

The problems associated with the incineration process are the following:

i) Large volume of effluent gases that need to be properly treated (the effluent gases are the summation of entrained air for the process, the gases resulted from the combustion of the organic toxic compounds, the gases from the burners and water vapor), since the gases can contain toxic compounds; although dedicated incineration units present off gases cleaning systems, the same is not the case of cement kilns (normally only a removal of entrained particulate material is conducted), which increases the problem.

ii) Poor energy efficiency, since a great deal of the energy resulted from the oil/gas burners leave the furnace with the off gases, with typical energy efficiencies of less than 30 % for the overall process;

iii) No recovery of the initial organic materials is possible, since the organic compounds are burnt in the furnace; in the case of oil or petroleum contaminated soil, for instance, it could represent a significant loss of raw materials;

iv) Large costs and environmental risks associated with the transportation of the material to dedicated incineration plants (the contaminated soil needs to be properly placed inside drums or other vessels in order to be carried to the incineration site);

b) Centrifuges

The use of centrifuges to treat contaminated soil or sludges is also a common practice. In this process the contaminated material, containing variable amounts of organic toxic or hazardous compounds and eventually water, is fed into a centrifuge. In the centrifuge vessel, due to centrifuge forces resulted from the rotation at high speeds, the liquid organic compounds contaminating the soil or sludges and eventual water are separated from the solid materials, using different types of screens. The result of the process would be in principle material (soil or sludge) free of liquid organic

contaminants and water, making it possible the recovery of such organic liquids in a separate vessel.

The main problems associated with that process are:

i) The impossibility of complete removal of the organic compounds; the soil or sludge after the treatment with centrifuges still contains typically more than 5 % in weight of organic contaminants (the legal limit for discarding hydrocarbon containing material is less than 1 %);
ii) Constant maintenance of the centrifuges required;
iii) Chemical agents need to be added to the charge regularly in order to improve the separation of the oil and the other components; this increase the costs of the process and the treatment of the recovered materials.

c) Steam extraction

The extraction of organic compounds from contaminated soil using steam consists in injecting saturated steam directly in the soil, resulting in a localized heating of the same, volatilizing, oxidizing and dissolving the organic compounds.

That process presents some problems:

i) Low removal efficiency, resulting in longer treatment periods;
ii) The off gases from the soil need, in principle, to be cleaned, since they may contain some organic compounds; the cleaning of the gases presents a difficult task.
iii) Some organic compounds will not be volatilized or oxidized by steam, remaining in the contaminated area.

d) Bioremediation

There are several variations of the bioremediation process, but all of them consist in the consumption of the organic compounds, present in the contaminated soil, by microorganisms or bacteria, resulting carbon dioxide and water vapor from the process.

Bioremediation presents some restrictions:

i) Can be used in cases where the contamination of the soil is not above 1 %;
ii) The soil can not present harmful compounds to the microorganisms (such as heavy metals);

iii) Normally only few types of organic compounds can be consumed by the microorganisms; in the cases of several organic compounds exist, some of them will not be eliminated by the process.

As shown above, all the existing processes for treating contaminated soil present technical and/or economical and/or environmental restrictions. A new process for treating contaminated soil (soil contaminated with petroleum, oil, gasoline, diesel, benzene, toluene, organo-chlorinated compounds, mercury, etc) or petroleum sludges was developed; the process uses a plasma system in a clean and efficient manner as shown below. The process was developed in a joint collaboration between TSL Environmental Corporation and the Technological Research Institute of São Paulo.

II. PLASMA PROCESS

A brief description of plasma is given below, followed by a description of the plasma process developed for treating contaminated soil and similar materials.

a) Thermal Plasmas

Thermal plasmas have been applied increasingly to industrial processes, in different areas. Thermal plasmas can be understood as an ionized gas, at high temperatures (above 10,000 ^{0}C) when compared to temperatures normally found in combustion or using electrical resistance heating. Thermal plasmas are produced using an electric arc, that strikes between two (metallic) electrodes, inside an equipment called plasma torch. When a common gas, such as air, argon, nitrogen, steam and many others, are injected into the plasma torch, the molecules / atoms of the gases collided with the electrons present in the electric arc (the electrons are being produced in one electrode, accelerated and collected in the other electrode). The result of that process is the heating and ionization of the gas, producing a (thermal) plasma jet, that reaches very high temperatures as mentioned above. .

Thermal plasmas have been used for:

i) Environmental applications, such as for the treatment of industrial residues (1), treatment of hospital wastes (2), vitrification of incineration ashes (3), treatment of radioactive materials (4), recovery of aluminum from drosses (5) and others;

ii) Metallurgy applications, such as for tundish heating for continuous casting (6), ferroalloys production (7), blast furnaces (8) and others;

iii) Materials applications, such as the production of titanium oxide (9), zirconia (10) and several nitrites and carbides (11).

A thermal plasma process was developed for the treatment of contaminated soil and similar materials. The plasma process utilizes a plasma torch, operating at

approximately 15,000 ^{0}C, for volatilizing the organic compounds present in the contaminated soil, in a controlled ambient; the volatilized organic compounds are recovered in the form of an oil, and can be readily reused. The process presents several advantages when compared to conventional technologies, as described below.

b) Process Description

The developed plasma process can be understood as a controlled volatilization of the organic compounds initially present in the contaminated soil, in an ambient that does not contain oxygen. The energy for the process is provide by a plasma torch; a plasma gas, such as argon or nitrogen (not containing oxygen), is used in the torch. The organic vapors that leave the plasma reactor, with the plasma gas, passes through a series of condensers; the vapors after cooling, are recovered in the form of a light oil (diesel type) that is 100 % reusable. The plasma gas can be recycled in the process.

The normal operating temperatures of the proposed plasma process is from 800 to 1,200 ^{0}C, in order to volatilize all the hydrocarbons contained in the treated material. The contaminated soil or sludge is continuously fed into the reactor from one end, while the oil free soil is removed from the other end of the reactor. The contaminated material, as it travel through the reactor, becomes increasingly free of organic contaminants; and it is clean once it has reached the outlet chute for removal from the reactor. The atmosphere inside the plasma reactor is maintained neutral or reducing in order to prevent the oxidation of the hydrocarbons and to permit their recovery after volatilizing them inside the reactor and condensing the hydrocarbons outside the plasma reactor.

The developed process presents several interesting characteristics and advantages when compared to conventional technologies, such as:

i) Higher energy efficiency, since the plasma jet is at much higher temperature than, for instance, the flame produced by oil or gas burners employed in incineration (typically 15,000 ^{0} C for the plasma jet and 2,000 ^{0} C for the oil or gas flame), so that the heat transfer, dependent on the temperatures of the energy source and the heated substance, is significantly higher in the plasma process, increasing substantially the energy efficiency of the plasma process. A typical energy efficiency above 80 %, is achieved with the plasma process as compared to around 20 % for the normal gas or oil burners);

ii) Possibility of recovering the organic compounds that were initially contaminating the soil, which can be a significant asset for the process specially when the soil or sludge contains more than 10 % in weight of hydrocarbons;

iii) Nil or almost nil off gases are produced in the process, since the plasma torch can operate with small amounts of gases (and the plasma gases can be recycled in the process) and the volatilized organic compounds are condensed and recovered.

iv) Soil after the plasma treatment contains less than 0.01 % in weight of hydrocarbons, even when treating soil containing more than 50 % organic

compounds;which is less than 100 times the legal limit for discarding or reusing the soil.

v) Continuous operation process.

A schematic representation of the equipment can be seen in Figure 1 below.

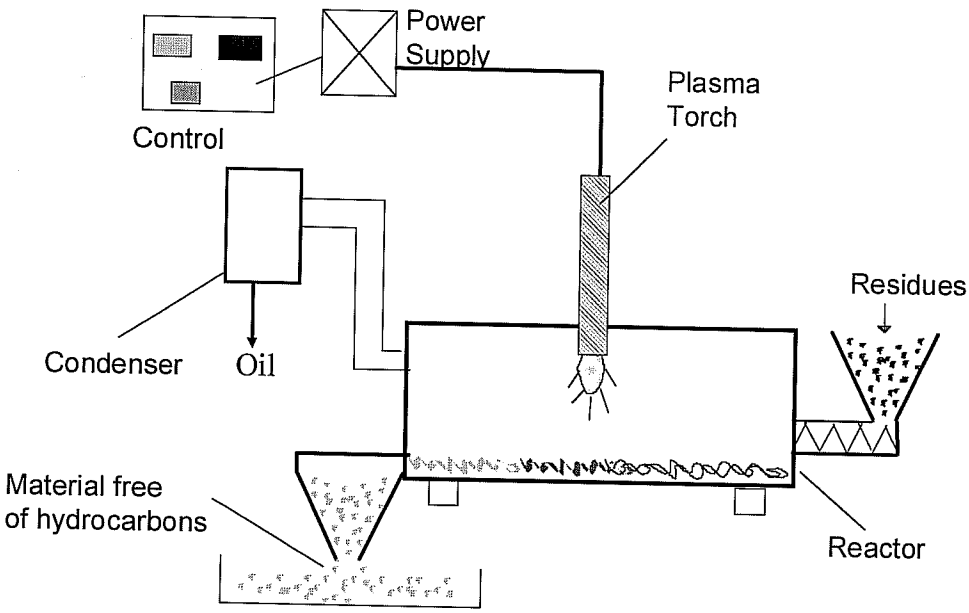

Figure 1 – Schematic representation of the plasma process

III. Results and Discussion

Several experiments were performed in a demonstration unit capable of treating up to 200 kg/h of contaminated material. Different materials were treated in the plasma unit, including soil containing from 1 to 50 % hydrocarbons (petroleum) and 25 % water in average. A summary of those results is given below.

a) Material (soil) after treatment:
Less than 0.01 % hydrocarbon when treating soil containing up to 50 % hydrocarbons;

b) Off gases
Less than 1 % of the amount of gases that would be generated if the soil containing hydrocarbons would be burnt in an incineration, for all the experiments and

conditions; gas analysis indicated only the presence of water vapor, carbon dioxide, nitrogen, oxygen and argon (plasma gas); no sulfur or chloride compounds detected.

c) Recovered oil
Diesel type for petroleum contaminated soil or petroleum sludge (analysis conducted by Petrobras – brazilian national oil company);

d) Specific energy for the process
0.5 kWh/kg.

The developed plasma process is well adapted for treating soil contaminated with several other compounds and elements, including mercury, organic chlorinated compounds and others. Economical evaluation of the process, based on the energy requirement and investments for the plasma units, indicate that the developed process can be even less costly than the existing technologies, without the environmental and technical limitations that those processes have as mentioned above.

Industrial units are being planned for treating contaminated soil on the site; those units will be able to process from 100 kg/h up to 5,000 kg/h (up to 2,000 kg/h the units are mobile; above that, the units are semi-mobile).

IV. Conclusions

A new process was developed, using a plasma system, for treating contaminated soil. The process removes the contaminants to a level several orders lower than the minimum required by environmental standards, at the same time that the organic contaminants can be recovered in the form of a light oil, completely reusable, reducing to almost zero the off gases that would be generated if the residues would be incinerated. The plasma units can be made mobile, treating in situ the contaminated area, avoiding therefore the risks and costs of transportation of toxic materials. Economical evaluation indicates that the process is very competitive with existing technologies, without presenting the environmental and technical limitations of those processes.

References

1) R.N. Szente, R.A. Schroter, M. G. Garcia, O.W. Bender; " Thermal Plasma Treatment of Galvanizing Residues", Journal of The Minerals, Metals & Materials Society - JOM, pg. 32-35, July 1998.
2) G.W. Carter, A.V. Tsangaris, " Plasma Gasification of Biomedical Waste", Proc. Internationa. Symposium on Environmental Technologies: Plasma Systems and Applications, Georgia, USA, October 1995.

3) N. Cerqueira, I. Ghiloufi, C. Vandensteendam, J.M. Baronnet, " Heavy metals volatility modeling for fly-ash plasma vitrification", Proc. International Symposium on Plasma Chemistry, Orleans, France, July 2001.
4) C. Girold, B. Barthelemy, N. Cerqueira, C. Vandensteendam, J.M. Baronnet, " Medium level burnable radioactive waste incineration/vitrification under oxygen trasnferred arc plasma", Proc. International Symposium on Plasma Chemistry, Orleans, France, July 2001.
5) R.N. Szente, M. Garcia, R. Schoeter, O Bender, L. Barbosa, "Recovering Aluminum via Plasma Processing", Journal of The Minerals, Metals & Materials Society - JOM, pg. 52-55, November 1997.
6) Z. Yamazaki, H. Hashimoto, First International EPRI Plasma Symposium, California, USA, 1990.
7) D.R. MacRae, " Application of Plasma Technology to Ferroalloy Processing", Plasma Technology in Metallurgical Processing, Jerome Feinman Editor, Iron and Steel Society, 1987.
8) S.Santen, L. Bentell, B. Johansson, P. Westerlund, " Applications of Plasma Technology in Ironmaking", Plasma Technology in Metallurgical Processing, Jerome Feinman Editor, Iron and Steel Society, 1987.
9) R.N. Szente, " Industrial Applications of Thermal Plasmas", AAIP Conf. Proceedings, n. 345, p. 487-494, 1995.
10) G. Clarke, Materials Edge, September-October, 1987.
11) E. Bouyer, M. Muller, G. Schiller, " Thermal plasma synthesis of ceramic materials from liquid precursors", Proc. International Symposium on Plasma Chemistry, Orleans, France, July 2001.

Remediation of TPH/PAHs Contaminated Soil Using Soil Washing

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ABSTRACT

This work deals with the treatment of a site contaminated mainly by gasoline and diesel, showing the presence of PAHs, MTBE, and BTEX. Soil washing was applied in three washing ditches of approximately 100 m^3. Every ditch had one recycling and one sedimentation tank.

A non-ionic surfactant, previously characterized, was employed in this work. Approximately 104 tons of soil were poured into each ditch and 18 m^3 of a 0.5% surfactant solution was introduced to each basin. Then, soil and surfactant solution were mechanically agitated. After that, the surfactant solution with dissolved hydrocarbons was pumped out to the sedimentation tank. When solids sedimented, the solution was transferred to the recycling tank and then, to the washing tank. The process was repeated three times. As a polishing stage, 18 m^3 of water were added to the soil.

At the beginning and after every stage, samples of soil were taken and analyzed in accordance to EPA analytic techniques. Average soil washing TPH removal was 83%. The soil treated reached the legislation limits (TPH values under 2,000 mg/kg) and had a significant reduction in PAHs concentrations. At the end of the process the washed soil was poured at the original site.

INTRODUCTION

A contaminated industrial site, which operated in Mexico from 1966 to 2000, was contaminated with hydrocarbons. The site was characterized by our research group in 2000 (Iturbe *et al.* 2003a). The main conclusions were that the soil was contaminated mainly by gasoline and diesel, showing the presence of methyl-tert-butyl-ether (MTBE), benzene, toluene, ethyl benzene and xylenes (BTEX). Nine of the 16 polycyclic aromatic hydrocarbons were found, as well as Fe, Pb, V, and Zn. The health risk assessment (HRA) suggested the necessity of reducing three of the PAHs (benzo(a)anthracene, benzo(a)pyrene, and benzo(b)fluoranthene), and vanadium. The estimated amount of soil contaminated was 1,640 m^3.

There are many available soil remediation methodologies, such as vapor extraction systems, soil stabilization and solidification, thermal treatments, electrokinetic systems, flushing and washing of soils, and biological methods, *i.e,* land farming, biopiles, bioaugmentation, and phytoremediation (Iturbe *et al.* 1998). We have learned from our experience in soil washing treatments that this methodology is cost-effective and easy to apply in conditions similar to those found on the site under study. We have explored the use of different anionic, and nonionic surfactants for washing highly contaminated sandy soils (Torres *et al.* 2003), and the successful use of *in situ* flushing techniques (Iturbe *et al.* 2003b) for remediation of oil-contaminated soils.

The aim of this work is to show that soil washing is an excellent remediation methodology to treat soils contaminated with petroleum derivates and metals. Applying them, it is possible to reach the goal value of 2,000 mg TPH/kg, requested by Mexican legislation, in a few months.

MATERIALS AND METHODS

Soil excavation and characterization

Three zones were mainly contaminated by TPH, PAH, and gasoline fractions. The first zone is where mobile-tanks were filled. The second zone corresponds to the railway, and the third zone is around the wastewater treatment plant (map not shown). After abandonment, pavement was retired, railway sleepers were removed and soil from these zones was excavated with the appropriate equipment (backhoe/loader and skid steer-loaders). Many times, rock was reached at about 0.5 m. Where necessary, extracted stones, walls and floors were washed with surfactant solution. On table 1, some physical-chemical properties of the contaminated soil are shown.

Analytical methods

Soil samples were evaluated in accordance to EPA analytic techniques: EPA 418.1 for TPH; and EPA 8100 method for PAHs.

Soil washing

For the soil washing processes, three washing ditches were built. Figure 1 shows the dimensions of ditches (8.7 m x 7.4 m x 1.25 m). Every ditch has one recycling and one sedimentation tank of about 4.3 m x 3.5 m x 1.25 m.

A non-ionic surfactant, previously characterized (Torres *et al.*, 2003) was employed in this work (Canarcel TW80). Soil washing process was as follows. Approximately 104 tons of soil were poured into each ditch and 18 m^3 of a 0.5% surfactant solution was introduced to each basin. Then, soil and surfactant solution were mechanically mixed. After that, the surfactant dissolved hydrocarbons solution was pumped out to the sedimentation tank. When solids sedimented, the solution was transferred to the recycling tank, and then to the washing tank. The process was repeated three times. As a polishing stage, 18 m^3 of clean water were added to the soil. At the beginning, and after every stage, samples of soil were taken in order to evaluate TPH concentrations. Composed

samples were analyzed for PAH removal determination. Wastewater was pumped out, and mixed with the washing solution for its appropriate treatment.

RESULTS AND DISCUSSION

Table 2 shows TPH concentrations for soil washing experimental batches (*i.e.,* 1, 2, 3, and 4), for every ditch. Initial concentrations Co, are compared with the TPH values found at the end of stages 1, 2, and 3. As observed, only 3 of the washing experiments required 3 stages (1A, 1B, and 1C). Most of the batches required 2 stages, and only two of them needed only one washing stage (4A, and 4B). The TPH initial concentrations were quite different (form 3,037 to 17,238 mg/kg soil). An average of 9,172 mg/kg. At the end of the washing process, the TPH concentrations were quite variable, from 942 to 2,317 mg/kg (average = 1,520 mg/kg). For this reason, removal values fluctuated form 50.3 to 92.8 % (average = 83.42%). As observed, the higher the initial soil TPH concentration, the higher the removal value. On figure 2, the relationship between initial concentration and removal efficiencies is shown. This behavior is well represented by the equation:

$$\textbf{Removal \%= 0.0026 TPH initial concentration + 53.629} \quad R^2 = 0.7308 \ldots \quad (1)$$

Figures 3a and 3b show the TPH concentrations for the first and final washing batches respectively in the three ditches. The washing process was carried out until reaching a TPH concentration equal or below 2,000 mg/kg, as suggested by PROFEPA (2000). Note that batch 1 required 3 washing stages, batches 2, and 3 needed two stages, and batch 4 required only one stage, except for ditch 4C, which required of 2 stages. On the same figures, it is noticeable that TPH concentration decaying curves have the form of an exponential curve (figure 3a, as an example). Values were fitted to the form:

$$\textbf{TPH=a exp (b*number of washing stages)}, R^2 = 0.8565 \quad (2)$$

Correlation factors are good enough, except for experiment 1C (0.5602). This kind of expression could help as a rule of thumb for anticipating how many washing stages are necessary in order to get a desired final TPH concentration during the washing process.

It is possible to estimate the amount of TPH removed from soil for every washing process using the initial and final TPH concentrations, and the amount of soil. During washing process, 104 tons of soils were processed on ditches A, and B, while approximately 143 tons of soils were processed at ditch C (average soil density of 1.7 g/cm^3). On the other hand, it can be assumed that the amount of surfactant employed in every washing process is 0.18 m^3 water x 5 kg/m^3 surfactant = 90 kg of surfactant, for ditches A and B. As every surfactant solution is employed thrice, it can be assumed that every batch consumes 30 kg of surfactant. For ditch C, the amount of employed water is 24.8 tons, giving a total of 123 kg and 123/4 kg per batch process. Defining a new removal efficiency as the amount (in grams) of TPH removed per g of employed surfactant, values between 7.88 and 55.45 mg TPH/mg surfactant can be achieved, as observed in table 2. Note that, in general, the higher the initial TPH soil concentration, the higher the removal efficiency as g TPH/g surfactant.

Figure 4 shows the relationship between that removal efficiency (g TPH/g surfactant), and the percent removal. It is remarkable that the higher the percent removal, the higher the amount in g of TPH removed by g of surfactant, but the function is no linear. Data were adjusted to an exponential curve, giving the following equation:

$$\textbf{Removal efficiency} = 0.4305 \exp(0.05 * \text{removal}),\ R^2 = 0.8565 \qquad (3)$$

This means that with the washing of soils with low TPH concentrations by means of a 0.5% surfactant solution, low percent removals are obtained, besides with very low removal efficiencies, therefore wasting a lot of surfactant.

It is noteworthy that the soil initial TPHs concentration affects the whole washing process. Three blocks were considered. The first one shows the experiences within a high concentration range (12,000-18,00 mg/kg). Runs 1A, 4C, 3B, and 1B were included. They had an average initial concentration of 14,379, an average percent removal of 89.35%, and a removal efficiency of 44 g TPH/g surfactant. The second block considers the moderate concentration range (8,000-11,000 mg/kg), runs 3C, 2B, 2A and 3A. As noted, they had an initial soil TPH concentration of 9,346, an average percent removal of 83.6%, and an average removal efficiency of 28.62 g TPH/g surfactant. At the end, the block of low range concentrations (3,000-5,000 mg/kg) include the runs 2C, 1C, 4B, and 4A. They had an average initial concentration of 3,804 mg/kg, an average percent removal of 60%, and average removal efficiency of 11.63 g TPH/g surfactant. This means that using a 0.5% surfactant solution for washing low TPH concentration soils, losses in removal efficiency of 16 and 32 mg TPH/g surfactant are obtained, if compared with the moderate TPH concentration and high TPH concentration soils, respectively. These figures suggest the future use of surfactant solutions with lower concentrations, appropriated for the TPG amount to remove.

Table 3 shows the PAHs concentrations in a composed sample of soil, before and after the soil washing process. Carcinogenic PAHs are highlighted in italics. In addition, the percent removals, and required cleaning levels suggested by the health risk assessment (PROFEPA 2000), are included for comparison purposes. As noted, from the 16 PAH considered by USEPA, 14 were found in the soil under treatment. Only acenaphthylene, and benzo(k)fluoranthene were not detected. The PAH which appeared in higher concentrations were pyrene (9.88 mg/kg), naphthalene, and benzo(a)anthracene, both with 6.69 mg/kg. PAHs removals due to the soil washing process were in the range of 47.8 to 100%. The case of fluoranthene is quite unusual, since an increase of 33% was observed due to the washing process. This fact could be related with soil heterogeneities. The PAH less removed from soils was chrysene (47.8%), but no required cleaning level is suggested for this aromatic hydrocarbon. On the other hand, naphthalene, benzo(g,h,i)perylene, fluorene, dibenzo(a,h)anthracene, indene(1,2,3-cd)pyrene, and acenaphthene were removed in a 100%.

A very rough calculation of washing soil process costs, including labor, building materials, pumping and tubing, ditches construction, storage tanks, and surfactant costs, among others, gives a total cost of \$140/m^3 or \$67/kg TPH removed. Lowe *et al.* (1999) report cost estimations for flushing technologies in the following ranges: the minimum and maximum are between 84 and 774 \$/m^3. Finally, if volume of NAPL removed is the target parameter, costs between 6 and 63 \$/L are the typical. As noted, the costs involved in the washing process are on the range of the typical costs for *in situ* flushing methodologies.

CONCLUSIONS

- Soil washing process (approximately 1,540 m^3) started with TPH average concentrations of 10 138 mg/kg. Percent removals in the range of 55.3 to 92.8% were observed (83.4% in average). Removal resulted in a direct function of the initial TPH concentration. The ratio g TPH/g surfactant showed values between 6.8 and 55.4 for the different washing batches, and resulted a quadratic function of the percent removal values.

- The contaminated soil was treated successfully, reaching the legislation limits *i.e.*, TPH values under 2,000 mg/kg, and a significant reduction in PAHs concentrations.

- A very rough calculation of washing soil process costs, including labor, building materials, pumping and tubing, ditches construction, storage tanks, and surfactant costs, among others, gives a total cost of \$140/$m^{3,}$ or \$67/kg TPH removed.

REFERENCES

Iturbe R, Castro A, and Madrigal I., "Soil and aquifer remediation techniques", (In Spanish). Series del Instituto de Ingeniería. Mexico. ISSN 0185-2345. **612** (1998).

Iturbe R, Flores RM, and Torres LG., "Subsoil contaminated by hydrocarbons in an out of service oil distribution and storage station in Zacatecas, Mexico," Env. Geol.. ,608-620 (2003a).

Iturbe R, Flores C, Chávez C, Ramírez A, and Torres LG., "In situ flushing of contaminated soils from a refinery organic compounds and metal removals", Remediation, submitted. (2003 b).

Lowe DF, Oubre CL and Ward C.H, Surfactants and Cosolvents for NAPL Remediation,USA,. Lewis Publishers (1999).

Mulligan CN, Yong RN, and Gibbs BF., "Surfactant-enhanced remediation of contaminated soil: a review", Eng. Geol., **60**, 371-380, (2001)

Simpkin T, Sale T, Kueper B, Pitts M., and Wyatt K., Surfactants and cosolvents for NAPL remediation, A technology manual, USA, Lewis Publishers, USA,(1999).

Torres LG, Orantes JL and Iturbe R "Three surfactants CMC and diesel removal efficiencies from sandy soils highly contaminated", Env. Geosc., In press. (2003).

Table 1. Physical-chemical properties of the contaminated soil

	Initial characterization (Iturbe *et al.*, 2003a)
Bulk density	1.7 g/cm^3
Porosity	0.38
Organic carbon fraction	0.0074
Hydraulic conductivity	8.6x10^{-4} cm/s
pH	7.8

Table 2. Analysis of the washing of soils as a function of the soil TPH-concentration range.

