

TUESDAY (GROUP 1) POSTERS


This year, more than 400 posters are on display in the Exhibit Hall, Group 1 on Tuesday and Group 2 on Wednesday. These posters, many representing current and recently completed SERDP and ESTCP projects, highlight research within the SERDP and ESTCP focus areas (Environmental Restoration, Munitions Management, Sustainable Infrastructure, and Weapons Systems and Platforms). To help attendees find their areas of interest, posters are grouped to keep similar technologies together. In addition to the SERDP and ESTCP Partners in Environmental Technology exhibit booth, there are other exhibitors at this event with booths representing funding and partnering opportunities or information resources.

While many SERDP and ESTCP projects are showcased in the Exhibit Hall, more information about past and present SERDP and ESTCP research projects is available by visiting our web sites (www.serdp.org and www.estcp.org). In addition, both sites enable you to access the SERDP/ESTCP Online Library (<http://docs.serdp-estcp.org>) where you can search for technical reports using criteria such as focus area, sub-focus, contaminant, or other specific environmental concerns.

You are encouraged to tour the posters and exhibit booths during the hours noted below when presenters will be available for discussion.

Tuesday Exhibit Hall Hours

7:30 a.m. – 8:45 a.m.
12:30 p.m. – 1:45 p.m.
3:10 p.m. – 3:35 p.m.
5:00 p.m. – 6:30 p.m.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Weapons Systems and Platforms (WP)			
WP: Heavy Metal Elimination			
Mike Audino <i>Benet Labs</i>	Chromium Replacement and Erosion Mitigation Technology for Medium Caliber Gun Barrels	21	E-1
Phillip Miller <i>Faraday Technology, Inc.</i>	Faradayic Process for Functional Trivalent Chromium Electroplating	22	E-2
Steven A. Brown <i>NAVAIR 4.3.4.2</i>	Cadmium Alternatives for DoD and NASA Applications—Phase II Testing Results	23	E-3
Ryan Josephson <i>U.S. Air Force Landing Gear Engineering</i>	Corrosion Resistant Ultrahigh Strength Steel to Replace Cadmium Plated 300m	24	E-4
Professor Gerald Frankel <i>The Ohio State University</i>	 Development of Ni-Cu-Ru Consumables for Welding of Austenitic Stainless Steels	25	E-5
Dr. Elizabeth Berman <i>Air Force Research Laboratory/MLSC</i>	Investigation of Chemical Vapor Deposition of Aluminum as a Replacement Coating for Cadmium	41	E-6

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Professor Roland A. Levy <i>New Jersey Institute of Technology</i>	Investigation of Chemically Vapor Deposited Tantalum for Medium Caliber Gun Barrel Protection	42	E-7
Victor Kenneth Champagne, Jr. <i>U.S. Army Research</i>	Supersonic Particle Deposition Technology for Repair of Magnesium Aircraft Components	43	E-8
E.I. Meletis <i>University of Texas at Arlington</i>	Electrolytic Plasma Technology: A Novel Cleaning and Coating Technology	44	E-9
Diana Facchini <i>Integran Technologies, Inc.</i>	Nanocrystalline Cobalt-Alloy Coatings for Non-Line-of-Sight Chrome Replacement Applications	45	E-10
WP: ODS and VOCs			
Dr. K. James Hay <i>U.S. Army ERDC-CERL</i>	Vapor Recovery by Electrothermal Swing Adsorption	26	E-11
Dr. Michael R. Kessler <i>Iowa State University</i>	Environmentally Benign Repair of Composites Using High Temperature Cyanate Ester Nanocomposites: Resin Development	27	E-12
Richard G. Gann <i>National Institute of Standards and Technology</i>	Advanced Technology for Fire Suppression in Aircraft	28	E-13
Andy Del Collo <i>Environmental Readiness Division (N451)</i>	Deep Web Search Portal for Environmental Applications	29	E-14
Dr. Michael E. Wright <i>U.S. Navy-NAVAIR</i>	New Reactive Diluents for VOC-Free Repair Resins	30	E-15
Dr. Shridhar Yarlagadda <i>Center for Composite Materials</i>	Environmentally Benign Approaches for the Repair of Composites for Military Applications	31	E-16
Les Bowman <i>Naval Air Warfare Center Weapons Division</i>	Alternative to Halon 1211 Flightline Fire Extinguisher	32	E-17
Dr. John J. La Scala <i>Army Research Laboratory</i>	Environmentally Friendly Coatings Systems for DoD Applications	33	E-18
WP: Coatings/De-Coatings			
Dr. John J. La Scala <i>Army Research Laboratory</i>	Demonstration of Composites with Low Hazardous Air Pollutant Contents for Military Applications	34	E-19
Yushan Yan, Professor <i>University of California Riverside</i>	Zeolite Coating System for Corrosion Control to Eliminate Hexavalent Chromium from DoD Applications	35	E-20
Dr. Wim Van Ooij, Professor <i>University of Cincinnati</i>	Improved Superprimers for DoD Applications	36	E-21
Dr. Peter Zarras <i>Naval Air Warfare Center Weapons Division</i>	Validation of Novel Electroactive Polymers as Environmentally Compliant Coatings for Replacement of Hexavalent Chromium Pretreatments	37	E-22
Professor Christopher K. Ober <i>Cornell University</i>	Environmentally Benign Multilayer Polymer Coatings with Controlled Surface Properties for Marine Antifouling Applications	38	E-23
Dr. El Sayed Arafat <i>NAVAIR</i>	Demonstration/Validation of High Performance Corrosion Preventive Compound (CPC) for Interior Aircraft Applications	39	E-24
Meng-Dawn Cheng <i>Oak Ridge National Laboratory</i>	Assessing the Pulmonary Toxicity of Single-Walled Carbon Nanohorns	40	E-25

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Matt O'Keefe <i>University of Missouri-Rolla</i>	Performance of Zero VOC, Multifunctional UV (MUV) Curable Corrosion Coatings on Metallic Substrates	61	E-26
Randel Bowman <i>Oklahoma City Air Logistics Center</i>	Robotic Laser Coating Removal System	62	E-27
Jim Tankersley <i>Battelle</i>	Progress Report: Qualification, Demonstration, & Validation of Compliant Removers for Aircraft Sealants and Specialty Coatings	63	E-28
Wayne Patterson <i>OO-ALC/MADL Science and Engineering Laboratory</i>	Low Temperature Cure Powder Coatings	64	E-29
John E. Benfer <i>NAVAIR Jacksonville</i>	Environmentally Friendly Inspection Through Coatings	65	E-30
Dr. Nese Orbey <i>Foster-Miller Inc.</i>	UV Curable Non-Chrome Primer and Advanced Topcoat System	66	E-31
Sustainable Infrastructure (SI)			
SI: Facilities Management — Facility Waste			
Dr. Jo Ann Ratto <i>U.S. Army Natick Soldier Research Development and Engineering Center (NSRDEC)</i>	Lightweight and Compostable Fiberboard for the Army	46	E-32
Dr. Chris Schwier <i>Metabolix, Inc.</i>	PHA Bioplastic Packaging Materials	47	E-33
Jiong Hu <i>Iowa State University</i>	Sequestering Lead in Paint by Utilizing Deconstructed Masonry Materials as Recycled Aggregate in Concrete	48	E-34
Stephen D. Cospers <i>ERDC-CERL</i>	Determining Environmental Solubility of Pb from Recycled Concrete Aggregate	49	E-35
Satya P. Chauhan <i>Battelle</i>	Development of Environmentally Benign and Reduced Corrosion Runway Deicing Fluid	50	E-36
Nancy Ruiz, Ph.D. <i>Naval Facilities Engineering Service Center</i>	Application of a Bimetallic Solvent Paste Technology for PCB Removal from Older Structures on DoD Facilities	51	E-37
Rance T. Kudo <i>Naval Facilities Engineering Service Center</i>	Demonstration of NoFoam System Technology for Aircraft Hangar and Fuel Farm Fire Suppression Foam System	52	E-38
SI: Facilities Management — Air Quality			
Byung J. Kim <i>U.S. Army Engineer Research and Development Center</i>	Measurement of Particulate Matter Emission Factors from Rotary Wing Aircraft Operations	53	E-39
John A. Gillies <i>Desert Research Institute</i>	Particulate Matter Emissions for Dust from Unique Military Activities: Rotary-Winged Aircraft	54	E-40
Charles E. Rodes, Ph.D. <i>RTI International</i>	A New-Technology Personal Aerosol Exposure Assessment Methodology for Deployed Troops	55	E-41
SI: Natural Resources Management — Maritime Sustainability			
Dr. Jay Barlow <i>NOAA Southwest Fisheries Science Center</i>	Predictive Modeling of Marine Mammal Density from Existing Survey Data and Model Validation Using Upcoming Surveys	56	E-42

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Dr. Pat Halpin <i>Duke University</i>	Predictive Habitat and Density Modeling of Marine Mammals for Naval Environmental Compliance	57	E-43
R. Pamela Reid <i>University of Miami-RSMAS</i>	Application of ROV-Based Video Technology to Complement Coral Reef Resource Mapping and Monitoring	58	E-44
Peter L. Tyack <i>Woods Hole Oceanographic Institution</i>	Studying Responses of Beaked and Other Whales to Sonar and Other Sounds	59	E-45
SI: Natural Resources Management — Threatened and Endangered Species			
Mary E. Cablk, Ph.D. <i>Desert Research Institute</i>	Maintaining Real-Time Calibration of Detection Dog Teams During Field Deployment Given Uncertainty in Target Location	60	E-46
Richard A. Fischer, Ph.D. <i>U.S. Army Engineer Research and Development Center</i>	Identification and Investigation of Migratory Bird Stopover Hotspot Habitats on U.S. Military Installations	73	E-47
Anna M. Pidgeon, Ph.D. <i>University of Wisconsin-Madison</i>	Predicting the Abundance of Desert Birds Using Landsat TM/ETM+ Imagery	74	E-48
Dr. Joseph M. Szewczak <i>Humboldt State University</i>	Automated Monitoring and Assessment of Bat and Bird Populations	75	E-49
Dr. Cynthia Hartway <i>University of Montana</i>	New Tools for Prioritizing Management Actions for Species of Concern on Department of Defense Lands	76	E-50
Maile C. Neel, Assistant Professor <i>University of Maryland</i>	An Ecoinformatic Approach to Developing Recovery Goals and Objectives	77	E-51
SI: Natural Resources Management — Ecosystem Management			
Paul R. Grossl <i>Utah State University</i>	Allelochemical Behavior in Soil Environments	78	E-52
Mark W. Paschke <i>Colorado State University</i>	Allelopathy and the Control of Exotic Weeds on Military Training Grounds	79	E-53
Thomas D. Sisk <i>Northern Arizona University</i>	The Ecological Impacts of Alternative Management Scenarios: The Use of the Effective Area Model on Military Bases	80	E-54
Patricia Cunningham, Ph.D. <i>RTI International</i>	SERDP's Defense Coastal/Estuarine Research Program (DCERP) - Project Update: Completion of Planning Phase	81	E-55
Dr. Lisa J. Rew <i>Montana State University</i>	Preventing the Spread of Invasive Species: Evaluating Plant Propagule Transport by Vehicles	82	E-56
Dr. Claudia Husseneder <i>Louisiana State University Agricultural Center</i>	Paratransgenesis for Termite Control	93	E-57
Dr. Joan L. Walker <i>USDA Forest Service, Southern Research Station</i>	Evaluating the Effects of Environmental Factors on the Loblolly Pine Decline at the Stand Level	94	E-58
Dr. Joan L. Walker <i>USDA Forest Service, Southern Research Station</i>	Predicting the Occurrence of Loblolly Pine Decline in Potential Red-Cockaded Woodpecker Habitat at Fort Benning, Georgia	95	E-59


Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Dr. Joan L. Walker <i>USDA Forest Service, Southern Research Station</i>	Effects of Site Preparation on Native Ground Layer Vegetation Diminish Three Years after Application on a Hydric Soil in North Carolina	96	E-60
Dr. Ann Hild, Associate Professor <i>University of Wyoming</i>	Selecting Promising Grass Genotypes to Limit Weed Reinvasion	97	E-61
SI: Natural Resources Management — Land Management and Watershed Protection			
Dr. Virginia H. Dale <i>Oak Ridge National Laboratory</i>	Comparing Model Projections Generated by RSim and Leam for Fort Benning	100	E-62
Dr. Patrick Mulholland <i>Oak Ridge National Laboratory</i>	 Restoration of Stream and Riparian Ecosystems at Fort Benning, Georgia	101	E-63
Antonio J. Palazzo <i>ERDC-CRREL</i>	 Improved Methods and Materials for Revegetating Military Training Lands	102	E-64
SI: Cultural Resources			
Dr. Jeffrey H. Altschul <i>SRI Foundation</i>	Intergrating Archaeological Modeling in DoD Cultural Resource Compliance	98	E-65
Dr. Michael L. Hargrave <i>ERDC-CERL</i>	Integrated Multi-Sensor Characterization of Archaeological Sites Using Archaeomapper	99	E-66
Munitions Management (MM)			
MM: Underwater			
Dr. Raymond Lim <i>Naval Surface Warfare Center Panama City</i>	Sonar Performance Against Underwater UXO	70	E-67
Dr. J. A. Bucaro <i>Naval Research Laboratory</i>	Broadband, Multi-Aspect Scattering Measurements from Shells, Rockets, and False Targets in the Structural Acoustic Domain	71	E-68
Barbara Sugiyama <i>Naval Facilities Engineering Service Center</i>	Predicting the Mobility and Burial of Underwater UXO	72	E-69
Chet Bassani <i>SAIC</i>	Deep Water Munitions Detection System	83	E-70
Steven A. Arcone <i>U.S. Army ERDC</i>	Factors Affecting Lake Subbottom UXO Surveys with Ground-Penetrating Radar	84	E-71
Eugene Lavelly <i>BAE Systems AIT</i>	Synthetic Aperture Sonar for Detection and Discrimination of Underwater	85	E-72
MM: Wide Area Assessment			
Dale Bennett <i>URS Corporation</i>	Lidar and Orthophotos in UXO Wide Area Assessment Summary of Lessons Learned	67	E-73
Christopher Jekeli <i>Ohio State University</i>	A Comparison of Filter Strategies for Precision Geolocation of UXO Detection Instrumentation Using Integrated IMU Systems	68	E-74
Barry Roberts <i>Sandia National Labs</i>	Testing and Analysis of Geostatistical Characterization Techniques Using Full-Coverage Magnetometer Data Sets	69	E-75


Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Brent Pulsipher <i>Pacific Northwest National Laboratory</i>	Camp Beale Wide Area Assessment Transect Design and Target Area Identification	86	E-76
John E. Foley, Ph.D. <i>Sky Research, Inc.</i>	Helicopter Magnetometry Characterization: Integrated Technology for Wide Area Assessment	87	E-77
David Wright <i>Sky Research, Inc.</i>	Next Generation Helimag Technology	88	E-78
Dr. Kevin Johnson <i>U.S. Naval Research Laboratory</i>	Intelligent Data Fusion for Wide-Area Assessment of UXO Contamination	89	E-79
Dr. Stephen Billings <i>Sky Research, Inc.</i>	Wide Area UXO Screening with the Minimum Altitude Remote Sensing (MARS) Fixed Wing Airborne System	90	E-80
Dr. William E. Doll <i>Battelle</i>	Demonstration of Two Airborne Vertical Magnetic Gradient Systems for UXO Surveying	91	E-81
MM: Ground-Based Detection and Discrimination — EMI and Magnetometers/Modeling and Processing			
Dr. Yaoguo Li <i>Colorado School of Mines</i>	 MM-1414: Improving Detection and Discrimination of UXO in Magnetic Environments	92	E-82
MM: Ground-Based Detection and Discrimination — Geolocation			
John E. Foley, Ph.D. <i>Sky Research, Inc.</i>	Improving Geospatial Positioning Accuracy to Support UXO Discrimination	108	E-83
MM: Recovery and Disposal			
Bill Lewis <i>AFRL/MLQF, Robotics Research Group</i>	The Magnetic UXO Recovery System (MURS)	115	E-84
MM: Ground-Based Detection and Discrimination — EMI and Magnetometers/Sensors			
Dr. Stanko R. Brankovic <i>University of Houston</i>	Electrodeposition at Nanoscale: The Prospect for Magnetic Field Sensors Fabrication	103	E-85
Dr. Ben Barrowes <i>CRREL-ERDC</i>	High Fidelity Electromagnetic Induction Instruments and Physically Complete Models	104	E-86
Herb Nelson <i>Naval Research Laboratory</i>	EMI Array for Cued UXO Discrimination	105	E-87
Dr. David L. Wright <i>U.S. Geological Survey</i>	ALLTEM UXO Detection Sensitivity and Inversions for Target Parameters from Yuma Proving Ground and Test Stand Data	106	E-88
Lynn Helms <i>U.S. Army Engineering and Development Center, Huntsville</i>	Sub-Audio Magnetics. The Application of a New Dual Mode Geophysical System to the Simultaneous Acquisition of Total Magnetic Intensity and Total Field Electromagnetic Responses from Buried UXO	107	E-89
Dr. Mark D. Prouty <i>Geometrics, Inc.</i>	Miniature Total Field Magnetometers	109	E-90
Dr. Mark D. Prouty <i>Geometrics, Inc.</i>	Metalmapper: A Multi-Sensor Tem and Magnetic Gradiometer System for UXO Detection and Classification	110	E-91
Dr. Michael W. Asten <i>Flagstaff GeoConsultants Technology Pty Ltd.</i>	Superior Depth of Detection and UXO Target Characterization Using an Array of Fluxgate Magnetic Sensors	111	E-92