Concentration Range (mg/kg)	**Batch/Ditch**	**Initial concentration (mg/kg)**	**Removal**	**Removal efficiency (gTPH/g surfactant)**
High (12,000-18,000)	1A	17,238	92.8	55.45
	4C	15,064	90.4	47.11
	3B	12,989	87.2	39.27
	1B	12,224	87.0	36.90
	Average	14,379	89.3	44.68
Moderate (8,000-12,000)				
	3C	10,291	85.2	30.34
	2B	9,483	81.6	26.84
	2A	9,438	90.0	29.61
	3A	8,171	77.6	22.00
	Average	9,346	83.6	27.20
Low (3,000-8,000)				
	2C	4,666	50.3	8.13
	1C	4,252	55.3	8.13
	4B	3,261	69.7	7.88
	4A	3,037	64.6	6.80
	Average	3,804	60.0	7.73

Table 3. PAH concentrations in a composed sample of soil before and after soil washing process

Compound	Initial concentration (mg/kg)	Final concentration (mg/kg)	Removal (%)
Pyrene	9.88	1.08	89
Naphthalene	6.69	ND	100
Benzo(a)anthracene	6.69	0.57	91.5
Benzo(g,h,i)perylene	6.42	ND	100
Anthracene	4.43	0.39	91.2
Fluorene	4.25	ND	100
Phenanthrene	3.14	1.08	65.6
Benzo(b)fluoranthene	2.35	0.76	67.6
Chrysene	2.03	1.06	47.8
Dibenzo(ah)anthracene	1.94	ND	100
Benzo(a)pyrene	1.42	0.56	60.6
Fluoranthene	0.767	1.02	-
Indene(1,2,3-cd)pyrene	0.414	ND	100
Acenaphthene	0.102	ND	100
Acenaphthylene	ND	ND	-
Benzo(k)fluoranthene	ND	ND	-
Total PAHs	50.52	6.52	87.1

ND, not detected, NR not reported, **carcinogenic PAHs in bold**

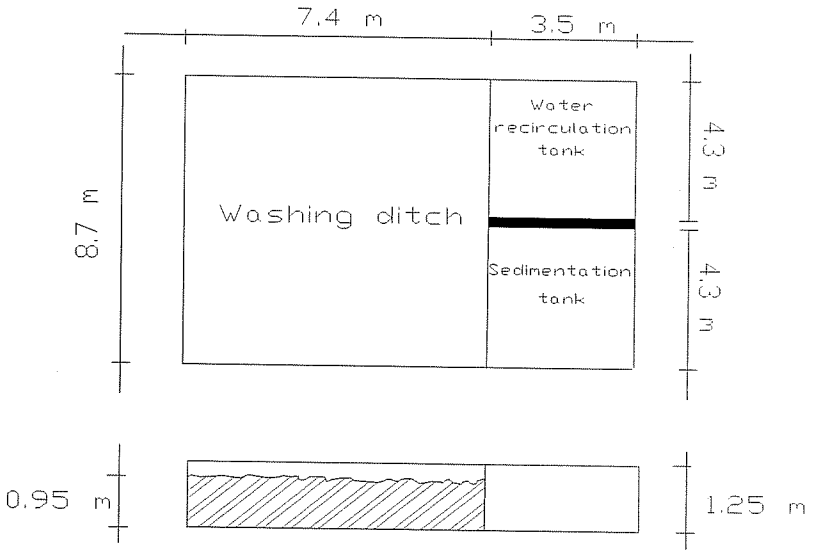

Figure 1. Soil washing ditch diagram

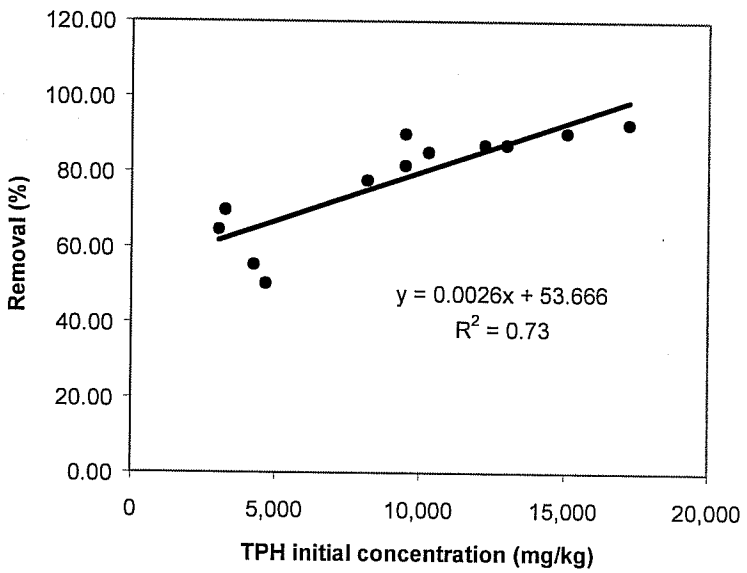

Figure 2. TPH Removal as a function of TPH initial concentrations

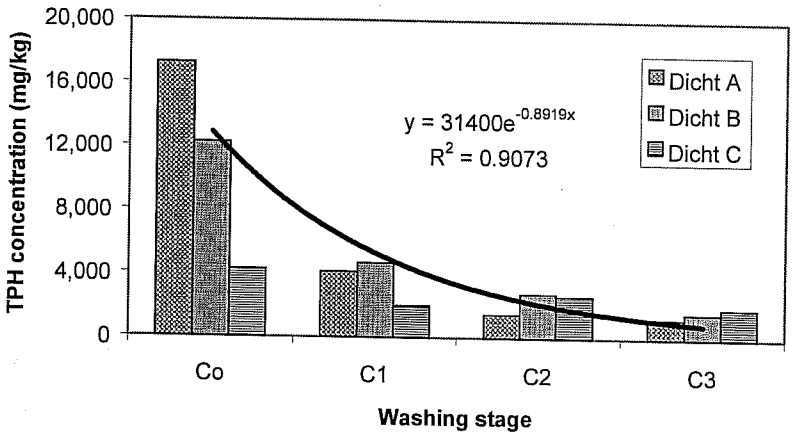

Figure 3 a. TPH concentrations. Batch 1, ditch A, B, and C

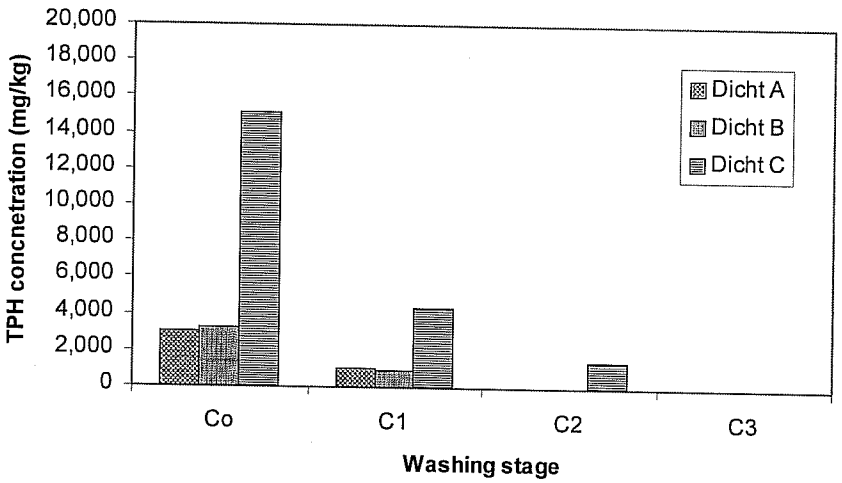

Figure 3b. TPH concentrations. Batch 4, ditch A, B, and C

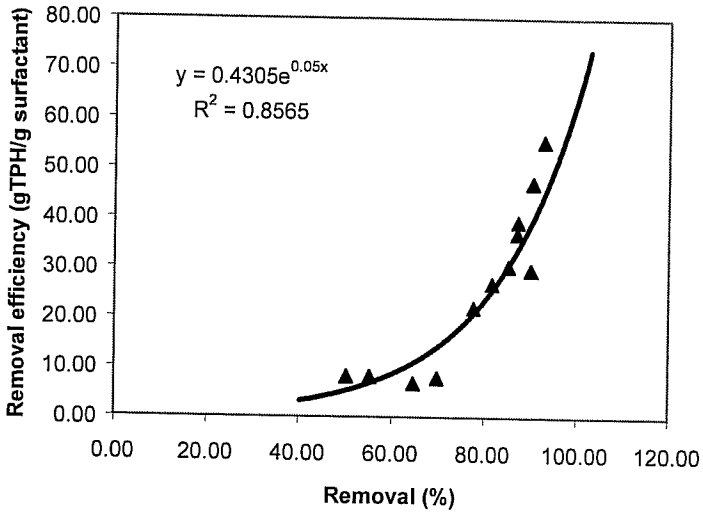

Figure 4. Removal efficiency as a function of TPH removal

ICF Consulting's GHG Emissions Management System (GEMS™)

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ABSTRACT

The natural gas industry is a major source of methane emissions -- a significant greenhouse gas (GHG). General approaches used today to estimate emissions from natural gas systems are based on EPA/GRI's 1996 study: "Methane Emissions from the Natural Gas Industry." This study developed emissions factors for natural gas system operations, e.g. dehydration, compression etc., that bundled different technologies and processes. These bundled factors -- adequate for estimating total emissions -- are less useful if companies intend to design an emissions reduction management program.

ICF Consulting's "GHG Emissions Management System" (GEMS) allows users to build GHG emissions inventories in a way that users can plan economic reductions. GEMS structures methane emissions inventories by source and technology. Users can estimate emissions reductions, costs, and economics of alternative technologies and evaluate benefits of trading carbon reductions. GEMS presents outputs at facility, business unit and corporate levels. A global U.S. gas company currently uses GEMS.

INTRODUCTION

Fossil fuels are significant sources of greenhouse gas emissions. Although, most of the emissions arising from fossil fuel are due to end-use combustion, a substantial amount can be attributed to fugitives from the Oil and Natural gas Industry. In 2000, as reported by the United Nations Framework Convention on Climate Change, fugitive greenhouse gases emitted from oil and natural gas totaled 326 Teragrams of CO_2 equivalent. Methane formed nearly 77% and carbon dioxide constituted another 21.7% of these emissions. Many oil and natural gas companies are beginning to develop inventories of their GHG emissions in anticipation of more stringent requirements, to better understand their carbon footprint, and to identify opportunities to profitably reduce methane emissions. What most inventory efforts lack however is an inventory approach that is integrated with mitigation strategies. ICF Consulting provides a GHG Emissions Management System (GEMS™) that structures an inventory in a way that helps companies to evaluate the economics of alternative, lower emitting technologies. This system makes planning and tracking of emissions reductions more robust. The GEMS™ concept can be applied to the inventory of any greenhouse gas emissions, and even conventional pollutants. This paper discusses a version of GEMS™ built for methane emissions from the natural gas industry. Methane was chosen because it is the main constituent of GHG emissions from the oil production and natural gas industries and has an economic value apart from the environmental benefits associated with its emission reduction.

GREENHOUSE GAS EMISSIONS INVENTORY

In the absence of a globally adopted strategy for GHG emission reductions, many companies have voluntarily taken steps to prepare in advance by measuring their GHG emissions. These initial steps often include a GHG inventory to identify emissions sources, a baseline estimation of emissions, and annual updating of the inventory. Through the U.S. Environmental Protection Agency's Natural Gas STAR Program, natural gas companies also identify economic GHG emission reduction measures.

Features of a GHG Inventory

A complete GHG inventory consists of protocols and reporting guidelines. Protocols provide a methodology for estimating GHG emissions and baseline reference case. The methodology will define all emissions sources, emissions factors and activity factors. The baseline is the historical start-up year or business-as-usual forecast against which annual emission inventories can be compared. Reporting guidelines define data requirements and controls, company or project boundaries (e.g. direct and indirect emissions), record retention and auditing policies, and change management (acquisitions/divestitures, consistency, transparency).

Risks Associated With Emissions Reduction Initiatives

Without internationally accepted guidelines, corporations implementing a GHG reduction program face policy and project-related risks. Policy risks stem from valuation and recognition of GHG emissions reductions that are subject to the uncertainties associated with national government regulations on GHGs. These risks include types of GHGs and sources included in national programs, time horizons (reference year for baseline and compliance periods), and geographic location (important for multi-national corporations with facilities in several countries with differing GHG policies).

Project risks are also significant. Developing a baseline that is representative of corporate activity is critical. Should the company account for both direct and indirect emissions? Legal entitlement to claimed reductions needs to be clear. Project monitoring and verification procedures must be defined. Data management systems must be adequate for intended uses.

GHG EMISSIONS MANAGEMENT – BEYOND GHG INVENTORY

Benefits of GHG Emissions Management

An effective GHG emissions management strategy is one that evaluates environmental and economic benefits, enables a corporation to manage policy and project risks, and is integrated into all levels of a corporation's operating and capital planning decisions. To facilitate these objectives, the GHG inventory data must be available at a level that is useful and actionable. In the absence of these features, a GHG inventory is simply a snapshot, rather than a motion picture with a story. The data must identify both sources of emissions and the operational practices or technologies of each source. Constructed in this detail, the inventory allows evaluation of alternative cost-effective emission reductions. Further, the data should enable annual comparisons with a set baseline to better account for real changes in emissions as opposed to changes in accounting methods.

Available Methane Emissions Inventory Software

Other available methane inventory software products provide a Tier 3 inventory (Table 1). These tools rely on a widely accepted approach used for estimating emissions from the natural gas and oil industries based on a 1996 study by the U.S. EPA and Gas Research Institute (GRI): "Methane Emissions from the Natural Gas Industry," and a 1998 U.S. EPA study "Estimates of Methane Emissions from the U.S. Oil Industry." The objective of these landmark studies was to characterize U.S. natural gas and oil industry methane emissions by sources. The studies developed emission and activity factors based on natural gas and oil facilities such as wells, dehydration units, compressors, tanks, pipelines, etc. The field data for emission factors incorporated a cross section of many different technologies and practices. While this approach is entirely adequate for estimating industry-wide emissions, it is not suited to company-specific emissions management decision-making or analyzing the emission reductions possible from alternative technologies and practices.

For example, the EPA/GRI study determined an emissions factor for gas pneumatic instruments for the production, transmission and processing sectors. These factors are based on survey data that bundled together low bleed and high bleed devices in the proportions that existed in 1993 and 1994 (when the field data was collected). Using these emissions factors will provide an average total emissions estimate that does not reflect the changing distribution from high- to low-bleed pneumatic devices. Further, if a corporation chooses to install low-bleed devices in place of high-bleed, these bundled emissions factors will not reflect the reduction in the emissions inventories for years following the replacements.

ICF CONSULTING'S GREENHOUSE GAS EMISSIONS MANAGEMENT SYSTEM (GEMS™)

ICF's GEMS™ goes beyond Tier 3 based tools. GEMS™ is not just a more detailed emissions inventory tool, it also allows the user to manage their emission reduction program. Some of the key features of ICF's GEMS™ are:

- It uses a bottoms-up approach to report GHG emissions by technology and operating/maintenance practice for each source and sector.
- It segregates all fugitive and vented emissions to better evaluate and track emissions reductions.
- It provides choices in emission factors, ranging from simple defaults to operationally tailored emission factors.
- It evaluates emission reduction economics that can be achieved by selecting alternative technologies and practices.
- It provides robust quantification and valuation of emission reduction credits.
- It evaluates the potential value of trading in a carbon market through potential emissions reductions.
- It establishes a more rigorous emissions baseline and can identify causes of emissions reductions/changes in the future years through an annual comparison.
- It is scalable in that it can be implemented at a single facility or at a corporate-wide level.
- It is available in a user-friendly Microsoft Excel® format. It can also be configured for Microsoft Access® or a web-based platform.

GEMS™ is a suite of three tools that can be configured to the client needs:

- Inventory Reporting Tool
- Inventory Compilation Tool
- Alternative Technology Analytical Tool

GEMS™ is a very powerful tool at the corporate, business unit or facility level. Users can develop an inventory and build summary reports at any level, from the plant to the corporation using only the inventory and compilation tools. However, the maximum benefit is the ability to evaluate and plan changes. GEMS™ can help evaluate alternative technologies that achieve emissions reductions cost-effectively.

Inventory Tool

Figure 1 shows a snapshot of the data entry form for vented methane emissions from the gathering/boosting sector of natural gas operations. For each emissions source, e.g. pneumatic devices, the user has the option of selecting a "recommended" or a "simple" methodology. The recommended methodology disaggregates the source into specific technologies. For pneumatic devices this includes high-bleed, low-bleed and non-bleeding isolation valves. This enables the user to quantify emissions at the most disaggregated equipment level. The simple method is consistent with a Tier 3 approach that group devices together for an industry average plant or operating site.

The emissions factors used in the recommended methodology are based on published studies including the original data collected by EPA/GRI, unbundled by source and then rebundled by technology

type. Data gaps were thus identified and supplemented with published technical surveys of field measurements, process simulation model analyses, equipment vendor specifications, and in rare cases industry expert judgments.

One feature in the inventory tool is the option to tailor emission factors to operating conditions. In the inventory spreadsheet, Figure 1, the user selects "Get Default" which presents a table like Figure 2. Here the user may enter site specific operating values, or choose an industry average default value for any variable: the more site-specific data that is used in the inventory, the more accurate the emissions estimate, and subsequently, the more accurate the analysis of technology alternatives in the Analytical Tool.

The recommended method also enables the user to enter "user-defined" activity and emission factors. Figure 1 shows this as the last option in the Recommended method for each emission source. This option may be used to input direct measurement of emissions, or user developed factors. By selecting the button "Consult Table" the user can see industry sector average values for activity factors and emission factors.

Compilation Tool

The compilation workbook electronically compiles and provides management reports on all inventories received from reporting entities. Emissions are presented in metric or English units for methane and CO_2 equivalent, grouped by fugitive sources, vented sources and total sources. An exception report on the emission inventories compiled is also generated as part of quality assurance and control. The compiled emissions inventories can be sorted by eleven options including similar facilities, industry sectors, business unit, the whole company, etc. Each sort includes output reports in the form of tables, bar charts and pie charts.

Emissions Management Tool

The analytical tool, shown in Figure 3, enables a user to evaluate alternative technologies that would result in lower methane emissions. This worksheet is based on the "source and technology" sort of the compiled inventories in the inventory workbook. The activity factors and total emissions represent the company's actual inventory, for all reporting entities compiled. The user can compile the whole company, or any sub-sector of the company, and then analyze the alternative technologies and economics for that compilation.

For sources and technologies that have lower methane emitting alternatives, the user can open a "drop-down" menu in the Alternative Technologies or Practices column. This presents the lower emitting alternatives. Selecting any alternative, and clicking the "Calculate" button, results in the analysis shown in the columns to the right for that source and technology. Emissions reductions are displayed in million cubic feet of methane per year, or carbon credits (expressed in alternative units selected in the global settings above; i.e. metric tonnes per year CO_2e). The values represent costs, benefits and economics for replacing all technologies compiled to the alternate choice. For example, if the user compiled just one business unit of the company, the reductions and economics apply to all of the selected source and technologies represented in the inventory for that BU.

Values calculated for the alternate choice include, in addition to the emissions reductions: number of new technologies required, net first year investment costs, net annual savings (including saved gas value and other differential operations and maintenance costs), and economic indicators of relative value. If the economics of the alternate are positive, then a positive net present value, an internal rate of return, and a simple payback are displayed. If the economics are negative, then a break-even carbon credit is calculated, indicating the value that would have to be recovered in a carbon trading market to bring the economics up to a break-even.

The economics are based on a five-year discounted cash flow analysis. In the upper-left corner of the worksheet in Figure 3 are global settings for these calculations. The user may specify a price for the natural gas (including zero), a price for a carbon market credit (or zero), a discount rate, and cost indices for the year of analysis. These cost indices are published quarterly, and the reference is shown in the instructions. The indices update equipment investment costs and labor costs from the bases in the GEMS™ program to real dollars for the date of analysis. The global setting also include choices in units, which will include both English and metric volumes and weights, and U.S. and foreign currencies.

The user may choose alternatives for any and all sources in the compiled inventory. The user can then test different mitigation alternatives for sources. The results can be expressed as a marginal abatement cost (MAC) curve that ranks the mitigation opportunities in a way useful for managers. Managers then can choose to implement those technology alternatives that appear attractive with the gas price and prospective carbon market in an entire program of change for the compiled inventory. The sum of all chosen alternates is displayed on the bottom of the spreadsheet.

Inter-year comparisons in GEMS™ allow a company to distinguish between emission changes resulting from reduction efforts and those resulting from business climate changes, and separately, the emissions changes associated with changing calculation methods or acquiring/divesting facilities. This is a powerful tool in substantiating real GHG emission reductions.

CONCLUSION

ICF's GEMS™ is not just an inventory tool, it is a new concept in GHG emissions management. The concept can be applied to any GHG gas, any industry, and updated periodically to reflect new alternatives and changing economics.

Identifying Fugitive Emissions with Optical Imaging

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ABSTRACT

A recent API study showed that less than 1 percent of potential leak sources at refineries contribute over 90 percent of fugitive emissions. Finding these few leaks in a cost-effective way is a challenge. Current programs require operators to visit and measure each of the thousands of regulated components at industrial plants. This is time consuming, labor intensive, and costly. A large U.S. refinery can spend $1MM annually in monitoring, repair, and record keeping.

Optical imaging (OI) allows the user to "see" live images of leaking gas. Several OI technologies are being developed; one is commercially available. These devices allow a user to scan hundreds of components in minutes and identify those few that are leaking.

This paper will describe different OI technologies, possibilities in fugitive emission detection, and future outlook for optical imaging. The presentation will show actual video of gas leaks detected with an optical imager.

INTRODUCTION

Fugitive emissions can be a significant contributor to air pollution from chemical plants and petroleum refineries. To control these emissions, U.S. refineries are required to implement a Leak Detection and Repair (LDAR) program for processes and streams described in the National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries (40 CFR 63 subpart CC) known commonly as "Refinery MACT Rule" (MACT is an acronym for Maximum Available Control Technology). While current LDAR programs have been successful in identifying and significantly reducing fugitive emissions from regulated components, monitoring procedures outlined by the current rule are time consuming, labor intensive and costly. An inspector must visit and measure each potential leak site; of which there are thousands at an industrial plant. A large refinery in the U.S. can spend over $1MM annually in monitoring, control measures, and record keeping. However, a recent API study based on 11.5 million refinery component monitoring events showed that over 90% of controllable fugitive emissions at refineries come from about 0.1% of components. (1)

Emerging optical imaging technologies provide a tool to more quickly identify high leaking components. Remote sensing and instantaneous detection capabilities of these optical imaging technologies allow an inspector to quickly scan large areas containing tens to hundreds of potential leaks. Significant leaks are identified immediately, allowing quicker repair, and ensuring efficient use of resources. Two types of optical imagers are being tested:

- Infrared laser cameras based on Backscatter Absorption Gas Imaging (BAGI) techniques, and
- An infrared camera based on Image Multi-spectral Sensor (IMSS) technology.

BACKSCATTER ABSORPTION GAS IMAGING (BAGI) LASER CAMERAS

Two types of BAGI cameras suitable for detecting hydrocarbon emissions at refineries and chemical plants are:

- A long-wave infrared (IR) camera. This is a commercially available instrument, manufactured and marketed by Laser Imaging Systems (LIS), under the trademark "Gas Vue®." Gas Vue® utilizes a long-wave IR laser. Among refinery fugitive emissions of interest, the Gas Vue®" has been shown to be suitable for detecting olefinic hydrocarbons. The Gas Vue® was successfully tested at two chemical plants and is referred to as a long-wave laser imager throughout this paper.

- A mid-wave IR laser imager. This instrument, developed by Sandia National Laboratory's (SNL) Lawrence Livermore facility utilizes a BAGI technique patented by LIS. The camera has been shown to be is suitable for aliphatic, olefinic and some aromatic hydrocarbons. It was successfully tested at two refineries and a chemical plant.

Backscatter Absorption Gas Imaging (BAGI) Principle

In Backscatter Absorption Gas Imaging (BAGI), a live video image is produced by illuminating the view area with laser light in the infrared frequency range. The reflected (backscattered) laser light is detected with an infrared camera sensitive to that light. When the chosen laser wavelength is strongly absorbed by the gas of interest, a cloud of that gas is revealed as a dark image. Figure 1 shows how BAGI works. Also see U.S. Patent #4,555,627.

A video camera-type scanner both sends out the laser beam and picks up the backscattered infrared light. The camera converts this backscattered infrared light to an electronic signal, which is displayed in real-time as a black and white image on both the viewfinder eye-piece and a video monitor. The same image will be seen whether the scanning is done in daylight or at night because the scanner is only sensitive to illumination coming from the infrared light source, not the sun. The imager can be switched between visible and infrared light views; an important attribute when the operator needs to differentiate between steam plumes and gas plumes (see discussion of Atmospheric Window below). Video recording of the image in both visible and infrared light provides a record of the inspection and leaks detected. Figures 2 and 3 show a leaking valve and flange detected with the BAGI cameras in visible and infrared light.

In the current state of development, the technology makes visible the size of a vapor cloud of hydrocarbons that are invisible to the naked eye, but does not quantify the mass emissions rate of the leak cloud. A detailed technical description of BAGI technology is presented in (2).

Three parameters that influence the performance of the two BAGI lasers are background, laser wavelength and atmospheric window.

Background. For the technology to visualize a leak, there must be a reflective, or backscattering, surface close behind the leak. It is not possible to visualize a gas plume against the sky or a distant background because insufficient laser light is reflected to create a bright image in the camera. It is, however, possible in many circumstances to image a leak against the component itself, with a distant or sky background appearing black. The operator knows that the imager is beyond detection range when the camera no longer produces a bright image of the components under inspection: the more distant the component or background, the darker the image. The operator can also switch the camera between infrared and visible light viewing to determine whether there is an adequate background surface behind the leak point being inspected.

Laser Wavelength. Gas leak detection sensitivity by optical imaging depends most strongly on the match between the laser wavelength and the wavelengths of strong absorption by the gas of interest. To produce an image in the viewfinder of a black cloud where the hydrocarbon gas is present, the gas cloud must be capable of absorbing the laser wavelength. Different hydrocarbon chemicals have characteristic IR light absorption spectra, and both laser imagers are tuneable within certain ranges.

Wind speed, optical resolution, gas plume motion and viewing angle also affect detection sensitivity. The higher the wind speed, the more quickly the gas is dispersed as it leaves the leak source, and the less visible it becomes to the optical imager. However, some motion is beneficial for detecting a

leak, as the human eye is particularly sensitive to movement. A stationary gas cloud is very difficult to distinguish against a non-uniform background.

Atmospheric Window. An "atmospheric window" is defined as a region of the spectrum where there is minimal or no light absorption by oxygen, nitrogen, carbon dioxide, and water vapor that are normally present in air. The major atmospheric windows in the infrared region are found in the 3 to 4.2 micron and in the 8 to 13 micron wavelength regions. A laser beam propagating through the atmosphere at wavelengths within these atmospheric windows will experience minimal attenuation. LIS's long-wave OI camera is discreetly tunable in the 8-10 micron region; SNL's mid-wave OI camera is continuously tunable in the 3-4 micron region.

Laser light within these IR windows may still be attenuated by particulates in the air, including water droplets as in fog and steam. Consequently, these particulates will appear as dark clouds in the BAGI image as do the fugitive gases that absorb the laser light. However, since these particulates are also visible to the naked eye (while the fugitive gases are not), the BAGI operator can easily distinguish between the two types of clouds by switching between visible and IR light displays.

For example, if the cloud can be seen with the unaided eye AND with the BAGI camera – the cloud is likely particulates or steam. If the cloud can only be seen with the BAGI camera, it is likely gas.

BAGI Cameras

The mid-wave and long-wave IR lasers, which weigh between 20 and 30 lbs, are about the size of a portable TV camera and consist of two systems: a camera unit and a power/control unit (Figure 4). The camera portion of LIS's laser is connected to a mobile power pack that plugs into an external 110V AC outlet. The power pack converts AC to DC. The camera portion of SNL's prototype plugs into a backpack borne power/control that is powered by a 28V lithium-ion battery. Battery lifetime while the mid-wave IR laser is operational is between 1 and 1½ hrs; batteries recharge in twelve hours. Batteries can be changed without shutting down the device. SNL's mid-wave IR imager can also be operated on a 110 volt AC outlet through the power unit's 28-volt DC converter.

Both laser cameras can be operated in a shoulder-mounted position or with a tripod-mounted position (Figure 5). The tripod has a swivel fitting that permits the operator to move the instrument from left to right and up and down while scanning for leaks. A zoom lens allows the operator to adjust the focal distance to obtain a better view. The operator can switch between the infrared view and visible light, and can record video of the image seen in the viewfinder in both views. Both cameras have simple start up procedures requiring 10 – 15 minutes after power is switched on.

THE IMSS CAMERA

The IMSS camera shown in Figure 6 is also a hand-held or tripod mounted, battery-operated device that is based on IMSS technology developed and patented by Pacific Advanced Technology (PAT) (US Patent 5,479,258 and 5,867,264). It is marketed under the Sherlock name. The current prototype of

the IMSS camera weighs 12 lb (including battery) and is 12 (L) x 6 (W) x 8 (H) inches in size. The system consists of the: Sherlock Camera, which holds a patented IMSS lens, and a PC to acquire and process hyperspectral images.

The IMSS camera also does not quantify leaks; however, while it can image leaks against the sky and distant backgrounds, and can identify chemical species within a leak, it does require a differential emissivity between the gas cloud and background. It can be used in un-manned aerial vehicles and controlled from remote locations. It can also detect chemical species from great distances. In one test, the camera was able to screen a flare on an offshore oil platform 10 miles away and provide a spectrum showing the composition of the flare.

The Image Multi-spectral Sensing (IMSS) Principle

Image Multi-spectral Sensing (IMSS) is based on the principal of diffractive optics. It is a combination of a diffractive imaging spectrometer and an adaptive tunable filter. The basic concept is shown in Figure 7.

A basic monochrometer has an entrance and exit slit combined with a dispersing medium such as a prism. In order to obtain high resolution, the entrance and exit slits must be very narrow, thus reducing the optical throughput of the system. The light is dispersed perpendicular to the axis of the exit slit and is spectrally scanned across the slit.

In the IMSS approach, a diffractive element is used to perform both imaging and dispersion of light. The diffractive optical element disperses the light along the optical axis and the detector array/lens focal length is scanned to produce images of different wavelengths ("colors"). The advantage of this approach is that the entire input aperture collects the light as opposed to the narrow entrance slit and thus the throughput is greater. The detector element acts as the exit slit and must be matched with the blur diameter of the diffractive lens. The disadvantage of this approach is that the image must be processed in order to sharpen it and the resulting spectrum. A detailed description of the process is presented in (3). Figure 8 shows the IMSS camera being demonstrated at an oil refinery.

Figure 9 shows an image of tests of a valve leaking methane at 0.1 standard cubic feet per min (scfm). The test setup is shown on the left. The center and right hand pictures show the leak profile (detected in the infrared) superimposed in a false color image on the image of the test valve.

TESTS AND DEMONSTRATIONS OF OPTICAL IMAGING

Table 1 summarizes data from some of the field and laboratory studies that have been conducted to demonstrate the use of optical imaging for fugitive emissions monitoring. Details of two field demonstrations are discussed below.

Refinery Test of SNL's Mid-wave IR Laser

A 2003 field study was conducted at a Texas refinery to evaluate the performance of a SNL prototype OI under normal field conditions. Specific aims of the study were to:

- Demonstrate that the prototype portable BAGI device detects and successfully images fugitive emissions under normal refinery operating conditions.
- Gather data that can be used to establish the mass-emission detection capabilities of the gas imaging technology.
- Gather data that can begin to establish the sensitivity of the BAGI technology to various factors that might be encountered during routine use at a refinery. Such factors include distance from scanned component, sight lines and angle-of-view, infrared backscatter and absorption properties of background components, weather conditions, and chemical composition of the emissions.

Study Findings and Results

The study concluded that the SNL's mid-wave laser can detect leaks of mixtures of olefinic and aliphatic hydrocarbons from LDAR components at leak rates of 20 g/hr and higher under normal refinery operating conditions, against typical reflective surfaces found at a refinery. Data and analyses to support this conclusion are presented below.

Study Data

This field study collected data from 41 leak sources within four process areas. The screened process areas were: the Alkylation Plant, Saturated Gas Plant, Unsaturated Gas Plant, and the Isomerization plant. Thirty of the 41 leaks were detected in the Saturated Gas Plant (SGP); five in the Unsaturated Gas Plant (USGP); and the remaining 6 leaks at the Isomerization (ISOM) Plant. No leaks were found at the Alkylation Plant. Both regulated LDAR components (valves, pump seals, compressor seals, open-ended lines) and non-regulated components (flanges, connectors, heat exchanger bundle heads) were screened.

Twenty-eight of the 41 leak sources were bagged and analyzed for mass leak rate and chemical composition. Analysis of the bagged samples indicated that the leaks consisted of mixtures of hydrocarbons from C1 to C6 and above.

Performance of the Mid-wave IR Laser (Detected Mass Leak Rate)

Figure 10 illustrates the performance of the SNL's mid-wave IR laser imager in detecting mass leak rate (note: the Y axis is used just do separate the data sets for viewing results). As the plot illustrates, the imager detected all bagged leaks above about 20 g/hr. Below about 20 g/hr the imager missed 3 of the 12 recorded leaks (one each at the SGP, USGP, and ISOM). With a brightly reflecting Styrofoam background held behind two known leaks, the SNL camera imaged a 16 g/hr leak at USGP and a 0.12 g/hr leak at SGP.

Testing the Long-wave IR for Ethylene at Production Facilities

Two tests were commissioned in 2002 by the Houston Area Advanced Research Center (HARC) at olefin plants in Texas. The objectives of these tests were to:

- Conduct a demonstration of the long-wave OI device in two industrial sites (ethylene producers) to evaluate the capability of the device in detecting fugitive emissions under normal chemical plant operating conditions.

- Gather data that could be used to establish the mass emission detection capability of the portable optical gas imaging device.

- Gather data that could begin to establish the sensitivity of the portable optical gas imaging device to various factors that might be encountered during routine use at a chemical plant including, but not limited to, distance from scanned components, sight lines and angle-of-view, infrared backscatter and absorption properties of background components, weather conditions, and chemical composition of emissions.

Study Findings and Results

The study concluded that LIS's long-wave IR laser imager could detect leaks of ethylene from regulated LDAR and non-regulated components at a rate of about 1 g/hr and above under normal plant operating conditions, against typical reflective surfaces found at a plant. Ethylene was the only species studied during testing at both sites. Data and analyses to support this conclusion are presented below.

The tests were conducted at two ethylene facilities in Texas (referred to as Site A and Site B). The process areas monitored were: cold ends, ethylene product pumps and heater, compressors, and drying areas. Mass rates of several leaks detected by the long-wave IR laser were determined using bagging techniques. The distance between the imager and the leaking component was recorded, as was local wind speed in the vicinity of the leak. Leaks were found at connectors, flanges, valves, and from seams in insulation metal sheathing.

Figure 11 illustrates the performance of the long-wave IR laser imager in detecting mass leak rate (note: the Y axis is used just do separate the data sets for viewing results). As the plot illustrates, the imager detected all leaks above about 1 g/hr, and 66% of the leaks below 1 g/hr.

The tests with the long-wave IR laser determined that current Method 21 techniques sometimes inaccurately attribute leaks. Several LDAR components tagged for repair were found not to be leaking. Instead, the imager determined that the tagged components were in the path of the plume emanating from another (often, overlooked and hence untagged) component. As the wind direction changed these tagged "non-leaking" components are no longer in the plume's path, and would be found not to be leaking (e.g. at the time of repair). Plant personnel at one site indicated that they have, on many occasions, detected and tagged components for repair, only to find no leak at the component on a later date when a crew arrives to perform repairs.

SAVINGS WITH OPTICAL IMAGING

Optical imaging offers facilities subject to LDAR requirements significant savings in time and labor costs over current monitoring requirements. Under existing Method 21 guidelines, an operator must visit and manually screen each regulated component – of which there are several thousands at a facility – for leaks. Current experience indicates that operators can screen between 500 and 700 components daily. With optical imaging an operator can screen thousands of components per hour and instantaneously detect leaks. For example, during 2003 testing at a Texas refinery, Sandia's laser operators screened at 35 components per minute or 2,100 components per hour. Leaking components are identified – and implicitly could be repaired -- more quickly with optical imaging.

Sandia National Labs has conducted preliminary analyses of the potential savings offered by OI. The analysis, presented in Table 2, shows that savings (combination labor and/or equipment) could range from $600,000 to $5,000,000 over 5 years.

FUTURE OF OPTICAL IMAGING FOR FUGITIVE EMISSIONS MONITORING

OI is currently used in the U.S. to identify SF6 leaks at power facilities and has shown great promise for fugitive emissions control at refineries and chemical plants. The U.S. EPA and state of Texas have taken the lead in testing the applicability of OI for fugitive emissions monitoring. In addition to the test results presented above, several lab tests have been completed and negotiations are currently underway between regulators and industry to begin long-term testing of the BAGI and IMSS cameras at refineries and/or chemical plants. OI technology offers a means to overcome cost and efficiency issues at facilities where hundreds or thousands of components are to be monitored. An important step in R&D that is currently being discussed is a means to quantify the mass emission rate of detected leaks. The future appears promising. As OI is more widely used greater strides will be made in technology improvements, the more cost-effective it will become to detect and ultimately repair fugitive emissions leaks at refineries and chemical plants.

REFERENCES

1. American Petroleum Institute, "Analysis of Refinery Screening Data," Publication # 310, Washington, DC, November 1997.

2. McRae, T. G. and Kulp, T. G., "Backscatter Absorption Gas Imaging: a New Technique for Gas Visualization" *Applied Optics*, 1993, Vol. 32, 4037-4050.

3. Pacific Advanced Technology, "Sherlock Gas Leak Detection Camera," Santa Ynez, CA, 2003

Environmental Management Systems After Sarbanes-Oxley

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1.0 Introduction

The recent wave of corporate scandals involving Enron, WorldCom, Arthur Anderson, and others has had an enormous impact on investor confidence and produced federal legislation designed to halt the breaches of security laws, fiduciary duty, and financial responsibility. Congress responded to the spiraling decline of the stock market, levels of retirement funding, and investor confidence by passing legislation designed to curb corporate misconduct and restore investor confidence. The Sarbanes-Oxley Act of 2002[2] (SOX) was passed to make the financial information about publicly traded companies more accessible, more reliable, and more available to those who are responsible for corporate reporting and disclosures. This new regulatory posture has brought the need for accurate environmental disclose back into the spotlight with a new focus. Many corporations have begun to re-evaluate their internal procedures for assessing and disclosing environmental liabilities and the relationship of these procedures to financial disclosure requirements.

The primary sections of SOX that are of concern to environmental professionals set standards and higher levels of accountability for certification of financial reports and require attestation as to accuracy of internal controls and procedures for financial reporting. As a result of this higher level of accountability for top executives, the level of supervision and control over environmental issues is expected to significantly increase. Moreover, at the same time that these SEC reforms are forcing more corporate oversight, environmental management issues and systems have been experiencing increasing pressure from other directions. Some of this pressure comes from the following:

- formalization and industry-wide adoption of environmental management systems and review under ISO 14001,
- adoption of ASTM standards for estimating costs and disclosing environmental liabilities, and
- broader consideration of environmental management systems in the regulatory enforcement context.

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[2] The full text of the Act, H.R. 3763, is available at http://www.law.uc.edu/CCL/SOact/soact.pdf.

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Environmental and Other Issues Respecting Exploration For and Development of Sour Natural Gas in Alberta, Canada and Means to Address the Issues

Presented by:
J.D. (Jim) Dilay, P.Eng. - Board Member, Alberta Energy and Utilities Board (EUB)

ABSTRACT – ENVIRONMENTAL AND OTHER ISSUES – DEVELOPMENT OF SOUR NATURAL GAS IN ALBERTA, CANADA

Vast deposits of oil, gas, oil sands, coal and other resources underlie the Province of Alberta, Canada. A significant proportion of the gas contains hydrogen sulphide, which is extremely toxic in small concentrations and corrosive. Thus, the exploration for and development of this gas presents many special issues, including environmental ones. Recently, these issues were reviewed in a province-wide initiative that resulted in a large number of recommendations for action and change being presented to the Alberta Energy and Utilities Board (EUB), the province's energy regulator.

The paper will briefly review the extent of sour gas operations in the province. The sour gas regulatory system and requirements will also be briefly described. The paper will also review some of the more substantive recommendations, the status of them in terms of their implementation, and plans for the future.

Design Enhancements to Eliminate Sump Recrystalization in Zero-Emissions Non-Regenerative Desiccant Dryer

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ABSTRACT

Non-regenerative or deliquescing desiccant dryers can be an effective means to remove moisture from natural gas in transmission lines. A deliquescing desiccant dryer offers many advantages over traditional drying methods such as triethylene glycol dehydration. However, a problem exists with gas dryers and desiccants, in that the generally high concentrated solution of desiccant salt that drain into the sump tend to crystallize and come out of solution. The re-crystallized salt has a tendency to remain in the sump when the solution is drained. Gas transmission lines and dryers are placed throughout a wide range of climates and seasonal conditions. The problem of solids formation is more relevant in locations where temperatures are low, but even in warmer climates it presents itself because the salts will come out of solution in the cooler evening temperatures.

Design enhancements have added to the ease of using deliquescing desiccant systems due to patent pending technology which decreases the recrystalization in the sump section of the vessel while at the same time increasing the life of the desiccant bed. The method enables the brine water collected at the bottom of the vessel to make contact with the gas before it reaches the desiccant bed. The brine water is circulated using a technique that allows the incoming gas to pass through a mist of hydroscopic brine water. The hydroscopic brine water pulls water from the inlet gas prior to contact with the desiccant. The application of this technology resulted in a decreased or elimination of recrystalization in the sump area, and a decrease in desiccant consumption.

Solving the Next Impediment to Coal Bed Methane Development in the Powder River Basin

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ABSTRACT

Although viewed as a primary solution to our nation's energy problems, the in-situ extraction of methane from coal is a new technology and development is proceeding on a scale and pace that are unprecedented in arid regions of the western U.S. where much of this resource is located. A Record of Decision for the Powder River Basin (PRB) Oil and Gas Project has been signed, yet development of the additional 31,000 gas wells allowed under that decision may yet be at risk. With airborne particulates and regional haze already beginning to exceed existing air quality standards, the effect of over 20,000 miles of additional unpaved roads may soon exceed legal limits, imposing an early cap on further development. This paper summarizes applied research and outreach efforts underway to enable developers and county-road supervisors to deal with this problem cost-effectively.

International Petroleum Environmental Conference
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TEXAS EMS PROGRAM REQUIREMENTS
WITH RESPECT TO
ISO 14001:1996 AND RESPONSIBLE CARE

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ABSTRACT

The State of Texas has passed House Bill 2997 and House Bill 2912 that provides regulatory incentives for establishing and maintaining Environmental Management Systems (EMS). The Bill defines the minimum standards for a site's EMS and also the regulatory benefits that may accrue to an organization that establishes and maintains an EMS that is in accordance with the program. The Texas Commission on Environmental Quality (TCEQ) administers the program and will evaluate and determine if the organizations EMS system meets the requirements of the program. Those organizations that are evaluated and found to meet the criteria of the Texas EMS program will then be able to benefit from the incentives that the Bill provides.

The Texas EMS program has some similarities to ISO 14001:1996 and also to the Responsible Care program which is common in the chemical industry, but is different in emphasis (For example Regulatory Compliance and Performance Achievement). This paper will detail the provisions of the Program in non-legal language and will also show the similarities to ISO 14001:1996, Responsible Care and the differences. The Texas EMS rules are in Texas Administrative Code 30, Chapter 90, and Subchapter C: Regulatory Incentives for Using Environmental Management Systems.

OVERVIEW

The TCEQ EMS program has many similar elements as ISO14001 and RCMS, but it differs in several key ways. First the focus is more on performance. From the TCEQ Interim Audit Protocols: *"The TCEQ is providing regulatory incentives, some of which reduce regulatory oversight. The TCEQ is also responsible for environmental protection in Texas, and public trust is critical to the development of additional incentives and program success. For these reasons, the TCEQ rules and audit protocols are more focused on end results including both compliance and environmental performance, instead of only being focused on system or element auditing."* Second, the TCEQ program has differences in how the scope of the EMS must be defined (see below).

The diagram shows the overlap between TCEQ EMS Program and ISO 14001 and RC 14001

Anaerobic Bio-Oxidation of MTBE and 1,2-DCA

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ABSTRACT

Many hydrocarbons are biodegradeable by oxidation. This includes petroleum hydrocarbons, di- and mono-substituted halogenated hydrocarbons, and other xenobiotic hydrocarbons such as MTBE. In addition to aerobic, anaeriobic bio-oxidation processes can be stimulated using alternate electron acceptors such as nitrate, ferric iron, or sulfate.

A field scale anaerobic bio-oxidation system has been designed and installed at a large storage terminal along the Houston Ship Channel. A discrete plume of MTBE and a mixed plume of benzene and 1,2 DCA are the focus of a remediation program. Each of the constituent systems were evalatued in two bench scale design studies in which the bio-oxidation systems tested included: oxygen; nitrate; ferric chloride; ferric sulfate; sodium sulfate; and humate-catalyzed ferric chloride and ferric sulfate. Data descibing the heterogeneitc response to these stimulation regiems will be presented from the bench scale design study and the on-going field pilot applications.

Source Zone Natural Attenuation Investigations at a Former Oil Field

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ABSTRACT

Spills of petroleum often create "source zones" for groundwater pollution. Source zones are petroleum-impacted soils that are either in direct contact with groundwater, or are in indirect contact through dissolution and soil moisture infiltration. The transient behavior of source zones is a determining factor of the longevity and character of dissolved phase plumes. A groundwater plume of dissolved petroleum will persist as long as the associated source zone exists, although the chemical character of the dissolved phase will change as the petroleum in the source zones weathers.

At the former Guadalupe Oil Field in California, source zone natural attenuation is the focus of field and laboratory investigations. Source zone mass loss processes and their rates are being assessed by acquisition of data from nested groundwater wells and soil gas probes around several large source zones. By quantifying fluxes of electron acceptors and degradation products in groundwater and soil gas, mass loss rates are being estimated. Current rates of mass loss related to gas diffusion through the vadose zone are much greater than those related to dissolution and dissolved phase electron acceptor transport. In addition, vertical chemical profiles through the source zones provides evidence of chemical weathering and suggests the long-term effects expected throughout the source zones.

Misconceptions Concerning the Behavior, Fate and Transport of the Fuel Oxygenates TBA and MTBE

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ABSTRACT

The release of gasoline from underground storage tanks and the subsequent appearance of dissolved constituents in drinking water has led to misconceptions about the behavior of fuel oxygenates in storage and in the subsurface. Critical review of several misconceptions about methyl-tertiary-butyl ether (MTBE) and tert-butyl alcohol (TBA) in gasoline reveals the concepts were conceived to rationalize early field observations and/or incomplete data sets. Closer scrutiny, in light of recent laboratory investigations, field data, case studies and world literature, clarifies these misconceptions and assumptions about the behavior of ether oxygenates and their degradation products in the environment. Commonly held misconceptions focus on four general areas of fuel and fuel oxygenate management: storage/dispensing, hydrology, remediation, and health effects. Generally MTBE and TBA are manageable by the same processes and precautions used for gasoline and other fuel hydrocarbons. Indeed specific physical properties of ethers and alcohols expedite their treatment by traditional remediation methods of pump and treat, soil vapor extraction and bioventing.

Co-Composting of PAH-Contaminated Soil With Poultry Manure

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ABSTRACT

Mispah form (FAO: Lithosol) soil contaminated with PAHs was co-composted with poultry manure for nineteen months. The soil was mixed with wood chips to improve aeration and then mixed with poultry manure in a ratio of 4:1. Moisture, temperature, pH, ash content, C:N ratios, and the concentrations of selected PAHs in the compost were monitored monthly. Temperature increased to 60°C in the poultry manure compost within three months before decreasing to about 45°C and then fluctuating between 35 and 50°C, while temperature in the control remained about 30°C for most of the composting period. PAHs concentrations decreased by between 96% and 100% at the end of the composting period. The 2- and 3- ring PAHs were more easily degraded while the 4- and 5- ring compounds were more recalcitrant, persisting until the end of the composting. The consortia of microorganisms isolated from the compost system included fungi, bacteria and actinomycetes. Microbial activity, monitored by CO_2 evolution correlated with reduction in PAHs concentrations.

INTRODUCTION

Compost bioremediation is carried out by co-composting the contaminated soil with suitable compost materials to effect biodegradation of the contaminant. Previous studies have examined the degradation of organic pollutants in composts (Reid *et al.,* 1999). For example, it has been shown that the microbes present in windrow composts are capable of mineralizing pentachlorophenol (Valo and Slakinoja-Salonen, 1986). Although composting has been used in the remediation of soils contaminated with a number of organic compounds, including PAHs, the use of composting as a bioremediation technology has been given very little attention (Potter *et al.,* 1999). Much of the work on treatment of contaminated soils by composting (Valo and Slakinoja-Salonen, 1986; Potter *et al.,* 1999; Reid *et al.,* 1999) has been done on soils with lower concentrations of the contaminating substance than were present in the present study, in spite of the fact that composts have been reported to have good potential for remediation of heavily contaminated sites (Reid *et al.*, 1999).

The soil used for this study is a mispah form (FAO: lithosol) contaminated with a wide range of PAHs among which the most prominent are naphthalene 158mg kg^{-1}, anthrecene 72.3mg kg^{-1}, phenanthrene 256 mg kg^{-1}, fluorene 68.3mg kg^{-1}, pyrrole 77.3mg kg^{-1}, pyrene 182.1 mg kg^{-1}, fluoranthene 188.5mg kg^{-1}, chrysene 93.3 mg kg^{-1} and benzo(a)pyrene 68.4 mg kg^{-1}. These high levels of PAHs provided a good opportunity to study and further understand the potentials of composting in soil bioremediation. Earlier, studies (Atagana, 2002; Atagana, 2003) showed that reasonable amounts of higher molecular mass PAHs remained in the soil at the end of 16 weeks and 11 months of pilot-scale and full-scale landfarming respectively. This study intends to exploit the high temperatures prevalent during composting, the high nutrient contents of poultry manure and the heavy microbial load of the compost system in enhancing the biodegrataion of high molecular weight PAHs in the soil system under investigation.

The aim of this study therefore is to investigate the effects of co-composting poultry manure with soil contaminated with different concentrations of polycyclic aromatic hydrocarbons (PAHs), on the degradation of selected PAHs in a static-pile compost system. It is also study the temperature regimes in the compost system and the changes in nutrient composition and moisture

occurring therein, during the treatment period. This would help determine the requirements of the compost type and its practical application on large-scale treatment of PAHs-contaminated soils. The remediation target set in this experiment was 1 mg kg^{-1} for the selected PAHs.

MATERIALS AND METHODS

About 2 000kg of PAHs-contaminated mispah form (FAO: lithosol) soil were excavated from the experimental site and transported in clean nylon fibre bags to the laboratory, where it was stored in a cold-room at 4 ^{O} C. Samples of the soil (250g each) were taken to an independent commercial laboratory for determination of the PAHs concentrations by GC/FID. The bulk soil was homogenized in an electric concrete mixer before being used to make the soil compost mixture. Poultry manure and hay for covering the compost heaps were obtained from the University of Natal Experimental Farm, Ukulinga, Pietermaritzburg. Compost heaps were made on slatted, sawn wood pallets overlaid with nylon fibre bags, which allowed passage of air and excess water in and out of the compost heaps.

Homogenized contaminated soil (350 kg) was mixed with wood chips (20cm x 4cm) in a ratio of 1:1 (v/v) and then mixed with poultry manure in ratio of 4:1(contaminated soil + wood chips : compost material) (v/v). The experiments were set up in triplicates. The control was a mixture of contaminated soil and wood chips without poultry manure. The mixtures were placed on a palette and covered with hay for insulation. The experiments were incubated for a total of nineteen months.

A temperature data logger with thermocouples located in the middle of the compost heaps measured temperature hourly. Moisture content was measured weekly and water added as necessary. The pH of the compost mixture was measured at monthly intervals in triplicate by using a standard pH meter (Crison Micro pH 2000^{TM}). The ash content of the compost mixture was determined at the start and at the end of the experiment by heating 10g of the mixture in a furnace at 400°C for 6 hours.

Respiration rates of compost-inhabiting microorganisms were determined by the closed jar method (Forster, 1995). Microbial plate counts of samples taken from three different levels (20cm, 35cm, and 50cm) in the compost heaps were done on nutrient agar and represented as colony forming units per gram (cfu g^{-1}). Total organic carbon, extractable phosphorus and total nitrogen were determined by the University of Natal Chemistry Department and KwaZulu-Natal Department of Agriculture, Cedara.

Changes in the concentrations of PAHs were determined by Soxhlet extraction and GC/FID. The GC was a Varian-3800 with argon as the carrier gas and fitted with a 3m capillary column with 0.25μm film thickness. Two temperature programmes were used (Eriksson *et al.*, 2000) in order to obtain good separation and quantification of the more volatile compounds.

Identification of bacterial isolates was done by biochemical tests using Buchanan and Gibbon's Bergey's Manual of Determinative Bacteriology and MacFaddin's Biocemical Tests for Identification of Medical Bacteria. Fungal isolates were identified by microscopic examination with reference to Barnett and Hunter's illustrated genera of imperfect fungi and Raper and Thom's manual of the penicillia.

RESULTS AND DISCUSSION

Changes in pH of The Compost During Composting

The pH of the compost and the control increased in the first four months reaching 8.4 in the compost and 7.6 in the control. The compost pH decreased after the fifth month reaching 6.6 in the ninth month before increasing again to 7.6 in the thirteenth month. The decrease after the thirteenth month was gradual and reached 6.7 at the end of the experiment. The pH of the control followed the same pattern of decrease and reached 6.3 at the end of the experiment. For most of the experiment the pH remained between 6.2 and 7.6, which is well within the recommended

range for composting organic materials (Hunter et al., 1981; Kubota and Nakasaki, 1991). The increase in the first four months could be due to the high ammonium content of the poultry manure. The decreases observed in subsequent months are attributed to the degradation of the compost and the hydrocarbons, which resulted in the release of intermediate and final products that probably had lowering effects on the pH of the mixture (Alexander, 1999; Lee and Lee, 2001; Piccolo, 2002).

Changes in The C:N Ratio of The Compost During Composting

A relatively high nitrogen concentration (C:N 25:1 to 35:1) is required to facilitate the effective compost bioremediation (Anderson, 1991; Kubota and Nakasaki, 1991). The C:N ratio in the present study is shown in Tables 1 and 2. The initial C:N ratio of the contaminated soil was 306:1. this ratio was considerably reduced after mixing with wood chips and poultry manure (Table 2). Although the nitrogen content in these C:N ratios are higher than those recommended by Anderson (1991), they are considered adequate for composting organic materials, considering the amount of compost materials used. The C:N ratio in the compost and control changed as the incubation progressed (Table 2). The decrease in nitrogen content in the compost was faster than in the control probably due to higher microbial activity and higher rate of breakdown of the hydrocarbon substrate in the poultry manure compost than in the control.

There was only a slight change in ash component of the compost mixture (4.1 to 4.15) and the control (6.37.6.41), which indicates that there was no significant change in the mineral components of the soil at the end of the experiment.

Microbial population and PAH degradation

The results show that there was a significant difference between the poultry manure compost and the control in the degradation of the PAHs (Fig. 1-9). The poultry manure microflora removed the PAHs faster than the control. Poultry manure has been reported to enhance the degradation of hydrocarbons in soil-compost mixtures (Hill and McCarthy, 1967; Deever and White, 1978). The rapid degradation observed in the compost was expected since poultry manure is rich in carbon and mineral nutrients particularly nitrogen (Kellog-Johnson, 1996). The organisms growing on the nutrients present in the poultry manure were found to readily metabolise the contaminant PAHs in the compost mixture while still growing on the manure. The manure afforded the organisms the opportunity to grow while adapting to the hydrocarbons. It also afforded the organisms the opportunity to produce enzymes that are required to metabolise hydrocarbons in the compost matrix (Sutherland, 1995; Bardos et al., 1996; Diaz et al., 1996). The high microbial load in the compost (7.39E+05) at the start of the composting afforded the population the opportunity to remain high while adapting to and attacking the hydrocarbon substrate.

During the second month of the experiment, counts of heterotrophic microorganisms increased from 7.39E+05 to 3.67E+07 in the compost mixture. During the same period, the largest amounts of reduction in hydrocarbon concentrations were observed (Fig. 1-9). This population increase is probably attributable to the abundance of readily available nutrients in the manure. It can also be attributed to the loss of excess nitrogen as gaseous ammonia (Piccinini *et al.,* 1996). High nitrogen content in soil can be inhibitory to microbial growth, affecting the rate of hydrocarbon degradation (Baker and Herson, 1994; Alexander, 1999). Increase in microbial populations and rapid degradation of some of the hydrocarbons continued after the fourth month probably due to further loss of nitrogen as a result of the increased microbial activity and high temperatures (60°C) reached at the start of the treatment (Piccinini *et al.,* 1996). The population reached a maximum of 4.88E+07 in the eight before it started to decrease, probably as a result of increasing release of ammonia during decomposition of the manure, which eventually became toxic to the microorganisms, explaining the decline in the microbial population to 3.88E+07 in the ninth month. The high temperatures generated by the decomposing manure, which resulted in

the increased loss of water from the soil-compost matrix may also have resulted in the decrease in microbial population after the eighth month (Fan and Tafuri, 1994). Regular watering when necessary kept the temperature from increasing higher than 60°C. The 2- and 3- ring PAHs (naphthalene, anthracene, phenanthrene and pyrrole were removed the remediation target of 1 mg kg^{-1} by the third and fourth months (Fig. 1-4) except for fluorene, which persisted until the seventh month (Fig. 5). Degradation of 4- and 5- ring PAHs (pyrene, chrysene, fluoranthene and benzo(a)pyrene became slower from about the eighth month (Fig. 6-9) and residual concentrations of chrysene continued to be above 1 mg kg^{-1} until the sixteenth month (Fig. 7). A decrease in temperature in the poultry manure-contaminated soil mixture in the fifth month from 60 to 45°C resulted in an increase in microbial population from 3.7E+07 to 4.12E+07 and subsequently an increase in removal of pyrene, chrysene and fluoranthene (Fig. 6-8). The effect only became evident in benzo(a)pyrene in the sixth month (Fig. 9).

Respiration of compost-inhabiting microorganisms (Fig. 10) and counts of heterotrophic microorganisms showed that microbial activity correlates with hydrocarbon degradation. Although the rapid increase in microbial activity in the first month did not translate into a similar amount of loss in hydrocarbon concentration, the effect of this increase manifested in the second month. This delayed effect is attributed to the time used by the organisms to adapt to the hydrocarbon medium and also other factors such as high initial nitrogen content and high temperatures as discussed earlier.

The removal of PAHs from the control experiment was similar to the compost system in the first month (Fig.1-9). However, while degradation continued very slowly for the rest of the experimental period in the control, degradation in the compost system increased rapidly from the second month.

In comparison to earlier studies using the same contaminated soil in which more than 20% of the 4- and 5- ring PAHs persisted at the end of eleven months of treatment (Atagana, 2003), all the PAHs except chrysene were removed to below the remediation target (1 mg kg^{-1}) by the eleventh month in the present experiment. The experiment was extended for six months during which period chrysene was degraded to below the target concentration. However, the experiment was extended for a further three months to achieve complete degradation of the compounds. It was observed that degradation became very slow after the fourth month for the 2- and 3- ring PAHs and after the eighth month for the 4- and 5- ring PAHs and in many cases, traces of the compounds (0.1-0.5 mg kg^{-1}) persisted until the end of the treatment period. This slow degradation is attributed to the very low concentrations of the PAHs remaining in the soil at those times. Eartlier reports have suggested decline in hydrocarbon degradation by soil microorganisms at very low concentrations (Baker and Herson, 1994; Alexander, 1999). This may also be due to incomplete desorption of the sorped hydrocarbon molecules to soil particles.

Contrary to expectations, high nitrogen content and high temperatures had limited effects on the microbial load and degradation capacity of the compost probably due to the reasons discussed earlier.

At the start of composting, a mixed population of bacteria and fungi dominated the compost. The dominant bacteria isolates were *Pseudomonas* sp., *Bacillus* sp., *Rhodococcus* sp. and *Mycobacterium* sp. among others that were not readily identified. The dominant fungal isolates were *Mucor, Rhizopus, Fusarium, Aspergillus, Penicillium and Pleurotus*. By the end of the fourth month, the dominant species were mainly fungi with *Pleurotus*, becoming more prominent. *Fusarium* and *Aspergillus* and *Penicillium* persisted in relatively low amounts but *Mucor* and *Rhizopus* were not evident any more. *Phanerochaete* was also isolated after the fourth month. Three *Pseudomonas* species and A*rthrobacter* sp. were isolated after the fourth month. Although there was a dynamic change in the microbial population of the compost system during the composting period, *Pleurotu, Phanerochaete, Fusarium, Pseudomonas and Arthrobacter* were the most persistent species that were identified.

CONCLUSIONS

Although poultry manure has been found to accelerate the composting of garden refuse, its application in bioremediation has not been fully explored. The results in the present experiment have shown that under controlled conditions co-composting of poultry manure with contaminated soil can effectively decontaminate soils heavily contaminated with PAHs. A temperature range of between 35 and 60OC is effective for composting hydrocarbon pollutants in soil with poultry manure.

REFERENCES CITED

Alexander, M., Biodegradation and bioremediation, San Diego, Academic Press (1999).

Anderson, J.G., Treatment of wastes by composting. In Senior, E. (ed), Microbiology of Landfill Sites. Boca Raton, CRC Press Inc., pp. 59-77. (1991).

Atagana, H. I., Bioremediation of creosote contaminated soil: A Pilot-scale landfarming evaluation. *World J. Microbiol and Biotechnol* 19: 571-581(2003).

Atagana, H.I., Bioremediation of creosote-contaminated soil by microbial intervention. A Ph.D. dissertation submitted to the University of Natal, Pietermaritzburg, South Africa (2002.).

Baker, K.H. and D.S., Herson. Bioremediation. McGraw-Hill, Toronto (1994).

Bardos, R.P., Forsythe, S., Westlake, K., The co-treatment of municipal and industrial waste. In M. de Bertoldi, P. Sequi, B. Lemmes and T Papi (eds), The Science of Composting. Blackie Academic and Professional, London. pp. 767-783 (1996).

Barnett, H.L. and Hunter, B.B., Illustrated genera of imperfect fungi. USA, Burgress Publishing, (1972).

Deever, W.R. and White, R.C. 1978. Cited by Wilson, G.B. Sikora, L.J. and Parr, J.F., Composting of chemical industrial wastes prior to land application. In Parr, J.F., Marsh, P.B. and Kla, J.M. (eds), Treatment of hazardous wastes, Noyes Data Corporation, New Jersey, pp. 263-273 (1983).

Diaz, L.F., Savage, G.M. and Golueke, C.G., Stabilization of hazardous wastes through biotreatment. In de Bertoldi, M., Bert, P. and Tiziano, P. (eds), The Science of Composting. Blackie Academic and Professional, London, pp. 1152-1156 (1996).

Eriksson, M., Dalhammar, G. and Borg-Karlson, A.-K., Biological degradation of selected hydrocarbons in an old PAH/creosote contaminated soil from a gas work site. *Appl Microbiol Biotechnol.* 53: 619-626 (2000).

Hill, D.W. and McCarty, P.L., Anaerobic degradation of selected chlorinated pesticides. *J. Water Poll. Cont. Fed.* 39: 1259-1277 (1967).

Hunter, J.V., Finstein, M.S., Suler, D.J and Bopal, R.R. 1981. Cited by Feinstein, M .S., Miller, F.C. and Strom, P.E., Waste treatment composting as a controlled system. In Rhelm, H.J.and Reed, G. (eds), Biotechnology Vol. 8 Microbial degradation. VCH Publishers, NY. 363-398 (1986).