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Ryan E. North <i>U.S. Army Engineer Research & Development Center</i>	Repeatability of Common UXO Detection & Discrimination Instruments	112	E-93
David C. George <i>G&G Sciences, Inc.</i>	An EM System with Dynamic Multi-Axis Transmitter and Tensor Gradiometer Receiver	113	E-94
David V. Smith <i>U.S. Geological Survey</i>	The Active Tensor Magnetic Gradiometer System: A Dual Mode System for Mapping and Discrimination of UXO	114	E-95
<i>Environmental Restoration (ER)</i>			
ER: Perchlorate			
Gregory J. Harvey, CIH <i>USAF</i>	 Unconventional Sources of Perchlorate	116	E-96
W. Andrew Jackson Ph.D., P.E. <i>Texas Tech University</i>	Occurrence and Deposition of Atmospherically Generated Perchlorate	117	E-97
Professor Mary Jo Kirisits <i>University of Texas at Austin</i>	Characterizing the Microbial Community in a Bioreactor Treating Perchlorate-Contaminated Groundwater	118	E-98
Ronald L. Crawford, Ph.D. <i>University of Idaho</i>	Engineered Intrinsic Bioremediation of Ammonium Perchlorate in Groundwater	119	E-99
David R. Lippincott <i>Shaw Environmental</i>	Successful Field-Scale Bioremediation of Perchlorate in Groundwater Utilizing an Active-Passive Treatment Approach	120	E-100
Yuehe Lin <i>Pacific Northwest National Laboratory</i>	Novel Electrochemical Process for Treatment of Perchlorate in Waste Water	121	E-101
Dr. John D. Coates <i>University of California, Berkeley</i>	A Colorimetric Bioassay for Perchlorate	122	E-102
Dr. John D. Coates <i>University of California, Berkeley</i>	Continuous Bioelectrical Perchlorate Treatment	123	E-103
Sheri L. Knox, P.E. <i>Solutions-IES</i>	Lines of Evidence for Monitored Natural Attenuation of Perchlorate	124	E-104
Carol Aziz, Ph.D., P.E. <i>Geosyntec Consultants</i>	Evaluation of Alternative Causes of Wide-Spread, Low Concentration Perchlorate Impacts to Groundwater	125	E-105
Se Chang Ahn <i>University of Delaware</i>	Enhancing Microbial Reduction of Perchlorate in Ammunitions Wastewater by Zero-Valent Iron	127	E-106
Greta J. Orris, Ph.D. <i>U.S. Geological Survey</i>	A Preliminary Look at Climatic Controls on Levels of Atmospherically-Derived Perchlorate in Natural Materials	128	E-107
Paul B. Hatzinger, Ph.D. <i>Shaw Environmental, Inc.</i>	Evaluation of Perchlorate Origin Using Stable Isotope Analysis	129	E-108
Richard R. Bernhardt, Ph.D. Candidate <i>University of Alaska</i>	The Effects of Perchlorate Exposure on a Model Vertebrate Species: The Threespine Stickleback	130	E-109
ER: Heavy Metals			
Professor Janet G. Hering <i>California Institute of Technology</i>	Possible Sequestration Mechanisms for Naturally-Occurring Arsenic Mobilized During In Situ Bioremediation of Chlorinated Solvents (ER-1374)	126	E-110

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Desmond I. Bannon, Ph.D. DABT <i>United States Army Center for Health Promotion and Preventive Medicine</i>	Bioavailability of Lead in Small Arms Range Soils	131	E-111
Amy Hawkins <i>Naval Facilities Engineering Service Center</i>	Species Sensitivity Variations in Amphibians Exposed to Lead and Copper	132	E-112
Amy Hawkins <i>Naval Facilities Engineering Service Center</i>	Reactive Capping Mat Development	133	E-113
Amy Hawkins <i>Naval Facilities Engineering Service Center</i>	The Effect of Soil Properties on Toxic Metal Bioavailability	134	E-114
Steven Larson <i>U.S. Army Corps of Engineers</i>	 Grenade Range Management Using Lime for Dual Role of Metals Immobilization and Explosives Transformation	135	E-115
David A. Cacciatore, Ph.D., P.E. <i>Shaw Environmental, Inc.</i>	Mass Balance Evaluation of Mechano-Chemical Destruction of PCBs	144	E-116
Mathieu Laporte-Saumure <i>Québec University</i>	Characterization and Treatability of Pb, Cu and Zn in Backstops Soils of Four Canadian Small Arm Shooting Ranges	145	E-117
Dr. Mary F. DeFlaun <i>Geosyntec Consultants, Inc.</i>	Precipitation of Arsenic Under Sulfate Reducing Conditions and Subsequent Leaching Under Aerobic Conditions	146	E-118
ER: Site Characterization, Monitoring, and Processing			
Joey Trotsky <i>Naval Facilities Engineering Service Center</i>	Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Ground-Water Quality and Remediation Progress at DoD Sites	147	E-119
Frank Löffler, Ph.D. <i>Georgia Institute of Technology</i>	BioReD: Biomarkers and Tools for Reductive Dechlorination Site Assessment, Monitoring, and Management	148	E-120
Dr. Matthew Feller <i>LuSyl Environmental Services</i>	Ex Situ Soil Remediation of Both Arsenic and Cyanide Contamination	149	E-121
Carl McElwee <i>University of Kansas</i>	Oscillatory Pressure Waves as Energy Source for Hydraulic Tomography	150	E-122
Philip M. Hunter, P.G. <i>AFCEE</i>	Tools for Long-Term Groundwater Monitoring Optimization: Improving GTS	151	E-123
Dr. H Zhang <i>Shanghai Jiaotong University</i>	The Arsenic in Groundwater and Arseniasis from the Hetao Area, Inner Mongolia	159	E-124
Donna E. Fennell, Assistant Professor <i>Rutgers University</i>	Kinetics of Reductive Dechlorination of PCDD/Fs by a Dehalococcoides-Containing Culture	160	E-125
Karla Harre <i>Naval Facilities Engineering Service Center</i>	Adaptive Long-Term Monitoring at Environmental Restoration Sites	161	E-126
Louise V. Parker <i>USA ERDC-CRREL</i>	Demonstration of the Snap Sampler Passive Ground Water Sampling Device for Inorganic Analytes	162	E-127

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Dr. Mark Kram <i>NFESC Code 413</i>	Mass Flux Distribution Using the High-Resolution Piezocone and GMS	163	E-128
Roelof Versteeg <i>Idaho National Laboratory</i>	Optimized Enhanced Bioremediation through 4D Geophysical Monitoring and Autonomous Data Collection, Processing and Analysis	164	E-129
Dr. Stephen Moysey <i>Clemson University</i>	Improved Management of Groundwater Contaminant Risks Using Dynamic, Model-Based Fusion of Hydrologic Processes and Electrical Resistivity Surveys	165	E-130
Dr. Ronald W. Falta <i>Clemson University a</i>	Contaminant Mass Transfer During Boiling in Fractured Geologic Media	166	E-131
ER: Sediments			
Gregory V. Lowry Associate Professor <i>Carnegie Mellon University</i>	Effects of Biogeochemical Factors on the Performance of In Situ Activated Carbon Sediment Caps for PCB Sequestration	174	E-132
Professor Upal Ghosh <i>University of Maryland Baltimore County</i>	PAH Transport Through Sediment Caps With and Without Sorbent Amendments	175	E-133
Professor Upal Ghosh <i>University of Maryland Baltimore County</i>	In Situ Remediation of Metal and Organic Pollutants in Sediments Using Sorbent Amendments	176	E-134
Victor M. Magar <i>ENVIRON International Corporation</i>	Guidance for Monitored Natural Recovery at Contaminated Sediment Sites	177	E-135
Dr. Danny Reible <i>University of Texas</i>	Evaluation of the Applicability and Effectiveness of Organoclays as Active Capping Materials	178	E-136
Dr. Danny Reible <i>University of Texas</i>	Evaluation of the Applicability and Effectiveness of Organoclays as Active Capping Materials	179	E-137
M.H. Paller <i>Savannah River National Laboratory</i>	Evaluation of the Potential Side-Effects of Sequestering Agents Used for the Development of Active Caps for Contaminated Sediments	180	E-138
Dr. Anna Sophia Knox <i>Savannah River national Laboratory</i>	Active Caps for Remediation of Mixtures of Contaminants and Resistance to Erosion – A Comprehensive Evaluation	181	E-139
Dr. Joel E. Baker <i>University of Maryland Center for Environmental Science</i>	Application of Tools to Measure PCB Microbial Dechlorination and Flux into Water During In-Situ Treatment of Sediments	189	E-140
Dr. Jeanne M. Vanbriesen <i>Carnegie Mellon University</i>	Bayesian Modeling of Polychlorinated Biphenyl Dechlorination in Sediment for Remediation Decision Support	190	E-141
Professor Nicholas Fisher <i>Stony Brook University</i>	Bioavailability of Sediment-Bound Metals for Marine Polychaetes	191	E-142
G. Allen Burton, Professor and Chair <i>Wright State University</i>	Sediment Ecosystem Assessment Protocol (SEAP): An Accurate and Integrated Weight-of-Evidence Based System	192	E-143
Philip Gschwend <i>Massachusetts Institute of Technology</i>	In Situ Measurement of PAH Activities in Submerged Marine Sediments Using Low Density Polyethylene Passive Sampler	193	E-144

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Dr. Joseph Z. Gailani <i>U.S. Army Engineer Research and Development Center</i>	Technical Objective 1 Experimental Investigation of a Wall Shear Stress in a Pulsating Channel Flow With Strong Bulk Flow Reversal	194	E-145
Y. Meriah Arias-Thode, Ph.D. <i>SPAWARSYSCEN San Diego</i>	Bacterial and Benthic Community Response to Inorganic and Organic Sediment Amendments	195	E-146
Hui Liu <i>Rutgers, the State University of New Jersey</i>	Ex Situ Dechlorination of Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans in Kymijoki River Sediment, Finland	196	E-147
ER: Energetics			
Marianne E. Walsh <i>U.S. Army ERDC/CRREL</i>	Persistence of High Explosives from Low-Order Detonations within a Salt Marsh Impact Area	202	E-148
Dr. Guy Ampleman <i>DRDC Valcartier</i>	Study of Propellant Residues and Gases Emitted During 105-mm Howitzer Live Firing at the Muffler Installation in Nicolet, Lac St-Pierre, Canada	203	E-149
Dr. Sonia Thiboutot <i>DRDC Valcartier</i>	Energetic Residues Deposition from 84-mm Carl Gustav Antitank Live Firing	204	E-150
Man Jae Kwon <i>University of Illinois</i>	Metabolite Distribution as Influenced by Abiotic, Biotic, and Mixed (Biotic-Abiotic) Pathways, pH and Bioavailable Fe(III) in Electron Shuttle-Mediated Biotransformation of RDX	205	E-151
Paul B. Hatzinger, Ph.D. <i>Shaw Environmental, Inc.</i>	Field Demonstration of In Situ Bioremediation of Energetic Compounds in Groundwater	206	E-152
Farrukh Ahmad, Ph.D., P.E. <i>GSI Environmental, Inc.</i>	Monitored Natural Attenuation of Explosives in Groundwater Using Stable Isotope Ratio Analysis	207	E-153
Dr. Susan Taylor <i>U.S. Army ERDC</i>	Outdoor Dissolution of Composition B, TNT, and Tritonal	208	E-154
Dr. Mohammad Qasim <i>ERDC USACE</i>	Molecular Structure Determines Trends Between Chemical and Physical Properties of Nitramines, Cage Nitramines, and Nitroaromatic Energetics	209	E-155
Dr. Mohammad Qasim <i>ERDC USACE</i>	A Study of Molecular Structure and Reactivity of TNT and Selected Derivatives	210	E-156
June Sup Song <i>University of Delaware</i>	Pilot-Scale Evaluation of Zero-Valent Iron Technology: Treatment of RDX Wastewater	211	E-157
Jim Szecsody <i>Pacific Northwest National Laboratories</i>	Subsurface Sediment Treatments for Mineralization of RDX, HMX, and TNT	212	E-158
Dr. Katerina Dontsova <i>U. S. Army Engineer Research and Development Center</i>	Dissolution and Transport of M9 and M30 Propellants in Soil Columns	213	E-159
Dr. Mark S. Johnson <i>U.S. Army Center for Health Promotion and Preventive Medicine</i>	Development of Toxicity Data for Munition Compounds to Support Toxicity Reference Value Derivations for Wildlife	214	E-160
Kathleen Savard, M.Sc. <i>Biotechnology Research Institute</i>	Effect of Soil Properties on Partitioning of RDX Among Soil, Interstitial Water, and Earthworm Tissue	215	E-161
Dr. Jerzy Leszczynski <i>ERDC USACE</i>	2D QSAR Analysis of Nitroaromatic Toxicity of the Tetrahymena Pyriformis	216	E-162

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Stuart Strand <i>College of Engineering-University of Washington</i>	Enhancing Rhizosphere Bacterial Degradation of RDX	217	E-163
Dr. Neil C. Bruce <i>University of York</i>	Engineering Transgenic Plants for In Situ Treatment of RDX	218	E-164
Dr. Neil C. Bruce <i>University of York</i>	The Role of Glycosyltransferases in the Phytodetoxification of TNT	219	E-165
Brittany R. Flokstra <i>The University of Iowa</i>	Phytoremediation for the Containment and Treatment of Energetic and Propellant Material Releases on Testing and Training Ranges	220	E-166
Christopher Abate, Ph.D. <i>AMEC Earth & Environmental, Inc.</i>	In-Situ Evaluation of Release of Explosives Compounds from a Cracked UXO Item	221	E-167
Dr. Thomas F. Jenkins <i>U.S. Army ERDC-CRREL</i>	Distribution and Fate of Propellant Residues on Military Training Ranges	222	E-168
Dr. Thomas F. Jenkins <i>U.S. Army ERDC-CRREL</i>	Accumulation of Propellant Residues at Small Arms Firing Points	223	E-169
Yuehe Lin <i>Pacific Northwest National Laboratory</i>	Displacement Immunoassay of TNT Based on Electroactive Silica Nanoparticle Label	224	E-170
ER: Emerging Contaminants			
Robert J. Steffan, Ph.D. <i>Shaw Environmental, Inc.</i>	Biodegradation of 1,4-Dioxane	201	E-171
ER: Chlorinated Solvents — Dissolved Phase Remediation			
Professor David L. Freedman <i>Clemson University</i>	Characterization of Microbes Capable of Using Vinyl Chloride as a Sole Carbon and Energy Source by Anaerobic Oxidation	187	E-172
Bahngmi Jung, Ph.D., Research Associate <i>Wright State University</i>	Characterization of Degradation of Chlorinated Ethenes and Redox-Sensitive Constituents in Column Reactors Simulating Constructed Wetland Conditions	188	E-173
Bruce M. Henry, P.G. <i>Parsons</i>	Loading Rates and Impacts of Substrate Delivery for Enhanced In Situ Anaerobic Bioremediation	197	E-174
Dr. M. Hope Lee <i>North Wind, Inc.</i>	Determining Intrinsic TCE Degradation at DOE EM Sites: Enzyme Probes	198	E-175
Dr. Paul M. Bradley <i>U.S. Geological Survey</i>	Kinetics of DCE and VC Mineralization Under Anoxic Conditions	199	E-176
Robert J. Steffan, Ph.D. <i>Shaw Environmental, Inc.</i>	Substrate Range and Microbial Diversity of SDC-9	200	E-177
ER: Chlorinated Solvents — Site Characterization			
Carmen Lebron <i>Naval Facilities Engineering Services Center</i>	Standardized Procedures for Use of Nucleic Acid-Based Tools for Microbial Monitoring	183	E-178
Gregory V. Lowry Associate Professor <i>Carnegie Mellon University</i>	Polyelectrolyte-Modified Nanoscale Zerovalent Iron: Characteristics of the Adsorbed Polyelectrolyte Layer and Their Effects on Dispersion Stability and TCE Dechlorination	184	E-179

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Lewis Semprini, Professor <i>Oregon State University</i>	Continuous-Flow Column Studies to Evaluate the Effects of Different PCE and TCE Concentrations and Lactate Addition on Reductive Dehalogenation	185	E-180
ER: Chlorinated Solvents — DNAPL			
Dr. Robert (Bob) C. Borden, P.E. <i>North Carolina State University</i>	Impact of pH Adjustment and Bioaugmentation on Enhanced Reductive Dechlorination of Trichloroethene	136	E-181
Dr. Robert (Bob) C. Borden, P.E. <i>North Carolina State University</i>	Developing a Design Tool for Planning Emulsified Oil Injection Projects	137	E-182
Robert L. Siegrist, Ph.D., P.E., DEE <i>Colorado School of Mines</i>	Performance Assessment During Remediation of Chlorinated Solvent Contaminated Sites: Potential for and Methods to Mitigate Errors Based on Sampling Using Direct-Push Cores and Groundwater Wells	138	E-183
Richard J. Watts, Ph.D. <i>Washington State University</i>	Development of Treatability Study Protocol for the Remediation of Contaminated Groundwater by In Situ Chemical Oxidation (ISCO)	139	E-184
Tom Sale <i>Colorado State University</i>	Field Applications of ZVI-Clay Technology for Chlorinated Solvent Source Zones	140	E-185
Thomas J. Simpkin, P.E., Ph.D. <i>CH2M HILL</i>	Dnapl Remediation at Camp Lejeune Using Soil Mixing with ZVI-Clay	141	E-186
Megan M. Smith <i>Colorado School of Mines</i>	Coupled Techniques for More Efficient Groundwater Remediation: Polymer Floods and Oxidation Treatment	142	E-187
Jeff A. K. Silva, MS, PG <i>Colorado School of Mines</i>	Water-Soluble Polymers to Enhance the Sweep-Efficiency of In Situ Remediation Agents	143	E-188
Charles Schaefer, Ph.D. <i>Shaw Environmental, Inc.</i>	DNAPL Dissolution in Fractures and Fracture Networks	152	E-189
Pierre Lacombe <i>U. S. Geological Survey</i>	First Things First--Investigating DNAPL Contaminated Fractured Rock Aquifers	153	E-190
Linda M. Abriola, Ph.D. <i>Tufts University – Department of Civil & Environmental Engineering</i>	Delivery of Reactive Iron Particles for Treatment of DNAPL Source Zones	154	E-191
Linda M. Abriola, Ph.D. <i>Tufts University – Department of Civil & Environmental Engineering</i>	Investigating the Benefits of DNAPL Source Zone Treatment: Source Zone Architecture, Partial Mass Removal, and Contaminant Flux Reduction	155	E-192
Purshotam K. Juriasingani, P.E. <i>Tetra Tech, Inc.</i>	Implementation of Thermal Treatment Technology Using Innovative Decision Making Tools for the Treatment of DNAPL	156	E-193
Denise Yaffe, Ph.D., P.E. <i>Earth Tech</i>	Utchem Model Simulations of Various Treatment Technologies for Chlorobenzenes-DDT-DNA	157	E-194
Ralph S. Baker, Ph.D. <i>TerraTherm, Inc.</i>	Improved Understanding of Thermal Mechanisms Obtained During Meter-Scale Experiments Simulating DNAPL Sources in Aquifers	158	E-195
Dr. Barry Cole <i>Honeywell Laboratories</i>	Honeywell Technologies to Address DNAPL Detection/Remediation	Newly Added Poster	Newly Added Poster
Jennifer Triplett Kingston <i>Arizona State University</i>	A Preliminary Assessment Tool for Use of In-Situ Thermal Technologies at DNAPL-Impacted Sites	167	E-196

Refer to the Exhibit Level map located within the General Information section for poster locations.

PRESENTER ORGANIZATION	POSTER TITLE	POSTER	PAGE
Rick Johnson <i>Oregon Health & Science University</i>	Cryogenic Collection of Complete Subsurface Samples for Molecular Biological Analysis	168	E-197
Michael Kavanaugh, Ph.D., P.E. <i>Malcolm Pirnie, Inc.</i>	Diagnostic Tools for Performance Evaluation of Innovative In-Situ Remediation Technologies at Chlorinated Solvent Contaminated Sites (ER-0318)	169	E-198
Gregory V. Lowry, Ph.D. Associate Professor <i>Carnegie Mellon University</i>	NZVI Treatability Study for a TCE Source Area at Alameda Point, CA	170	E-199
Gregory V. Lowry Associate Professor <i>Carnegie Mellon University</i>	Effect of pH, Pore Water Velocity, Grain Size, and Clay Content on the Transportability of Surface-Modified NZVI in Saturated Sand Columns	171	E-200
Dr. Ronald W. Falta <i>Clemson University</i>	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	172	E-201
Mark Leeper, P.G. <i>Defense Supply Center Richmond</i>	Mulch Biowall used for Chlorinated Solvent Remediation	173	E-202
Carmen Lebron <i>Naval Facilities Engineering Services Center</i>	Improving Effectiveness of Bioremediation at Dnapl Source Zone Sites by Applying Partitioning Electron Donors (PEDs)	182	E-203
Dr. John Freim <i>OnMaterials</i>	Optimizing the Performance of Injectable Zero Valent Metals	186	E-204

CHROMIUM REPLACEMENT AND EROSION MITIGATION TECHNOLOGY FOR MEDIUM CALIBER GUN BARRELS

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Medium Caliber Guns use electrodeposited chrome to protect the bore surface from the harsh environment of propellant gases. The electrodeposition process uses Chrome IV, a known carcinogen. Various laws and statutes exist to eliminate Chrome IV. In addition, advanced propellants used in higher lethality medium caliber ammunition increases cannon wear and erosion, and shortens barrel service life for current and future gun barrels. The solution is to develop environmentally-friendly, erosion resistant, gun bore coatings that meet or exceed current performance requirements. The technical objective of this program is to eliminate chromium plating in the production of medium caliber guns by developing an environmentally acceptable method for depositing wear and erosion resistant materials onto the gun bore surface through the exploitation of explosive cladding technology.

Benet Labs, in conjunction with High Energy Metals Inc. (HEMI) in Sequim, WA has successfully cladded numerous environmentally-friendly materials onto both 12” and 36” truncated sections of a medium caliber 25mm Bushmaster gun barrel using explosive cladding technology. After successful liner rifling, firing tests are expected to validate performance equivalency.

This work is funded by SERDP through Project WP-1426: Chromium Elimination In Medium Caliber Guns, WP-1426.

FARADAYIC PROCESS FOR FUNCTIONAL TRIVALENT CHROMIUM ELECTROPLATING

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Faraday will present research work performed to develop a functional trivalent chromium plating process from a simple to control trivalent-based electrolyte to replace hexavalent chromium plating. Hexavalent chromium plating has been used for many years to provide hard, durable coatings with excellent wear and corrosion resistance properties. However, hexavalent chromium baths have come under increasing scrutiny due to the toxic nature of the bath, effects on the environment, and workers' health. In this poster, Faraday will present its accomplishments to date to achieve properties comparable to existing hexavalent chromium plating for both functional and decorative applications. Continuing work on the bath chemistry, diffusion layer, hydrodynamics, and electrically mediated process parameters will also be discussed. Also presented will be brief details on Faraday's other environmentally benign technologies that may be of interest to SERDP participants.

CADMIUM ALTERNATIVES FOR DOD AND NASA APPLICATIONS— PHASE II TESTING RESULTS

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A Joint Test Protocol (JTP) for evaluation of cadmium alternatives for high-strength steel structural components has been developed through the Joint Cadmium Alternatives Team (JCAT). The test protocol combines the joint requirements of the aviation and ground platform community for defense and commercial users, and builds upon previous work including screening tests for cadmium alternatives and the Air Force's landing gear effort. Phase I testing, completed in 2006, focused on embrittlement/re-embrittlement and adhesion testing of alternative coatings and repair methods. Coatings selected for Phase II testing were: LHE Zinc-Nickel, Sputtered Aluminum, Electroplated Aluminum, Brush Zinc-Nickel, Brush Tin-Zinc, and SermeTel[®] 249/273. Control coatings included both LHE cadmium and IVD aluminum. Phase II tests, conducted in FY07, consisted of stress corrosion cracking, corrosion fatigue, SO₂ salt fog corrosion, throwing power, compositional uniformity, galvanic corrosion, salt spray corrosion, fluid corrosion, coating adhesion, paint adhesion, repairability, and lubricity. Test data reported here have been generated by various government and commercial labs including NAVAIR, Army Research Labs, Concurrent Technologies Corporation, and Westmoreland Mechanical Testing and Research. Portions of this effort were funded by ESTCP WP-0022.

CORROSION RESISTANT ULTRAHIGH STRENGTH STEEL TO REPLACE CADMIUM PLATED 300M

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An innovative approach to the computational engineering of new materials has been undertaken to develop a stainless steel replacement for cadmium coated 300M in aerospace structural components. Computational modeling and systems engineering has optimized an alloy composition and processing to achieve a superior combination of strength, toughness, and resistance to corrosion and stress-corrosion-cracking. A program targeting applications in Landing Gear (WP-0304) is now nearing completion and will result in AMS specification for the new alloy, Ferrium[®] S53, by the end of 2007. Component qualification testing on A10 main landing gear pistons is currently in process. JTP test data has been completed and documented in a JTR. A separate program targeting rotary gear actuator applications (WP-0619) is underway and addresses corrosion and wear issues not common to landing gear. Program results to date indicate the alloy can replace 300M steel with significant improvements to general corrosion resistance and stress corrosion cracking resistance. Results from JTP testing and demonstration activities will be presented.

DEVELOPMENT OF NI-CU-RU CONSUMABLES FOR WELDING OF AUSTENITIC STAINLESS STEELS

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Welding of stainless steel can produce fumes that contain carcinogenic hexavalent chromium (Cr^{+6}) species. OSHA recently has dramatically reduced the Permissible Exposure Limit (PEL) for hexavalent chromium, which may severely restrict the use of conventional weld consumables containing 12-25% Cr. The motivation of this SERDP-funded study (WP-1415) is to develop a Cr-free filler metal based on the Ni-Cu alloy system that is compatible with common austenitic stainless steels, including Types 304 and 316.

Last year, we presented results from shielded metal arc (SMA) welds made with a Ni-209 (Ni-4Ti-0.7Al-0.4Si-0.3Mn) core wire with Cu and Pd additions in the wire coating. It was difficult to achieve the desired weld deposit composition with those consumables. This year, wire was made with the composition Ni-7.5Cu-0.5Ti-0.5Al-0.02C. SMA consumables were produced by Special Metals Corp. and Euroweld Ltd. using this wire. Welds were made with the fabricated Ni-Cu-Ru electrodes and weldability and corrosion testing was performed on those welds. The target composition of Cu and Ru was achieved in the weld deposits.

Weldability testing was performed using a cast-pin test designed to evaluate susceptibility to solidification cracking. It was found that the Ni-Cu-Ru weld metal has only a moderate susceptibility to solidification cracking similar to other Ni-based weld metals. Testing of solid-state weld cracking susceptibility was also performed on weld deposits made with the Ni-Cu-Pd consumables. The solid-state cracking phenomenon, known as ductility dip cracking (DDC), was found in those weld deposits. The susceptibility to DDC is similar to other Ni-based weld metals with a moderate to high susceptibility. Fume studies were performed on fume produced by the Ni-Cu-Pd and off-the-shelf E308-16 welding consumables. Fume generation rates were considerably higher for the Ni-Cu-Pd consumables, as compared to E308-16, though the levels of Cr+6 were reduced dramatically from 2.6 wt-% (E308-16 fume) to 0.02 wt-% (Ni-Cu-Pd).

Corrosion resistance of welds made with Ni-Cu-Pd consumables was assessed by cyclic polarization and immersion crevice corrosion tests. The results of the two tests were in agreement. The lower breakdown potential and higher repassivation potential of the samples with Ni-Cu-Pd welds compared to 308L welds are associated with the location of crevices at the weld metal for the Ni-Cu-Pd weld samples but shallower crevice depth. The beneficial effects of Pd on the critical potentials, even at levels as low as 0.12%, are also reflected in the improved crevice corrosion behavior of the Pd weld samples.

INVESTIGATION OF CHEMICAL VAPOR DEPOSITION OF ALUMINUM AS A REPLACEMENT COATING FOR CADMIUM

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Cadmium is widely accepted as the coating of choice on high strength steels due to its excellent corrosion resistance, adhesion, and lubricity characteristics. However, cadmium is a carcinogen, a teratogen, and a toxic metal that can be leached easily causing potential contamination of the ground water supply and food chain.

The objective of this SERDP project (WP-1405) is to evaluate the use of atmospheric pressure chemical vapor deposition techniques to produce uniform and conformal aluminum coatings on high strength steel substrates. This approach offers an environmentally benign alternative to cadmium plating, as well as promises to provide high production throughput, low cost, and coatings with desirable properties and performance. Efforts during the third year of this project have focused on using tri-isobutyl aluminum as a precursor to deposit coatings 10-25 mm thick at temperatures in the range from 275°C to 300°C. These aluminum coatings have been characterized in terms of their composition, structure, and morphology. Additionally, performance tests are being used to determine their properties compared to those of cadmium and Ion Vapor Deposited (IVD) aluminum. Results indicate that the coatings consist essentially of pure aluminum with traces of oxygen, carbon, and hydrogen. The presence of hydrogen in the coatings necessitates a post deposition, hydrogen relief bake (such as used for cadmium coatings) to avoid causing hydrogen embrittlement and/or a fatigue debit. The performance tests include chemical resistance, paint adhesion, corrosion resistance, electrochemical characterization, hardness and tensile strength debit, hydrogen embrittlement susceptibility, as well as fatigue debit. Further work is needed to produce pure coatings at lower deposition temperatures that will not have an adverse effect on high strength steel substrates used for landing gear components, as well as producing optimized coatings for other applications that require lower strength steels.

INVESTIGATION OF CHEMICALLY VAPOR DEPOSITED TANTALUM FOR MEDIUM CALIBER GUN BARREL PROTECTION

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Chromium (Cr) has been widely used as a protective coating on the interior bore surfaces of medium caliber gun barrels. Chromium coatings are currently electro-deposited from aqueous solutions of hexavalent chromium, a known carcinogen and toxic substance that is strictly regulated and entails high disposal costs. Tantalum (Ta) in the α phase is an attractive candidate for Cr replacement because it is environmentally friendly and exhibits excellent physical and chemical properties such as a high melting point (3017°C), good ductility, and excellent corrosion resistance in aggressive environments. Although internally magnetized cylindrical magnetron sputtering (IM-CMS) has been demonstrated to be capable of depositing Ta coatings to protect large caliber gun bores, it has proven not to perform well on cylinders with diameters below 45 mm due to the critical ionization distance required by this process.

This program investigates the use of chemical vapor deposition (CVD) to produce high quality Ta coatings for Cr replacement. In addition to offering an environmentally benign alternative to Cr plating, this relatively low deposition temperature process promises to provide high throughput, low cost, conformal step coverage, and coatings with desirable properties and performance. In this SERDP-supported study (WP-1425), tantalum pentachloride (TaCl_5) has been selected as the preferred precursor while a downstream-type plasma enhanced CVD (PECVD) reactor with 13.56 MHz RF power source was used to produce the coatings. The interrelationships governing the growth kinetics, compositions, and coating properties have been established as a function of deposition temperature, total pressure, RF power, and reactant concentration. The Ta coatings have been characterized with respect to their chemical, structural, and morphological properties. Results of AES and XPS indicate that the coatings consist essentially of pure Ta with trace amounts of oxygen and chlorine. The SEM results revealed that the coatings exhibit conformal coverage while the XRR and XRD results indicated that the coatings are dense and exhibit a mixture of the α (BCC) and β (tetragonal) Ta phases. Challenges currently being addressed include enhancement of the growth rate and production of the pure α phase at lower temperature on steel substrates.

SUPERSONIC PARTICLE DEPOSITION TECHNOLOGY FOR REPAIR OF MAGNESIUM AIRCRAFT COMPONENTS

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Magnesium alloys are widely used for fabrication of many components on DoD aircraft, because of their high strength-to-weight characteristics, especially for complex components such as transmission and gearbox housings on helicopters and gearbox housings on fixed-wing aircraft. The acquisition cost for these components ranges from several thousand to over one-hundred-thousand dollars. However, magnesium alloys are highly susceptible to corrosion in-service and to surface damage due to impact such as during handling, assembly, or repair. To provide some level of protection, OEMs hard anodize the surface using a process designated Dow 17 which uses compounds containing hexavalent chromium. Repair depots use a chromate conversion process designated MIL-M-3171. On most surfaces, these processes are followed with a resin sealer and then a chromated primer and topcoat. Even with these processes, several million dollars are expended by DoD each year to either repair or replace Mg alloy components that are corroded or damaged in service. In addition, the proposed new permissible exposure limit for hexavalent chromium will make the replacement of processes using this compound almost mandatory. As part of an overall solution to the problem, supersonic particle deposition (SPD) of aluminum alloys is considered one of the most viable methods of imparting surface protection to Mg alloys. Test data relating to the demonstration and validation of SPD of Al alloy coatings as a cost-effective, environmentally acceptable technology to impart surface protection and restore dimensional tolerances to Mg alloy components on DoD helicopters and fixed-wing aircraft will be presented. The work includes establishment of a demonstration SPD facility at NADEP Cherry Point (NADEP-CP), development and execution of a materials joint test protocol that would include field testing, and application of coatings to actual components for lead-the-fleet flight testing.

This work is funded by ESTCP as Project WP-0620.

ELECTROLYTIC PLASMA TECHNOLOGY: A NOVEL CLEANING AND COATING TECHNOLOGY

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Electrolytic Plasma Technology (EPT) is a novel environmentally friendly, surface cleaning and coating technique which involves a combination of electrolysis and wet plasma phenomena. The electrolytic-plasma results in fine bubble formation and collapsing with concomitant forceful disruptions and shock wave production, along with local melting of the materials surface layer. These wet plasma/material surface interactions result in a complete removal of mill-scale or other contaminants and produce an effectively clean surface. Furthermore, the local surface melting and subsequent quenching results in ultra-fine grain structures and a favorable ‘anchor’ surface profile providing a key or mechanical interlocking for a coating. Deposition of coatings predominantly occurs by ion acceleration through the plasma, ion bubble adsorption, and transport to the surface via bubble collapsing. These processes eliminate boundary layer diffusion and result in unrealistically high deposition rates.

In the present work, the EPT was applied for cleaning 4340 steel surfaces and subsequently depositing Zn-Ni coatings. The objective of the present SERDP Project (WP-1406) is to assess the potential of EPT as an alternative for Cd coating replacement. The cleaning process was carried out in a NaHCO₃ solution; whereas, coating treatments were conducted using a mixture of ZnSO₄·7H₂O and NiSO₄·6H₂O solutions. The Ni content in the coatings was varied by changing the composition of the electrolyte. The coating microstructure and composition and the coating/substrate interface were investigated by scanning electron microscopy (SEM) in conjunction with energy dispersive x-ray spectroscopy (EDS). The chemical state of the coatings was studied by X-ray photoelectron spectroscopy (XPS) and the phase structure was determined by X-ray diffraction (XRD). Corrosion performance of the coatings was evaluated by corrosion potential and potentiodynamic polarization measurements. The results show that EPP presents high promise as a viable alternative for Cd coating replacement.

NANOCRYSTALLINE COBALT-ALLOY COATINGS FOR NON-LINE-OF-SIGHT CHROME REPLACEMENT APPLICATIONS

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The replacement of hard chromium (Cr) plating, in aircraft manufacturing activities and maintenance depots, is a high priority for the U.S. Department of Defense. Hard Cr plating is a technique that has been in commercial production for over 50 years and is a critical process that is used both for applying hard coatings to a variety of aircraft components in manufacturing operations and for general re-build of worn or corroded components that have been removed from aircraft during overhaul. Chromium plating baths contain chromium in the hexavalent state, a known carcinogen. Wastes generated from plating operations must be disposed of as hazardous waste and plating operations must abide by EPA emissions standards and OSHA permissible exposure limits (PEL). OSHA recently reduced the PEL for hexavalent Cr and all hexavalent Cr compounds from $52\mu\text{g}/\text{m}^3$ to $5\mu\text{g}/\text{m}^3$. Due to the expected increase in operational costs associated with compliance to the revised rules and the expected increased turnaround times for processing of components, there is tremendous pressure to find an environmentally benign alternative to hard chrome.