Kubota, H. and Nakasaki, K., Accelerated thermophilic composting of garbage. *BioCycle* 32: 66-68 (1991).

MacFaddin, J.F., Biochemical tests for identification of medical bacteria, Baltimore, (1980).

Piccinini, S., Rossi, L., Bonazzi, G. and Dall= Orso, G., The Emilia-Romaga Experiment in animal manure composting. In M. de Bertoldi, P. Sequi, B. Lemmes and T Papi (eds), The Science of Composting. Blackie Academic and Professional, London. pp. 1275-1280 (1996).

Potter, C.L., Glaser, J.A., Hermann, R. and Dosani, M.A., Remediation of contaminated East River sediment by composting technology. In A. Leeson and B.C. Alleman (eds), Bioremediation technologies for polyclic aromatic hydrocarbon compounds. The fifth international *in situ* and on-site bioremediation symposium. San Diego, California, April 19-22, 1999. Battelle Press, Columbus. pp. 31-36 (1999).

Raper, K.B. and Thom, C., A manual of the penicillia. New York, Hafner Publishing Co., (1968).

Sutherland, J.B., Rafti, F., Khan, A.A. and Cerniglia, C.E., Mechanisms of polycyclic aromatic hydrocarbon degradation. In: Microbial transformation and degradation of toxic organic chemicals (Eds) Young, L.Y. and Cerniglia, C.E. Wiley Liss, New York. pp 269-306 (1995).
Valo, R. and Salkinoja-Salonen, M., Bioremediation of chlorophenol-contaminated land. *Appl. Microbiol. Biotechnol.* 25: 68-75 (1986).

Table 1. C:N ratios of contaminated soil and poultry manure before mixing. Values are means of three ± 1 standard Deviation.

Compost materials before mixing	**C (g kg^{-1})**	**N (g kg^{-1})**	**C:N**
Contaminated soil	24.53 x 10	0.08 x 10	306:1
Poultry manure	36.03 x10	3.63 x 10	10:1

Table 2. Changes in C:N ratios of compost mixtureduring incubation. Values are means of three ± 1 Standard Deviation.

Compost-soil mixture	**0 Time**	**6 Months**	**12 Months**	**18 Months**
Contaminated soil (Control)	306:1	326:1	322:1	289:1
Poultry Manure Compost	2:1	3:1	5:1	8:1

PHYTOREMEDIATION POTENTIAL OF *AMARANTHUS SP.* FOR HEAVY METALS CONTAMINATED SOIL OF OIL PRODUCING TERRYTORY

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It is well established that all higher plants can accumulate heavy metals in different concentrations. However, significant differences in metal accumulation were shown between and within plant populations. There are an indications in the literature that amaranth plant species may accumulate heavy metals in their organs. In our investigations 7 subspecies of Amaranthus, *A. hibridus, A. paniculatus, A. hypochondriacus, A.tricolor, A. retroflexus* and two hybrids *between A. hybridus and A. hypochondriacus, K-343 and K-422*, were used. Seeds of these subspecies were obtained from the "Amarant" scientific-technical corporation (Russia) and the Institute of Botany and Phytointroduction of Kazakh Science Academy in Almaty.

Materials and Methods

The following salts of heavy metals were used in our study: Cd $(CH_2COO)_2 . 2 H_2O$; HgC_{12}; $NiSO_4$; $ZnSO_4.7H_2O$) and $CuSO_4.5H_2O$. For coloring the heavy metals the reagent 4-(2-pyridilazo) -resorcin was used.

1.Seeds of these plants were grown in laboratory and field conditions. In laboratory seeds were germinated on filter paper in Petri dishes, then transferred to the hydroponic dishes with Knopp growth medium, and also in the pots with natural soils of Almaty region (pH 6.3). Since the growth of amaranth plants in Knopp growth medium is not natural, in our research the main attention was paid to the growth and development of amaranth plants in the natural conditions. Plants were grown in the room temperature at 23^0 C and with 14 hrs light period. For analysis the samples of plant material were harvested on 10, 20 and 30 days after planting. Length of roots and leaves, total fresh and dry weights of the seedlings and whole plants were determined and their viability were estimated. These experiments were carried out with 5 parallel replications.

2. Laboratory experiments. Seeds of amaranth plants were grown in flowerpot containing 1 kg of soil, according Z.Zhurbickii (1). Soils preliminarily mixed thoroughly with water (distilled) solutions of heavy metals achieving their following concentrations in soil: Cd - 50, 75 and 100 mg/kg dry soil (DS); Cu - 75, 100 and 150 mg/kg DS and Zn - 150, 225 and 300 mg/kg DS.

Preliminary growth experiments on filter paper showed that the concentrations of Cd higher than 125 mg/l of water, Cu - 175 mg/l and Zn - 350 mg/l inhibited seed germination and growth of the plants. Control soils were mixed with the same volume of distilled water and also were thoroughly mixed. Plants were grown for 120 -145 days after planting. These experiments were carried out using 3 parallel replications.

3. In order to study the changes of heavy metal content in such an artificially contaminated soils: (a) whole plants were removed from soils (from water, in case of hydroponica) after vegetative (35-40 days), bud forming (25-30 days) and flowering (40-50 days) stages and their fresh and dry weights were determined; (b) then the soils (or hydroponica water) were removed from pots and mixed thoroughly; (c) after drying in certain soils mass (or in 10 ml of hydroponic water) the content of heavy metals were determined. Control soils (or hydroponic water) with different concentrations of heavy metals were kept without planting throughout the experimental time (these soils regularly cleaned up from any weeds appeared). In control soils at corresponding stages also determined the content of heavy metals. In such control soils (water) the content of heavy metals were not changed during 145 days experiments.

4. Field experiments were carried out in the "Ecos" agrobiostation of Al-Farabi Kazakh State university in Almaty. Seeds of amaranth plants were grown in porous bags containing 10 kg of soil. Such a bags were

placed into the field soil according to the method of U.V. Alekseev (2). Seeds of amaranth were planted in first quarter of Mai 1999 and 2000. Growth bags were irrigated regularly every 7 days using the water-spraying tractor. These experiments were carried out using also 3 parallel replications.
Content of heavy metals was determined by using the atomic-absorption spectrophotometer AAS-IN (Karl Zeiss, FRG). From plant material and soil the heavy metals were extracted by the method of dry and humid mineralizing.

Effects of heavy metals on amaranth plants growth and their accumulation in the plant organs.

Seed germination and seedling growth are the critical stages of plant development. First of all we investigated seed germinating ability and viability seedlings of seven subspecies of amaranth plant under different concentrations of heavy metals such as Zn, Cu, Cd, Hg and Ni. Seeds of different subspecies of amaranth were grown on filter paper moistened with water solutions of different heavy metal concentrations. Results of our experiments showed that among the seven subspecies of amaranth mentioned above, *A. paniculatus, A. tricolor, A. hypocondriacus* and *hybrid K-343* were able to germinate and grow under corresponding high concentrations of heavy metals. Further, the growth of seedlingsof *A. paniculatus* and *A. tricolor* were more tolerant to heavy metals than *A. hypocondriacus* and *hybrid K-343*. According to the results relative high 300 mg/l concentrations of Zn and Ni slightly improved the growth of amaranth seedlings, whilst the 125 mg/l concentrations of Cd and Hg inhibited seed germination and seedling development. Phytotoxic concentrations of heavy metals are shown in the Materials and Methods. Toxicity range of heavy metals for seed germination and seedling growth of amaranth plants was determined as: Hg > Cd > Cu > Ni > Zn.
Since in Kazakhstan the populations of two amaranth subspecies *A. paniculatus* and *A. tricolor* are widespread and Cd, Cu and Zn are more important pollutants in the industrial regions, further experiments were carried out with these heavy metals using the Kazakh populations of these two amaranth subspecies. We studied therefore the effects of increased concentrations Cu, Cd and Zn on the growth and development of the subspecies of amaranth. Growth rate and biomass production of amaranth plants were used for determination of the toxic levels of heavy metals. Considerable effects of high concentrations of heavy metals were observed during the early stage of plant development. At concentrations of Cd 125 mg/kg and Cu 175 mg/kg the germination of amaranth seeds decreased by 20-30%.
Zink (Zn). Control seeds in water germinated in 4-6 days, whilst at high concentrations of heavy metals (Hg and Cd - 100, Cu - 150, Cu and Ni - 300 mg/l), it observed in 7-9 days after planting. During ontogenesis of plants the heavy metals showed different effects. At vegetative phase (in 1.5 month) Zn in concentrations of 200-300 mg/kg markedly stimulated the growth of amaranth, particularly *A. Tricolor.* The maximum biomass production of leaves (113% compared to the control plants) was observed in these concentrations of Zn. At the same time at Zn concentrations of 225 - 300 mg/kg the growth rate of amaranth roots was more slowly. However, at flowering stage these concentrations of Zn resulted in the minimum biomass production (95% of control plants), i.e. the maximum biomass production was occurred in vegetative and bud formation stages of plant development. At the flowering stage of plants the concentration of Zn of 150-200 mg/kg was optimal for maximal biomass production (106% of control plants). Thus, in our experiments among the heavy metals used, Zn only at higher concentrations showed stimulating effect on the growth and biomass production of A. tricolor and A. paniculatus.
Further we investigated the accumulation of Zn in the roots and aerial parts of amaranth. Our results showed that in these parts of plants the maximum metal accumulation was observed at vegetative and bud formation stages of plant development. Whilst at the flowering stage the increase of Zn content in the organs was negligible. At this stage amaranth subspecies were found to be more sensitive to higher concentrations of Zn than 300 mg/kg of soil.
In next experiments we studied the changes of Zn content in amaranth-growing soils in pots. In this case the soils containing 300 mg Zn/kg were analyzed in detail. At vegetative phase of plant development in soil with growing A. paniculatus, the metal content decreased to 245 mg/kg of dry soil (DS). At flowering stage the decrease of metal content in soil reached 149 mg/kg DS. In the case of A. tricolor at vegetative phase the metal content in soil decreased to 230 mg/kg DS, and further at flowering stage it was 126 mg/kg DS. Thus, A. tricolor was found to be more effective Zn-accumulator compared to A. paniculatus, and by

the end of bud formation and at the beginning of flowering stage the plants accumulated maximum content of the metal in their organs. During the bud formation stage copper at concentration of 100 mg/kg DS and higher begun to be phytotoxic for amaranth plants inhibiting their further growth and biomass production. As a result of such inhibition the flowering of plants begun to 10-15 days later than that of control plants. Levels of Cu accumulation in the roots and aerial organs of amaranth were positively correlated with the metal content in soil. A. paniculatus accumulated more Cu in its organs than A. tricolor. During flowering stage the roots of A. tricolor grown in soil containing 150 mg Cu/kg accumulated the metal up to 3.1 g/kg DW, whilst that of A. paniculatus accumulated 3.5 g/kg DW. Throughout all the stages of development of amaranth plants their roots were found to be the main metal-accumulating organ. Roots, stem and leaves accumulated 2.1 mg, 7.0 mg and 5.0 g/kg DW, respectively. At flowering stage in the roots of control plants of A. paniculatus grown in soils without Cu the metal content was 41,4 times less, and in those of A. tricolor - 14.4 times.

As a result of Cu uptake and accumulation of the metal by amaranth plants, the metal content in soil progressively decreased with plant growth. At vegetative stage of development of A. paniculatus, Cu content in growth soil decreased from original 150 mg/kg DS to 123 mg/kg DS, and then at flowering stage - to 84 mg/kg DS. Whilst, at flowering stage A. tricolor decreased the metal content in growth soil to 90 mg/kg DS. Thus, A. paniculatus decreased Cu content in its growth soil almost 2 times and A. tricolor - 1.6 times.

Cadmium. Though Cd is chemically analog of Zn, its phytotoxicity is considerably higher than Zn. At higher concentrations Cd may replace Zn in an active center of several enzymes inhibiting their catalytic activities, and as a consequence plant development. During the vegetative stage Cd concentrations up to 100 mg/kg DS did not show any negative effect on plant development. However, from the bud formation stage Cd concentrations of 75 - 100 mg/kg DS showed toxic effects on amaranth roots. Furthermore, these concentrations of the metal delayed the formation the buds to 8-10 days.

Determinations of Cd content in different organs of amaranth plants grown in Cd-containing and control soils showed that this metal accumulated mostly in roots and the in leaves. Accumulation of Cd in the organs of A .paniculatus was higher than A. tricolor. For example, at flowering stage Cd content in roots of A. paniculatus was 9.0 g/kg DW, and in those of A. tricolor it was 7.0 g/kg DW. In roots of control plants grown in soils without Cd the content of the metal was between 0.2 - 0.5 g/kg DW.

Further the role of amaranth plants in the changes of Cd content in soils were studied. Planting and growing of amaranth plants in Cd-containing soils resulted in gradually decrease of heavy metal content in the soils. The plants were grown in soils containing 100 mg/kg of Cd. At vegetative stage of A. paniculatus Cd content in soil decreased to 78 mg/kg DS, and further, at flowering stage it decreased to 49 mg/kg DS. Whilst A.tricolor at flowering stage decreased Cd content in soil to 63 mg/kg DS. Thus, at flowering stage of the plants Cd content in the soil of A. paniculatus- decreased 2 times, and of A. tricolor it was 1.4 times.

Results of field experiments

Field experiments were carried out according to the Materials and Methods. As in laboratory experiments, in the field conditions higher concentrations of Zn showed the same effects on plant growth and development. Height of aerial part, length of roots and biomass production of flowering A. paniculatus grown in soil containing 300 mg/kg DS, Zn contents were 105%, 90% and 108% of control plants, respectively. This result showed that at later stage of plant development the heavy metal begun to inhibit root growth, but not of aerial organs. Whilst biomass production of A. tricolor at the same conditions dramatically increased, i.e. it was 182% compared to the control plants. It is necessary to note that amaranth plants grown in field conditions with high concentrations of Zn had dark-green colored leaves with larger surface and thicker stems compared to the control plants grown without the metal.

In field conditions for both amaranth subspecies the main organs accumulating Zn were their roots and then leaves. As in the case of laboratory experiments, in the field conditions A. tricolor showed more effective accumulation of Zn than A. paniculatus. During plant development the content of the metal in their roots and leaves gradually increased. At vegetative stage *A. tricolor* accumulated from 650 mg/kg to 690 mg/kg DW of Zn. Effective uptake and accumulation of Zn by amaranth were observed at vegetative and bud formation stages of plant development. At flowering stages the increase of metal accumulation was negligible. After flowering stage of amaranth the content of Zn in plant-grown soils (in bags) was

determined. As mentioned above, originally these soils had Zn concentration of 300 mg/kg DS. At vegetative stage of plant development in soil of *A. paniculatus* the content of Zn decreased to 183 mg/kg DS, whilst in the case of A. tricolor - it decreased to 165 mg/kg DS. Further, in flowering stage these indications were 98 and 74 mg/kg DS, respectively. It is necessary to note that maximum accumulation of the metal by amaranth plants was observed during bud formation stage and at the beginning of flowering. In field conditions all the plants showed more improved growth and development than in model experiments carried out in laboratory conditions. Effects of cutting of the apical parts of amaranth plants on their heavy metal accumulating ability. It is known that the prune (cut) of stem apex causes the intensive growth of lateral branches (limbs). Moreover, K.S. Safarov and coworkers (3) using this approach increased the biomass production amaranth plants. In the next field experiments, at the end of vegetative stage, we cut the stem apex of amaranth plants. Central stem apex was cut 1 cm below than apical bud. It resulted in the increase of density and growth rate of lateral branches in aerial part of amaranth, and as a consequence the biomass production also considerably increased. After such a cutting of the apex, at the end of bud formation stage the total plant biomass of A. paniculatus increased to 121% compared to the control plants, whilst A. tricolor - to 133%. Our experiments showed that the removal of stem apex of amaranth plants at the beginning of bud formation stage definitely resulted in the increase of Zn accumulation in the roots and leaves. At flowering stage the roots of A. tricolor without apex accumulated the metal up to 650 mg/kg DW and leaves - up to 690 mg/kg DW. In the same conditions the roots and leaves of A. tricolor accumulated up to 1,5. and 1,8g/kg DW, respectively. The content of Zn in growth soil decreased more effectively by amaranth plants without apex. At flowering stage *A. tricolor* without apex decreased Zn content in soil up to 40 mg/kg DS. Thus, the removal of apical part of amaranth plants significantly increases Zn accumulation and decreases the metal content in growth soil. *A.tricolor* accumulated Zn more then 30-40 time then control plants and *A.paniculatus* accumulated Cd more then 5--60 time then control plants.

The use of special technology (see below) we can increase accumulation ability of A.tricolor on one order and take line of *A.tricolor* which accumulation ability of Zn to 10-15g/kg DW .

The following experiments are in progress:

1. Seeds of two amaranth subspecies were treated using the method priming. Priming carried out with use of water extract of biohumus (WBH). Their germination ability and growth rate, the metal accumulating abilities of their cut forms are being studied in contaminated soils of oil production area (Caspian see region).
2. Two given amaranth subspecies are being grown in higher concentrations of Cd and Cu. Effects of presowing treatments on accumulation of these metals are also being studied.
3. Effects of application of EDTA to soil on heavy metal uptake and accumulation by the amaranth plants are being studied.
4. Experiments of 1, 2 and 3 are being carried out in different combinations.
5. Contaminated soils from oil production sites are being used for phytoremediation by amaranth plants.

REFERENCES CITED

1. Zhurbickii Z.I . The Theory and practice of vegetative methods. 46-68, Moscow, Nauka (1968).

2. Alekseev U.V.,. Heavy metals in soil and plants. 25-65, Leningrad., Agropromizdat (1987)

3. Safarov K.S., Musaev D.A., Sultanov A.S, Usupov Ch., "Studying of morphobiologycal and economic characters of amaranth for creation of a genetic collection," presented at the International scientific conference Biology and ecology of agricultural plants, Tashkent, Uzbekistan (February, 15-18 , 1995).

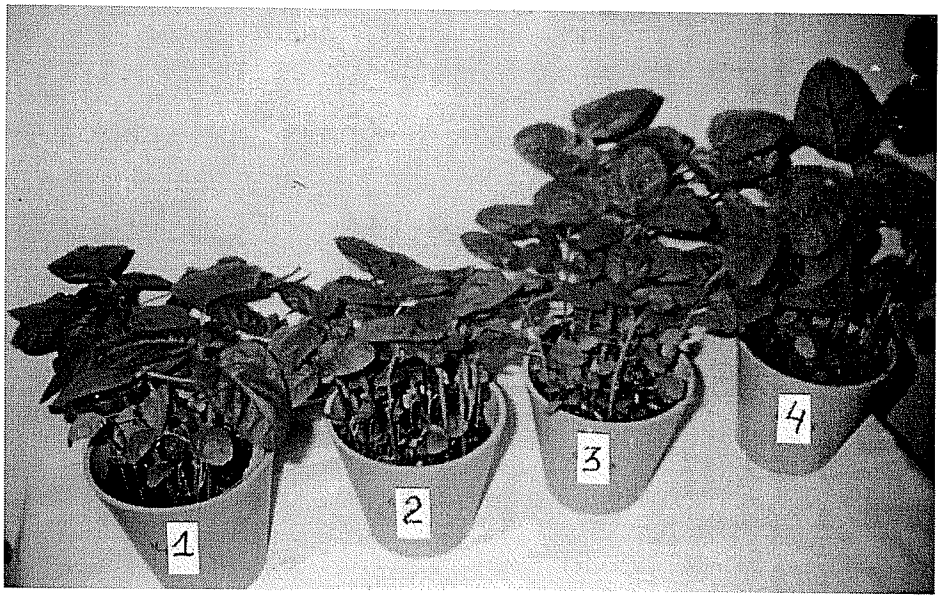

Figure 1. Influence of heavy metals on growth of *A.Tricolor*.1-control, 2-Cu (150mg/kg), 3-Cd (100 mg/kg), 4-Zn (300 mg/kg).

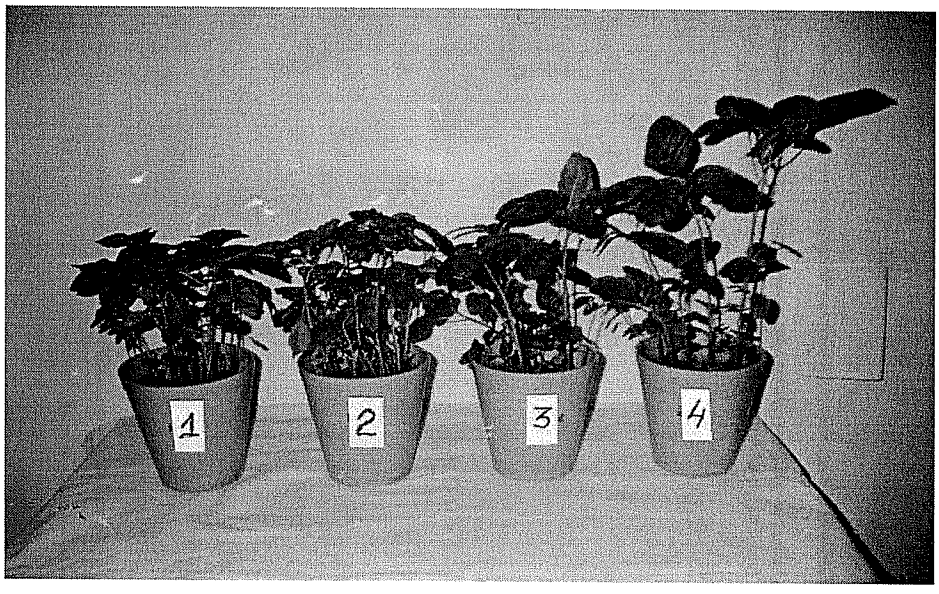

Figure 2. Influence of different Zn concentration on growth of *A.tricolor*
(Zn concentration : 1 - control, 2 - 150mg/kg, 3 - 225mg/kg, 4 - 300mg/kg)

Issues Related to Oil/Water/Solids Separation at a Commercial Produced Water Treatment Facility Operating in South Central Wyoming

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ABSTRACT

Since 1999, Crystal Solutions (CS) has been treating natural gas produced water using a freeze-thaw/evaporation (FTE®) facility located in south central Wyoming. Oil/water/solids separation is an important step in the operation of the facility. This is accomplished using conventional oil/water/solids separation equipment in the system design. Produced water unloaded from trucks flows into and through two 400 bbl vertical tanks connected in series. These tanks are each equipped with fire tubes fueled with propane and controlled to a selected temperature set point. Inlet and outlet piping enter and exit the top of the tanks and extend vertically to the middle of the tanks. Oil collected in the upper portion of each tank is manually fed to a 300 bbl condensate storage tank by gravity. Water from the second 400 bbl tank flows into a lined separation pond one-quarter acre in size. This pond, equipped with duck netting, provides additional residence time to insure complete separation is achieved. Water is pumped from the lower portion of the separation pond to one of the eight facility treatment ponds. Oil collecting on the top of the separation pond is recycled into the first 400 bbl separation tank as required.

The operational history of the separation system is discussed along with economic issues related to the system operation. In addition, recommendations for design modifications to future systems are provided.

Cost Factors Associated With Managing Produced Water at CBM Properties In the Rocky Mountain Region

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ABSTRACT

The issue of produced water management must be addressed by producers of coalbed natural gas fields in the Rocky Mountain region. In a study recently completed for the Gas Research Institute, producers throughout the Rocky Mountain states were interviewed by telephone to determine localized produced water management strategies and associated produced water disposal costs. During the interviews, many producers reported recycling produced water generated at their leases for a variety of beneficial uses including enhanced recovery projects, dust abatement, irrigation, cement mix and for watering livestock. However, when asked, most producers could not place a direct value on the recycled water.

This paper will examine the economic and regulatory issues that oil and gas producers associate with beneficially using or "recycling" produced water at coalbed methane fields in Wyoming, Colorado, New Mexico and Utah; and will also provide an economic overview of both perceived and actual cost savings that producers realize when they recycle oil and gas field produced water. It will also include a discussion of treatment technologies that are currently utilized by coalbed methane producers to improve the quality of water prior to recycling or disposal, or that are used to reduce the volume of water they generate.

Onshore Drilling Waste Management: Beneficial Reuse of Cuttings

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ABSTRACT

Marathon Oil Company, in collaboration with the Alaska Department of Environmental Conservation (ADEC), successfully implemented an Exploration and Production (E&P) Drilling Waste Beneficial Reuse Management Plan (Plan) in its Cook Inlet, Alaska operations in 2001. Since that time, all drill well oversize cuttings associated with E&P activities have been beneficially reused within Marathon's existing infrastructure.

The overall objectives of the Plan are to ensure that drill cuttings do not pose a threat to the environment, to treat and beneficially reuse the oversize fraction of sand and gravel associated with E&P drill wells, and to reduce the disposal volume of cuttings and associated costs. The two products of treatment are cutting fines which are slurrified and injected into a disposal well and clean sand and gravel that can be used for the maintenance and/or construction of roads and berm. The following paper presents Marathon's approach to managing these wastes.

Chemical Method for Cleanup of Produced Oil-Coated Solids from Oilwell Operations

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ABSTRACT

Disposal of solids waste, such as drill cuttings and produced sand, from oil/gas well operations is strictly regulated, and there is an urgent need to develop cost-effective and energy-efficient methods for cleaning the solids before disposal. This is particularly so with respect to disposal of (1) oil-coated solids, such as those generated from drilling using non-aqueous fluids, and (2) produced sand/formation solids from the oil-bearing zone.

Current technologies depend mainly on energy-intensive thermal treatment of the solids to lower the oil content to meet regulations. This treatment is followed by either re-injecting the solids into the formation or disposing of the solids in a landfill.

This paper discusses a simple, new chemical process that uses a biopolymer-based aqueous treatment for reducing the oil content of the drill cuttings and oil-coated sand to levels that meet the requirements of regulatory agencies. The oil-removal efficiency of the aqueous treatment can be enhanced by coating the solids with suitable surfactant combinations before the treatment. The removed oil is collected as flocculated mass. Using this procedure, it was shown in laboratory studies that the oil content can be reduced by 95 to 99%.

DRILLING FLUID CHEMICALS AND EARTHWORM TOXICITY

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ABSTRACT

Earthworms can be used to assess toxicity in terrestrial systems and the survival rate of the worms, or changes in other parameters such as biomass, can be used to calculate an LC_{50} value (lethal concentration to 50% of the population) for test chemicals spiked into soil. This type of information can be useful in predicting the likely toxicological effect of oily drill cuttings on the soil environment and may be useful for calculating application rates for fluids with different toxicological characteristics if the oily cuttings are to be land farmed.

Another remediation option is to treat the cuttings using worm farming, or vermiculture. This is a well-established method of treating organic wastes, but it has only recently been applied to drilling fluids. When drill cuttings and other organic materials are fed to earthworms such as *Eisenia foetida* the oil content of the cuttings is rapidly degraded and the mixture converted into a high quality soil-like compost that can be used as a soil improver or fertiliser. To date this approach has only been used with specially designed and engineered low toxicity, highly biodegradable, synthetic-based drilling fluids that have a chloride-free brine phase. The data presented in this report can be used to evaluate what other types of oil-based drilling fluids can be treated and also how much fluid the worms can tolerate before it reaches a toxic level and reduces the efficiency of the process.

The results presented in this paper form part of a larger study to investigate the limitations of vermicomposting as well as evaluate the feasibility and practicality of this approach in other locations and using other types of drilling fluid chemicals.

Toxicity data for some commonly used drilling fluid additives show that while some chemicals are toxic and unsuitable for vermicomposting, linear paraffin/potassium acetate containing fluids showed the lowest toxicity and may be considered to give the optimum potential for remediation by vermiculture. The toxicity data was used to calculate suitable cuttings treatment rates, and the concentration of salt in the blend was shown to be the limiting factor.

A Model to Rank the Risk of Environmental Impact on the Biodiversity around Pollution Systems

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ABSTRACT

A model that ranks the risk of impact on flora/fauna species in a typical biodiversity environment under the influence of pollution source(s) is presented. This model, which is based on the weighting concept for risk analysis, allows a structured technique to quantify and prioritize the risk of impact on flora/fauna population under the influence of pollution source(s) in a particular biodiversity environment. In this way the risk of degradation of the environment can adequately and proactively be predicted. An overall risk model was developed for flora/fauna species in a typical ecological biodiversity environment around a gas flare system of an operating Oil and Gas Company. The risk potential was evaluated as a product of the risk variable and reciprocal of the remedial function. The maximum risk scenarios were obtained from the differential of the potential risk of extinction with time. The air pollution dispersion model of the flare system was obtained using the eulerian technique and the second order differential equation resulting, was solved using the Crank Nicholson method. The concentration of the space vector was evaluated. A doze and response effect of flora/fauna species under the impact of a pollution sources was simulated using a computer program utilizing a model that relates the effect of the contaminants' concentration dispersed in the air pollution pathways to the growth profile of the flora/fauna population. The simulation of the doze-response effect of the biodiversity was obtained using a computer simulation program. The plots of concentration with time of different contaminants at ground level up to 60 minutes were plotted. A parabolic profile with peak concentrations of plots was observed. Also the growth profile (response effect) of different Macro fauna species in different environment under different contaminants (doze), CO, NO, NO_2, SO_2 concentration with time shows exponential decrease with time, except for contaminant CO_2 effect on Macro Fauna biodiversity, which shows a different trend (Population/Mass increases almost exponentially with time after a time lag, where population/mass remain constant. Hence a model has been presented that allows environmentalist, regulators and operator have a reliable tool to assess the risk to biodiversity ecology their operation(s), impacts on the environment and the optimum time for remedial action that would allow operators comply proactively with HSE (Health, Safety, Environment) requirements.

Soil Clean-Up Levels for Residential and Industrial Land Use in Mexico: A Case Study Applying RBCA on a Site Contaminated by Hydrocarbons

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ABSTRACT

RBCA (Risk Based Corrective Action) framework was applied in two contaminated sites located on the east coast of Mexico in order to assess the risks of the exposed population to the hydrocarbons and metals found on the soil and groundwater, as well as to obtain the soil clean-up concentration levels required to protect these populations. Soil physical and chemical properties of both sites were similar, differences were observed on hydraulic conductivity, depth to the water table, extension of the contaminated area, and land use (one was classified as industrial and the other one as residential). Almost in all cases hydrocarbon and metal soil concentrations were greater on the industrial site, and soil clean-up concentrations were less restrictive on this site.