Electrodeposited nanocrystalline cobalt-phosphorus (nCoP) coatings have been developed as an environmentally benign alternative to hard Cr coatings for non-line-of-sight (NLOS) applications under the SERDP Project WP-1152, and are currently going through demonstration-validation testing in a project under ESTCP Project WP-0411. Nanocrystalline CoP coatings show great potential as an alternative coating to hard chrome for NLOS applications due to: higher cathode efficiency, higher deposition rates, high hardness and good sliding wear, and corrosion resistance. Originally developed on the laboratory scale, the nCoP deposition process has been scaled up to the industrial/production scale.

Outlined here are the process and properties of various nanocrystalline cobalt-alloy coatings in comparison to hard Cr, and the broad areas of application for the various coatings. A general overview of nanocrystalline materials will be presented with particular emphasis on reviewing the process and properties of nCoP coatings as they pertain to a hard Cr alternative. A review of the ongoing demonstration/validation program for nCoP, currently being carried out at the Naval Aviation Depot (NADEP) in Jacksonville, Florida, will also be presented.

VAPOR RECOVERY BY ELECTROTHERMAL SWING ADSORPTION

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The development of new vapor recovery technologies can allow for the continued use of higher-performance chemicals, re-use of those chemicals, and lower overall emissions of Hazardous Air Pollutants/Volatile Organic Compounds (HAPs/VOCs). They may also alleviate concerns of greenhouse gas emissions from oxidative technologies. The most energy efficient method is adsorption, which is often economically or practically unfeasible with current technologies, such as granular activated carbon (GAC) with steam regeneration. VaPRRS™ was developed cooperatively by the University of Illinois, ERDC-CERL, and Air Force Research Laboratory (AFRL) as an economical adsorption technology to control emissions from Department of Defense (DoD) HAP/VOC emissions sources such as painting operations

VaPRRS™ is a new type of regenerative filter system, which uses a high-performance activated carbon fabric cloth (ACFC) contained within a vessel. Applying an electrical current regenerates the fabric by rapidly heating the fabric, which efficiently desorbs the contaminant with minimal heating of the vessel. The adsorbate is released and condensed onto the inner surface of the vessel and is collected as a liquid. The filter is ready for reuse after it cools. A major advantage of this technology over conventional systems is that the entire adsorption, desorption, and recovery process occurs in the same vessel. This ultimately reduces the size, complexity, and cost of the system.

During a pilot field study at a paint booth at Fort Hood, TX, the system achieved greater than 99% control efficiency. Through ESTCP Project WP-0521, VaPRRS™ is being demonstrated at Hill Air Force Base on a portable system for painting the wheel wells of the C-130 aircraft. The portable paint booth encloses the painting operation so that evacuation of the hangar is not necessary during painting. However, control efficiency is important because the booth vents back into the hangar. A bed of GAC is currently used to adsorb the HAPs/VOCs in the paint booth exhaust. When the bed has become saturated, it is sent offsite for disposal or regeneration and a new bed is installed. This demonstration replaces that GAC bed with a VaPRRS™ unit. The VaPRRS™ unit has been scaled from an 80 cubic feet per minute (cfm) flow rate pilot system to approximately 1,000 cfm. Scale-up required a significant redesign of the system, including modification of the ACFC filters from cylindrical to a bag-type configuration.

ENVIRONMENTALLY BENIGN REPAIR OF COMPOSITES USING HIGH TEMPERATURE CYANATE ESTER NANOCOMPOSITES: RESIN DEVELOPMENT

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High-temperature polymer matrix composites (PMCs) are widely used in applications, such as aircraft exhaust and engine cowlings, requiring stability at temperatures up to 260°C. PMCs are especially susceptible to matrix micro-cracking when subjected to repeated thermo-mechanical loadings. Often these matrix micro-cracks coalesce and lead to other damage modes including fiber/matrix debonding and ply delamination. Low velocity impacts are also common causes of delamination damage in fiber reinforced PMCs. Resin injection repair is one of the common methods to repair delamination damage in PMCs. To repair high-temperature PMCs by this method, the resin should have a very low viscosity, yet cure into a compatible adhesive with high temperature stability. Normally, thermosetting polymers with high glass transition temperatures (T_g) are made from resins with high room temperature viscosities. Among the high temperature resins, such as bismaleimides, polyimides, and cyanate esters, an exception is a unique type of cyanate ester monomer: bisphenol E cyanate ester (BECy), which has an extremely low viscosity of ~100 cP at room temperature and polymerizes as a cross-linked thermoset with a high T_g of nearly 300°C.

Addition of nanoparticles to the repair resin causes a thixotropic response: viscosity decreases under applied shear force. This property allows the repair resin to be easily injected into micro-cracks under shear and remain in the damage zone after the shear force is removed until the polymer is cured. The incorporation of nanoparticles can also improve the adhesive strength and may reduce the required high cure temperature by influencing the cure kinetics of the resin. BECy monomer is cured via an addition trimerization reaction, without volatile products, to form a high T_g amorphous network. The cure kinetics of BECy was investigated by differential scanning calorimetry (DSC) in dynamic and isothermal mode. The activation energy (E_a) of catalyzed BECy was calculated as 67 kJ/mol and 69 kJ/mol based on Kissinger and Flynn-Wall-Ozawa methods, respectively. A T_g vs. conversion diagram was plotted by using isothermal curing data and the empirical DiBenedetto equation was used to evaluate the relationship between T_g and conversion. Alumina nanoparticles were found to have a profound catalytic effect on the cure kinetics of BECy, reducing the (peak exothermic) cure temperature over 70°C with a 10 wt% loading of alumina nanoparticles.

This work is funded by SERDP through Project WP-1580.

ADVANCED TECHNOLOGY FOR FIRE SUPPRESSION IN AIRCRAFT

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Production of halon 1301 (CF_3Br), long the agent of choice for suppressing in-flight fires, had ceased as of January 1, 1994 due to its high ozone depleting potential. The Department of Defense's Next Generation Fire Suppression Technology Program (NGP), supported by SERDP as Project WP-1059, reached its conclusion in FY 2006 after ten years of research with a goal to develop and demonstrate technology for economically feasible, environmentally acceptable and user-safe processes, techniques, and fluids that meet the operational requirements currently satisfied by halon 1301 systems in aircraft. The NGP has completed its development of a suite of tests for screening candidate fire suppressants, delineated the desirable properties of gaseous and aerosol suppressants, advanced the technology for estimating the environmental properties of candidate suppressants, and developed a methodology for comparing the life cycle cost of alternate suppressants for both back fit and forward fit. The Program has also completed a search for alternative chemicals, leading to a focus on compounds containing bromine, iodine, or phosphorus atoms, having a boiling point low enough to ensure rapid dispersion in cold operational temperatures; containing chemical features that ensure rapid decay in the lower atmosphere; and manifesting low toxicity. The NGP has developed guidance in deploying a suppressant as efficiently as possible. This includes modeling of agent transport through clutter and determination of the effects of a cold environment on the effectiveness of agent dispersion throughout the space to be protected. Finally, the NGP has made significant advancements in fire suppression techniques other than dispensing of a compressed fluid. This includes solid propellant-based fire extinguishment systems in which coolants or chemical additives are incorporated directly into the propellant composition and those in which an auxiliary fluid is discharged with the propellant effluent. Dramatic improvements have also been realized in powder panel technology, an approach that provides passive, lightweight protection of aircraft dry bays against ballistic impact by releasing powder into the fire zone to inert the space before the adjoining fuel spills into the space and is ignited by incendiaries.

The final report, a 1,240 page book, is available on CD from the author.

DEEP WEB SEARCH PORTAL FOR ENVIRONMENTAL APPLICATIONS

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Department of Defense (DoD) decision makers require current, accurate, and focused information on commercial and emerging environmental technologies—sometimes on short notice—to ensure the best performance and economic returns for their technology investments. Large amounts of this information are widely available and rapidly increasing, but timely access to key sources is difficult and unreliable. Moreover, useful data is scattered across many sources (such as technical reports, press releases, trade journals, conference proceedings, and government web sites) and exists in different formats. Traditional search engines like Google index only about 16% of information on the Internet and locating sources outside this category in the “hidden web” can be time-consuming. Many commercial-off-the-shelf (COTS) data search technologies exist to access this variety of sources, but no single system design meets the range of DoD environmental data gathering needs. This presentation will describe and demonstrate a recently developed, user-friendly Internet Data Search Portal to support search, organization, analysis, and content extraction from the environmental hidden web for DoD users. The Data Search Portal incorporates a COTS web-based search engine, along with a user interface, selected environmental technology Internet sites and data processing features. Potential search portal applications include scouting for environmental technology solutions, monitoring emerging technologies, and collecting data for technology assessments.

NEW REACTIVE DILUENTS FOR VOC-FREE REPAIR RESINS

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Composite polyester repair resins using styrene as the reactive diluent pose significant health and environmental risks. Our SERDP SEED program (WP-1596) is targeting alternative and cost competitive reactive diluents that will lead to a 0% VOC repair resin that possesses equal or better mechanical properties. The initial work has focused on creating new diphenyl ether analogs that will diminish or eliminate VOCs and deliver a cost effective drop-in replacement for existing styrene-based repair systems. Currently, we have made diphenyl ether systems, that indeed produce low viscosity polyester mixes, that nicely wet out the repairs, fully cure using standard free-radical initiators, and have virtually no detectable VOCs. Results will be presented on: (1) chemical synthesis and characterization, (2) VOC determination, (3) and use in composite repairs with mechanical test data. Direct comparison to styrene based repair resins will be presented as well.

ENVIRONMENTALLY BENIGN APPROACHES FOR THE REPAIR OF COMPOSITES FOR MILITARY APPLICATIONS

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Thermoset adhesives used in composite joining and repair include: epoxy, polyurethane, organo-silane, and vinyl ester. These adhesives are applied as films or liquids in volatile and toxic solvents including: toluene, MEK, acetone, and xylene which are both VOCs and HAPs and are hazardous to the workers health. In addition, the primary chemical components and plasticizers that constitute the uncured adhesives are toxic waste on the EPA Toxic Release Inventory (TRI). The uncured adhesive materials require low temperature storage and have a shelf life of approximately one year. If not used, the uncured materials must be discarded and disposed of as hazardous and toxic waste.

This SERDP SEED effort (WP-1581) proposes to evaluate the feasibility of using thermoplastics as adhesives instead of standard thermosets, using Kubota's near-infrared (NIR) PWave welding technology. The proposed one-year effort will address scientific and technical barriers, such as, selection of thermoplastic polymers as alternatives, understanding and optimizing adhesion mechanisms between thermoplastics and thermosets, optimizing the NIR system for selective heating of the thermoplastic, and mechanical performance of the thermoplastic alternatives. The main barrier is the level of adhesion that is possible between a thermoplastic and a pre-cured thermoset interface. Two mechanisms, surface roughness and chemical bonding facilitated by plasma treatment of the thermoplastic, will be evaluated to improve and optimize adhesion. The NIR system will be used to provide heat locally at the bondline, without heating the substrate and process optimization will be performed to identify the optimal parameters to maximize adhesion.

The use of thermoplastics eliminates the generation of VOC's and HAPs, has infinite shelf life, no storage restrictions or disposal issues allowing it to be carried into the operating theater. The NIR source is portable and low energy with the potential for **battery operation** in the field. This is extremely attractive as it allows in-field repair (due to battle damage or other reasons) of components restoring platform performance. The radiation heating process only heats and melts the resin at the bonding interface, minimizing heating and cooling time in the repair cycle to provide a fast repair (order of minutes). The short repair time allows easy application of external pressure (rollers), rather than the autoclave or other expensive alternatives.

ALTERNATIVE TO HALON 1211 FLIGHTLINE FIRE EXTINGUISHER

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ESTCP Project WP-0618, Qualification of an Acceptable Alternative to Halon 1211 DoD Flightline Extinguishers, is in its second of a two-year funded effort. This is a joint Navy/Air Force initiative to identify an acceptable alternative to the 150 pound Halon 1211 flightline fire extinguishers. These units are used at airfields as the first responder to an aircraft fire emergency on the ground. During the first year of the program, suitable alternative agents were identified along with performance metrics to be used during testing. Candidate agents for testing were required to meet the following requirements: (1) be on the EPA SNAP list, (2) meet NFPA 2001 criteria for “clean agent,” (3) and be commercialized in a streaming and/or flooding application. Several agents met these screening criteria. Additionally, a joint test protocol was developed. During the second year, the team is conducting testing of industry-submitted alternative agents/systems against fire scenarios of interest to the two services. Testing is being conducted at Tyndall Air Force Base.

DEMONSTRATION OF COMPOSITES WITH LOW HAZARDOUS AIR POLLUTANT CONTENTS FOR MILITARY APPLICATIONS

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Liquid resins used for molding composite structures are a significant source of hazardous air pollutant (HAP) emissions. One method of reducing styrene emissions from vinyl ester (VE) resins is to replace some or all of the styrene with fatty acid-based monomers. Fatty acid monomers are ideal candidates because they are inexpensive, have low volatilities, and promote global sustainability because they are derived from renewable resources. This patent pending technology allows for the formulation of high performance composite resins with no more than 25 wt% styrene. As a result, these resins are currently being demonstrated/validated under ESTCP WP-0617 for DoD use in Marines HMMWV helmet hardtops, Air Force T-38 dorsal covers, MCM composite rudders for the Navy, and Army tactical vehicles, including HMMWV hoods, HMMWV transmission containers, and M35A3 truck hoods. This work has validated the commercially produced low HAP vinyl ester resins from Applied Poleramics, Inc. for use in DoD composite structures. Army tests have shown that the established resin formulations meet the property requirements. The low HAP composites have similar modulus, strength, and short-beam shear properties relative to composites made using the conventional high HAP vinyl ester resin and have superior ballistic performance. Yet, AF and Navy testing showed that a very low HAP resin with 20% styrene had insufficient properties. As a result, an established resin formulation with 25 wt% styrene is currently being evaluated. Weathering tests are currently being conducted to determine the environmental durability of the low HAP resins. Next, the performance of full-scale parts will be rigorously tested to properly demonstrate this alternative resin technology. For the truck hoods, the ability of this structure to withstand static load, cyclic load, high service temperatures, and impact will be demonstrated by simulating the forces the structure would be exposed to in the field. The transmission container will undergo critical tests to simulate impact, low service temperatures, and assembly, cargo, and storage loads typical during fielding. The T-38 dorsal cover will be tested as per applicable sections of the Joint Services Specifications Guide 2006 (JSSG-2006). Following this guide should ensure proper durability and strength of candidate resins. The flexural and fatigue properties of the composite rudder will be rigorously tested to assure at least a five year service life. Furthermore, each of these parts will be fielded in real service conditions. The part performance will be monitored for damage and compatibility, while being compared to parts made with commercial resins.

ENVIRONMENTALLY FRIENDLY COATINGS SYSTEMS FOR DOD APPLICATIONS

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Military coating systems for metals typically consist of an inorganic pretreatment, an epoxy primer, and a polyurethane topcoat. Designed for harsh environments, including intense sunlight, corrosive sea water, thermal extremes, exposure to fuel and oxidizers, and damage from shrapnel, weapons fire, and collisions, these coatings also provide superior barrier properties, maintain good camouflage (low gloss, etc.), and continue to protect the soldier from chemical and biological attack. Traditional coating systems contain hexavalent chromium (Cr^{6+}) and produce significant amounts of volatile organic compound (VOC) emissions. However, the latest OSHA's regulations impose strict environmental standards forcing all industrial sectors and the Department of Defense to reduce VOC and Cr^{6+} exposure limits. As a result, we have examined the use of the trivalent chromium process (TCP) and non-chromium process (NCP) developed by NAVAIR to reduce Cr^{6+} use. We have developed modifications to increase corrosion resistance through the addition of an organic chelating compound and other additives to TCP at low concentrations. Furthermore, we have performed ISO titration studies on TCP and a hexavalent-based pretreatment, Alodine 1200, liquid pretreatments and pretreated panels. The results show that the amount of Cr^{6+} found in TCP samples is 1-2 orders of magnitude lower than that in Alodine 1200. We have developed water-based topcoats using low contents of fluorinated additives that improve cleanability, while having no discernible detrimental effects on performance. We also have reformulated water dispersible CARC to contain essentially no VOC content through the use of new high performance water dispersible polyols. The performance of the resulting polyurethanes is similar to that of the current polyurethane, but full military specification testing has not been completed yet.

This program is funded by SERDP through Project WP-1521.