A 2^k factorial design was applied to determine the factors (Hydraulic Conductivity, Depth to the Water Table, Contaminated Area, and Land Use) and their interactions that posed the main influence on the soil clean-up concentrations obtained with RBCA Tool Kit for one of the contaminants present at the sites. The contaminant analysed was MTBE, because of its great potential of contaminating groundwater and its adverse health effects. The results showed that the main influence on the soil concentrations obtained with RBCA Tool Kit are Land Use x Depth to Water Table, followed by the interaction of Hydraulic Conductivity x Depth to water Table.

HEALTH RISK ANALYSIS CARRIED OUT IN AN OIL STORAGE AND DISTRIBUTION STATION IN EASTERN CENTRAL MEXICO TO DETERMINE REQUIRED CLEANING LEVELS

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ABSTRACT

Subsoil of an oil storage and distribution station (ODSS) located in Eastern Central Mexico was characterized in terms of total petroleum hydrocarbons (TPHs), the 16 polynuclear aromatic hydrocarbons (PAHs) suggested by USEPA as priority contaminants, benzene, ethyl benzene, toluene, and xylenes (BTEX), methyl tert butyl ether (MTBE) tertamyl methyl ether (TAME), and four metals *i.e*, Fe, V, Pb, Ni and Zn. ODSS resulted contaminated mainly by TPHs in a concentration higher than that legislated in Mexico (NOM-EM-138-ECOL-2002). It was detected the presence of BTEX and 11 of the 16 PAHs suggested by USEPA as prioritary pollutants. MTBE was found in only one sampling point, but TAME was not found anywhere. Metals were under the suggested limits, so they do not need to be reduced. The health risk assessment carried out indicated that only dibenzo(a,h)anthracene is in a concentration that exceeds the previously fixed maximum acceptable risk of $1x10^{-5}$. Hence, dibenzo(a,h)anthracene must be reduced from 2.36 mg/kg to 2.0 mg/kg. Soil must be treated to reduce the TPHs actual concentration up to a value of 2,000 mg/kg, as suggested by the Mexican Norm.

INTRODUCTION

Petróleos Mexicanos (PEMEX) is very concerned of the environmental problems associated to the exploration, extraction, refining, distribution and storage of crude oil and its fractions.

Our research group has developed different media characterizations of refineries and ODSS along the country (Iturbe *et al.,* 2003 a, b, c, d, among others). In most sites, after soil and water characterization, risk health assessment has been carried out to

determine the state of the facilities and the required cleaning levels for industrial soil uses. After that stage the appropriated remediation methodologies to clean-up soils and aquifers affected by hydrocarbon pollution have been suggested. Pilot plant-level treatments as well as full-scale remediation processes have been carried out in some of those sites.

The aim of this work is to show the entire characterization process carried out in Eastern central Mexico ODSS subsoil. A step-by-step health risk assessment HRA procedure is showed. The tools for this HRA procedure were ASTM RBCA Tools Kit for Chemical Releases (GSI, 2000.

MATERIALS AND METHODS

Soil sampling procedure

Soil samples were taken in 19 points distributed in the ODSS area, at different depths. Samples were taken at 1.0 - 3.8 m below surface. They were extracted with pneumatic perforation equipment. This equipment has a 12 HP motor, variable speed and 2,000 pounds working pressure. A helicoidal 3-inch tube was employed for drilling. For sampling, a 0.6 m long and 1.5 in diameter tube screwed on both sides was used and was driven into the soil at the bottom of a borehole by means of a 63.5 hammer having a free ball of 760 mm similar to that used in standard penetration test (SPT). Inside there is an aluminum tube where the sample is accumulated. In that way, there is no contact between the soil and air. Samples were stored at low temperature (4 °C) until they were analyzed. Parameters evaluated in the soil samples were total petroleum hydrocarbons (TPH); hydrocarbons profile, including diesel fraction, gasoline fraction, methyl tertbutyl ether (MTBE), and tertamyl methyl ether (TAME); and BTEX (benzene, toluene, ethyl benzene, and xylenes). Additionally, 16 polynuclear aromatic hydrocarbons (PAH) were analyzed: Acenaphthene, phenathrene, fluoranthene, fluorene, anthracene, indene(1,2,3-cd)pyrene, acenaphthylene, naphthalene, pyrene, benzo(a)anthracene, benzo(a)pyrene, benzo(a)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene and dibenzo(a,h)anthracene. Finally, four metals were measured—Zn, Cr, Fe, and Pb.

Analytical methods

Soil samples were evaluated in accordance to USEPA analytic techniques: EPA418.1 for TPH concentrations; EPA6010 for Pb, Cr, Fe and Zn; EPA8240 for hydrocarbons *i.e.* diesel and gasoline, MTBE, and BTEX. PAHs were analyzed using the EPA8100 method.

Explosivity index

19 sampling points were distributed in the ODSS, for evaluating explosivity indexes. Explosivity index was measured with a COSMOS XP-311 ALPHA A system (New Cosmos Electric Co. LTD; Japan). Measurements were done at the same depth than the rest of the parameters.

Health risk assessment

In order to establish soil and groundwater clean-up levels protective to the health of the population exposed (workers of the facility and residents living in the neighborhood) the HRA approach was carried out by means of RBCA Tool Kit for Chemical Releases v 1.3. HRA considers four main steps: 1) Hazard Identification, 2) Dose-Response or Toxicity Assessment, 3) Exposure Assessment, and 4) Risk Characterization (Boguski 2001, Kaplan & McTernan 1995), and depending on the site specific conditions, the chemical characteristics, and the risk that is set as *acceptable* the clean up remediation goals can be more or less restrictive.

RESULTS AND DISCUSSION

Site characterization

Hydrocarbons distribution

Table 1 shows the minimum, maximum, average (including standard deviations) concentrations found at the Eastern Mexico ODSS as well as the number of points where contaminates were detected. As shown, TPH concentrations ranged between 7,452 and 21,307 mg/kg (average of 13,360 +/- 5,346 mg/kg). These hydrocarbons were detected in only 6 points of the studied area. Diesel fraction was found at 7 sampling points in the range of 2.83-478 mg/kg (average of 279.02+/- 189.05 mg/kg). Gasoline fraction was detected at 6 points between 3.2 and 629 mg/kg (average of 175.58 +/- 23.07 mg/kg). BTEX were found in 8-15 ODSS sampling points in the following intervals. Benzene: 0.001 to 7.93 mg/kg, ethyl benzene: 0.001 to 58.4 mg/kg, toluene: 0.001 to 1.79 mg/kg, and xylenes: 0.001 to 74.66 mg/kg.

TAME was not found anywhere, but MTBE was detected in one point at a concentration of 0.0085 mg/kg. Regarding the 16 PAHs considered by USEPA as priority pollutants, 11 were found at the ODSS in rather low concentrations. The most abundant PAH was naphthalene (found at 6 sampling points) in concentrations between 5.37 and 14.51 mg/kg. Dibenzo(a,h)anthracene was detected in only two points, in concentrations between 0.01 and 2.36 mg/kg. Phenanthrene in the third place of abundance appeared in 6 sampling points in concentrations between 3.26 and 6.62 mg/kg. Naphthalene and phenanthrene are non-carcinogenic compounds, but dibenzo(a,h)anthracene is considered as carcinogenic, as well as chrysene, benzo(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, and indene(1,2,3,c,d)pyrene, also present in some points at the ODSS. Explosivity was detected in 7 sampling points in values from 20 to 100%.

Figure 1 shows a spatial distribution of TPH inside the ODSS. As observed, high TPH values are quite located at specific zones inside the ODSS. There seems to be two hot spots where TPH concentrations are higher. Those points correspond to sampling points 1 (815,773 mg/kg), and 4 (21,307 mg/kg). Both points are located on the railroad. From these points on, TPH concentrations tend to vanish gradually up to 2,000-5,000 mg/kg concentrations. Figure 2 shows the distribution of PAHs on the ODSS. As noted,

points where PAHs were identified are located also on the railroad. They correspond to points 1, 4, 5 and B. Total PAHs concentrations for these points are 13.62, 11.35, 26.18 and 31.47 mg/kg, respectively.

Metals distribution and accumulation indexes

Regarding the metals analyzed, Fe, V, Pb, Ni and Zn were measured in the soil samples. Fe fluctuated between 4,598 and 20,976 mg/kg, V between 16.2 and 56 mg/kg. On the other hand, Pb was in the 3.4 to 29.9 mg/kg, Ni in the range of 4.8 to 14.8 mg/kg, and Zn between 12.7 and 47.6 mg/kg (see table 1).

Metals were present in all the sampled points, as expected, but concentrations were quite variable along the studied zone. Figure 3 shows the vanadium concentrations along the ODSS. It is remarkable that there is a hot spot located on sampling point number 6. Figure 4 shows the explosivity levels higher than 50% at the ODSS. It is noteworthy the fact that explosivity values higher than 50% are located on the railroad, coinciding with the high TPH concentration hot spots. Points where this condition was achieved are 1, 4, 5, and A.

On table 2, sampling points were no hydrocarbons were detected are showed (*i.e.* TPH, gasoline fraction, diesel fraction, BTEX, PAH, MTBE). Ten points are in this category. Average and standard deviations for every metal were calculated and reported on Table 2. Detection limits for every metal are reported in the same table. As observed, standard deviations are rather high. They represent 17.2, 21.3, 36.2, 14.6, and 19.5% of the average, for Fe, V, Pb, Ni, and Zn, respectively. These average values will be assigned as the metal background concentrations. In an effort to discuss the possibility of metal contamination (due to oil spills inside the ODSS), the equation proposed by Muller (1969) for calculation of geo-accumulation will be employed:

$$\text{I-geo} = \log_2 (Cn/1.5Bn) \qquad (1)$$

Where Cn is the analyzed metal concentration, and
Bn is the background content for the metal.

From table 2, it is noticeable that I-geo values for Fe, V, Pb, Ni and Zn are –0.3402, -0.4237, 0.3535, -0.4288, and –0.2311. It is clear that only Pb seems to be accumulated in the ODSS soil, *i.e.,* shows a positive value.

Relationship between organic compounds and metals

With the purpose of getting more information in order to explain some organic compounds and metal distribution behaviors in the ODSS, relationships among TPH, diesel fraction, gasoline fraction, BTEX, PAHs, MTBE, and the five measured metals were investigated. Most interesting relationships are reported on Table 3. As shown, TPHs seems to be not related with gasoline, but with diesel, though r^2 coefficient is not good enough, (-0.1088 and 0.7001, respectively). Diesel fraction seems to be related with naphthalene (again, r^2 coefficient is not very good *i.e.*, 0.7355), but not with Fe or Pb (r^2 coefficients of –0.1493 and –0.2861, respectively). Gasoline fraction, on the other hand, seems to be related with benzene, ethyl benzene toluene, and xylenes, as expected (r^2 coefficients of 0.9601, 0.7515, 0.9569, and 0.9624, respectively). Finally, gasoline

resulted related with lead (r^2 coefficient of 0.9464), and perhaps with iron (r^2 coefficient of 0.7057).

In an effort of understanding the relationship between gasoline and these two last mentioned metals *i.e.,* Fe and Pb, they were plotted as a function of the gasoline fraction concentration on Figure 5. As observed on figure 5, a) Fe has the tendency of augment as the gasoline fractions increases, but r^2 coefficient is not very good. The explanation for this behavior could be related with the fact that where contamination with gasoline is present, allows the movement of Fe more freely, concentrating the metal in some hot spots. This behavior was found in the study of other ODSS in Mexico (Iturbe *et al.*, 2003a and b). b) Pb has also the tendency of growing as the gasoline fraction increases, with a quite good r^2 coefficient (0.8958), which means that the lead contamination in the ODSS soil is probably coming from gasoline contamination. The use of gasoline in Mexico started since the 1930's to the end of 1990's, approximately in 1997 (Thomas *et al.,* 1999), when unleaded gasolines (*Magna sin* and *Premium*) substituted the old leaded gasolines (*Nova* was the last one of a list). Regarding the amount of lead present in gasolines was quite variable. From 1988 to 1993 it was reduced from 0.2 to 0.06 g/L (Thomas *et al.,* 1999). These arguments are confirmed by the fact that Pb was the only one metal that seems to be geo-accumulated at the ODSS soil.

Health risk assessment results

The general scenario considered for the evaluation was set in two kinds of receptors: On-site and Off-site, the first ones are the workers of the facility and the latter ones are the neighbors living in the houses located next to the facility (at the north and west sides of the facility) with an estimated population of 2,000 people. Land use for the On-Site receptors was classified as industrial and for the Off-Site receptors was set as residential. Information regarding to geo-hydrological and climatic conditions was gathered, and physical and chemical properties of the soil were measured. A summary of this information is presented on Table 4.

For the HRA, the maximum soil concentrations found were used. These results are shown on third column, Table 1. No samples of groundwater were analyzed because the aquifer beneath the facility is about 200 m depth and the water used by the workers and the neighbors come from a well located 10 km down gradient the facility.

Soil sampling showed the presence of contaminants in the soil and subsoil (PAHs were found at 3.8 m depth). The migration pathways considered for the site were air and groundwater migration, considering soil to air volatilization or particulate re-suspension due to the action of the wind, and leaching from soil to groundwater; the latter one was considered even though the aquifer is very depth because it was established the worst scenario for the extraction well located down-gradient the facility, where the drinking water comes from. The exposure routes considered were dermal contact and ingestion of soil, vapor and particulate inhalation, and ingestion of water (water contaminated due to the leaching of substances from soil to groundwater).

The software calculates the doses received by the population considered to be exposed (workers of the facility on an industrial land use, and neighbors on a residential land use) through the different exposure routes (ingestion, inhalation and dermal contact), and calculates the Hazard Quotient for non carcinogen effects (exposure dose/ RfD), and

the Risk for carcinogen effects (exposure dose x SF). Acceptable HQ was set as 1, and acceptable Risk was set as $1x10^{-5}$.

The HQ calculated by the software. ranged from $2.1x10^{-10}$ (Naphthalene, On-Site receptors dedicated to construction operations, via inhalation of vapors and particulates) to $2.2x10^{-1}$ (Fluoranthene, Off-Site receptors with residential land use, via ingestion of groundwater contaminated by the leaching from soil). This shows that none of the contaminants is expected to be above the HQ established as acceptable, therefore the population exposed under the scenario proposed for the site is not likely to present the systemic effects associated to the contaminants

The Risks calculated by the software (Table 8) ranged from $6.7x10^{-15}$ (Benzo(k)fluoranthene, Off-Site receptors with residential land use, via ingestion of groundwater contaminated by the leaching from soil) to $1.2x10^{-5}$ (Dibenzo(a,h)anthracene, On-Site receptors dedicated to construction operations, via soil ingestion and dermal contact). This shows that only the On-Site population is at risk of developing cancer (Risk value established as acceptable, $1x10^{-5}$, was exceeded), and this happens by the soil exposure to Dibenzo(a,h)anthracene, so it is necessary to reduce soil concentration of this contaminant to a level that assures that the acceptable Risk is not going to be exceeded.

Table 9 shows soil concentrations necessary for all the contaminants to assure that the HQ and Risks are not going to be exceeded; comparing these concentrations to the actual concentrations present at the site. On the same table, the Mexican NOM values, and Louisiana State (USA) Standards are included for comparison purposes. It is concluded that only Dibenzo(a,h)anthracene soil concentration has to be reduced from 2.36 mg/kg to the value suggested by HRA, *i.e,* 2.0 mg/kg. If maximum concentrations found at ODSS are compared to the Mexican NOM, only TPHs value overpasses the suggested value of 2,000 mg/kg. If the same concentrations are compared to the Louisiana State Standards, TPHs, benzene, dibenzo(ah)anthracene, and naphthalene exceed those standards (*i.e*, 500, 3.2, 0.36, and 5.2 mg/kg, respectively).

From the HRA, and Mexican NOM, it was concluded that TPHs concentrations must be under 2,000 mg/kg, and dibenzo(a,h)anthracene must be reduced up to 2 mg/kg. Lead is not present in a harmful concentration. The ODSS under study can be remedied using available techniques so in a short period ODSS soil can be in conditions for any industrial use.

Biopiles and soil washing are widely recommended; since they have showed their easiness and cost-effective development in treating similar refineries or ODSS contaminated soils in Mexico (Iturbe *et al*, 2001; Iturbe *et al*, 2003d)

CONCLUSIONS

Main conclusions derived form this study are the following.

- The ODSS under study resulted contaminated in terms of TPHs, BTEX, diesel and gasoline fractions, and some PAHs *i.e.,* phenanthrene, fluoranthene, fluorene, naphthalene, pyrene and chrysene. Explosivity indexes higher than 50% were

observed. Fe, V, Pb, Ni and Zn concentrations are high, but at this point it is not clear if they are geologically determined or they are contamination product.

- There seems to be two hot spots where TPH concentrations are higher. Those points correspond to sampling points 1 (815,773 mg/kg), and 4 8 (21,307 mg/kg). Both points are located on the railroad. Explosivity index higher than 50% are located in the same area (over the railroad).

- Geo-accumulation indexes values for Fe, V, Pb, Ni and Zn are –0.3402, -0.4237, 0.3535, -0.4288, and –0.2311. In basis to these indexes, it can be concluded that only Pb seems to be accumulated in the ODSS soil, *i.e.,* shows a positive value.

- TPHs seem to be not related with gasoline, but with diesel. This fraction seems to be related with naphthalene, but not with Fe or Pb. Gasoline fraction, on the other hand, seems to be related with BTEX, as expected. Finally, gasoline resulted related with lead and perhaps with iron. This would mean that gasoline is responsible of metal and BTEX concentration in a major way, and diesel would be for PAHs and TPH contamination.

- Only dibenzo(a,h)anthracene soil concentration represents a risk to the health of the population exposed. Even though the soil is permeable, there are some attenuating factors as the depth of the exploitable aquifer and the distance to the point of contact (extraction well), which reduces the magnitude of the potential impacts.

- From the HRA, and Mexican Norm, it was concluded that ODSS TPHs concentrations may be reduced up to 2,000 mg/kg and dibenzo(a,h)anthracene must be reduced up to 2 mg/kg. Lead is not present in a harmful concentration.

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REFERENCES

Boguski, T.K. (2001). "Human Health Risk Assessment. Environmental Science and Technology Briefs for Citizens". Hazardous Substance Research Centers. http://www.envirotools.org/ factsheets/fs_health_risks.pdf.

GIS (2000) Ground Water Service Inc. RBCA Tool Kit Chemical releases v.1.3 Software for Excell 2000, Groundwater Services Ins. Houston, USA.

Iturbe R, C Chavez and C Flores (2001) Biopiles: a remediation option for soils contaminated by hydrocarbons. XV International conference on soil mechanics. Turkey.

Iturbe R, Flores, R.M. and Torres L.G. (2003a) Soil and water contamination levels in an out-of-service oil distribution and storage station in Michoacan, Mexico. Water, Air and Soil Pollution146(1-4) 261-281.

Iturbe R., R.M. Flores, and L.G. Torres (2003b) Subsoil contaminated by hydrocarbons in an out-of-service oil distribution and storage station in Zacatecas, Mexico. Environmental Geology. In press.

Iturbe, R., R. M. Flores, C.R. Flores, and LG Torres. TPH-contaminated Mexican-refinery soil: Health risk assessment and the first year of changes (2003c). Environmental Monitoring and Assessment. Published on-line in forthcoming papers section.

Iturbe R, C Flores, C Chávez, A Ramírez and LG Torres (2003d) In situ flushing of contaminated soils from a refinery: organic compounds and metal removals. Remediation. Submitted.

Kaplan, E. & McTernan, W.F. (1995). Overview of the Risk Assessment Process in Relation to Groundwater Contamination. In J. Lemons (ed.), Readings from the Environmental Professional. Risk Assessment. Michigan: National Association of Environmental Professionals and Blackwell Science Inc.

Muller G. (1969) Index of geoaccumulation in sediments of the Rhine River. Geojournal 2: 108-118.

Thomas, V M, R.H. Scolow, J F Fanelli, and T Spiro (1999) Effects of reducing lead in gasoline: an analysis of the international experience. Environmental Since and Technology 33 (22): 3942-3948.

USEPA (1996a) Recommendations of the Technical Review Workgroup for Lead for an Interim Approach to Assessing Risks Associated with Adult Exposures to Lead in Soil, U.S. Environmental Protection Agency, Technical Review Workgroup for Lead, Washington, DC.

USEPA (1996b) Calculations of Preliminary Remediation Goals (PRGs), U.S. Environmental Protection Agency, Technical Review Workgroup for Lead, Washington, DC.

CHARACTERIZING RISKS TO LIVESTOCK FROM PETROLEUM HYDROCARBONS

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ABSTRACT

Livestock may be exposed to petroleum hydrocarbons at or near exploration and production sites and, in these cases, there may be a need to estimate potential risks to these receptors. A framework was developed to 1) determine when livestock should be included in a risk evaluation and 2) estimate risks of petroleum hydrocarbon exposure to livestock. A conceptual site model was developed to assess whether complete and significant exposure pathways exist at a given site. To estimate potential risks, toxicity reference values (TRVs) and drinking water and soil risk-based screening levels (RBSLs) for petroleum hydrocarbons, including crude oil; benzene, toluene, ethylbenzene, and xylene; and polycyclic aromatic hydrocarbons were developed for a variety of livestock receptors. The TRVs and RBSLs developed for this framework were comparable to human health RBSLs and other published livestock guidelines.

Realistic Soil Cleanup Standards With Dual Equilibrium Desorption

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ABSTRACT

The desorption of contaminants from soils/sediments is one of the most important processes controlling hydrocarbon transport and environmental risks. None of the currently adopted desorption models can accurately quantify desorption at relatively low concentrations; these models often overestimate the desorption and thus the risks of hydrophobic organic chemicals, such as BTEX and PAHs. In reality, desorption is generally found to be biphasic, with two soil-phase compartments. A new duel-equilibrium desorption (DED) model has been developed to account for the biphasic desorption. This model has been tested using a wide range of laboratory and field data and has been used to explain key observations related to underground storage tank (UST) plumes. The DED model relates the amount of a chemical sorbed to the aqueous concentration, with simple parameters including octanol-water partition coefficient, solubility and fractional organic carbon; thus, it is the only biphasic model, to date, that is based on readily available parameters. The DED model can be easily incorporated into standard risk and transport models. According to this model, many regulatory standards of soils and sediments could be increased without increasing the risks.

Microbial Activity in Soil During Gasoline-Ethanol Degradation

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ABSTRACT

In Brazil, ethanol has been mixed to gasoline for many years, both compounds entering the environment when leaks occur. In the aquifer, ethanol seems to be preferentially degraded, depleting soil of electron acceptors and consequently delaying BTEX degradation. However, processes in the vadose zone are still poorly understood. Previous studies showed a decrease in culturable bacterial populations in unsaturated residual soils with gasoline and gasoline-ethanol mixture. Recovery of gasoline-contaminated soils happened sooner than for ethanol-containing ones, suggesting a similar situation to the one observed in saturated soil. This study monitored the biodegradation of BTEX-ethanol mixture in unsaturated soil and the influence of ethanol on BTEX degradation. Bioventing was applied to contaminated soils; measures of fluorescein-diacetate hydrolysis ascertained microbial activity, and Time Domain Reflectometry monitored soil dielectric constant shifts. Contaminant residues were analysed by Gas Chromatography. Results show the effect of contamination and bioventing on microbial activity during BTEX degradation in the presence of ethanol.

Bioremediation of Soil Contaminated with Alkyllead Compounds: Laboratory Investigations and Field Trials

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Tetraethyllead (TEL) and tetramethyllead (TML) were produced world-wide as anti-knocking additives for gasoline to increase octane numbers. The use of leaded gasoline over almost one century caused an ubiquiteous pollution of the environment with lead ions or alkyllead compounds (Rhue et al. 1992). Nowadays, tertiär-butylether (Europe) or in future ethanol (U.S.) are used to increase the octane numbers.
Whereas car emissions led to an ubiquiteous distribution of low concentrations of organolead compounds and in greater amounts of inorganic lead in the upper layers of soil, spillages of highly toxic tetraalkyllead (TAL) compounds during production, transportation or blending at oil refineries and petrol stations caused more severe soil and groundwater contaminations. The toxicity of alkyllead compounds decreases in the sequence: $R_4Pb > R_3Pb^+ > R_2Pb^{2+}$ with R = $-CH_3$ or $-C_2H_5$. Methylated lead species are less toxic than the ethylated compounds. In the atmosphere TAL is decomposed photocatalytically by UV irradiation, by ozone or by hydroxyl radicals to the more stable, water soluble ionic tri- and dialkylated species. Monoalkyllead cations are assumed to be very instable. After chemical decay and/or biological degradation of organic lead compounds, the inorganic, less toxic lead is immobilized by precipitation as $PbCO_3$ or $Pb_5(PO_4)_3Cl$ in soil. In addition to photodecomposition or oxidative decay, TAL can be decomposed into trialkylated lead species by catalysis of Cu^{2+} or Fe^{2+} ions (Rhue et al. 1992). The ionic trialkyl- and dialkyllead species were stable in an aqueous solution and could not be decomposed by catalysis of Cu^{2+} or Fe^{2+} cations. A sulfide-mediated transalkylation of two moles of trialkyllead compounds into a tetraalkyllead and dialkyllead species was observed by Jarvie et al. (1983). In laboratory experiments and in field studies with soil from an industrial site, that was contaminated with organolead and inorganic mercury, the inorganic mercury was alkylated to ethylmercury by tetraethyllead (Hempel et al. 2000). In addition to photochemical or chemical transformation of alkyllead compounds, microbial degradation in soil occured (Macaskie and Dean 1990, Blais et al. 1990). Biologically mediated multiple dealkylations resulted finally in the formation of inorganic lead.
In Germany TEL and TML were manufactured by two chemical factories until the end of the 1980´s. At both production sites significant amounts of organolead compounds were spilled and drained into the underground and still endanger the aquifer. The subsurface soil at the TAL-contaminated site contains mainly fluvial sand deposits with a hydraulic conductivity of 3.5×10^{-4} m s^{-1}. The groundwater table starts at 3 m depth (Gommeringer and Luber 2000). The groundwater flows about 70 m·$year^{-1}$ towards the Rhine river. Upstream it contains about 0.4 mg·l^{-1} oxygen. No oxygen was found in the groundwater downstream of the industrial site. Soil and groundwater samples from bore holes, brought up from the center of the polluted area from 3 - 10 m depth, were highly contaminated with organolead compounds, whereas samples from bore holes in the periphery were less or not contaminated.

For determination of soil respiration activity of contaminated soil, samples M 8-10 (volatile solids content 0.3 %, alkyllead content of the this soil only 0.24 mg·kg^{-1} dry matter) and S 70 (volatile solids content 0.9 %, alkyllead concentration 185.1 mg kg^{-1}

dry matter) with and without mineral amendment (N, P, K, Mg fertilizer) were compared in batch assays. Aliquots of 500 g of the soil sample M 8-10 (as a control to determine endogeneous soil respiration) and S 70 (respiration of alkyllead compounds and hydrocarbons) were transfered into 1.2 l glass bottles, closed air-tight and incubated in the dark under aerobic conditions (~21 % O_2). When the oxygen concentration in the bottles had decreased to below 2 %, the gas phase of the bottles was evaccuated and replaced by fresh air.
In both soil samples oxygen consumption and CO_2 production was highly enhanced by mineral addition (Fig. 1a, 1b). In the absence or presence of fertilizer much more oxygen was consumed by the soil containing the high alkyllead and volatile solids concentrations than by the soil, that was only little contaminated with alkyllead and contained less volatile solids (Figure 1a, 1b). The oxygen was, however, not consumed for respiration of alkyllead compounds, but apparently for respiration of oily co-contaminants.

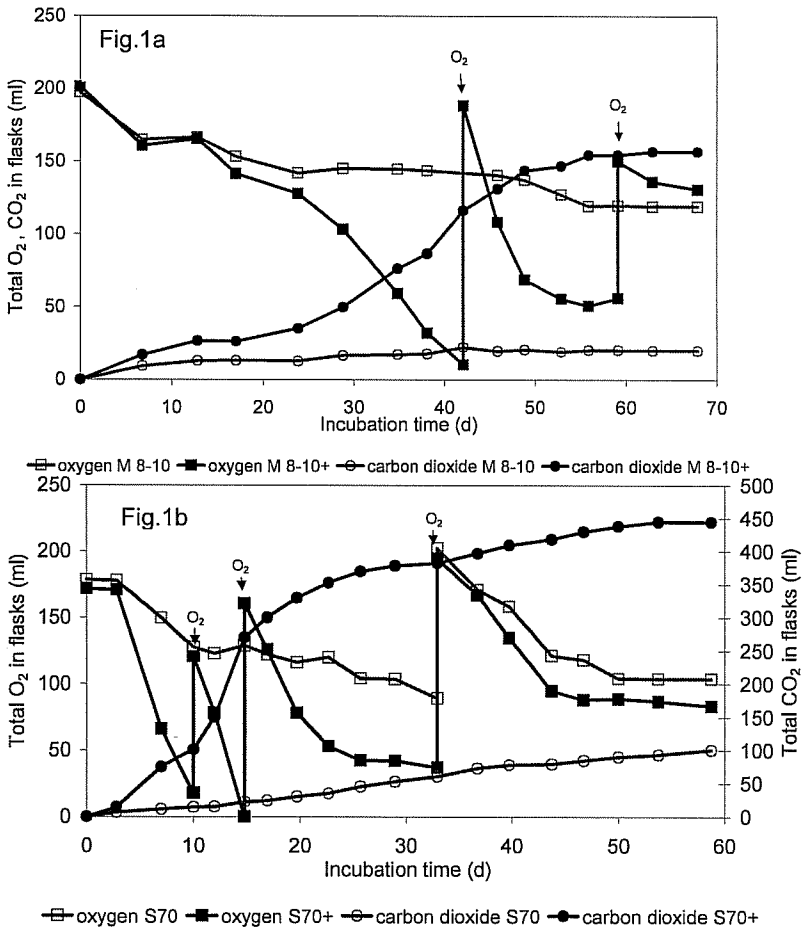

Fig 1a, b: Oxygen consumption and carbon dioxide production by mixed soil samples M 8-10 (Fig. 1a) or S 70 (Fig. 1b) in the presence or absence of minerals. + indicates fertilization with minerals, arrows mark an exchange of the headspace of the assays against air.