ZEOLITE COATING SYSTEM FOR CORROSION CONTROL TO ELIMINATE HEXAVALENT CHROMIUM FROM DOD APPLICATIONS

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Zeolites are microporous crystalline aluminosilicates with uniform and molecular sized pores. They are non-toxic and have been explored for medical applications. We have been investigating the application of zeolite films as chromium-free protective coatings on aluminum alloys^[1-4]. We have shown that as-synthesized organic template containing high-silica-zeolite (HSZ) MFI coatings on AA-2024-T3 are non-porous and have excellent corrosion resistance in strong acids, bases, and pitting aggressive media^[1, 4]. We have demonstrated that high silica coatings including MFI, BEA, and MTW are all good corrosion resistant coatings^[2]. We have also shown that the in-situ crystallization coating deposition process we use can coat surfaces of complex shapes and in confined spaces^[1]. We successfully expanded our investigations to include other aluminum alloys (6061-T4, 5052-H32, 7075-T6)^[4] and steels (SS304-2b, S1008, S4130). We were able to use one simple pretreatment and a single zeolite formulation on all aluminum alloys and steels to synthesize MFI coatings. Corrosion protection was measured by DC polarization in several corrosive media. Salt-fog accelerated weathering tests were performed according to ASTM 117-B on scribed and non-scribed HSZ MFI coated 2024-T3. The non-scribed HSZ MFI coated 2024-T3 panels had no observable corrosion after more than 2,000 hrs. continuous salt fog exposure. The scribed HSZ-MFI coated 2024-T3 panels exhibited no delamination of the zeolite coating after 1,000 hrs. continuous salt fog exposure and corrosion was limited to the scribe. The compatibility between zeolite coatings with primer and topcoat systems has been investigated. A coating system of zeolite-primer (chromated) and zeolite-primer (chromated)-topcoat passed 3,100 hrs. continuous salt fog exposure with no observable corrosion and delamination. Currently, ionothermal synthesis of zeolite coatings is being investigated to reduce autogeneous pressure produced during the current hydrothermal deposition process for HSZ-MFI coatings. Corrosion resistant zeolite conductive coatings also are being investigated. Uniform electrical conduction throughout the zeolite coating is conferred through high density Ni/Au pillars imbedded within the HSZ-MFI coating. Detailed preparation procedure of the zeolite coatings and their corrosion resistance will be presented.

This work is funded by SERDP as Project WP-1342.

IMPROVED SUPERPRIMERS FOR DOD APPLICATIONS

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The results reported in this abstract are based on SERDP Project WP-1341 with the title “Improved superprimers for DoD applications”. The project started in 2003 and ended in September 2007. The objective of this project is to develop environmentally-benign coating systems for alloys used in DoD applications.

Heavy use of hexavalent chromium and VOCs in current primer coatings in DoD and other industrial applications poses a great threat to the environment. This has led researchers to pursue development of alternative environmentally-friendly coatings with a comparable performance. Our approach is to utilize organofunctional silane and waterborne resins, together with environmental-benign inhibitors, to develop a novel one-step primer coating system (termed superprimer). In this project, we have developed novolac epoxy-based superprimer and epoxy-acrylate-based superprimer. Both of them are chromate-free, containing very low VOC, and do not require any conversion coating. In accelerated corrosion test, these superprimers demonstrated strong protection for aluminum alloy, HDG, and CRS substrates. Improved superprimers can provide more than 3,500 hours of protection for AA2024-T3 in ASTM B117 test.

The microstructures of superprimer coatings and the protection mechanism were studied by different characterization techniques. SEM/EDAX revealed that some superprimers have unique stratified structure which accounts for their strong corrosion inhibition. Silane was found to improve adhesion and anticorrosion of the coating. The presence of silane on the interface between the coating and substrate was confirmed by ToF-SIMS studies. Pigment was found to leach out when the coating was damaged. The leaching rate of zinc phosphate (a typical pigment used in superprimers) from the coating was measured. How leached-out zinc phosphate protects the damaged area was investigated.

Electrodeposition, as a new application method for superprimer, was explored with initial success. Preliminary study found electrodeposited superprimer coating had a more organized structure and showed improved performance on certain substrates.

VALIDATION OF NOVEL ELECTROACTIVE POLYMERS AS ENVIRONMENTALLY COMPLIANT COATINGS FOR REPLACEMENT OF HEXAVALENT CHROMIUM PRETREATMENTS

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This ESTCP program (WP-0527), a follow-on to SERDP Project WP-1148, is currently demonstrating an effective, environmentally benign, repairable coating system using electroactive polymers (EAPs) as the replacements for chromate conversion coating (CCC) pretreatments on aluminum and steel alloys. The Naval Air Warfare Center – Weapons Division (NAWCWD), China Lake, CA is leading this effort in collaboration with Wright Patterson Air Force Base (WPAFB); Naval Air Warfare Center Aircraft Division (NAWCAD); Patuxent River, MD; and the Army Research Laboratory (ARL), Aberdeen Proving Grounds, MD.

The EAP polymers, that are being evaluated for this ESTCP program, are poly (2, 5-bis (N-methyl-N-hexylamino) phenylene vinylene), (BAM-PPV) and poly ((2-(2-ethylhexyl) oxy-5-methoxy)-*p*-phenylene) vinylene), (MEH-PPV). Both of these polymers have demonstrated acceptable performance as military alternatives to CCC on aluminum alloys. Each service (Air Force (AF), Navy and Army) have nearly completed all laboratory testing prior to field testing these two polymers. The laboratory testing by each service follows their specific military requirements for CCC replacements on metals. To date, nearly all NAWCWD/AD laboratory testing (neutral salt fog, filiform, SO₂ fog and contact resistance) for BAM-PPV and MEH-PPV panels has been completed. The AF has done extensive testing of these two polymers using a VOC-exempt solvent (Oxsol-100). A viable coating was produced with each polymer and could withstand 168 hours neutral salt fog exposure (ASTM B 117). These two polymers also were incorporated into standard coating systems (MIL-PRF-23377 and MIL-PRF-85285 APC) and provided acceptable adhesion performance and corrosion resistance in a neutral salt fog chamber. The Army adhesion testing for these two polymers has been completed with the MEH-PPV performing best with Navy primers and BAM-PPV performing best with Army primers. Both polymer systems (BAM-PPV and MEH-PPV) will be field tested starting in FY07 and continuing through FY08 using non-critical equipment from each service.

ENVIRONMENTALLY BENIGN MULTILAYER POLYMER COATINGS WITH CONTROLLED SURFACE PROPERTIES FOR MARINE ANTIFOULING APPLICATIONS

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Marine biofouling is the undesirable accumulation of microorganisms, plants, and animals on artificial surfaces submerged in seawater. Biofouling causes unwanted drag, which in turn leads to significantly higher consumption of fuel by marine interests. Novel, environmentally friendly multilayer antifouling coatings, based on the control of surface energy and coating modulus, are being developed to replace traditional toxic copper and tributyl-tin containing anti-fouling coatings. These multilayer coatings consist of a surface-active block copolymer (SABC) layer supported by a thick elastomeric layer. This work seeks to tackle both the energy consumption issues caused by biofouling and the environmental concerns of the previous generation of marine antifouling coatings.

Polystyrene-block-polyethylene/butylene-block-polystyrene (SEBS) produced by Kraton Polymers was selected as the bottom rubbery layer. This triblock copolymer provides the necessary low modulus, corrosion protection, adhesion, and durability needed for a multilayer coating system. Several approaches to the synthesis of side-chain functionalized SABC have been developed. Semifluorinated alkyl chains, poly(ethylene glycol), and Zonyl[®] amphiphilic fluorosurfactants are all being explored as grafted surface-active side-chains. Spray coating provides a realistic approach to apply these coating systems onto a ship's hull, and surface analysis using X-ray photo electron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS), and scanning force microscopy (SFM) has demonstrated that the elastomeric layer is fully covered by SABC. Biofouling tests are being performed in several marine labs, and samples have exhibited encouraging antifouling performance with regards to both soft and hard marine fouling. Promising coating compositions have been identified and further development is on-going.

Acknowledgement: This work is supported by SERDP WP-1454 with additional analytical support provided by the Office of Naval Research.

DEMONSTRATION/VALIDATION OF HIGH PERFORMANCE CORROSION PREVENTIVE COMPOUND (CPC) FOR INTERIOR AIRCRAFT APPLICATIONS

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The main goal of this ESTCP Project (WP-0615) is to demonstrate and validate a newly developed high performance, long lasting, corrosion preventive compound (Navguard) for internal airframe application to minimize the costs attributed to the aging aircraft. Navguard CPC was developed by NAVAIR through the Office of Naval Research-Future Naval Capabilities Total Ownership Cost (FNC-TOC) research project. The key benefits of using Navguard CPC are reducing the VOC emission by 50% or more, eliminating HAPs materials, and reducing the maintenance intervals for re-application of CPCs. Navguard CPC has been tested through Lead-The-Fleet demonstration on F-18, Oceana, VA, and EFV, Camp Pendleton, CA. The last field test inspection for Navguard on F-18, NAS Oceana, showed no sign of corrosion in the applied test area (24 months exposure). The second field test for Navguard was performed on the Expeditionary Fighting Vehicle (EFV) at USMC Camp Pendleton, CA, 24 months evaluation showed no sign of corrosion (Parker Seal Frame). The qualification testing for Navguard products (manufactured by Armick, Inc. and Corrosion Technologies) to MIL-PRF-81309F specification has been completed with exception of the storage stability testing.

Navguard CPC has been applied on multiple of platforms, such as H-46 (4), EA-6B (3), EFV (8), EH-60 (1), UH-1 (1), and F-18 (12) at several DoD (Army, Navy, and Marine Corps) organizational and FRC locations (Cherry Point, NC, and North Island, CA). For successful demonstration of the new technology, the demonstration periods will be at least two years and two-deployments for any carrier-based assets. Service evaluations will be used to document the results of the Navguard versus currently qualified CPCs. During the first two years, periodic inspections have been scheduled with Fleet Support Teams and FRC representatives. After successful demonstration, the new product will be recommended for aircraft maintenance manuals.

The outcome of this effort should be a significant contribution in the fight against corrosion. The application of this newly developed product is expected to increase fleet readiness and provide a significant cost savings to the end user.

ASSESSING THE PULMONARY TOXICITY OF SINGLE-WALLED CARBON NANOHORNS

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Previous studies have suggested that single-walled carbon nanotubes (SWCNTs) may pose a pulmonary hazard. We investigated the pulmonary toxicity of single-walled carbon nanohorns (SWCNHs), a relatively new carbon-based nanomaterial that is structurally similar to SWCNTs. Mice were exposed to 30 μg of surfactant-suspended SWCNHs or an equal volume of vehicle control by pharyngeal aspiration and sacrificed 24 hours or 7 days post-exposure. Total and differential cell counts and cytokine analysis of bronchoalveolar lavage fluid demonstrated a mild inflammatory response which was mitigated by day 7 post-exposure. Whole lung microarray analysis demonstrated that SWCNH-exposure did not lead to robust changes in gene expression. Finally, histological analysis showed no evidence of granuloma formation or fibrosis following SWCNH aspiration. These combined results suggest that SWCNH is a relatively innocuous nanomaterial when delivered to mice in vivo using aspiration as a delivery mechanism.

PERFORMANCE OF ZERO VOC, MULTIFUNCTIONAL UV (MUV) CURABLE CORROSION COATINGS ON METALLIC SUBSTRATES

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Multifunctional UV (MUV) curable corrosion coatings that contain no volatile organic compounds (VOCs), no chemicals on the toxic release inventory (TRI) list, and that do not release any hazardous air pollutants (HAPs) are being developed to replace existing coatings used on military weapon systems that contain VOC/TRI/HAP chemicals and use hexavalent chromium as the corrosion inhibitor. Previous efforts have demonstrated the feasibility of using UV curable coating systems with non-chromate corrosion inhibitors to protect high strength aluminum alloys against neutral salt spray corrosion out to 1,000 hours. The coatings also have good pencil hardness and adhesion strength on chromate (CrCC) or cerium conversion coated (CeCC) Al 2024-T3 substrates. Duplicate experiments have been conducted to verify the initial results. Follow on efforts also have used trivalent chromium passivation (TCP) and bare Al 2024-T3 panels with MUV coatings for comparison with CrCC and CeCC. Three different corrosion inhibitors were evaluated in MUV coatings and the results were compared to commercially available chrome and chrome-free coating systems. Results indicated that the performance of the MUV coatings was affected by the type of corrosion inhibitor more than any other factor. While two of the corrosion inhibitors were ineffective at preventing corrosion on MUV coated Al 2024-T3 substrates during ASTM B117 salt spray testing, one corrosion inhibitor was able to prevent corrosion on scribed Al 2024-T3 panels out to 3,000 hours of neutral salt spray testing. The best MUV coating was as good as or better than the chrome and chrome-free coated panels subjected to the same test conditions. In general, the performance of the MUV coating, with the effective corrosion inhibitor, was best on CrCC coated panels; but CeCC and TCP panels also performed well in certain cases. The non-conversion coated, bare Al -2024-T3 panels with a MUV coating showed significant blistering. Optimization of the performance of the MUV with the effective corrosion inhibitor is on-going.

This work was funded through SERDP Project WP-1519.

ROBOTIC LASER COATING REMOVAL SYSTEM

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Oklahoma City Air Logistics Center (OC-ALC), Headquarters Air Force Material Command (HQ AFMC/LGPE), and the Air Force Research Laboratory (AFRL) are currently leading the Robotic Laser Coating Removal System (RLCRS) program to demonstrate and validate a RLCRS, as an alternative technology, to the current chemical and mechanical methods that are used to remove coatings from large off-equipment aircraft components at Tinker Air Force Base, OK. This project will demonstrate the ability of this technology to meet the requirements for coatings removal in a production environment as well as the pollution reduction that can be achieved through its use across the Department of Defense (DoD). The RLCRS system will be designed to accommodate processing of large parts that are currently subjected to coatings removal operations once they are removed from the airframe. This project is funded by the Environmental Security Technology Certification Program (WP-0526) and HQ AFMC.

This technology has the potential to reduce the environmental burden associated with coatings removal operations while reducing the labor and chemical costs and positively impacting the production schedule. The implementation of the RLCRS also will provide the maintenance facility with the flexibility to remove coatings from components of various sizes and geometries using a single system.

Integration of the various components into the robotic system has been completed at Concurrent Technologies Corporation (CTC) Demonstration Factory in Johnstown, PA. So as to avoid interruptions to the depot production schedule, the system will be assembled, debugged, tested, and validated at these facilities prior to implementation at OC-ALC. Debugging of the control system, operational testing of all of the components, and system optimization testing has been completed. The optimization testing resulted in settings that allow the system to strip a 10 mil thick coating at a rate of greater than 1 ft²/min while keeping substrate temperatures below the 300°F temperature limitation. Following optimization, testing of the material compatibility testing of the effects of operation of the system on various substrates began. This material compatibility testing is being performed on aluminum and metallic honeycomb panels which are undergoing four coating/laser stripping cycles, in accordance with the approved Joint Test Protocol (JTP). Currently this testing is in the second stripping cycle.

PROGRESS REPORT: QUALIFICATION, DEMONSTRATION, & VALIDATION OF COMPLIANT REMOVERS FOR AIRCRAFT SEALANTS AND SPECIALTY COATINGS

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The Air Force, Navy, and commercial airline industry have funded numerous studies to identify and evaluate non-chemical, environmentally friendly technologies or processes for safely and efficiently removing degraded sealants and specialty coatings from the internal and external surfaces of aircraft structures. Technologies have included mechanical (i.e., pressurized water, bio-based and nano-engineered dry media blends, ultrasonic scrapers, and bristle brushes), light energy (i.e., handheld lasers and Flashjet), as well as various combinations of these processes. Advantages and disadvantages have been identified for each process; however, the underlying conclusion from these studies is that there is no one technology, method, or procedure that efficiently removes the various types of sealant or specialty coating materials without the risk of damaging the underlying substrates or surface sealants.

The subject ESTCP-funded project (WP-0621), led by the Air Force Research Laboratory, has focused on identifying, qualifying, demonstrating, and validating an environmentally friendly (contains no TRI chemicals, no HAP, or chlorinated compounds) substitute material or product for removing sealants, adhesives, and specialty coatings from aircraft structures. Candidate materials examined are Commercially-Off-The-Shelf (COTS), and being assessed on how effectively each material removes different sealants (e.g., polysulfide and polythioether) used by Air Force, Navy, and commercial aircraft maintenance, repair, and overhaul (MRO) facilities. Structural aerospace materials included in all process assessments and field demonstrations are 2024-T3 aluminum alloy and two types of composites.

To date, the project has completed baselining procedures performed at USAF and NAVAIR MRO facilities, downselected vendors for further screening, and an initiation of a controlled set of laboratory testing of these COTS materials on selected samples. The laboratory testing phase of this project is scheduled to conclude in mid-October, with field-level demonstration/validation testing to be performed in January of 2008.

The poster presented at this session will detail the results achieved thus far, and will also report on anticipated demonstration/validation activities.

LOW TEMPERATURE CURE POWDER COATINGS

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The Department of Defense (DoD) currently spends millions of dollars each year to procure, use, and dispose of toxic and hazardous materials associated with the use of solvent-borne organic paint coatings for corrosion protection. Powder coatings have the potential to eliminate a significant amount of the toxic and hazardous materials used in the aerospace industry during application of corrosion protection coatings. Powder coatings are a VOC/HAP-Free alternative to solvent-based paints and feature performance properties equal to or better than specification driven solvent-based coatings such as MIL-C-22750 (epoxy) and MIL-C-85285 (polyurethane). High temperature cure powder coatings meeting DoD performance requirements have been commercially available for many years and have been utilized extensively on DoD hardware such as tactical missiles. However, although numerous aircraft, weapon systems, and ground support equipment could benefit from corrosion resistant powder coatings, they are made from temperature-sensitive materials, such as low-tempered aluminum or composites, and simply cannot withstand traditional high temperature cure (300°F - 400°F) powder coatings. Over the last few years, lower temperature curing powders (less than 300°F) have become available having a 280°F maximum allowable cure temperature. One such low temperature powder coating, developed under SERDP (Project WP-1268) by GE Global Research and Crosslink Powder Coatings, targets the displacement of military paints conforming to MIL-C-85285 in non-critical military support applications. The objective of the ESTCP Low Temperature Powder Coatings project (WP-0614) has been to build on the work already accomplished by the previous SERDP Project and demonstrate, validate and successfully implement low temperature powder coatings on DoD production hardware in a depot production environment. The current demonstration is verifying the environmental and economic advantages of the proposed technology relative to the currently utilized technologies and is validating that the new technology is better in terms of cost, schedule, and performance when compared to the baseline solvent-based coatings. Laboratory coupon validation testing is completed, and target hardware is selected that will be coated with the ESTCP powder coating. These will be engine gearboxes, engine starter cases, and ground support equipment carts. Additionally, a Field Service Evaluation is being performed to evaluate how well the powder coating behaves on operational equipment in the field. The expected benefits of this project to the DoD are: Greener—no VOC's or HAP's, Safer—minimized worker exposure to hazardous materials, Less Expensive—powder coatings eliminate the disposal of solvents and hazardous wastes.

ENVIRONMENTALLY FRIENDLY INSPECTION THROUGH COATINGS

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This ESTCP Pollution Prevention project (WP-0407) addresses the reduction of hazardous chemical/waste by employing non-destructive techniques to inspect aircraft interior and exterior structures through coating, thus reducing the amount of stripping and repainting that occurs at military rework facilities. It is anticipated that hazardous pollutants will be significantly reduced by eliminating scheduled organic coating removal and moving to a process where IR inspection results will be used to determine when and if coating removal is required.

The technology exploits an optically transparent spectral window in military paint systems within the Mid-IR spectrum and also the difference in infrared (IR) reflection properties between corroded and non-corroded metallic surfaces. The IR energy passes directly through the coating and then reflects off the metallic substrate back through the coating and into an IR camera. Since the corroded areas do not reflect the IR energy as well as the non-corroded areas, a picture or image is generated by the IR camera much the same as observing the corrosion under standard visual techniques.

The demonstration and validation measurements at NAVAIR Jacksonville and Oklahoma City Air Logistics Center on P-3, B-52, and KC-135 aircraft illustrate clearly that the IR imaging is an improved method of corrosion inspection compared to the visual inspection method. IR imaging will give engineering and corrosion control personnel the capability to make sound decisions regarding coating removal based upon improved detection of corrosion through coatings. A level of 70-80% accuracy was achieved with this technique as compared to the 5-25% accuracy of the visual inspection method.

The cost and environmental benefit criteria for pollution prevention was projected and applied based on actual usage data of materials plus projected waste savings scenarios from the demonstration and validation measurements at NAVAIR Jacksonville and Oklahoma City Air Logistics Center. The study, based upon a medium sized aircraft (6,500 square feet surface area), confirms a potential environmental savings of 300,000 pounds of Volatile Organic Compounds, 2,500 pounds of Chromates, and 1,100,00 pounds of Hazardous Materials can be saved for a fleet of 100 aircraft over a four year period. Additionally, labor and material savings of \$135,000 per aircraft can be realized. Technology deployment across DoD platforms and weapon systems can result in an estimated 15 year savings of 2M pounds VOC, 7M pounds Hazmat, 20K pounds Chromate and a \$115M cost avoidance.

UV CURABLE NON-CHROME PRIMER AND ADVANCED TOPCOAT SYSTEM

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Foster-Miller (FMI), Deft, Inc. and Northrop Grumman (NGC) are working to develop an environmentally benign surface pretreatment, primer, and topcoat system for aircraft applications. FMI has a patented chemistry for single-component coating formulations that contain no VOC, HAP, or TRI constituents and cures rapidly by chemical reaction on exposure to UV irradiation. FMI is using this coating chemistry in conjunction with Deft's proprietary corrosion inhibiting pigments to develop high-performance materials that will ultimately comprise a corrosion inhibiting coating system that doesn't contain VOCs, HAP, or SARA 313-reportable chemicals. Specifically, we are developing sprayable, UV-curable corrosion-inhibiting primers and high-performance topcoats that will provide superior protection to aluminum substrates even when non-chromated surface pretreatments are employed. Further, a one-coat formulation will be developed in an attempt to combine the corrosion inhibiting properties of the primer and superior durability of the topcoat into a single, high-performance coating. Work done to date and results obtained will be presented.

This work is funded by SERDP through Project WP-1520.

LIGHTWEIGHT AND COMPOSTABLE FIBERBOARD FOR THE ARMY

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The U.S. Military consumes approximately 46.6 million operational rations each year generating over 14,000 tons of packaging waste. Due to the operational requirements for combat rations (i.e., air-droppable, minimum three year shelf life at 80°F, six months at 100°F for MREs), the rations must be packaged appropriately to meet these requirements. Shipping containers fabricated from fiberboard are necessary to safely transport and store food and other military items to all the Services. However, there are numerous disadvantages in the process used to produce paper and fiberboard: the process is costly, uses hazardous chemicals, depletes natural resources in our environment, and creates hazardous waste.

A SERDP project (SI-1479) “Lightweight and Compostable Packaging for the Military” is funded for FY06-FY09 to develop new environmentally friendly, lightweight biodegradable fiberboard that can be converted to a valuable byproduct, compost.

In particular, some of the research focuses on producing a medium density fiberboard (MDF) using soybean protein-based adhesive to replace the existing MRE fiberboard. The soy protein adhesive was developed using modified soybean flour. Commercial wood fibers were mixed with 15% soy protein solution, and then were processed into fiberboard using a hot-press. This fiberboard had a medium density at about 0.73 g/cm² in comparison to the military fiberboard (V2S) density of 0.81 g/cm². The biodegradable MDF had stronger internal bond, modulus of rupture, and modulus of elasticity in comparison to V2S. The MDF had significantly lower linear and thickness expansion, and higher wet strength than those of current V2S board.

Simultaneously, corrugated fiberboard coated with a biodegradable material is also being investigated as an alternative. Compression tests of the boxes show that it is comparable to the existing military solid fiberboard boxes. In addition, compost studies demonstrate that these fiberboard samples and their components are readily biodegradable. This research suggests that the biodegradable fiberboard has great potential as alternative secondary packaging for the military.

PHA BIOPLASTIC PACKAGING MATERIALS

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Plastic packaging materials represent a significant portion of the world plastics consumption, estimated in excess of 300 billion lbs in 2004. In North America alone, consumption of plastic shrink/stretch film is estimated to be over 1.5 billion lbs/year by 2006, and foamed product consumption is estimated at 8.5 billion lbs/year by 2006. While these packaging materials are low-cost and effective, the logistics of managing packaging waste is becoming increasingly problematic and costly. Military operations in remote areas and/or foreign countries face serious logistic hurdles dealing with large volumes of packaging waste.

The objective of this project is to demonstrate the applicability of biodegradable PHA Natural Plastics for foamed packaging and stretch/shrink film applications. PHA packaging foams and stretch/shrink films that match form and function of existing packaging materials will be produced and tested for functional performance and biodegradability. In order to produce PHA film and foamed packaging products, Metabolix will develop PHA formulations with the proper physical and rheological properties. For packaging foam products, a balance between elastic and viscous polymer melt properties will be obtained to achieve low density and acceptable foam cell structure. Rheological properties will be optimized for cell formation, the key aspect in foaming. For pallet wrap products, which are typically stretch or shrink film, a suitable PHA formulation will be developed that has the proper mix of tensile and tear strength, puncture resistance, and stretch-ability to match performance of existing polyolefin stretch films.

PHA Natural Plastics are produced by Metabolix from renewable agricultural resources. Because they are biodegradable in marine and soil environments, products made with PHAs can be disposed of easily and without any adverse environmental impacts. Non-hazardous solid packaging materials are used by DoD personnel in virtually all aspects of operations. Using PHA Natural Plastics packaging materials instead of conventional petrochemical plastic packaging materials will dramatically reduce solid waste management problems such as transport and disposal. PHA Natural Plastics are ideally suited for use in packaging application due to the range of physical properties attainable, water resistance, heat resistance, strength, and barrier properties. Other biodegradable materials, particularly starch-based materials, do not have the required water resistance, temperature resistance, or range of properties needed for film and foam packaging applications. PHAs biodegrade benignly to CO₂ and water with no residual toxic byproducts, allowing DoD forces to minimize the environmental impact of their presence. Metabolix is currently receiving SERDP funds for this effort (SI-1478).

SEQUESTERING LEAD IN PAINT BY UTILIZING DECONSTRUCTED MASONRY MATERIALS AS RECYCLED AGGREGATE IN CONCRETE

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A systematic study has been conducted to establish a rational mix design method for proportioning concrete utilizing recycled lead-contaminated aggregate for field construction. Different types of masonry materials (concrete blocks and clay bricks) were painted and crushed to simulate lead-based paint (LBP)-contaminated masonry materials. Physical properties of the masonry materials were measured as well as total and leachable lead. Two different kinds of cement, ordinary portland cement and phosphate cement, were selected for sequestering LBP in recycled aggregate. A concrete mix design matrix was developed to have three water-to-cement ratios, three aggregate-to-cement ratios, two types of cements, and four types of masonry materials. Concretes with different aggregate-to-cement ratios (3, 4.5, and 6) and different workability levels (slump of 1"-2", 3"-4", and 6"-7") were included in the mix design nomograph development. Workability and compressive strength at different ages were measured for various concrete mixes. The toxicity characteristic leaching procedure (TCLP) test, California Waste Extraction Test (WET), and total lead test were used to determine the leachability of lead from the different concrete mixes. Results showed that concretes with recycled aggregate have relatively lower compressive strength compared with concretes with natural aggregate. The compressive strength varied for different cement and masonry material types and content. The results showed that, in nearly all of the mixes, TCLP lead was less than 5 mg/L, which means that they are not hazardous wastes according to the Resource Conservation and Recovery Act (RCRA). Portland cement, was found to be able to effectively sequester LBP in the recycled aggregate because of the high alkalinity. The developed mix design nomograph can be used to ensure the proper selection of mix proportions that meet workability and strength requirements for concrete construction and to abate the lead hazard in recycled aggregates. Successful research results can significantly reduce the cost and environmental impact of DoD construction and deconstruction projects.

SERDP Project Number SI-1548

DETERMINING ENVIRONMENTAL SOLUBILITY OF PB FROM RECYCLED CONCRETE AGGREGATE

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The military has many concrete buildings constructed from the 1950s through the 1970s which are being replaced with contemporary complexes. This contributes greatly to, and can be the majority of, an installation's solid waste generation.

The past few years have seen a growing trend to reduce C&D waste by reusing or recycling of the materials available in excess buildings. Large Army installations have a continuous need for aggregate. The presence of LBP, however, presents regulatory uncertainty to the reuse for some of these building materials. This material is not a "waste," therefore RCRA definitions and numerical limits do not apply.

This study attempts to model real world applications of recycled concrete aggregate (RCA) with some Pb content. RCA was obtained from Fort Jackson, SC, derived from a building of known dimensions and paint history. Extraction experiments were set up to model Pb dissolution from common RCA reuse profiles.

It is hoped this work will remove some of the uncertainty of reusing RCA with LBP, and help to dramatically increase on-post use of RCA.

SERDP Project Number SI-1549

DEVELOPMENT OF ENVIRONMENTALLY BENIGN AND REDUCED CORROSION RUNWAY DEICING FLUID

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Due to the toxicity and high biological oxygen (BOD) and chemical oxygen demand (COD) of urea, the DoD and commercial airports have switched to organic salts, such as, potassium acetate, sodium or potassium formate, or propylene glycol (PG) runway deicers, and anti-icers. The acetate and formate deicers have a much lower BOD than PG and are significantly cheaper, but are unacceptably corrosive to runway and aircraft components. PG deicers are more slippery than desirable. In recent SAE G-12 Subcommittee meetings, there has been serious concern expressed about the more commonly used potassium acetate and formate deicers because of the corrosion of very expensive carbon-carbon brake pads as well as landing gear components containing cadmium. These concerns are likely to lead to the use of larger quantities of toxic corrosion-inhibitors and/or the use of less corrosive but high-BOD alternatives. Therefore, both the environmental and material compatibility concerns are currently threatening the runway maintenance and aircraft availability for both DoD and commercial sectors.

The objective of SERDP Project SI-1535 is to develop and evaluate novel chemistry to formulate Runway deicing fluids (RDFs) from bio-based raw materials. These new RDFs are expected to exhibit improved environmental and anti-corrosion properties with deicing performance being comparable to currently-available RDFs. The project activities include RDF preparation, conventional and specialized performance testing, and a cost-benefit analysis.

During the first year of this project, three new RDF formulations have been prepared. Two of the formulations have been fully certified under AMS 1435A. The results of this testing, as well as carbon-carbon brake pad oxidation testing, are very encouraging.

APPLICATION OF A BIMETALLIC SOLVENT PASTE TECHNOLOGY FOR PCB REMOVAL FROM OLDER STRUCTURES ON DOD FACILITIES

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Researchers from the Naval Facility Engineering Service Center (NFESC), NASA-Kennedy Space Center (NASA), University of Central Florida (UCF), and Geosyntec are working on an ESTCP-funded technology demonstration project (SI-0610) to demonstrate the efficacy of a Bimetallic Treatment System (BTS) to remove and rapidly degrade polychlorinated biphenyls (PCB) found in structural coatings.

The BTS technology, which consists of elemental magnesium coated with a small amount of palladium in a solvent solution capable of hydrogen donation, has two functions: (1) to extract PCBs from weathered, decades-old coating material such as paint, and (2) to rapidly degrade the extracted PCBs. Prior to 1979, PCBs were extensively used in industrial paints, caulking material and adhesives. Researchers from NASA and UCF previously demonstrated rapid and complete dechlorination of PCBs in aqueous/solvent systems containing Aroclors 1254, 1260, and 1268 (specific PCB mixtures). Significant, if not complete, PCB extraction and degradation from paint chips with total PCBs as high as 11,000 ppm has been achieved with as little as 48 hours of exposure. The solvent in BTS is used to open, but not destroy the polymeric lattice structure of the paint, allowing pathways for PCB movement out of the paint and into the solvent. Because of the wide variety of structural properties associated with each specific PCB-laden coating, the choice of solvents incorporated into BTS is specific to the material being treated. Additional BTS formulation properties that must be addressed for each site-specific application include viscosity and stability.

This paper will address the pre-demonstration laboratory testing conducted at all three of the demonstration sites and the field testing conducted at the first of the demonstration sites, the Vertical Integration Building (VIB), Cape Canaveral, Florida. Pre-demonstration laboratory testing was conducted to evaluate the concentrations of PCBs in the various materials tested at each facility, including paint, adhesives, caulking, and rubber gaskets material, and to determine which BTS formulation would work best for each material. The demonstration goal was to reach PCB concentrations below the Toxic Substances Control Act limit of 50 parts per million (ppm) in the paint on all structures tested. Details of the results from the field demonstration at the VIB will be presented.

DEMONSTRATION OF NOFOAM SYSTEM TECHNOLOGY FOR AIRCRAFT HANGAR AND FUEL FARM FIRE SUPPRESSION FOAM SYSTEM

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Serious environmental concerns have arisen from aircraft hangar fire suppression foam system discharge tests. These concerns stem from hundreds of thousands of gallons of aqueous film forming foam (AFFF) wastewater that is generated during testing. As a result of these environmental concerns, foam discharge checks are not being performed and has a negative impact on the facility mission readiness. As a result, the Navy has developed a real time evaluation NoFoam System that tests the aircraft hangar fire suppression system without releasing AFFF to the environment. This technology allows the activity to test the fire suppression system

The Naval Facilities Engineering Service Center (NFESC) is demonstrating and validating the NoFoam System for aircraft hangar fire suppression foam systems. This is being done under the sponsorship of the Environmental Security Technology Certification Program (ESTCP) and Naval Facilities Engineering Command (NAVFAC), project number SI-0525. The NoFoam System hardware is installed on a mobile platform and uses an environmental benign dye-water or water, providing a valid foam discharge array test that eliminates AFFF release. The technology provides real-time online measurements of discharge rates and requires no specially trained personnel to interpret the resulting data. Validations will be conducted at Arizona Air National Guard, Arizona (Tucson); Tyndall Air Force Base, Florida; Fort Belvoir, Virginia; Naval Air Station Lemoore, California; and Marine Corps Base, Hawaii (Kaneohe).

DoD cost savings will be accrued from eliminating AFFF wastewater collection and disposal and replenishment of spent AFFF concentrates during annual and maintenance discharge checks. DoD mission readiness will not be jeopardized.

MEASUREMENT OF PARTICULATE MATTER EMISSION FACTORS FROM ROTARY WING AIRCRAFT OPERATIONS

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Rotary wing aircraft training operations are one of the military's major unique fugitive particulate matter (PM) sources. We developed a monitoring protocol to measure PM emission factors from rotary wing aircraft operations and conducted a field campaign at Yuma Proving Grounds (YPG) in May 2007. We evaluated PM emissions at six different rotary wing aircraft speeds and at two different YPG helicopter test sites. One of the test sites had a desert pavement surface and the other a heavily disturbed desert soil surface. We combined several Optical Remote Sensing (ORS) instruments into an ORS measurement system for characterizing fugitive PM plumes. The ORS instruments included a Micro Pulse Lidar, two Fourier Transform InfraRed spectrometers, and two Laser Transmissometers. We used the ORS measurement system to construct time dependent two-dimensional size-specific mass concentration profiles of each fugitive PM plume. The PM mass concentration profiles from the plumes were then integrated with concurrent wind data to generate PM mass fluxes and PM mass emission factors. In this poster, we'll discuss the new ORS measurement protocol for developing rotary wing aircraft emission factors, analyze the relationship between emission factors and operational conditions (e.g., aircraft speed, surface conditions), and assess the impact of rotary wing aircraft in terms of national fugitive PM generation. We'll compare the results from the ORS measurement system with those from conventional in-situ measurements provided by the Desert Research Institute (DRI) from work on SERDP Project SI-1399. We will also compare rotary wing aircraft emission results with those from artillery back blasts and tracked vehicles.

This is an active SERDP project (SI-1400).