The elution and degradation of organolead compounds from contaminated soil was determined in water-saturated soil columns.

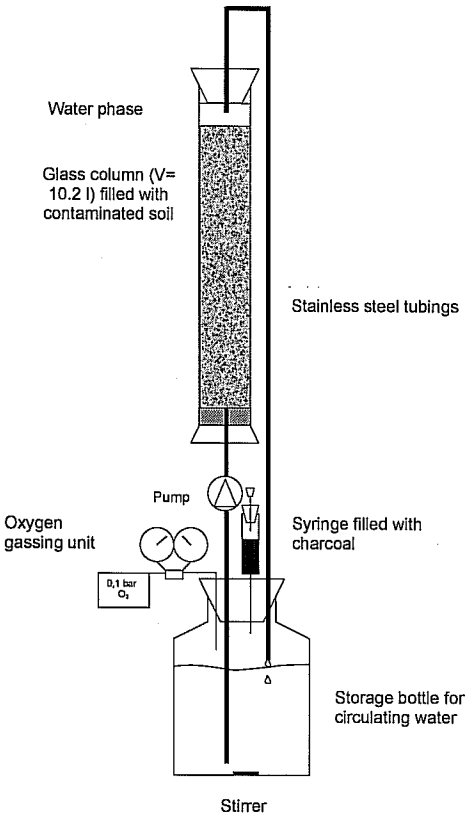

Fig.1: Scheme of the laboratory soil columns used for upflow percolation

Wet sandy soil from 6 m depth, obtained from drilling in the center of the TAL-contaminated site was homogenized in a technical-size blender (capacity 500 kg). All drain water was adsorbed after intensive mixing for 10 minutes. 18 kg portions of the homogenized soil sample S 80 (90 % dm) were immediately filled into each of 6 glass columns of 10 cm inner diameter and 150 cm length. The glass columns were plugged with rubber stoppers, rapped densely with a silicon tubing for cooling by cold water circulation and with aluminum foil to prevent photooxidation and photosynthesis. Figure 1 shows a scheme of the experimental set-up. For oxygen supply the water in the storage bottle was continuously saturated with pure oxygen to maximally 38 mg/l O_2 and circulated via stainless steel tubings (0.3 mm i.d.) through the column in an upflow mode (soil completely water-saturated). In three of the six columns (S1 – S3) oxygenated water and in the other three columns (S4 – S6) an oxygen-saturated mineral mix (N, P, K, Mg fertilizer) was circulated at a pumping rate of 2.2 l/d, which was about 4 times the flow velocity of the groundwater of ~70 m·year^{-1}.

The average initial content of R_4Pb of the soil samples S 80 was 274 mg kg^{-1} dm, of which 86 % were TEL. The initial concentration of R_3Pb^+ was 22 mg kg^{-1} dm, of which 86 % were triethyllead and the initial concentration of R_2Pb^{2+} was below the detection limit of < 0.5 mg kg^{-1} dm. The mineral hydrocarbon content was 539 mg kg^{-1} dm. No inorganic lead was detected, indicating that no previous mineralization of organolead in the soil samples had occured (Gallert and Winter 2002).

A mobilization of TAL compounds from soil into the circulating water and degradation of total alkyllead compounds (R_4Pb, R_3Pb^+ and R_2Pb^{2+}) in the circulating water of column S1 (no fertilizer, Figure 2a) and column S4+ (with fertilizer, Figure 2b) was shown. During the first 98 days of incubation more oxygen was consumed in the fertilized column than in the non-fertilized column, primarily for degradation of non-leaded organic matter. After 220 days of incubation, the maximum of total alkyl lead compounds, mainly trialkyllead compounds was eluted from the soil samples into the circulating water. After that, the concentration slowly decreased with an interim increase of dialkyllead compounds. Although tetraalkyllead compounds were considered insoluble in water, there was some intermediary appearance in the circulating water, presumably due to particle or colloid wash-out (Fig. 2a, 2b. Different scales!).
In order to obtain reliable mass balances of the alkyllead substances during more than 2 years of incubation the experiment was designed as a closed system with water leachate recycling. This led to very high concentrations of e.g. triethyllead, reaching 130 mg l^{-1} after 126 days or even higher than 200 mg l^{-1} after 220 days.

During air injection in the field, maximal concentrations of trialkyllead compounds were only 1.2 – 1.5 mg·l^{-1}.

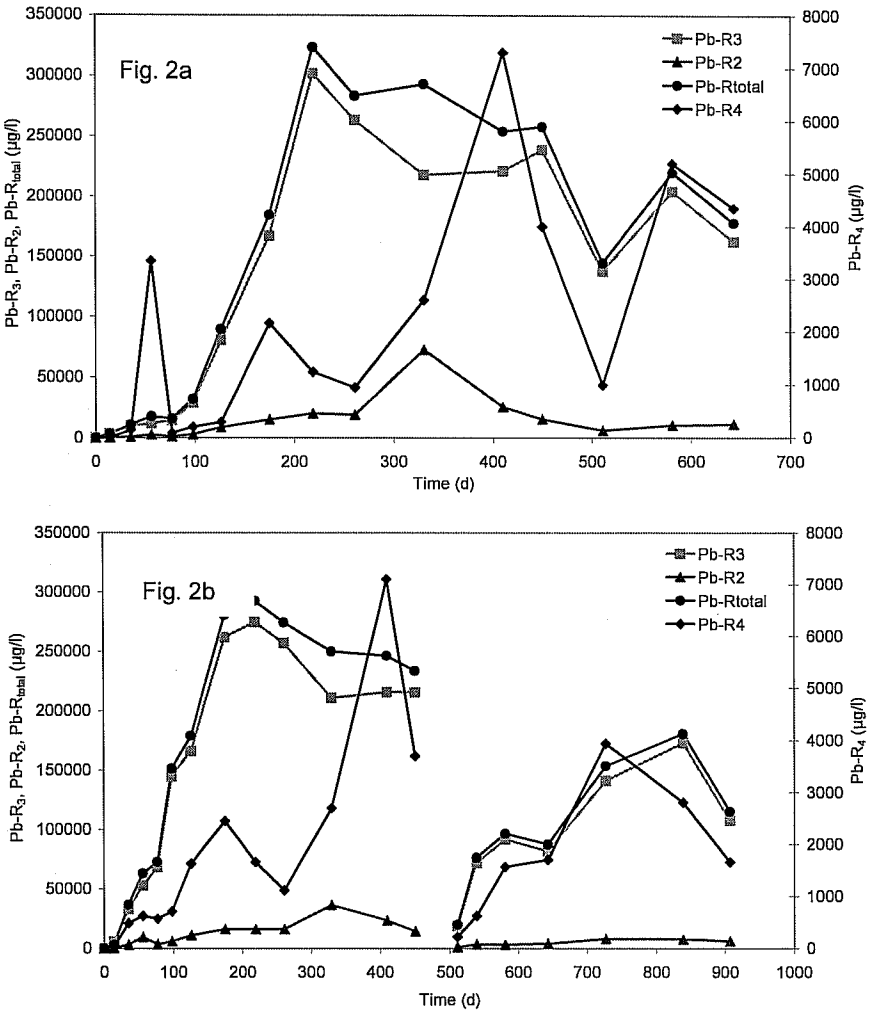

Fig. 2a, b: Elution of total alkyllead, tetraalkyllead-, trialkyllead- and dialkyllead-compounds from soil into circulating water and their degradation in the soil columns S1 (unamended) and S4 (amended with a mineral mix).

To examine whether alkyllead concentrations at field and laboratory conditions were toxic, toxicity was tested with *Photobacterium phosphoreum* (DEV, 1983) using a standard solution of triethyllead chloride and as a reference circulating water from one fertilized and one non-fertilized soil column. Triethyllead concentrations causing 25 (EC_{25}), 50 (EC_{50}) or 75 % (EC_{75}) inhibition were 0.2 mg l^{-1}, 1.4 mg·l^{-1} or 5.6 mg l^{-1}, respectively. Since the circulating water from soil columns contained much higher triethyllead concentrations, and in addition other trialkyllead-, tetra- and dialkyllead species, inhibition of luminescence could not be related to the triethyllead concentration alone. The inhibiting effect of all of these alkyllead compounds could be reduced to 40 % by a 256-fold dilution of the circulating water. At this high dilution the concentration of triethyllead was only around 0.9 mg l^{-1}. Since the triethyllead concentration in the circulating water was much higher, the soil bacteria must have

been much more resistent than the test organism, *Photobacterium phosphoreum*, which represents an unadapted species.
The high concentration and/or the toxicity found in the toxicity test for triethyllead may be the reasons for the slowly decrease of the alkyllead concentrations in the circulating water after reaching the maximum (~ 220 days) in fertilized and non fertilzed soil columns (Fig. 2a, b). An experimental modification after 450 days of incubation should demonstrate the effect of dilution with tap water to non toxic concentrations of triethlyllead concentrations: The circulating water of the 3 non-fertilized soil columns (Fig. 2a) was collected and the soil of each column was flooded three times with tap water. After about 2 weeks, the concentrations of the alkyllead compounds began slowly to increase in the fresh circulating water (Fig. 2a), similar as at the beginning of the experiments. After further 320 days of incubation the maximum of trialkyllead concentrations in the circulating water (not as high as the first maximum) was reached and degradation of alkyllead species was observed. The experiments will be continued until no alkyllead concentrations will be measured in the circulating water.
After 740 days of incubation, extraction and degradation of organolead compounds from contaminated soil in the water-saturated, fertilized soil columns was stopped in order to make a lead balance (Fig. 3). The circulating water was collected and the water-free soil was sampled from the columns. In three different hights the soil was analysed for the occurance of organic and inorganic lead species. The bacterial counts at the beginning and the end of the experiment are shown in Tab. 1.

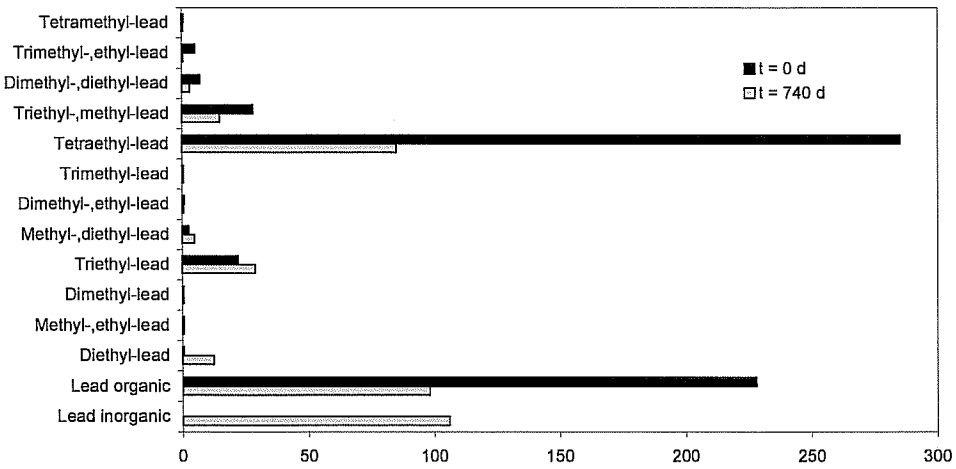

Fig. 3: Mass balance of organic and inorganic lead species of fertilized soil column after 643 days of incubation

Tab. 1: Determination of bacterial count in fertilized soil columns after 740 days of incubation

CFU (g^{-1} dm)	S4+	S5+	S6+
t = 0 d	7 - 10 x 10^3	1 - 6 x 10^3	1 - 2.4 x 10^4
t = 740 d	5.2 - 8.2 x 10^6	4.7 - 8.2 x 10^6	1.5 - 3 x 10^6

After almost 2 years of incubation, the alkyllead compounds of the fertilized soil were degraded to an extend of 58 %, wereas inorganic lead was formed to an extend of 54 % (Fig. 4). Mineral hydrocarbons were degraded to an extend of 37 %. With these experiments we were able to show the biological degradation of organic lead compounds to inorganic lead during an incubation time of almost 2 years. A negative influence of hydrocarbons on the degradation activity of tetraethyllead was described by Mulroy and Ou (1998). In soil, that was not contaminated with gasoline, TEL was degraded completely during 14 days, whereas in the gasoline-contaminated soil 83 – 96 % of the TEL was degraded only after 77 days. In TAL-contaminated soil columns transformation of tetraalkyllead into tri- and dialkyllead was slow and was not significantly influenced by a concomittant hydrocarbon degradation in the presence or absence of minerals.
The laboratory experiments were created as a "closed system" in order to make an accurate mass balance. The negative effects were the high and toxic concentrations of alkyllead compounds in the circulating water. The soil columns with diluted circulating water (Fig. 2a) were incubated for a longer time in order to degrade most of the organic alkyllead species to inorganic lead.

To simulate the conditions in the field which means concentrations of alkyllead species in the groundwater of 1-10 mg l^{-1}, a new set of soil columns was started. Non contaminated sand from the Rhine valley was filled into 3 columns and diluted circulating water of one of the contaminated laboratory columns was used. The time dependence of degradation of alkyllead species is shown in Fig. 4.

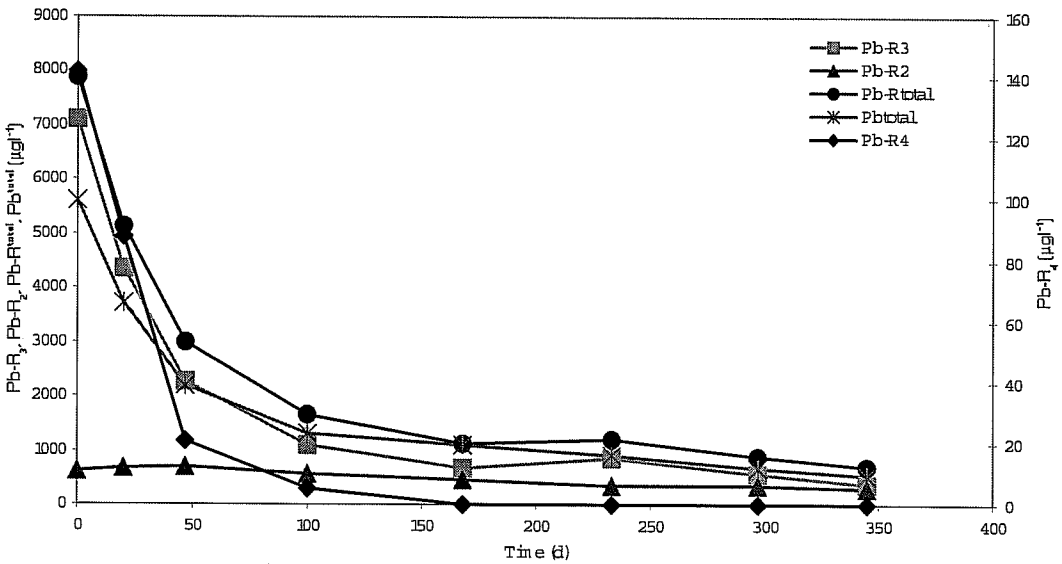

Fig. 4: Degradation of alkyllead compounds from ground water: application of field concentrations

If the initial concentrations did not exeed 8 mgl^{-1}, after 168 days of incubation, almost 100 % of tetraalkyllead compounds and after 345 days 95 % of trialkyllead compounds were degraded. The dialkyllead compounds, the degradation product of tetra- and trialkyllead species were degraded to an extend of 51 %. The time needed for degradation may be reduced by addition of an alkyllead degrading population or by feeding the almost "sterile" sand with more alkyllead contaminated water to enhance the biological activity.

Microorganisms that were capable of degrading tetraalkyllead have not jet been isolated, presumably due to the low water solubility of this substrate of 6 – 9 x 10^{-7} mol l^{-1} (Rhue et al. 1992). Macaskie and Dean (1990) worked with an *Arthrobacter* spec., which was able to grow in a medium that contained 100 µg Pb · l^{-1} as trimethyllead.

To increase the oxygen concentration of the groundwater, air injection wells (AIW) were installed at the contaminated industrial site. The well itself consists of a perforated metal tube reaching 4 m into the groundwater table (Fig. 5). A smaller air injection pipe is fitted into the perforated pipe to inject air from the surface. The air is released at the base of the tube and due to the buoyancy the air moves upwards lifting the water level in the perforated pipe above the ground water level. The result is a groundwater circulation aerea in the aquifer (Luber 1999) and an enrichment of the groundwater with oxygen or other supplements. In the first phase, 4 AIW with a distance of 5 m were installed. Meassurement of the oxygen concentration in monitoring wells showed an increase of oxygen of one order of magnitude during the first weeks of operation. Parallel with the enrichment of oxygen, the tri- and dialkyllead concentration in the groundwater increased due to a higher avilalability of oxygen.

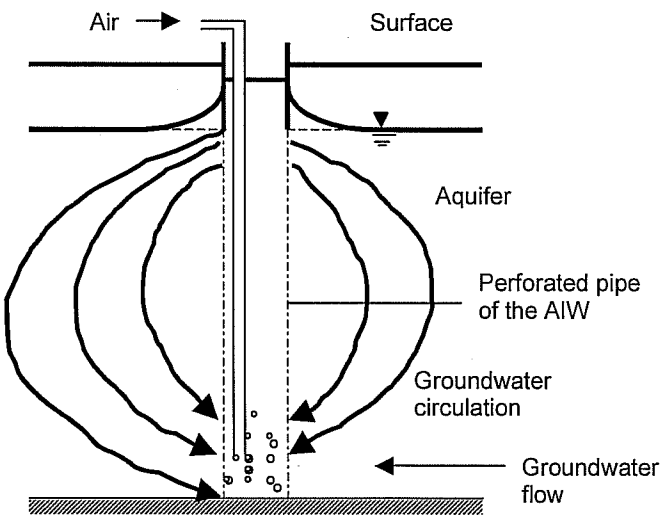

Fig. 5: Air injection well AIW and groundwater circulation during air injection according to Luber (1999)

Analyses of alkyllead compounds in the soil and groundwater at the industrial site before and after air injection led to the conclusion, that in the natural environment not sufficient oxygen is available for a chemical and/or biological transformation of tetraalkyllead compounds to tri- and dialkyllead species. Whether the in situ distance of the hot spot from the boundary of the property of about 150 m in the direction of the groundwater flow is sufficient for a complete degradation of water-soluble trialkyllead via dialkyl to inorganic lead, if enough oxygen is supplied, remains to be determined. From our laboratory experiments it can be concluded, that a bioremediation of alkyllead contaminants in principle is possible, if enough oxygen is supplied. Alternatively, nitrate or sulfate might be suitable electron acceptors.

References:

Blais, J. S., Doige, C. A., Marshall, W. D. and Knowles, R. (1990). Persistence and toxicity of alkyllead salts to anaerobic nitrogen transformations in soil. Arch. Environ. Contam. Toxicol., **19**: 227-234.

Gallert C., Winter, J. (2002) Bioremediation of Soil Contaminated with Alkyllead Compounds. Wat Res **36**: 3130-3140.

Gommeringer, K. and Luber, M. (2000). In situ groundwater remediation using air injection wells and the principle of groundwater circulation. International workshop „Contaminated Sites Assesment and Remediation", 10. Nov. 2000, Mailand.

Hempel, M., Kuballa, J. and Jantzen, E. (2000). Discovery of a transalkylation mechanism – Identification of ethylmercury+ at a tetraethyllead-contaminated site using sodiumtetrapropylborate, GC-AED and HPLC-AFS. Fresenius J. Anal. Chem., **366**: 470-475.

Jarvie, A. W. P., Withmore, A. P., Markall, R. N. and Potter, H. R. (1983). The sulfide assisted decomposition of trimethyllead chloride in aqueous systems. Environ. Pollut. Ser. B. Chem. Phys., **6**: 69-79.

Luber, M. (1999). Luftinjektionsbrunnen zur in situ Grundwassersanierung – Hydraulik und Stoffdurchgang. Doctoral Thesis at the Institute of Soil Mechanics and Rock Mechanics, University of Karlsruhe.

Macaskie, L. E. and Dean, A. C. R. (1990). Trimethyl lead degradation by free and immobilized cells of an *Arthrobacter* sp. and by the wood decay fungus *Phaelus schweinitzii*. Appl. Microbiol. Biotechnol., **33**: 81-87.

Mulroy, P. and Ou, L.-T. (1998). Degradation of tetraethyllead during the degradation of leaded gasoline hydrocarbons in soil. Environ. Toxicol. Chem., **5**: 777-782.

Rhue, R. D., Mansell, R. S., Ou, L.-T., Cox, R., Tang, S. R. and Ouyang, Y. (1992). The fate and behaviour of lead alkyls in the environment: A review. Crit. Rev. Environ. Control, **22**: 169-193.

Landfarming on the Alaskan North Slope – Historical Development and Recent Applications

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ABSTRACT

Arctic landfarming of diesel-impacted gravel is being evaluated by BP as a primary North Slope remediation and treatment technology. The method is gaining support with the State agencies and offers an attractive, low-cost alternative to thermal oxidation. Attempts at arctic landfarming in the early 1990s were marginally successful, although multiple (eight-week) seasons were required to reach the stringent cleanup level of 500 mg/kg DRO. Recent applications have demonstrated that thorough tilling of 18 inch gravel lifts on a three-day cycle maintains aerobic conditions and reduces hydrocarbon contaminant levels by 60-70% over a single summer season. Field experiments were performed in 2002 on large (1,000-3,000 cy) plots using various test parameters and vendor applications. Two applications of 20-10-10 fertilizer (0.9 lbs/cy) and utilization of the indigenous soil microbes provided the most effective results. No other enzyme additions or specialized microbial consortiums were required.

INTRODUCTION

Development of the Prudhoe Bay oilfield on the North Slope of Alaska began in 1970, shortly after field discovery in 1968. Production drill sites and processing facilities were constructed on gravel pads that were approximately five feet thick and designed to insulate and preserve the shallow permafrost. During the course of development, fuel spills (predominantly diesel) contaminated minor portions of some pads. BP is currently assessing and removing the now inactive pads in a field-wide remediation and rehabilitation program. Treatment of the contaminated gravel presents a challenge since winter excavation is frequently required and transport distances may exceed 30 miles. When included with the costs of traditional thermal oxidation, gravel remediation costs can approach or exceed $150 per cubic yard (cy).

Various pad remediation methodologies have been investigated over the past 15 years; on-site treatment of the contaminated gravel is preferred. Landfarming and other biotreatment alternatives have been evaluated since at least 1990. Initial in-situ and ex-situ attempts at landfarming experienced variable degrees of success; however, recent ex-situ treatments have demonstrated that the method provides a low-cost, effective alternative to thermal oxidation. Achievement of 500 mg/kg diesel range organics (DRO) cleanup goals and +70% hydrocarbon mass reduction have been demonstrated in a single, eight-week summer season. This report examines the North Slope landfarming methods attempted since 1990 and considers those variables that have potentially contributed to the different levels of success.

REGIONAL SITE CONDITIONS

Harsh, arctic field conditions undoubtedly pose the greatest challenge to landfarming on the North Slope. Temperature measurements and other climate information have been collected for at least 15 years (1) along the Beaufort Sea coastline at Prudhoe Bay and the Barrow (AK) Airport. Mean annual monthly temperature and, growing degree-day units (45°F base temperature) from 1971-2000 are summarized in Figure 1. These data demonstrate that surface and air temperatures are optimal for plant growth primarily during July and August. Summer warming is reflected in shallow subsurface temperatures by a 2-3 week lag time. Although the temperatures of frequently tilled, shallow (18-24 in) landfarm soil-lifts exceed undisturbed soil subsurface temperatures, the maximum extent of the treatment season is only a 6-8 week period. Soil temperatures in a 2001 landfarming experiment (2) ranged primarily between 35-50°F, with minimum and maximum spikes of 30 and 62°F, respectively.

The mean annual precipitation of only 4.16 inches demonstrates that the North Slope is a true desert. This seems contradictory when observing the numerous shallow lakes and saturated tundra. The short thaw season and shallow (12-24 in) depth of relatively impermeable permafrost hinders evaporation and infiltration of the surface water. Most of the precipitation falls during July and August although the amount is insufficient to maintain adequate moisture in the landfarm soil-lifts; water must be added periodically throughout the treatment season.

The pad gravel is mined locally from borrow pits along the major rivers in the Prudhoe Bay field. The material contains 3-10% clay and silt-sized particles, 30-40% sand, and 50-65% gravel (3) and is nutrient-depleted; fertilizer must be added prior to and during treatment (discussed below). The gravel is frequently re-used for pad and road maintenance after treatment.

DESCRIPTION OF INITIAL LANDFARMING ATTEMPTS (1990-1995)

Surfcote Pad

The Surfcote Pad was constructed and occupied during development of the eastern side of the Prudhoe Bay field. Diesel contamination was identified in an approximate 100 x 300 ft area in a former fuel storage area. A pilot test was conducted during 1990 and 1991 by constructing three 25 x 25 ft lined treatment cells on which two feet of contaminated gravel was spread. One control cell (A) was selected, a second (B) was treated with a microbial consortium and fertilizer (amount not specified), and the third (C) only received 200 pounds of ammonium nitrate fertilizer [~4.4 pounds per cubic yard (lbs/cy)]. Soil moisture checks and roto-trimmer tilling were performed approximately twice weekly (frequency of 3-7 days). Water was added to maintain the soil moisture at 3-10% (15-50% of soil capacity) in each plot. The initial DRO concentrations of the blended gravel in the three test plots ranged between 9160 and 9880 mg/kg, and the test was conducted for 41 days (July 26 – September 6, 1990). After that period, the DRO levels had decreased to between 5220 and 5690 mg/kg (44-45% decrease; 74-128 mg/kg/day). A statistical ANOVA demonstrated that no significant difference existed between the treatment types; each plot, including the control cell, decreased significantly and similarly.

The pilot test was continued in 1991. Plot A was again used as a control; Plots B and C received low- and high-dosages of ammonium nitrate fertilizer (22:4:4, NPK). Plot B received a 15:1 C:N ratio (3.0 lb/cy; assumed previous season DRO endpoint, one foot depth penetration) and Plot C received a 7:1 C:N ratio (6.0 lbs/cy). All other variables remained constant; a treatment period of 75 days was utilized (June 22 – September 5). At the end of the 1991 test, DRO levels in the three plots had decreased an additional 51-70%. This resulted in a total DRO decrease for the two years of 77% [Plot A (control); 2159 mg/k final DRO], whereas DRO in Plots B and C decreased by 86 and 87% (1297 and 1250 mg/kg final DRO, respectively). Although no statistically significant difference existed between the two application rates, a statistically significant difference (95% probability) was determined between the fertilized plots (B and C) and the control plot A. The addition of fertilizer increased the biodegradation rate.

Drill Site 1 and 2 Relief Pits

Relief pits are unlined, bermed areas once used to contain the pressure release of oil-water separators in case of an operational upset. In some historic cases, crude oil was discharged to the tundra pit floors; steel tanks are now used to capture such discharges. In-situ landfarming of the affected pit floors was investigated beginning in 1991 through 1995. Various techniques that were applied to the Drill Site 1 and 2 pits included 1) draining, pumping, and ditching in attempts to remove water and aerate the saturated tundra; 2) repeated tilling (8 inch depths); and, 3) fertilizing [0.3 lbs/cy each of 34-0-0 NPK (ammonium nitrate) and 8-32-16 NPK]. Hydrocarbon concentrations in the affected pit floors typically ranged from 500-8000 mg/kg DRO. Although seasonal decreases in the mean DRO levels were occasionally observed, statistical demonstration of a systematic decrease in contamination was not achieved in either pit. This failure was attributed to the saturated soil conditions that persisted despite attempts to de-water, and to high variability in the DRO concentrations in the pit floors.

Service City Pad

The site includes an abandoned gravel pad that was leased by oil field service contractors and served as a former storage, maintenance, and staging area. Diesel contamination was identified (2000-2500 mg/kg DRO) within an approximately 150 ft diameter area at a depth of three feet. Three 50 x 50 ft test plots were prepared in 1992 by installing forced aeration pipes at 3-5 ft depths in vertical trenches (10 ft spacings) and backfilling. Attempts were made to deliver air-flow at 80 standard cubic feet per minute (scfm), although frozen pore water in the deeper trenches restricted air-flow to 40 scfm until thawing occurred late in the summer. This method is considered a bioventing application although information can be gleaned that relates to in-situ landfarming. Each plot received a different treatment – one plot received air only (Plot A), another received air plus fertilizer (B), the third received air, fertilizer, and a bacteria consortium (C). A total of 1.1 lbs/cy of ammonium nitrate fertilizer (liquid form) was applied in 10 treatments to each plot. The test period was 75 days (July 3 – September 15). No statistically significant decrease in DRO concentrations occurred; the initial and final levels in Plots A, B, and C were 1520 vs. 1500, 2520 vs. 2390, and 160 vs. 330 mg/kg, respectively. Failure was attributed to insufficient aeration (frozen ground and saturated soil conditions) and to low in-situ pad temperatures (~38°F) that were assumed to limit bacterial activity.

DESCRIPTION OF RECENT LANDFARMING APPLICATIONS (2000-2003)

Haliburton Pad

The Haliburton Pad (4) is adjacent to the Prudhoe Bay field. Approximately 7400 cy of diesel-contaminated gravel (1010 mg/kg DRO, mean pad concentration) was identified in the lower half of the six-foot thick pad. Remediation of this large volume of contaminated material by conventional thermal methods was prohibitively expensive and landfarming was approved as a remedial alternative by the Alaska state agencies. An in-situ landfarming method was selected that included treatment amendments by a private vendor [Enzyme Technologies Inc. (ETEC)]. Five treatment cells were constructed within the pad by removing the upper three feet of clean gravel and stockpiling on site. French-drain catchment basins were then constructed within each cell to collect and remove the intra-pad pore water. The mean DRO concentrations for the five cells ranged between 400-1680 mg/kg. Each cell was inoculated on July 24, 2000 with ETEC nutrient enhancers (fertilizer type and quantities unknown), microbial enzymes, and a hydrocarbon-degrading bacterial consortium. Each cell was tilled daily the first week, the rate was reduced to three times per week for the remaining three weeks. A 30-day treatment period was used. At the end of the treatment the mean DRO levels in the five cells ranged between approximately 30-220 mg/kg. The mean pad DRO concentration (average of all treatment cell samples) was 162 mg/kg, reflecting an 84% reduction in hydrocarbon levels.