PARTICULATE MATTER EMISSIONS FOR DUST FROM UNIQUE MILITARY ACTIVITIES: ROTARY-WINGED AIRCRAFT

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Dust emissions are created by activities often unique to the testing and training activities of the DoD. As part of SERDP Project SI-1399, emissions of dust raised by rotary-winged aircraft activities were measured at the Yuma Proving Ground (YPG), Yuma, AZ, in May 2007. Dust emissions measurements, from which emission factors can be developed, were carried out with a three-tower system and in conjunction with optical remote sensing measurements made by SERDP Project SI-1400. Each of the towers is equipped with instruments to measure the vertical concentration of dust in the emitted plumes at 1 Hz. One of the three towers is also instrumented with cup anemometers to measure the vertical wind speed profile and a wind vane to measure wind direction. The meteorological measurements are combined with the dust concentration measurements to estimate the unit flux of dust emissions for each activity. The use of three towers allows better characterization of the emitted dust plumes in the vertical and horizontal planes and better estimation of emission fluxes than single point measurements. The strength of the rotor downwash and the shear stress created by the downwash, as it travels laterally across the surface, were measured with a sonic anemometer and Irwin sensors. Measurements of the emission potential of the surface and the threshold shear stress, at which dust is entrained, were also made using the DRI PI-SWERL instrument. The suspended dust was collected using filter samplers to develop representative samples of its chemical and mineralogical composition for this area.

The dust emissions were created by a UH-1H Huey traveling above two different desert surface types over a range of speeds with the rotor blade at the same height above the surface (8 m) for each test. In addition, dust emissions were measured for several landing and takeoff sequences as well as hovering maneuvers. The strength of the emission was observed to scale negatively with aircraft forward speed. This occurs for two reasons: (1) as the forward speed is increased, more thrust is directed to the rear of the aircraft due to change in blade pitch, and (2) as aircraft speed increases, the residence time per unit of travel distance is decreased. The dust emission measurements for the UH-1H aircraft and estimated emission factors for the activities tested will be included as part of this poster presentation.

A NEW-TECHNOLOGY PERSONAL AEROSOL EXPOSURE ASSESSMENT METHODOLOGY FOR DEPLOYED TROOPS

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A new technology personal aerosol exposure platform (the RTI MicroPEM) has been developed to facilitate very low burden assessments for difficult cohorts such as active duty troops in deployment settings. The design provides robust aerosol collection performance in a tiny package that provides wearing transparency (minimal impact on mission). The system provides PM_{2.5} or PM₁₀ collections (a dual channel version is also being built) in a package weighing less than 200 g and can also be deployed at fixed-location indoor, mobile, and outdoor locations. Aerosol filter collections match EPA referee methods. A separate polycarbonate filter can be used to provide morphological information by SEM/TEM. On-board, programmable electronics control the sampling and collect operational QC data to readily allow validation of the filter samples. The system includes a (patented) built-in activity sensor to assess both wearing compliance (% of time worn according to protocol) and estimated physical activity level. Multi-wavelength, non-destructive absorbance measurements of the sized and deposited aerosol indicate the level of confounding by environmental tobacco smoke and black carbon. The miniature aerosol collection assembly containing the inlet, impactors, and filters weighs only 25 g and can be pre-loaded to eliminate potential in-field contamination. High precision gravimetric analyses in clean-room settings (state-side) allows low-flowrate (0.5l pm) collections to be used onto Teflon filter substrates that can also be analyzed for standard PM elemental/ion analytical suites, plus endotoxin, if desired. Data will be presented on the system performance and plans discussed to test the system in-theater.

PREDICTIVE MODELING OF MARINE MAMMAL DENSITY FROM EXISTING SURVEY DATA AND MODEL VALIDATION USING UPCOMING SURVEYS

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The Navy and other users of the marine environment must be able to estimate cetacean density within their operational areas in order to comply with regulatory requirements. The goal of our SERDP-funded research (SI-1391) is to develop methods to predict cetacean densities within any arbitrarily defined region in the eastern Pacific Ocean using habitat variables. This poster highlights cetacean-habitat models that we have developed for the California Current Ecosystem (CCE) using in situ and remotely sensed oceanographic data.

In situ oceanographic data were used to assess the effect of spatial resolution on cetacean-habitat relationships in the CCE. In a previous study, we explored the effect of spatial resolution on cetacean-habitat relationships in the eastern tropical Pacific Ocean (ETP) using oceanographic habitat variables. Resolution did not affect the functional form of habitat relationships and interannual habitat variability had a greater impact on the predictive power of the habitat models than resolution. We expanded our analyses to the CCE because oceanography varies on smaller spatial scales in the CCE than the ETP. Specifically, we developed generalized additive models of cetacean-habitat relationships for six species at resolutions ranging from 2 to 120 km using four years of summer shipboard survey data. The results suggest that species-habitat responses in the CCE are resolution-specific, but that small-scale patches could not be identified using the available in situ oceanographic data.

We also compared the predictive performance of cetacean-habitat models built on a common cetacean sighting dataset collected during four years of shipboard surveys in the CCE and either remotely sensed or in situ oceanographic data. We examined the predictive power of six different spatial resolutions of satellite data. We developed generalized linear and generalized additive models to predict cetacean encounter rate, group size, and density based on static and dynamic environmental variables. The remotely sensed and in situ models with the greatest predictive ability were selected and compared to observed density estimates for ten species. Satellite-derived estimates of sea surface temperature variance were found to be the most effective at characterizing frontal activity due to their ability to measure heterogeneity in two dimensions. For species with sufficient sample sizes for modeling, predictions developed using broad-scale satellite data were comparable to those developed with analogous in situ data.

PREDICTIVE HABITAT AND DENSITY MODELING OF MARINE MAMMALS FOR NAVAL ENVIRONMENTAL COMPLIANCE

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Our ability to inform conservation and management of species is fundamentally limited by the availability of relevant biogeographic data, use of statistically robust predictive models, and presentation of results to decision makers. In order for the U.S. Navy to environmentally manage interactions with marine mammal species, we are incorporating dedicated surveys from the OBIS-SEAMAP archive (<http://seamap.env.duke.edu>) to develop predictive habitat models and deliver the results with a flexible spatial decision support system (SDSS). The SDSS, a browser-based interactive map server, enables viewing of original survey effort, marine mammal observations, oceanographic imagery, and model results. A suite of multivariate statistical models (CART, GLM, GAM, and Bayesian approaches) have been fitted to observations from at-sea surveys (boat and plane) with remotely-sensed environmental data (bathymetry, sea-surface temperature, and chlorophyll), as well as derived variables such as slope, temperature fronts, and chlorophyll aggregations. Environmental data from the JPL physical oceanographic data archive (PO.DAAC), of past remotely-sensed satellite imagery, is used to fit the model, while the oceanographic forecast data from the HYbrid Coordinate Ocean Model (HYCOM) is then applied to the model for future prediction. Model results yield predictive maps for the likelihood of encounter as well as the associated standard error. Given the uncertainty of these estimates, a loss function can be applied to different decision sets for determining the minimal-loss decision to take for a given area. Regions of interest can further be delineated within the SDSS for extracting summary statistical outputs, such as histograms.

SERDP Project SI-1390

APPLICATION OF ROV-BASED VIDEO TECHNOLOGY TO COMPLEMENT CORAL REEF RESOURCE MAPPING AND MONITORING

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Comprehensive assessment of reef condition is fundamental to DoD marine operations in tropical areas. Successful and legally defensible assessments of reef damage or documentation, of declines in reef vitality associated with DoD operations, require reef monitoring techniques that are simple, accurate, repeatable, and appropriate to the scale of the damage.

The aim of SERDP Project SI-1333 is to develop and evaluate an innovative technology, 2-D mosaics created from underwater video, to provide DoD with improved reef monitoring capability. Specific goals include the construction of plot-scale georeferenced images of habitat patches on a coral reef and the evaluation of these mosaics for extracting ecological indicators of reef health.

2-D mosaic technology presents significant advances in state-of-the-art capabilities for reef mapping and monitoring. Specific accomplishments have been to address limitations of former monitoring techniques while retaining strengths of traditional diver surveys. The most significant advances result from the fact that large areas can now be imaged at high spatial resolution resulting in spatially accurate, landscape views of the bottom that were previously unobtainable. These landscape mosaics will be useful for DoD reef monitoring requirements and open doors for new applications in reef mapping and change detection. We have demonstrated that 2-D mosaics are ideal tools for documenting damage and recovery patterns on reef habitats impacted by ship groundings and hurricanes. The ability to create spatially accurate landscape views of impacted reef communities provides scientists and resource managers with novel, powerful survey tools.

The mosaicing algorithm used in the project requires surveys to be conducted at an altitude above the seafloor that is significantly greater than the relief of the survey area. This requirement has led to two limitations: (1) the mosaicing algorithm does not function well in reefs with high topographic relief, and (2) taxonomic identification is limited to biota >10 cm in diameter. Solutions are currently being pursued to modify the existing imaging hardware and software. These improvements include addition of a self-contained heading sensor to reduce registration drift in high relief areas, and pairing the video camera with a high resolution still camera to improve spatial resolution for better taxonomic identification.

STUDYING RESPONSES OF BEAKED AND OTHER WHALES TO SONAR AND OTHER SOUNDS

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Some unusual mass strandings of several species of beaked whales have coincided with naval sonar exercises. In only two of these cases is it known when and where specific sonar signals were transmitted, and in these cases, it is not known where the whales were before the response that led to stranding. The other strandings coincided with naval exercises involving warships outfitted with mid-frequency active (MFA) sonars, but it has not been reported when and where specific sonar signals were transmitted. During the past seven years, with funding from SERDP Projects SI-1188 and SI-1539, we have tagged beaked whales of the species most involved in sonar-related strandings. We have defined their dive behavior and their echolocation clicks, which are used regularly during deep dives to find and select food. Data on the acoustic structure of these clicks were used by the Naval Underwater Systems Center (NUWC) marine mammal monitoring on Navy ranges (M3R) program to develop a detector for beaked whale clicks. When this detector was implemented on a system designed to monitor the Atlantic Undersea Test and Evaluation Center (AUTEK) range in real time, beaked whale clicks were regularly detected on the range, and the identification of the source as beaked whales was validated by visual observations. One Blainville's beaked whale (*Mesoplodon densirostris*) has been tagged on the AUTEK range while sounds from the hydrophone array was recorded. Clicks from the tagged whale were detected on the AUTEK array. These data are being used to measure the efficacy of the current M3R beaked whale detector and to validate and develop statistical density estimation methods, along with estimation of the 3-D beam pattern of the tagged whale. Here we report results from a study designed to use tags and acoustic monitoring on the AUTEK range to evaluate the responses of beaked and other whales to sounds of MFA sonars compared to several control stimuli. This experiment is the beginning of a research program designed to resolve several problems. By defining how beaked whales respond to sonar, we hope to decide which hypothesis about the cause of MFA sonar-related strandings is correct. By studying the exposure at which different whales start responding to these sounds, we hope to build a dose-response function to relate acoustic exposure and behavioral response. This research is designed to provide new science-based approaches for mitigating the risk of sonar to beaked and other whales.

MAINTAINING REAL-TIME CALIBRATION OF DETECTION DOG TEAMS DURING FIELD DEPLOYMENT GIVEN UNCERTAINTY IN TARGET LOCATION

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The objective of the spring 2007 research was to assess and refine dog training protocols developed for small desert tortoises under the ESTCP-funded (SI-0609) DTK9 Program in 2006. The activities were held at the Desert Tortoise Conservation Center (DTCC) near Las Vegas, NV, April 18 – May 3, 2007. The targets were small tortoises <100 mm in length (68 mm mean midline carapace length). A new concept for deploying working dogs under conditions of uncertainty in target location was developed, tested, and validated. This operational concept is termed ‘Read and Go’ and is a means for handlers to maintain calibration of their team given that they cannot reward their dog for finds that are not immediately validated by the handler. Most of the time, dog alerts will not be able to be validated immediately because small tortoises are extremely difficult to see and tend to occur in very small burrows. Read and Go involves three levels of reward to the dog based on dog behavior and target verification. It is implemented on the fly during deployment. Once the handlers understood and were comfortable executing Read and Go, assessment trials started. The objectives were to (1) evaluate degradation in alert behavior over time when dogs are given varying levels of reward for finding tortoises, and (2) evaluate degradation in handlers over time executing Read and Go. Handlers worked two different search areas each day. In the first area, the number and size classes of tortoises was unknown. The second area contained only transmittered small tortoises that were verified after the handlers completed their search. The dogs continued to alert on unknown and unverified targets over five days of trials given inconsistent reward levels for correct indications. The handlers also were able to correctly interpret their dog’s change in behavior over this time period. Although the ratio of independent alerts to change in behavior varied over time, the dogs’ performance, in terms of locating tortoises, did not significantly degrade over five days of trials. The results of this study indicate that operating under Read and Go is a viable means of maintaining calibration of detection dog teams during operational deployments when targets cannot be immediately verified and thus dogs do not receive full reward. The implications of this work extend to other military and law enforcement working dog disciplines such as accelerant, explosives, and human remains detection.

IDENTIFICATION AND INVESTIGATION OF MIGRATORY BIRD STOPOVER HOTSPOT HABITATS ON U.S. MILITARY INSTALLATIONS

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Mmilitary lands in the United States provide some of the highest quality habitats available for a wide diversity of bird species. Although significant emphasis has been placed on the conservation and management of breeding and wintering bird habitat on military installations, relatively little attention has been paid to stopover habitats used by migratory birds during spring and fall migration. Even less is known about the locations and extent of important stopover sites (i.e., hotspots), or areas where birds concentrate heavily to rest during migration. By identifying where, when, how long, and in what concentrations migratory birds inhabit temporary stopover sites, installations will be able to improve both flight safety and species conservation. The objectives of this three-year effort, which is being funded by SERDP (SI-1439), are to (1) use radar data to identify military installations that have important migratory bird hotspot habitats; (2) document the pattern of bird migration at these installations; (3) conduct intensive ground surveys to investigate these hotspots; (4) investigate habitat use by individual radio-collared landbirds; and (5) develop forecast models of bird migration at and around selected installations. The U.S. Army Engineer Research & Development Center, Environmental Laboratory; Clemson University Radar Ornithology Laboratory; and University of Southern Mississippi Department of Biological Resources have collaborated to (1) develop maps that show the relationship of selected military bases to important stopover areas across the country; (2) delineate hotspot stopover sites via intensive on-the-ground investigations of radar-identified concentrations of migrant birds; (3) provide information on the stopover ecology of migrants within these habitats; (4) correlate radar data with ground census information; and (5) develop spring and fall migration forecast models that will allow managers to predict when dense migrations of birds are likely to occur, and assist in improving planning for flight training, and ultimately, flight safety. This work is also assisting natural resource managers in the management and conservation of military lands for migratory birds.

PREDICTING THE ABUNDANCE OF DESERT BIRDS USING LANDSAT TM/ETM+ IMAGERY

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In order to efficiently monitor biodiversity within vast landscapes, methods using remotely sensed data to identify areas of high species richness and abundance are necessary. In this project, we constructed models of abundance of birds from remotely sensed correlates of habitat elements thought to be important to breeding birds in the northern Chihuahuan Desert. We developed models using three types of predictive variables: (1) NDVI, a measure of vegetation productivity, and (2) landscape indices based on vegetation life form (i.e., tree, shrub, or grass), and elevation. Landsat TM/ETM+ imagery was the source of the vegetation data. Preliminary results indicate that for some species (e.g., Black-tailed Gnatcatcher, Eastern Meadowlark, and Crissal Thrasher) the ability to predict variation in abundance was consistent among three years examined, and the variables included in models were also consistent among years. For other species, the variables that best predicted abundance varied among years, suggesting that the environmental conditions in a given year exert a strong influence on their distribution and abundance. This project, SI-1438, is funded within SERDP's Sustainable Infrastructure program.

AUTOMATED MONITORING AND ASSESSMENT OF BAT AND BIRD POPULATIONS

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All public land jurisdictions must monitor and manage sensitive species. For many species, this work accrues high costs because of the requisite specialized skills for the monitoring personnel. In addition, sensitive species are typically rare and require greater survey effort (thus higher cost) to acquire reliable data compared to more common species, particularly over the extensive landscapes of U.S. military installations. For species that emit acoustic signals, automated monitoring can provide a cost-effective solution to more confidently assess activity and confirm presence or absence of sensitive species, provide consistency by eliminating variability in the skill level of monitoring personnel, and operate continuously to better detect rare species that intermittent survey efforts may miss. Automated acoustic monitoring entails (1) autonomous field recording hardware, (2) software to automate signal detection and extraction of defining signal parameters, (3) a comprehensive library of reference recordings from target and sympatric species to cover their range of signals under various conditions, and (4) software to automate species identification based on the reference data. Our SERDP supported (SI-1394) team has completed these tasks to develop and deploy a functioning automated monitoring system. Much of our effort in developing the automated processing and identification system addressed the need for generating robust algorithms immune to the distorting effects of ambient noise and echoes. Acquiring a representative reference library for free-flying bats presented a considerable challenge because (1) many sympatric species emit echolocation calls overlapping in many acoustic characteristics, (2) bats exhibit considerable plasticity in their calls, and (3) unlike birds that can be identified at a distance while recording, most bats require capture to determine species. For most bats, acquiring representative free-flight echolocation calls entailed capturing the bat and light-tagging it to track and record it in free-flight; a necessary, but painstaking, method with low return. However, our field crews acquired in excess of 10,000 species-confirmed recording files from locations in 23 states, covering 34 species. Using this data, we have generated nine identification modules for all eastern bat species, and have modules under development for western bats. These modules divide species into regional and species acoustic clades to optimize utility and performance. The correct classification of these clades, depending upon algorithm approach, ranges from 73 to 100%, with the majority performing in excess of 90%. We anticipate improving overall performance with the addition of the 2007 field data and further refinement of the parameter extraction and identification algorithms.