Service City Pad

A second attempt was made to remediate contamination on the Service City Pad in 2002. Additional assessments revealed contamination over a much larger area than previously identified in the 1992 study. The study was performed by BP in cooperation with the Alaska Department of Environmental Conservation (ADEC) to assess various landfarming treatment methods on a production-sized scale. A total volume of 15,500 cy of contaminated gravel was excavated from an area with contaminant levels that exceeded 2000 mg/kg DRO and that included the former study. Several "hot spots" within this area exceeded 7000 mg/kg DRO. The excavated material was divided proportionally (by truckload) into four treatment plots (1.5 ft lift thickness) in an attempt to "normalize" the starting DRO levels between plots. One plot (1227 cy) was designed as a control cell and received no amendments. Plot A (1314 cy) received two fertilizer applications (20-10-10 NPK; 0.86 lbs/cy total); Plot B (2014 cy) received a proprietary vendor application of nutrients (type and quantity unknown) and a microbial consortium; and, Plot C (11,079 cy) received treatment products provided by ETEC (described above - see Haliburton Pad section). A greater quantity of contaminated gravel was treated with the ETEC products due to the success at the Haliburton Pad. Tilling of the complete lifts was performed with a tractor-led rotary tiller at a frequency of four times per week for the control cell and Plot C, once every three days for Plot A and once every five days for Plot B. The tractor and tiller were decontaminated between tillings of different test plots. A treatment period of 56 days was used. The mean DRO concentration range for each of the four plots was 913-1053 mg/kg at Day 0. Soil moisture was measured daily and maintained at 30-40% for the control cell and Plot A, whereas vendor-specified moisture levels were used in Plots B and C.

The results are summarized in Figures 2 and 3. The decline in DRO concentrations for the four plots ranged between 48-71% (261-506 mg/kg final mean DRO). The highest percentage

of DRO decline occurred in Plot A (nutrients only); however, Plot C (ETEC) compared favorably and began with a higher DRO concentration (1046 vs. 913 mg/kg). A non-parametric statistical analysis demonstrated that no significant difference existed between Plot A and C. Figure 2 demonstrates that no appreciable contaminant loss occurred in Plot B and the control plot after Days 14 and 28, respectively. These data suggest that the loss in the control cell and Plot B was due to volatilization and/or leaching since the gravel in the control cell was depleted of nutrients. The similarity in performance between Plots A and C indicate that additions of exotic microbial consortiums and enzymes are unnecessary for Prudhoe Bay remediation. Plate counts of hydrocarbon degrading bacteria were approximately equivalent in Plots A and C (1.2×10^7 vs. 1.0×10^7 colony forming units) at Day 56, demonstrating that indigenous hydrocarbon-degrading bacteria exist at the site and are capable of supporting biodegradation. The test results imply that frequent tilling and nutrient addition is primarily responsible for the contaminant loss at Service City, and that 60% of the loss may be associated with volatilization.

Sea Air Motive Pad

BP conducted an additional landfarming treatment in coordination with the ADEC at the Sea Air Motive pad in 2003 using the same treatment conditions as applied in Plot A (Service City Pad; nutrients only) during the 2002 test. A treatment period of 77 days was used. The pad adjoins the commercial airport (Deadhorse, AK; near Prudhoe Bay) and was used to dispense jet fuel [high gasoline-range organic (GRO) fraction]. Arctic landfarming of the fuel-contaminated gravel was tested; the results are shown in Figure 4. Initial starting concentrations (June 20) of GRO and DRO were 358 and 737 mg/kg, respectively, whereas the final concentrations (September 6) were 101 and 187 mg/kg. Hydrocarbon GRO and DRO reductions were 72 and 75%, respectively. The decline in DRO levels approximates the 71% value observed during the Service City test. Note that the GRO concentration of the freshly stockpiled material (May 23; 1020 mg/kg) declined to the starting level (358 mg/kg) in only 13 days. This reflects the high volatility of the jet fuel. Respiration tests performed during the study reflect a hydrocarbon decay rate of 14.0 mg/kg/day for the study period. Only 1.6 mg/kg/day (11%) was attributed to biodegradation, the remaining 12.4 mg/kg/day was attributed to volatilization and/or leaching.

SUMMARY AND CONCLUSIONS

A review of the various attempts at arctic landfarming over the past 13 years has provided information that will optimize future remediation treatments using this technology. Recent Prudhoe Bay landfarming treatments (since 2000) have been successful; contaminant reductions of approximately 70% of the initial DRO levels have been achieved in a single summer season (60-75 days). Earlier attempts experienced decays of less than 50% in a single season, or in some cases, no reductions at all. Saturated soil conditions and infrequent tilling, i.e. insufficient aeration, appears to be responsible for the poor performance. Recent treatments with multiple test plots have demonstrated that DRO declines of 70-75% over a summer season can be achieved simply by tilling on a 2-3 day schedule, fertilizing (1-1.5 lbs/cy of 20-10-10 NPK; 1000-2000 mg/kg DRO), and maintaining adequate soil moisture (30-40%). The indigenous hydrocarbon-degrading bacteria provide sufficient biodegradation capacity. Exotic nutrients, enzymes, or specialized bacterial consortiums appear to offer no added benefit in the Prudhoe Bay treatments. A hydrocarbon biodegradation decay rate of 1.6 mg/kg/day was recently measured, suggesting that only 11% of the observed decline is attributed to bacteria. The remaining decline is attributed to volatilization and/or leaching.

REFERENCES CITED

1. Western Regional Climate Center, Division of Atmospheric Sciences, Desert Research Institute; Reno, Nevada. http://www.wrcc.dri.edu/cgi-bin/cliGCStG.pl?akbarr.

2. SLR Alaska, "Final Corrective Action Report Service City Pad Prudhoe Bay, Alaska"; prepared for BP Exploration Alaska and submitted to Alaska Department of Environmental Conservation, Anchorage, AK; March 13, 2003.

3. Geosphere, Inc., "Assessing Hydrocarbon Cleanup Levels Appropriate for North Slope Gravel Pads"; prepared for BP Exploration Alaska; draft report, final in preparation.

4. URS Corporation, "Remediation of 17,000 Pounds of Hydrocarbons in One Month"; technical marketing publication; April, 2001.

5. SLR Alaska, "Final Corrective Action Report Sea Air Motive Pad Prudhoe Bay, Alaska"; draft report in preparation for BP Exploration Alaska for submittal to Alaska Department of Environmental Conservation, Anchorage, AK; September, 2003.

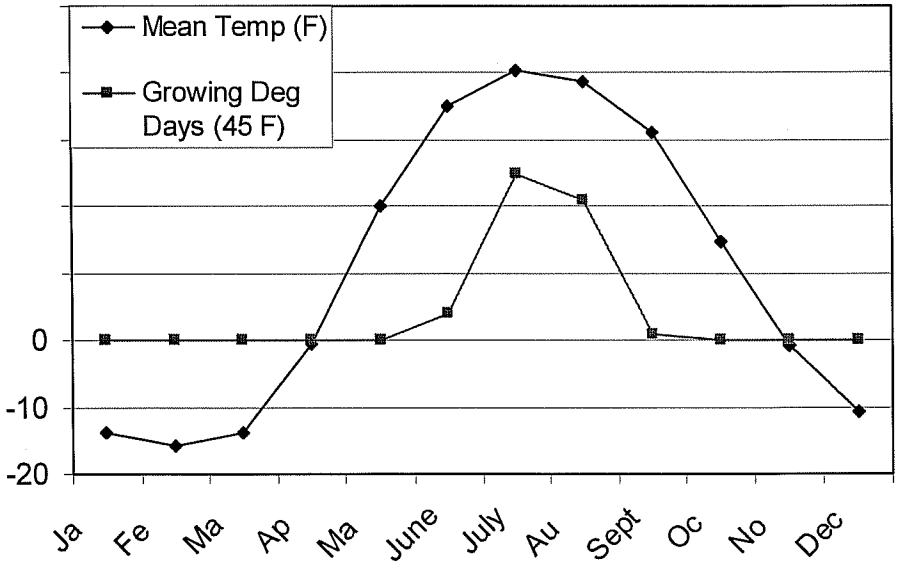

Figure 1. Mean annual monthly temperatures and 45°F growing degree-days at the Barrow Airport (North Slope, AK; approximately 150 miles west of Prudhoe Bay). Mean annual data from 1971-2000.

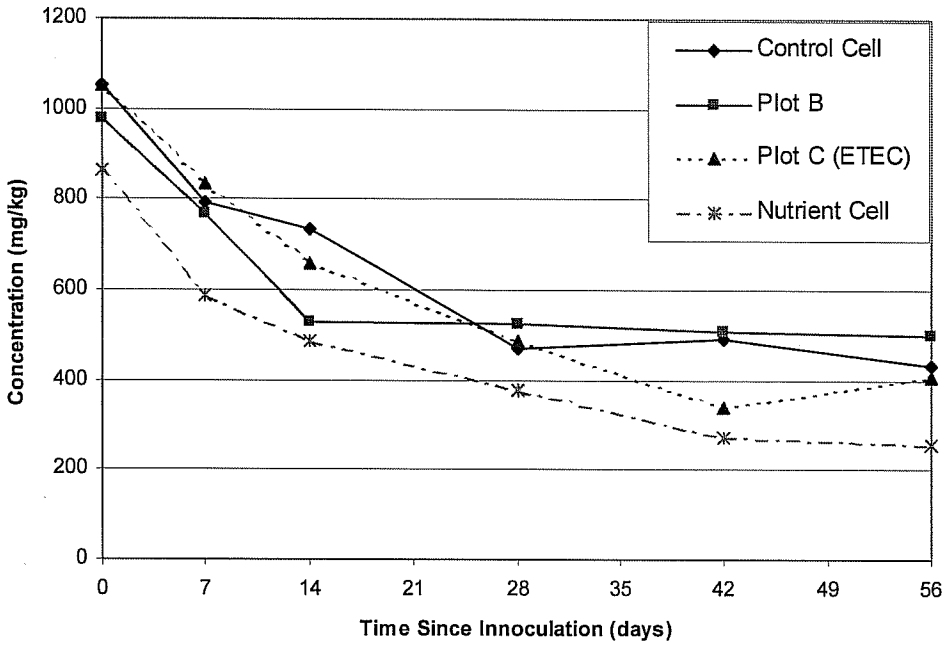

Figure 2. DRO concentrations for individual landfarming treatment plots at Service City pad.

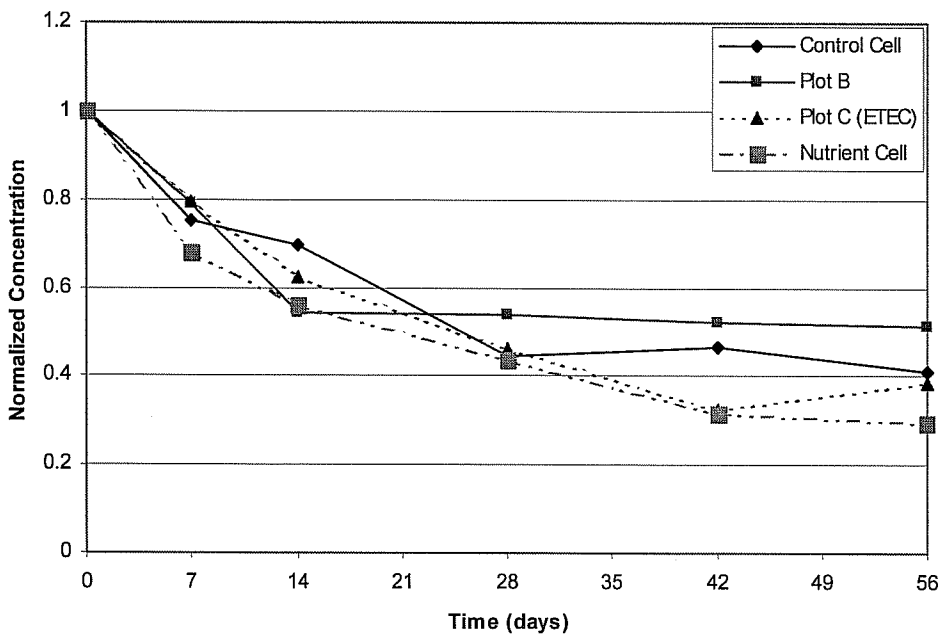

Figure 3. Normalized DRO concentrations for individual landfarming treatment plots at Service City pad.

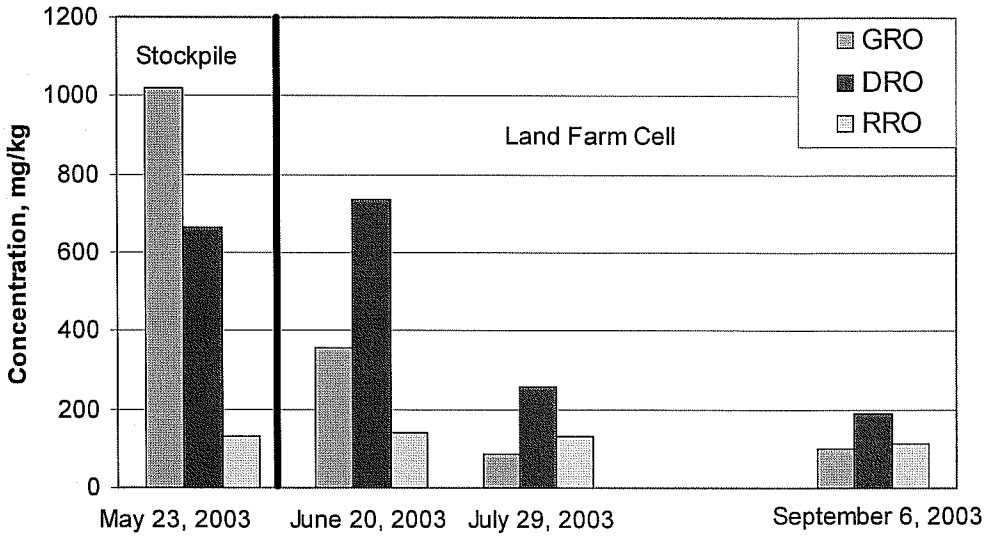

Figure 4. Hydrocarbon GRO, DRO, and RRO concentrations during a landfarming treatment period of 77 days at the Sea Air Motive pad.

Bioventing of Gasoline-Contaminated Soil: Some Aspects for Optimization.

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ABSTRACT

Underground storage tank leakage is a concern in North America because gasoline contaminated soil can cause significant groundwater contamination. São Paulo (Brazil) has leakage rates similar to North America. The typical in-situ remediation process is soil vapour extraction (SVE), but experience shows that tailing usually occurs. Bioventing is an innovative technology to address tailing in the remediation of contaminated sites, where natural occurring hydrocarbon degrading microorganisms are stimulated. The drawback is the prediction of time needed for bioventing to reach site closure. Encouraging laboratory results have not always translated into similar outcomes in the field. One reason for this inconsistency is the scale-dependent phenomenon that influences the process. Research is being conducted to develop correlations that incorporate a variety of factors including soil type, contaminant composition, and nutrient composition. These correlations will assist in better predicting the necessary time to reach site closure.

Biodegradation of Petroleum Hydrocarbons in a Soil Containing Polyacrylamide

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Abstract

The objective of this study was to evaluate the fate and toxicity of total petroleum hydrocarbons (TPH), polyacrylamide and acrylamide monomer in soil under aerobic conditions for mixtures of commercially available products that have application as an anti traction material (ATM) (Southwest Research Institute patent pending for ATM).

The aerobic biodegradability of petroleum hydrocarbons in several formulations was determined using a simple microcosm/respirometric method based on carbon dioxide production and TPH depletion. The microcosms consisted of 1L mason jars fitted with sealed rubber caps that allowed headspace gas samples to be collected in a sealed system. The analytical procedure included the detection of peaks for the compounds in TPH by gas chromatography and identification of peaks with a mass spectrometer (GCMS). Mole fractions of the major components in TPH (undecane, dodecane, tridecane and tetradecane) were calculated from the detected peaks. The extracted soil was analyzed for total organic carbon (TOC) content in order to examine the carbon balance. The method described here provides a simple and inexpensive method for determining the aerobic biodegradability of organics in soil.

Results indicated that, for the polyacrylamide (PAM) treatments in soil, there was no significant CO_2 production in the headspace of the microcosm within the experimental time period. Total organic carbon values obtained for the initial and final soil showed no significant PAM biodegradation within a time period of 161 days. This confirms that PAM biodegradation is a slow process and may take several years.

Reducing Remediation and Long-Term Monitoring Costs Through Accurate Site Assessment

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ABSTRACT

Environmental remediation and long-term monitoring can be a costly endeavor. A GORE™ Survey is one site assessment tool that can reduce costs by providing a more accurate view of the subsurface contamination. By reporting the presence or absence of a wide range of organic compounds -- from precursors to degraded by-products -- the survey can focus remediation efforts, thereby reducing the number of required monitoring wells and long-term sampling costs.

This presentation will provide an overview of this USEPA ETV performance verified technology, its applications, and two case studies related to petrochemical contaminants. The first study looks at a fuel storage terminal, where GORE™ Survey data resulted in a 55% reduction in the number of regulator-required monitoring wells. The second study reports on a long-term monitoring program of several retail gas stations. At one station, subsequent sampling revealed new contaminant releases when compared to the baseline, resulting in a modification to the site remedy plan, as well as proper assignment of liability.

THE EFFECT OF REGIONAL CONFLICTS AND POLITICAL RIVALRIES ON THE RELEASE OF PETROLEUM HYDROCARBONS TO THE ENVIRONMENT

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ABSTRACT

The twentieth century has shown us the economic and social importance of petroleum extraction from the Earth. In almost all of our daily activities, hydrocarbon plays a driving force. Commuting and traveling, building and fixing the house, mowing the lawn, etc., are all feasible with petroleum generated energy. Many of the products that we use are made from petroleum hydrocarbons. Hospital syringes, plastic bags, food containers, computers, etc., are things that are all or partly made with petroleum products and we take them for granted.

Control of petroleum resources has led to long eras of cold wars between nations and in some cases has led to disastrous conflicts. During any regional conflict, the environment is the last thing that the warring sides focus their attention on. The destruction of terrain, crops or the entire ecosystem is a military tactic practiced from ancient times. When large oil fields are shared among two or more countries, there is always a heated rivalry between neighboring countries to extract the maximum possible petroleum from the shared ground. Here, again, the environment falls victim to the abuse of Earth resources. In this article, the environmental damages caused by regional conflicts and political competitions are assesses and discussed. As two contemporary living cases of environmental disasters, the (land and sea) damages of the 1991 Persian Gulf War to the ecosystem and the ecological degradation of the Caspian Sea caused by the competition between the surrounding countries for petroleum extraction are discussed in this article.

Keywords: conflicts, environmental damage, petroleum release, politics

INTRODUCTION

The environment is always the victim of political conflicts and wars. During the Persian Gulf crisis of 1990 to early 1991, the Persian Gulf area experienced overwhelming environmental stress. Over 700 oil wells were destroyed and set on fire by the retreating Iraqi forces from Kuwait in February 1991 [1]. Large quantities of crude petroleum were released into the marine, terrestrial and atmospheric environments. Tidal currents and water mass circulations in the Gulf favoring northwest to southeast and east directions pushed the floating oil pools towards the northern shores of Saudi Arabia and southwestern Gulf States. At least 30,000

marine birds exposed to crude oil were killed. Over 20 per cent of mangroves on the eastern coast of Saudi Arabia and about 50 per cent of the coral reefs were affected by oil contamination. Hundreds of square kilometers of seagrass beds (feeding grounds for dugongs and turtles) as well as tidal mud flats were inundated with heavy petroleum products [2].

Due to the presence of large quantities of unextracted crude oil, Caspian Sea (the World's largest land-locked water body) which lies less than 1000 km north of the Persian Gulf has in recent years become the focal point for economic development of most of the Caspian countries. The Caspian Sea's ecological balance is already facing serious consequences [3] and if neglected, the World may soon face another dead water body similar to the Aral Sea that is located about 400 km northeast of the Caspian Sea in Asia Minor.

In this article the environmental problems related to oil extraction and spills in the Caspian Sea and the 1991 Gulf War impact on Persian Gulf contamination with petroleum products are discussed.

THE CASPIAN SEA CASE STUDY

The Caspian Sea is the largest lake in the world with an area of about 400,000 km^2 (equivalent to the size of Japan) (Figure 1). It is 1,200 km long and 170-450 km wide, and its water volume is 80,000 km^3. The total length of the shoreline is about 7,000 km. The average depth is 180 m and its maximum depth is 1,025 m. All these data are approximate, because they vary considerably depending on the water level of the Sea [4,5]. Morphologically, the Caspian Sea is divided into three main parts, which are more or less equal in area: a very shallow northern part with depths not exceeding 10 m, a middle part with an average depth of 170 m and a maximum depth of 790 m, and the deepest southern part, which has an average depth of 325 m and a maximum depth of 1,025 m [4]. The proportional volumes of the three parts are correspondingly 1/100, 1/3, and 2/3 of the total volume. The salinity of the Caspian Sea water ranges between 0.2 g/liter at the mouth of the Volga River to 12-13 g/liter in the central and southern parts. The northern section has the equivalent of 28% of total surface area and an average depth of 6.2 meters. The direction of either current in this section is clockwise. Central section, covers 36%. The southern section covers the remaining 36%. Water movement direction in the central and southern sections are counterclockwise [4].

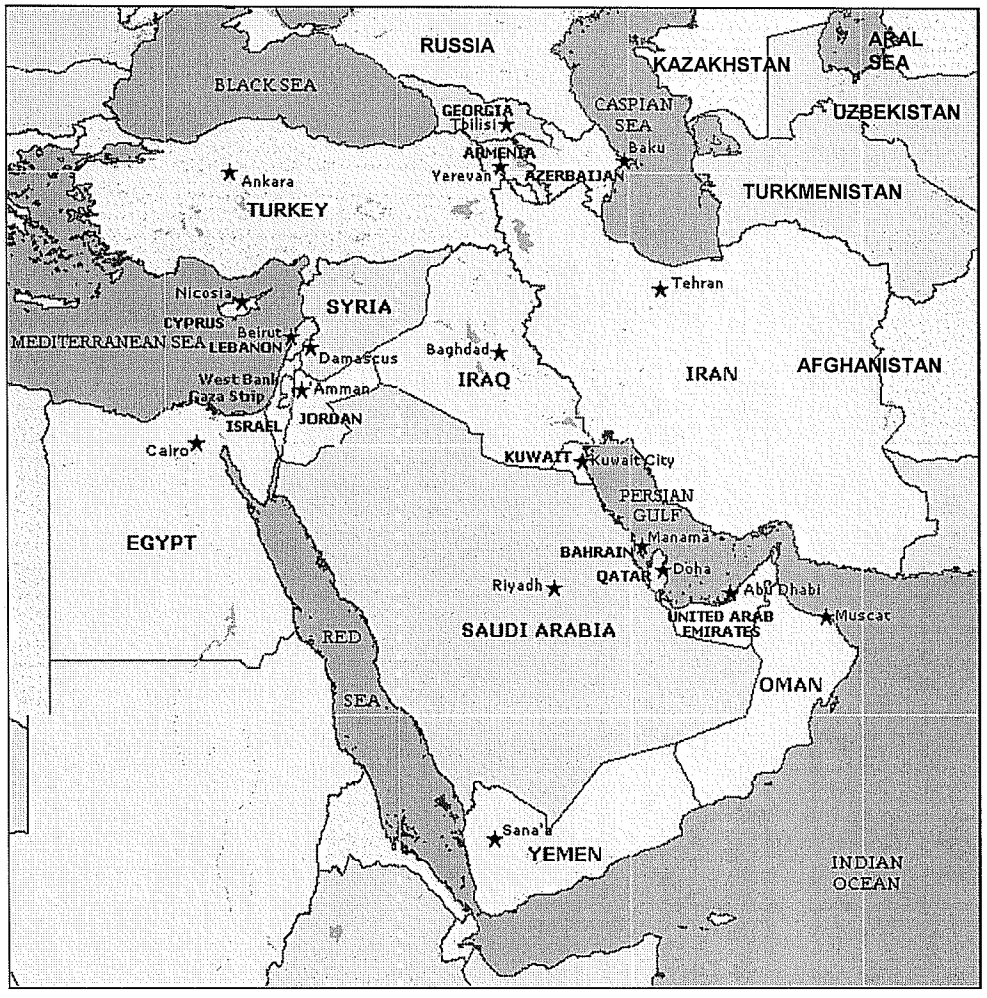

Figure 1. Map of the Persian Gulf, the Caspian Sea and Neighboring Countries.
(The Courtesy of World Sites Atlas, Madrid, Spain)
http://www.sitesatlas.com/Maps/Maps/MEast.htm

The level of water in the Caspian Sea is 26 meters below the mean sea level. The water level has demonstrated continuous up and down changes. No clear explanation is available for the reason of these changes. The local people believe that the Caspian Sea water level fluctuation is the results of frequent earthquakes in the area, affecting the structure under the sea. It could be noted here that global warming of the past two decades might have had its share of bringing the Caspian Sea water level higher than its average level recorded in the first eight

decades of the twentieth century. Warmer temperatures may have melted the glaciers located in northern Ural Mountains and northern Russia increasing the water volumes that discharges into the Caspian Sea from the northern rivers. The average water balance of the Caspian Sea from 1900 – 1985 has been tabulated in Table 1.

Table 1. The average water balance of the Caspian Sea, 1900-1985 [4]

Parameter	**km^3/year**
River inflow	+298
Precipitation on the Sea's surface	+74
Evaporation from the Sea's surface	-370
Outflow to the Bay of Kara-Bogaz-Gol	-14
Total	-12

As Table 1 indicates, from 1900 to 1985, there has been a net evaporative loss of 12 km3/year from the Caspian Sea. Since 1978 (The year of Tabas/Khorasan-Iran major earthquake) water level in the Caspian Sea has followed a rising path. Since 1985, the water level of the Caspian Sea has risen 2.5 meters and has flooded many coastal towns in Kazakhstan. At the present time, the level of the water is relatively stable. If water levels continue to rise and one day reach to the normal sea level again, areas as far as St. Pittsburgh in Russia could be flooded. Major rivers discharging into the Caspian Sea are Volga, Ural, Terek, Kuma (flowing through Russia), Sefid Rud, and Atrak (flowing through Iran). Caspian Sea is also an important inland water route. The Caspian occupies an enormous depression and was once linked with the Aral and Black Seas. Much of the land surrounding the sea is covered with a thick layer of yellowish-green clay that was deposited by the sea.

One of the major economic aspects of the Caspian Sea is the fishing industry. Caviar (sturgeon fish eggs) from the Caspian Sea is simply considered one of the most exquisite delicacies in the world. It is completely dependent upon the sea for development and taste.

Petroleum Reserves and Extraction

The local population surrounding the Caspian Sea learned to extract and use oil for domestic purposes in small-scale more than two millennia ago. Large-scale extraction of oil and

gas in the Caspian Sea oil fields started in the middle of 19th century, during which production has had a fluctuating trend. After the disintegration of the former Soviet Union, the newly formed countries of Azerbaijan, Kazakhstan, and Turkmenistan together with Russia and Iran have focused their attention on the oil reserves of the Caspian region [6]. Historical discharge of petroleum by-products and pollutants into the Caspian Sea environment has positioned it in an awkward situation. In terms of pollution discharge ranking Russia stands first, followed by Azerbaijan, Kazakhstan and Turkmenistan. Iran has a small share of polluting the Caspian Sea [3]. However, it should be noted that Iran has not yet conducted any petroleum related drilling and extraction on its Caspian Sea shores and offshore areas. Once these activities start, the possibility of higher pollution discharge into the Caspian Sea will rise significantly.

The petroleum reserves of the Caspian Sea region are detailed in Table 2. The bulk of the petroleum reserves are located in Kazakhstan, Azerbaijan, and Turkmenistan respectively.

Table 2. Petroleum Reserves and Oil Production of the Countries Surrounding the Caspian Sea. (production and export are in 1000 barrels/day) [6].

Country	**Total Reserves**	**Production**	**Exports**	**Major Exporting Cities**
Azerbaijan	31-38 BBL	198.7	42.6	Baku
Iran	12 BBL	0.0	0.0	Neka / Kharg Island
Kazakhstan	95-101 BBL	532.1	254.5	Tengiz/Aktyubinsk/ Atrau
Russia	5 BBL	52.0	0.0	Novorossisk / Terskoye
Turkmenistan	34 BBL	103.9	26.4	Turkmenbashi / Charjou
Uzbekistan	1 BBL	182.6	3.8	-
Total	178 – 191 BBL	1069.3	327.3	-

Geopolitical Aspects of the Caspian Sea

In 1941, during World War II, Hitler wanted to use Caspian oil to fuel his army. He declared that if he failed to seize the Caucasus region, he would be forced to end the war. The defeat for conquering the Caucasus oil came in late 1942 and was the first major setback for Germany. With an estimation of 50 to 200 billion barrels of oil reserves, It is projected that the Caspian Sea is the third largest oil and gas reservoirs of the world [7]. The political changes of the 90s led to diminishing attention that was given to the Caspian Sea environment during the 80s [8].

Ecological Impacts

Commercial oil and gas explorations have taken place in the Caspian Sea for over 150 years. The Volga River and oil drilling works are the two major sources of pollution in the Caspian Sea [8]. Based on published data, petroleum hydrocarbons, phenols, surfactants, and organochlorine pesticides are the priority pollutants entering the Caspian Sea mainly from rivers originating or flowing through Russia.

Scientists estimate that each year an average of 60,000 metric tons of petroleum byproducts, 24,000 tons of sulfites, and 400,000 tons of chlorine are discharged into the Caspian Sea [3]. The present level of contaminants entering the Caspian Sea are threatening the existence of the rare sturgeon and fresh water seals that live there. Since the year 2000, thousands of Caspian seals have died due to pollution that weakened their immune systems. Environmental scientists have warned that poaching of sturgeon and oil prospecting is threatening to push the sturgeon and fresh water seal species into extinction [9].

The deposits of mineral exploration, particularly oil extraction and pipeline construction, have contributed to the pollution of about 30,000 hectares of land [9]. Oil pollution in the Caspian Sea comes from flooded wells (due to rising Sea levels), offshore production, accidental releases of oil, natural seeps, and major rivers [7]. Table 3 lists the estimated total annual oil input to the Caspian Sea.

Table 3. Estimated Total Annual Oil Input to the Caspian Sea [7].

Source	Oil input (tons/year)	Oil input range (tons/year)	Percentage
Seepage and erosion	20,000	10,000 – 50,000	12.5
Oil industry activities	8,000	5,000 – 13,000	5.0
Municipalities	21,000	10,000 – 40,000	13.1
Other industries	35,000	15,000 – 50,000	21.9
Rivers	75,000	50,000 – 260,000	46.9
Atmosphere	1,000	300 – 2,000	0.6
Total	160,000	90,000 – 300,000	100.0

If a comprehensive plan is not set forth for the preservation of natural habitat of the Caspian Sea, there will be no doubt that in near future, sturgeon, caviar, and seals will become past legends and will only exist in science and history text books.

THE PERSIAN GULF CASE STUDY

The Persian Gulf, is a 960-km-long body of water which separates Iran from the Arabian Peninsula, and one of the most strategic waterways in the world due to its importance in world oil transportation. At its narrowest point (the Strait of Hormuz), the Gulf narrows to only 55-km wide (Figure 1).

During the Persian Gulf crisis from 1990 to early 1991, the Persian Gulf area experienced tremendous environmental stress. Over 700 oil wells were destroyed and set on fire by the retreating Iraqi forces from Kuwait in February 1991 [1]. Large quantities of crude petroleum were released into the marine, terrestrial and atmospheric environments. Tidal currents and water mass circulations in the Gulf favoring northwest to southeast and east directions pushed the floating oil pools towards the northern shores of Saudi Arabia and southwestern Gulf States. At least 30,000 marine birds exposed to oil were killed. Over 20 per cent of mangroves on the eastern coast of Saudi Arabia and about 50 per cent of the coral reefs were affected by oil contamination. Hundreds of square kilometers of seagrass beds (feeding grounds for dugongs and turtles) as well as tidal mud flats were inundated with heavy petroleum products [2]. In a study comparing the concentrations of heavy metals in sea sediments among nine major harbors in populous areas of the world, Al-Arefj and Alam (1993) found that the highest concentrations

of heavy metals belonged to northern shores of Saudi Arabia and the Bay of Kuwait following the end of the 1991 Gulf War [11].

Water Currents in the Persian Gulf

The Persian Gulf has an average depth of 35 meters with maximum depths of 110-160 m in current scoured channels near the islands [11]. It is connected to the western Gulf of Oman through the Strait of Hormuz (Figure 1). The evaporation rate is 1.4 m/yr., river runoff is 0.15-0.46 m/yr. and precipitation is 0.07-0.1 m/yr. The high evaporation rate combined with small connection to open oceans has lead to formation of saline, dense water mass known as Persian Gulf Water (PGW) and a reverse estuary circulation through the Strait of Hormuz [11]. Flow of water out of the Gulf is confined to the southern side of the Hormuz channel by geostrophy. The Indian Ocean surface water flows into the Gulf along the northern side of the Strait and continues northward along the Iranian coast. Surface water modeling conducted by Swift and Bower (2003) indicated that the strong, northwest winds in the winter and spring produce southeast flowing surface water. The major rivers flowing into the Persian Gulf have their origins in Iraq and Iran. The Tigris and Euphrates Rivers flow through Mesopotamia (Southeastern Iraq) and join Karoon and Karkheh that flow along the southwestern borders of Iran to form the navigable waterway called the Shat-al-Arab discharging into the northwestern end of the Persian Gulf. The flow of Shat-al-Arab into the Gulf helps in forcing the surface water flow direction towards south and southwest where northern shores of Saudi Arabia are located. High-salinity water flows out of the Persian Gulf into the Gulf of Oman and spreads at 200-350m depth within the Gulf of Oman [11]. The dense (highly saline) water forms during winter in shallow areas of the northern end of the Gulf from January to April.

Environmental Damages to the Persian Gulf

During the first Gulf War, the worst terrestrial damage was incurred on Kuwait and northern shores of Saudi Arabia. As a result of land contamination, ground water aquifers in the area have been severely contaminated and it may take decades before these lands and aquifers are restored to their background conditions. Recent satellite photos show that surface oil spills in Kuwait have virtually disappeared. Examination of topsoil on the ground has shown that dust accumulation over pools of oil have enhanced some growth of vegetation hiding the bulk of oil

spills underneath. The west and southwestern waters and sediments of the Persian Gulf were impacted worse than other areas. The deliberate burning of the oil fields in Kuwait sent 3×10^8 tons of carbon dioxide (~1.5% of the worldwide annual emissions from fossil fuel and biomass burning) into the atmosphere. The smoke plume widths ranged from 15 to 150 km extending as far as 1,000 km. Although local and regional temperatures and solar radiation were reduced beneath the plume, there was not enough evidence to prove that regional climate was consistently affected [2]. Evaporation studies in the Persian Gulf region have indicated that winter evaporations can be as high as double the rate in summer. Therefore, there was rapid evaporation of the oil spill, as it occurred during winter of 1991.

CONCLUSION

The Persian Gulf has been the scene of three major wars in the past two decades. During the Iraq-Iran war that lasted from 1980 to 1988, each side attacked the other's oil tankers causing massive oil spills into the Gulf. In 1991, the Persian Gulf was again the background for another battle known as the 'First Gulf War', as Iraq invaded Kuwait and was subsequently pushed back by allied forces led by the United States. During the First Gulf War, Kuwait oil fields were set on fire by retreating Iraqi forces resulting into irreversible atmospheric deterioration. Many oil tankers were sunk near the shores of Kuwait and Saudi Arabia causing massive oil contamination of the marine environment. During the 'Second Gulf War' that started in March of 2003, the Persian Gulf was again the scene of another major battle.

Less than 1000 km north of the Persian Gulf lies the biggest lake of the world known as the Caspian Sea. In the Caspian Sea, environmental pollutions are not triggered by wars. Political and economical rivalries existing between the countries surrounding the Caspian Sea have accelerated the pace of ecological damages in the region. Being the third (maybe the second) largest oil and gas reservoir of the world after the Persian Gulf Region, the future of the Caspian environment is grim. The Caspian sturgeon and seals are at the brink of becoming extinct and the large population living on the banks of this precious water body are being driven into all kinds of health risks and health hazards. Due to political instability and lack of cooperation between the countries in the Persian Gulf and the Caspian Sea regions, there has not been a comprehensive health study assessing the damages that petroleum spills has caused to the population living near these two water bodies. The future for these two regions does not look

any better than their past. To salvage the fragile habitat of the Persian Gulf and the Caspian Sea, there is a dire need for understanding and cooperation between the countries of these two regions and the United States, which is the dominating power in the area. Without such an understanding, two of the world's unique and precious water bodies will soon plunge into an irreversible environmental catastrophe.

REFERENCES

[1] Saeed, T., Al-Muzaini, S., and Al-Bloushi, A., Post-Gulf War Assessment of the Levels of PAHs in the Sediments from Shuaiba Industrial Area, Kuwait, *Water, Science Technology*, 34:7-8, 195-201. (1996)

[2] Gerges, M. M., On the Impacts of the 1991 Gulf War on the Environment of the Region: General Observations, Oceans and Coastal Areas Programme Activity Centre (OCA/PAC), *United Nations Environmental Programme*, P. O. Box 30552, Nairobi, Kenya, (1994).

[3] Aghai Diba, B., Pollution in the Caspian Sea, *Payvand Iran News*, 2003. http://www.payvand.com/news/02/jul/1073.html.

[4] Golubev, G. N., Environmental policy-making for sustainable development of the Caspian Sea area, Central Eurasian water crisis: Caspian, Aral, and Dead Seas, Edited by Iwao Kobori and Michael H. Glantz, The United Nations University, 1998

[5] Save Caspian Sea – Nature, 2003. http://www.savecaspiansea.com/nature.htm.

[6] El Saghir, K., Caspian Sea Region: The Checkboard of Oil and Minefields, "A Political Science Independent Study", University of Michigan in Anne Arbor, Michigan, USA, 1998. http://members.tripod.com/~KELSAGHIR/Caspian/index.

[7] Caspian Environment: Decline in Environmental Quality, 150 Years of Commercial Oil and Gas Gas Exploitation in the Caspian Sea, www.grida.no/caspian/priority-issues (2003).

[8] Lebedev, A. T., Poliakova, O. V., and Dianova, I. V., Contamination o the Caspian Sea Ecosystem with Organic Pollutants, *Water Pollution* VI, 291-297, 2003.

[9] Caspian Sea Region: Environmental Issues, EIA Country Analysis Briefs, www.eia.doe.gov/emeu/cabs/caspenv, 2003.

[10] Al-Arefaj, A., Alam, I. A., Chemical Characterization of Sediments from the Gulf Area after the 1991 Oil Spill, Marine Environmental Bulletin, 1993.

[11] Swift, S. A., and Bower, A. S., Formation and Circulation of Dense Water in the Persian Gulf, Woods Hole Oceanographic Institution, Woods Hole Oceanographic Contribution # 10625, Woods Hole, Massachusetts, USA, 2003.

The Use of GIS to Streamline Section 404 Permitting

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Devon Energy Corporation (Devon) is a major operator in the Fort Worth Basin Barnett Shale play. Drilling two hundred plus wells per year over a relatively small land area means that scheduling and timing for every step of the process is critical to success. Any lost time due to environmental permitting scan sometimes become a critical path in the process. Standard procedure for Devon is to avoid areas that would require Section 404 (Clean Water Act) permitting to help alleviate this potential bottleneck in the process. Section 404 involves the permitting for the discharge of dredge and fill material into waters of the United States. The U.S. Army Corps of Engineers (USACE) administers the permit process while the U.S. Environmental Protection Agency has oversight over the program. Waters of the U.S. (waters) include streams, rivers mudflats, lakes, wetlands and other various water bodies. Streams, in particular ephemeral and intermittent, comprise the majority of waters of the U.S. within the Fort Worth Basin area. At this time there is no convenient permitting process that allows for the development of petroleum well production sites in North Central Texas. The Nationwide General Permit Program can be used for distribution systems but the pads themselves require are a Regional General Permit or Individual Standard permit. Oftentimes, the

permitting process can take 2-8 months for the General Permits and can go much longer for the Individual permit.

As developments (residential, commercial and retail) progress in the area of eastern Wise and western Denton Counties, drilling sites are becoming less and less desirable, making avoidance to areas requiring Section 404 wetlands permitting more and more difficult. Prior to acquisition by Devon, Mitchell Energy began a search to determine if available GIS data could be assimilated into a database that would provide a screening tool for waters when determining potential well sites. The Center for Spatial Analysis and Mapping at the University of North Texas was contacted for assistance with a pilot project. Carter & Burgess, a consulting firm, was also contacted for their knowledge of Section 404 permitting, waters delineations, and contact with the Corps of Engineers in the Fort Worth District. An initial team meeting resulted in the conclusion that the pilot was possible with readily available data utilizing ArcView to produce the analysis.

Being a major operator in the Barnett Shale, Devon is continuously identifying new locations for drilling rigs, which move approximately every fifteen days. Locations are being staked and readied for a rig two to three months in advance of actual drilling. A delay of six weeks to two months for more than one location would create major scheduling problems in the process. Wells are scheduled and assigned to one of sixteen rigs several months in advance. Rig assignments are based on the physical location in addition to the type of hole being drilled. Some of the locations require city permits issued by the respective city council. These permits require going before the council and planning and zoning groups to assure the city that drilling requirements will be met. Once the site is permitted and then requires movement, the process has to begin again from the start. Re-staking the location also requires geology and reservoir professionals to review the movement in reference to their drilling objective.

If the sites could be screened prior to staking, time delays could be avoided or planned for. This is the premise that brought academia, industry and consulting together to find a solution or determine that it was not feasible. The pilot area is approximately 900 square miles, extending from Highway 287 on the west side in Wise County to Highway 35 on the east side in Denton County (Exhibit No.1). A very small portion of the top of Tarrant County is included near the Alliance Airport. Initial team meetings centered on data availability, requirements for waters, and sources for the data. SPOT, a French satellite was chosen to provide imagery for vegetation. SPOT imagery is limited to twenty by twenty meter resolution, which limits vegetation identification to some degree (20 m x 20m = 4,303 m^2). Overall accuracy is limited to approximately plus or minus one tenth of an acre. Initially one tenth of an acre was the goal since waters impacts less than that fall under the Corps Nation Wide Permit Program. As a reference, a tenth-of-an-acre is approximated by, a surface area of fifty feet by eighty feet or any combination of just over four thousand square feet. Soil data was acquired from the National Resource Conservation Service (NRCS) website for Denton and Wise Counties. The digitized data for Wise County was delayed while the NRCS completed the project. Soil attributes of frequently flooded and occasionally flooded areas provided the basis for areas that may contain hydric soils since these type soils are not identified as such in the Wise and

Denton Counties soil surveys. Elevation analysis was based upon 30 m resolution Digital Elevation Data (DEM), DEM data was used to evaluate slope along drainage to identify flat areas likely to be waters. High-resolution National Hydro Data sets were not available for the areas within the pilot. Drainage patterns were derived from the slope information, creating "low" order streams further "upstream" than in lower-resolution data and matching closely with drainage patterns in aerial photography. Digital Ortho Photography (1995), obtained from the Texas Natural Resource Information Service, provided an "aerial view" backdrop on which the other data sets were overlaid and compared. Roads and urban boundary files were overlaid with soil, vegetation, hydrology and elevation data to provide a visual reference for location. National Wetlands Inventory (NWI) maps were not utilized in the data sets because they do not match the wetlands criteria used by the Corps of Engineers. NWI waters maps identify wetlands based on visual observations from aerial photography with limited ground-truthing, whereas the USACE bases their determination of wetlands on three criteria, which must be present: hydrophytic vegetation, hydrology, and hydric soils. All files were projected to UTM, NAD 83, Zone 14 meters for analysis purposes.

Once complete, the datasets were incorporated into the existing Devon GIS database. The final version of the datasets contain layers or themes for topo maps of the area, derived waterways which project the head waters beyond the limit of the USGS data, four priority layers for potential wetlands, aerial photography and waterway (streams, lakes, rivers) buffers. The final four priority layers are based upon the union of the various data sets:

Priority Level 1 – Wet forest or stream buffer

Priority Level 2 – Low slopes contiguous to stream buffers

Priority Level 3 – Occasionally flooded soil but not wetland forest or low slope within stream buffer

Priority Level 4 - Within pond or lake buffer or frequently flooded soil or wetlands forest within stream buffer or occasionally flooded soil and wetland forest

Level 1 is the lowest potential whereas Level 4 is the highest potential for wetlands occurrence. Exhibits 2 – 4 respectively show examples of derived streams, priority levels with buffers, and aerial photography with overlays of the priority layers. Due to the volume of data, only the final four layers were incorporated. Once integrated into the existing database, viewers have the ability to locate leases with the option of adding the four priority layers to screen for potential issues. The database allows all interested parties to review the information on any lease within the pilot area. Database information is placed on a server in the respective office for viewing.

Data from 56 site visits were over-laid onto the database information for correlation of the pilot project data and actual ground proofing of the site. Results are as follows:

41 sites contained one of the four priority levels and waters of the U.S.

8 sites contained one of the four priority levels but did not have waters of the U.S.

5 sites did not contain any of the four priority levels and no waters of the U.S.

2 sites did not contain any of the four priority levels but did have waters of the U.S.

Of the 56 evaluated sites, the model correctly predicted 46 sites or 82% of the time. For the area involved with the pilot project, this is an insignificant number of samples to determine the future of the project. Overall, the number of correct predictions is very promising. From the very start this was meant to be only a screening tool. The potential exists for waters to be in any of the four priority layers. All final evaluations must be conducted on the ground and then if necessary presented to the USACE for final determination.

Changes and additions have been identified which could be incorporated into future versions, possibly enhancing the value of the analysis. Changing the theme menu to allow for viewing the priority areas singularly would aid in the accuracy determination of each layer. Areas with high incidence of forests could benefit from the soil data. Generally, forests in North Central Texas are associated with streams, however may also exist in areas having not been farmed for several decades. IR satellite imagery is of limited use in these areas due to the inability to "see" under the canopy. The availability of better resolution remote sensing, would certainly enhance the analysis. However, higher resolution imagery is more expensive an often requires higher processing costs. Data access time is a major constraint unless the data is uploaded onto a server in the local office. Loading time on the network from the Oklahoma City headquarters office to Bridgeport field office is approximately 20 minutes on a 2 GHz computer. Each time the display is altered, the entire screen must be redrawn. To be valuable to the end user, local access to the information is critical.

The project is unique only in the assimilation of data from different sources into one database used for screening potential drilling sites for waters and potential Section 404 permit applicability. If the analysis proves sufficient as a screening tool, the next step would be to incorporate the entire operating area for the Barnett Shale into the project. The addition of future data points, correlation of data, and ground proofing will ultimately prove the worth of the project. There are numerous potential applications for similar wetland identification analysis in areas other than petroleum exploration. For the oil and gas industry, the potential for this screening tool to be a useful addition to petroleum exploration is promising.

Step Change In Development of Environmentally Responsible Chemicals

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ABSTRACT

In the European chemical compliance arena, frequent regulatory changes potentially affect a complex chemical inventory of materials used in all parts of the well construction and production process. Active country-level management of the chemical portfolio is required, coupled with effective communication with technology departments to ensure research and development into new formulations and alternative wellsite practices that anticipate and maintain pace with trends in regulatory change. All of this must be achieved while minimizing testing and development costs.

This paper describes the mechanism by which a large service company maintains a proactive strategy toward chemical compliance in anticipating regulatory change and achieving an effective compliance strategy through application of technology. It also describes some cases where cementing and drilling chemicals have been replaced with effective alternatives that have reduced impact on the environment compared to their predecessors.

Development of an Environmentally Friendly and Economical Process for Plugging Abandoned Wells

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ABSTRACT

Fly ash has long been known for its cementitious properties. Presently, however, cement grout is used for plugging the abandoned wells. It has been reported in our previous research that the use of Class C fly ash as plugging material for the abandoned wells is an economically viable option. In that work the optimum fly ash slurry formulation was developed, tested, and compared with Class H cement. The results were very encouraging and now it appears that the fly ash plug could be an economical substitute for cement.

The objective of this paper is to report the progress on continuation of the previous work using fly ash grout. In this study, results of the additional laboratory tests with fly ash slurry as plugging material are reported. The chemical and physical compositions, and the thickening times are first investigated in order to verify the representation and consistency of fly ash samples from different sources and to use them as slurry for plugging abandoned wells. Then, frictional pressure loss data are determined by pumping the fly ash slurry through 2000 ft of 1 ½-in. coiled tubing as well as 20 ft of the same size straight tubing. Bonding properties of fly ash plug are also investigated by a specially designed apparatus. The future plans for performing the field tests with the optimum fly ash formulation and placement technique are also addressed.

Potential Environmental Impact from Mishandled Waxy Crude Oils

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ABSTRACT

Pipeline failures can occur in for a variety of reasons, including, but not limited to, corrosion, scale, and wax obstruction. Because failures are extremely costly and potentially disastrous to the environment, producers, transporters, and refiners often expend considerable amounts of capital toward their prevention. In addition to construction costs incurred by building high quality transport facilities, enormous financial resources are spent regularly on chemical treatments. Generally speaking producers, transporters, and refiners are little concerned with the preceeding or subsequent costs of the oil handling process. Consequently, each does only that which is absolutely required to move the product along its way to the consumer, nothing more. Although pipeline failures are rare, they do occur, and the appropriate chemical treatment can assure safer pipeline operation. If the producer would effectively treat the oil prior to transferring it to the transporter and refiner, he would reap considerable economic benefit. The following paper discusses paraffin wax obstruction and presents field and laboratory data supporting the above conclusion.

Nearby Lake Sediment Quality and Seedling Tree Survival on Eroded Oily Waste / Brine Contaminated Soil

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Summary

An ecosystem restoration study is being conducted at an old oil production area in Northeast Oklahoma. Surface soil samples from areas impacted by discarded crude oil and brine wastes have been chemically characterized. Surface erosion has occurred in areas impacted by waste discharges so only sparse native vegetation is present. Gullies have formed resulting in transport of impacted surface soil into an adjacent lake. Sediments have been collected and analyzed for total and bio-available metals to determine potential effects on the lake ecosystem. The sediments contained toxic levels of barium, cadmium, chromium, and lead. Test plots were established for Black Locust seedlings, Russian Olive seedlings, and Bermudagrass in several impacted areas. After three months growth, the survival rate was 20 and 90 percent for Russian Olive and Black Locust trees, respectively.

Introduction

Hydrocarbon and produced water releases can occur in oilfield operations as a result of equipment failures and other accidents. These releases, the disposal of water produced with oil and gas, and restoration of effected areas are natural issues that concern watershed managers as well as regulators, surface landowners and local residents. Most of the releases frequently were related to past acceptable oilfield practices. Studies are now needed to evaluate and restore the ecosystems by cost effective techniques.

The two research sites are located adjacent to a lake northwest of Tulsa, Oklahoma. Both sites have a long history of petroleum production with the highest activity occurring in the 1930's. Crude oil and brine water have impacted the landscape by erosion and contamination of the surface and disappearance of the native plants.

The objective of the study was to determine the heavy metals associated with eroded surface soil that is now lake sediment. Also, as study was conducted using test plots to determine survival of three plant species planted into impacted soil.

Experimental Methods

Lake shore-line sediments were collected with a seven inch wide LaMotte clam-type steel sampler in about six inches of water. The samples were placed in 125 mL polyethylene bottles, and then capped for transport back to the laboratory. The sediments were air-dried and digested in 10% nitric acid for total metals analysis using an ICP-Emission spectrometer. Duplicate dry sediment samples were extracted with a dilute calcium nitrate solution (An etal, 2003). The extract solutions were analyzed for metals and reported as bio-available metals.

Two 8x40 foot plots on bare ground were selected at each Site A and Site B location. The plots were tilled using a small powered rotor-tiller. Each 8x40 foot was divided into five 8x8 foot plots. Black Locust and Russian Olive seedlings were alternately planted equal distances apart in the 8x16 foot outer plots. The center 8x8 foot plot was planted with Bermudagrass seed. Straw mulch was placed on top of the planted grass seed. The plots were established during March. The field site was visited every six weeks and observations were recorded.

Besides metals, soil salt and nitrates were determined on the sediments and plot soil samples. Soil nitrates were measured on a dilute acid extract of 95% distilled water and 5% mix of sulfuric and hydrochloric acids using a cadmium reduction method (EPA Standard Method 353.3). Soil salt was determined using the IPEC Soil Salt Analysis Kit.

Results and Discussion

Regulatory limits of toxic heavy metals under RCRA guidelines are listed in Table 1. The concentrations listed are for water, but are shown for soil by assuming ppm for both water and soil are equivalent and that soil metals are all water extractable. Table 2 lists total metals present in the shore-line sediments. Toxic levels were exceeded for barium, cadmium, chromium, and lead. None of the samples contained measurable amounts which were > 1 mg/Kg of bio-available metals.

Analyses of the two Site A and two Site B test plot soils are listed in Table 3. Soil salt was much higher in the Site B plots. All plots had levels of barium, cadmium, chromium, and lead that exceeded the RCRA toxic levels. This may not actually be true because assumptions were made that all metals associated with the sediments were water extractable. Our approach was to show that the potential for toxicity does exist. The survival of seedling threes in the test plots after a 2003 March to June growth period is shown in Table 4. The establishment of Black Locust trees did not appear to show any detrimental effect of higher soil salt in the Site B plots. Russian Olive trees that survived after three months growth did not have a vigorous appearance characteristic of the Black Locust trees. Three months after planting the Bermudagrass seed the establishment of plants was rather sparse. Appearance was that the cool spring weather did not favor grass seed germination and growth.

The information obtained from the test plots showed that for developing an effective restoration program Black Locust trees should be established.

Notice: The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here through in-house efforts. This document has not been subjected to Agency review and therefore does not necessarily reflect the views for the Agency and an official endorsement should not be inferred.

References

1. An, Youn-Joo and D.H. Kampbell, "Total, Dissolved, and Bio-Available Metals at Lake Texoma Marinas". Environmental Pollution 122 (2003).

2. EPA Standard Method 353.3. Methods for Chemical Analysis of Water and Wastes. © March 1997 Cincinnati, OH; Environmental Monitoring & Support Laboratories, Environmental Protection Agency.

Table 1:
Regulatory Limits of Toxic Heavy Metals under RCRA

Metal	Regulatory Limit
Arsenic	5.0 mg/Kg
Barium	100.0 mg/Kg
Cadmium	1.0 mg/Kg
Chromium	5.0 mg/Kg
Lead	5.0 mg/Kg
Mercury	0.2 mg/Kg
Selenium	1.0 mg/Kg
Silver	5.0 mg/Kg

Toxic Heavy Metals Without Established Regulatory Limits

Antimony
Beryllium
Nickel
Thallium

Table 2:

Lake Shore-Line Sediments

(mg/kg)

	ASEL 1	ASEL 2	BSEL 1	BSEL 2	BSEL 3	Mean
Soil Salt	105	90	250	140	80	133.0
Nitrates	0.07	0.08	0.08	0.08	0.13	0.09
Arsenic	ND	ND	ND	ND	13.6	---
Barium	*221.0	*112.0	*145.0	*133.0	* 83.0	---
Beryllium	ND	ND	0.83	0.67	0.90	0.80
Cadmium	*1.2	0.9	*3.1	*2.5	*5.5	*2.6
Cobalt	3.3	4.2	6.8	6.0	9.4	5.9
Chromium	*10.0	*8.8	*26.0	*21.0	*35.2	*20.2
Copper	2.1	1.8	7.3	7.0	1.8	4.0
Manganese	130	262	192	288	634	301.2
Nickel	4.9	5.0	15.4	13.1	10.8	9.8
Lead	4.8	*6.6	*12.4	*11.8	*17.0	*10.5
Strontium	14	13	56	53	16	30.4
Titanium	81	76	151	143	113	112.8
Vanadium	14	11	36	29	52	28.4
Zinc	13	14	46	44	37	30.8

* Toxic Level Exceeded

Table 3:

Test Plot Soil

	A Plot 1	A Plot 2	B Plot 1	B Plot 2
Soil Salt (mg/kg)	70	50	2000	9500
pH	6.0	6.0	7.3	7.1
Nitrates (mg/kg)	0.05	0.05	0.06	1.30
(mg/kg)				
Arsenic	ND	ND	ND	ND
Barium	*126	*377	*124	*115
Beryllium	ND	ND	ND	ND
Cadmium	0.86	0.89	*1.41	*2.04
Chromium	*8.2	*6.5	*10.6	*12.9
Copper	2.7	2.7	3.1	4.1
Nickel	3.8	2.9	6.0	7.6
Lead	*7.2	*6.3	*6.4	*10.0
Strontium	30	31	49	68
Titanium	126	65	239	206
Vanadium	14	10	21	24
Zinc	15	19	20	28

* Toxic Level Exceeded

Table 4:

Survival Rate of Seedling Trees

Black Locust	90%
Russian Olive	20%

Effects of produced water and hydrocarbon releases on vegetation at site A of the Osage-Skiatook petroleum environmental research project, Osage County, Oklahoma

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ABSTRACT

To examine the impacts of past oilfield operations on forest stands of the "A" Site (Osage-Skiatook petroleum environmental research project northwest of Tulsa, OK) we sampleed the vegetation along 4 transects through an eroded salt scar caused by produced water disposal. Transects began and ended within the forest matrix on either side of the impact area, and 100 m^2 study plots were located at 15-m intervals along each transect. All trees greater than 2.5 cm in diameter in each plot were identified to species and measured. Saplings and shrubs within each plot were counted by species, while herbaceous species were counted in two 1 m^2 subplots. Tree ages were estimated from increment cores to provide a general age or age structure of the forest.

The forest matrix around the salt scar was composed predominately of post oak and blackjack oak with smaller amounts of hickory and very low numbers of black willow, ash, and American elm. Nine species, plum, eastern red cedar, buttonbush, red bud, honey locust, hackberry, buckbrush, winged sumac, and chittim wood (buckthorn bully), were found in the small tree/sapling/shrub layer. Vines included Virginia Creeper, catbrier, blackberry and grape. Nine of the 62 plots established, mostly in the salt scar area, contained no trees.

Age analysis indicates that many of the larger post oaks are greater than 100 years old while only a few of the blackjack oaks approach 100 years in age. Prior to oilfield operation the area was probably savannah with scattered post oak. The majority of trees currently in the area invaded during or after operation of the oil field, possibly as a result of fire exclusion.

Determining the distribution of subsurface salt contamination using the composition of oak leaves: a case study at an oil production site, northeast Oklahoma

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ABSTRACT

Leaves of blackjack oak (Quercus marilandica) were collected in November 2002 from 34 trees surrounding a former oil-production site in northeastern Oklahoma (Site A, Osage-Skiatook Project). The objective was to investigate the response of native oak trees to known NaCl contamination in the shallow (1-8 m depth) subsurface. Trees were sampled from a 225 X 300-m area that included locations at various distances (10-200 m) from a salt-scarred area at the site. Locations within about 30 m of the salt scar are subject to subsurface contamination by NaCl as indicated by ground-based geophysical surveys and by anomalous chloride contents of aqueous extracts of core samples. The Cl content of dried oak leaves was determined by ion chromatography and ranged from 184 to 918 ppm. Of the 14 samples with >400 ppm Cl, 6 plotted within 30 m of the salt scar and 10 within 45 m of the scar. The location of these trees confirmed, and also implied an expansion of, the area affected by subsurface salt. Two Cl-enriched trees more removed from the salt scar are spatially associated with a former tank battery site and a trench for transporting produced water. Analyses of 32 additional elements in leaf ash indicated no significant positive correlation with Cl in leaf ash. Biogeochemical sampling and analysis for Cl may provide a less costly alternative to geophysical measurements or drilling when assessing possible contamination by NaCl in the shallow subsurface.