NEW TOOLS FOR PRIORITIZING MANAGEMENT ACTIONS FOR SPECIES OF CONCERN ON DEPARTMENT OF DEFENSE LANDS

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Management of sensitive species on DoD installations is often complicated by incomplete information on the parameters necessary to properly assess population trends and by the lack of a framework to prioritize recovery actions. We report here, on three related projects, in which we address these problems. First, we are developing a technique to prioritize management actions when data are sparse. Using meta-analytic techniques, on data culled from a wide range of published and unpublished studies, we determined how key population attributes such as survival or reproduction respond to specific anthropogenic disturbance and/or management actions (e.g., grazing, removal of exotic predators), and whether these responses were consistent across taxa. For example, preliminary results suggest that for birds, removal of exotic predators has, on average, a much greater effect on reproductive rates than either cessation of grazing or implementing controlled burns. Furthermore, the extent to which certain management actions, such as the removal of exotic predators, boosts reproductive rates in birds can be predicted by life history attributes related to age at first reproduction. These early results suggest that when confronted with sparse data, land managers may be able to generalize from similar well-studied species about which types of management actions may best boost population growth for a species of concern. Our second related research topic explores the extent to which population viability models can be used to assess the impact of training/management activities on better-studied species. This includes identifying what types of empirical data are critical for estimating species viability and determining what level of model complexity is needed in order to determine the effect of site-specific management scenarios on overall species viability. Finally, we have analyzed methods for estimating simple population trends through time based on trajectories of count data, and have determined that one of these, the diffusion approximation method, is easy to implement and yet will accurately estimate population trends even when up to half of the counts in the trajectory are missing. This project (SI-1477) is funded by SERDP.

AN ECOINFORMATIC APPROACH TO DEVELOPING RECOVERY GOALS AND OBJECTIVES

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A lack of data hinders managers' abilities to set scientifically defensible recovery goals and criteria for all but a few species. The overall objective of our SERDP-funded project (SI-1475) is to develop methods that will help quantify scientifically defensible recovery goals for federally listed species on DoD-managed lands via sophisticated comparison of endangered species with a diverse set of well-studied species. We will build explicit links between established recovery goals of listed species and their biological traits and extrinsic threats. To date, we have focused on developing databases for life history and recovery information for federally listed species, as well as life history information and conservation recommendations for well studied species.

Analyses, thus far, have compared the number of populations required for recovery of plant species on the U.S. Endangered Species list with the current number of populations and historic number of populations. The dataset comprises the 638 plant taxa covered in one of the 267 recovery plans approved as of March, 2007. The recovery plans provided quantitative data on the numbers of historical populations for 404 taxa, ranging from 1 to 284 populations (mean=15.8; median=8). Numbers of extant populations were available for 596 taxa and ranged from 0 to 175 populations (mean=10.9; median=4). The percentage of populations remaining extant (n=404) ranged from 0%-100% and averaged 66.5%. Overall, 446 of the 650 taxa examined have suffered loss of whole populations; 378 have suffered reductions in population size; and 285 species, for which data were available, had suffered both types of losses. The number of populations deemed necessary to remove species from the endangered species list by recovery plans ranged from 1 to 115 and averaged 10.7 populations (n=409). Approximately 94% of taxa have recovery targets of at least five populations. Percentages of populations required for recovery represented 11.2%-800% of historical population numbers (n=284 species) and 12.0%-1,500% of current population numbers (n=383 species). At least all current populations were specified for 72.1% of taxa and numbers equivalent to at least all current and historical populations were required for 53.5% of taxa. On average, recovery objectives required 247.5% of current populations per taxon and 154.5% of all current and historical occurrences combined, indicating need for restoration actions. Recovery targets for 45.0% of species (n=128) exceeded the number of populations ever known to exist.

ALLELOCHEMICAL BEHAVIOR IN SOIL ENVIRONMENTS

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Knapweed species are an aggressive and highly invasive noxious group of weeds that, once established, can create large monocultures reducing biodiversity of wildland flora. In part, their successful spread is due to the elemental and organic allelopathic properties of the plants. Two of the knapweed species, *Acroptilon repens* (Russian knapweed, RK) and *Centaurea maculosa* (spotted knapweed, SK) have been found to exude allelopathic chemicals from their root systems that are toxic to some native plants; *A. repens* releases 7,8-benzoflavone (α -naphthoflavone) and *C. maculosa* releases (-)-catechin. The objective of this study (SERDP-funded project SI-1468) was to determine the conditions – via batch sorption and greenhouse bioassay studies – that result in optimum soil sorption of these chemicals. This information could provide an environmentally sound means of controlling the spread of RK and SK. Sorption of both 7,8-benzoflavone and (+)-catechin was nearly 100% in soil environments, thus, diminishing their importance as active allelochemicals. Greenhouse bioassay results, comparing RK growth with native bluebunch wheat grass (BBWG) when grown together and with and without activated carbon (AC), have made us reevaluate the mechanism we thought was responsible for the successful spread of RK. Initially we hypothesized that the AC would act as a sink for the allelochemical 7,8-benzoflavone, thus, BBWG would be able to successfully compete with RK only in those treatments where AC was present. What we actually observed was surprising. RK growth was inhibited by 75% in all cases where AC was applied, while BBWG growth increased by 15% in the presence of AC. Also, RK root growth was inhibited in presence of AC, while the opposite was found for BBWG. Root growth of BBWG was not inhibited in treatments where RK and BBWG were grown together with AC, whereas without AC, BBWG growth was limited. These promising results suggest that soils amended with AC could enhance growth of native grasses while suppressing the growth of RK. We are currently conducting analyses to determine if suppression of RK growth in the presence of AC may be due to the binding of trace metal nutrients to AC. We surmise that these nutrients are required in greater amounts by RK, and by binding to AC they are rendered unavailable to RK. Similar studies are currently underway with SK. Overall, the results are encouraging. If RK and SK are inhibited by organic carbon then management strategies can be established to control their spread at military bases.

ALLELOPATHY AND THE CONTROL OF EXOTIC WEEDS ON MILITARY TRAINING GROUNDS

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Discovering effective, environmentally sound, and economical methods for controlling exotic weeds is essential for conserving native ecosystems and preserving military training activities. Some exotic weeds that have invaded North America appear to be allelopathic; meaning that they produce phytotoxins that may negatively impact neighboring plants. We are investigating the linkage between invasiveness and allelopathy in several exotic weed species, as well as the potential use of native, allelopathic plant species as “smother crops” to reduce the dominance of exotic weeds. We are also exploring whether native plants that are known to be resistant to the allelochemicals produced by exotics increase restoration success.

To identify promising, native, allelopathic species useful in combating exotic weeds, we are conducting both greenhouse and field experiments. In both settings, we are testing for allelopathic effects by including an activated carbon treatment that effectively removes phytotoxins from the soil. In the field, we are investigating the effect of native, allelopathic and native, allelochemical-resistant seed mixes on target, exotic weeds. Two years after establishing the field experiments, results are encouraging. The native, perennial species we are studying, however, may require several years for establishment before long-term impacts within the plant community are discernable.

In greenhouse treatments, we grew desirable, native species in combination with exotic weeds in the presence or absence of native, allelopathic species. Our goal was to identify native, allelopathic species that negatively affect exotic weeds, but not desirable natives. Preliminary analyses from the greenhouse experiment suggest complex interactions, with several native, allelopathic species appearing to have negative impacts on target weeds. Results from our studies suggest the potential efficacy of a novel, economical, and environmentally sound approach using native, allelopathic species and allelochemical-resistant species to control exotic weeds.

This project (SI-1388) is funded by SERDP.

THE ECOLOGICAL IMPACTS OF ALTERNATIVE MANAGEMENT SCENARIOS: THE USE OF THE EFFECTIVE AREA MODEL ON MILITARY BASES

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Land managers on military bases face the same challenges as other conservation managers—balancing necessary land uses with conservation goals. Managers are under increasing pressures, not only to meet goals mandated by the endangered species act, but to manage for the long-term health of the larger ecological community. Despite these pressures, there are few tools to help them intergrate the many ecological consequences of their decisions while balancing land use and habitat conservation needs. We present an example of the use of the Effective Area Model (EAM), a spatial model developed with SERDP funding, to explore the potential ecological impacts of alternative management decisions on two military bases: Ft. Hood in Texas and Ft. Benning in Georgia. We modeled two types of decisions that military land managers frequently face: how much training activity to allow in an area (in this case, tank maneuver exercises) and which patches should receive prioritization for restoration for two competing endangered species (in this case, golden-cheeked warblers and black-capped vireos). We created a series of maps that reflect plausible future configurations of both sites under different land management scenarios, and then used the EAM to model the potential impacts of those decisions on the bird communities. We will present the preliminary results of these modeling exercises and our plans for improvements for the next generation of the model.

This project (SI-1597) is funded by SERDP.

SERDP'S DEFENSE COASTAL/ESTUARINE RESEARCH PROGRAM (DCERP) - PROJECT UPDATE: COMPLETION OF PLANNING PHASE

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DCERP (SERDP Project SI-1413) is being conducted at Marine Corps Base Camp Lejeune (MCBCL) in North Carolina and is designed to conduct mission-relevant research in support of an ecosystem-based management approach. MCBCL provides an ideal platform for DCERP because it encompasses diverse ecosystems including aquatic-estuarine waters, coastal wetlands, coastal barrier islands, and a variety of terrestrial habitats. Specific DCERP objectives include: (1) development of conceptual and mechanistic ecological models to guide research, monitoring, and adaptive management feedback loops; (2) identification of significant ecosystem stressors, their sources, and their level of impact on MCBCL's ecological systems; and (3) incorporation of stressor and other ecological indicator information into the models, with an aim to develop more effective management guidelines for sustainable ecosystems.

The planning phase produced (1) a mission-relevant strategic plan, (2) baseline monitoring plan, and (3) research plan for 13 separate research projects. Several workshops were also conducted to acquire technical and stakeholder input that integrated the basic monitoring and research needs of the DCERP team with the management needs of MCBCL. To facilitate better understanding of ecosystem state and dynamics, installation lands were subdivided into five distinct, but interdependent ecosystem modules: Aquatic/Estuarine, Coastal Barrier, Coastal Wetlands, Terrestrial, and Atmospheric. The DCERP team developed both module-specific conceptual models and detailed roadmaps that integrated monitoring and research activities and identified desired outcomes. The conceptual models provided a clear picture of the processes and stressors affecting each specific ecosystem. Module-specific roadmaps provided a view of monitoring activities and how the monitoring and research activities among all ecosystem modules were integrally connected, and identified appropriate end users for the information. DCERP's monitoring indicators, metrics, and techniques are intended to be transferable to other ecologically similar sites.

Implementation of DCERP will foster greater understanding of MCBCL's biologically diverse ecosystems and their interactions with military training activities. This information will assist in the successful long-term management and sustainability of these unique ecosystems which will in turn, provide for the sustainability and enhancement of the military training mission.

PREVENTING THE SPREAD OF INVASIVE SPECIES: EVALUATING PLANT PROPAGULE TRANSPORT BY VEHICLES

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Invasion by non-indigenous plant species (NIS) is a global-scale problem that threatens the ecological integrity of native plant communities and ecosystems. NIS are introduced to areas by a variety of natural and anthropogenic means, and the number of anthropogenic introductions has increased in recent decades. Roads are dispersal vectors for NIS due to transport of NIS propagules by vehicles and by natural population expansion in the more-disturbed environments along the right of way. Plant propagules (seeds and other reproductive parts) have been observed on vehicles, but the number of studies is limited. Transporting equipment, materiel, and personnel between sites, conducting off-road maneuvers, and simply driving on unpaved roads pose a measurable risk of transferring NIS within and between sites. More propagules are likely to be collected by vehicles driven off-road than on paved roads, and by tracked or all-terrain vehicles than civilian pattern vehicles, but there are no quantitative data to support this hypothesis. In the execution of SERDP Project SI-1545, our first objective was to quantify the potential of different vehicles to transport soil which could include NIS propagules. This was accomplished simultaneously with execution of our second objective, which was to evaluate the efficacy of commercially available relocatable vehicle washing units. These systems are designed to clean vehicles and contain the (NIS contaminated) waste. During the summer of 2007, five commercially available vehicle washing units were evaluated for effectiveness and efficiency of cleaning three different types of vehicles. Vehicles were cleaned meticulously prior to driving at a set speed around a predefined course, and then washed by the wash unit, this being replicated 18 times for both light 4-wheel drive vehicles and for heavier all-wheel-drive trucks, and once for tracked vehicles. At the end of each cycle, the vehicles were stripped down and cleaned meticulously again to quantify the amount of debris missed by the commercial wash units. To quantify how much seed was lost in the wash and filtering system process a known amount of soil and seed were placed in a tank bath and taken into the wash unit's filtering system. Samples were filtered using the individual unit's protocol. Waste samples (greater than 75 μ) were saved, placed in a greenhouse and germination recorded. These data, and those from future experiments, will be used to develop protocols which will aim to reduce the movement of non-indigenous plant propagules, within and between Department of Defense installations.

PARATRANSGENESIS FOR TERMITE CONTROL

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Wood feeding termites, such as the Formosan subterranean termite (FST), are some of the most devastating invasive insects that threaten strategically important locations in tropical and subtropical regions, including the U.S. The Department of Defense is a program leader in establishing environmental protection programs with a goal of minimizing pesticide application. A promising and novel alternative to conventional chemical and bait treatments for termite control is paratransgenesis, i.e., the use of microbes, which naturally live in the termite gut, but have been genetically modified to produce toxins that are detrimental to termites. The most important symbionts in the gut of the FST are three species of protozoa, which enable termites to digest wood efficiently. In this SERDP study (project number SI-1467), we developed a paratransgenic system to kill protozoa in the termite gut. Without their protozoa and the nutrients that they supply, termites die. Lytic peptides (LP) are part of the nonspecific immune system of eukaryotes that have been shown to kill a wide variety of protozoa but not to harm humans and higher eukaryotes. We tested four LPs (*Cecropin B*, *Melittin*, *L-Hecate*, *D-Hecate*) for their efficacy against protozoa, and 50 μM LP concentrations resulted in 100% mortality of all three protozoa species in culture within 5-10 minutes. LPs also were injected into termite hindguts and death of all protozoa in the guts (defaunation) was observed within 72 hours of treatment with 0.25-0.5 μl of a 500 μM lytic peptide solution. Termites were defaunated and died within a range of a few days (*Melittin*) to six weeks (*L- and D-Hecate*, *Cecropin B*). The genes of *L-Hecate* and *Melittin* were synthesized and integrated into the chromosome of the yeast, *Kluyveromyces lactis*, to generate strains that secreted either *L-Hecate* or *Melittin*. To date, activity of several *Hecate* producing yeast strains have been confirmed in bioassays against protozoa in culture. Termites feeding on *Hecate* secreting yeast strains were defaunated within four weeks. To increase environmental safety, work is in progress to construct fusion genes that cause the yeast to secrete inactive protoxins, i.e., LPs inactivated by C- and N-terminal peptide caps. The LPs would be activated in the termite gut by cleavage of the caps with gut specific proteases. The ultimate aim is to achieve inducible expression of LPs within the recently characterized termite specific anaerobic, gram-positive bacterium, *Pilibacter termitis*, to minimize environmental impacts and achieve efficient colony level control of FST.

EVALUATING THE EFFECTS OF ENVIRONMENTAL FACTORS ON THE LOBLOLLY PINE DECLINE AT THE STAND LEVEL

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Fire exclusion and artificial plantation have resulted in the replacement of historically dominant longleaf pine (LLP; *Pinus palustris*) with loblolly pine (LBP; *Pinus taeda*) throughout the southeastern U.S. Fort Benning, GA has 36,400 ha of upland pine forests that are currently dominated by LBP. Although LBP forests are considered inferior habitat for red-cockaded woodpeckers (RCW; *Picoides borealis*), about 2/3 of the base's RCW population must use LBP for nesting and foraging due to a lack of mature LLP. However, approximately 2/3 of the LBP stands show some level of decline that may negatively affect RCW populations. Thus, there is an urgent need for protocols to restore LLP, while retaining mature LBP to support RCWs. At the same time, it is critical to understand the status of decline on the installation. In 2006, land managers in Fort Benning conducted an extensive forest inventory including approximately half of the installation's pine stands. We retrieved and analyzed plot level data from 9,800 ha of LBP/hardwood, mature LBP, and LBP plantation stands to identify variables indicative of LBP decline. Feral hog ground disturbance or gopher tortoise burrows did not significantly ($p < 0.05$) affect the percentage of pine decline (%PD). Moreover, the stand aspect did not significantly ($p < 0.10$) influence crown vigor condition, insect disease condition, or pine decline. The number of hardwood trees larger than 35cm DBH showed a significant ($r = 0.46$, $p < 0.01$, $n = 67$) correlation with %PD in LBP/hardwood stands, while herbaceous and pine straw ground cover were correlated ($r = 0.12$, $p < 0.01$, $n = 603$ and $r = -0.12$, $p < 0.01$, $n = 603$, respectively) with %PD in natural LBP stands. Considering that ground cover is altered by management activities (e.g., prescribed burning or thinning), the results suggested the possible influence of management activity on LBP decline. Percent pine basal area (pine BA/total BA \times 100) correlated significantly with %PD ($r = -0.32$, $p < 0.01$, $n = 75$) in loblolly pine plantations.

SERP Project SI-1474

PREDICTING THE OCCURRENCE OF LOBLOLLY PINE DECLINE IN POTENTIAL RED-COCKADED WOODPECKER HABITAT AT FORT BENNING, GEORGIA

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Forest managers are challenged to restore longleaf pine (*Pinus palustris* Mill) forests to support red-cockaded woodpeckers across the southeast U.S. while retaining critical habitat features, specifically mature pine trees. The need for such restoration protocols are critical at Fort Benning, GA, where as many as 70% of the active RCW cavities are located in mature loblolly pine (*Pinus taeda* L.) stands with trees that are reported to be declining at an alarming rate. At the landscape level, selecting stands for restoration requires a firm understanding of loblolly decline in relation to stand conditions, site conditions, and management history. The goal of our study is to develop a probability model to identify the loblolly pine stands facing the highest risk of decline. In each plot, we measured or sampled parameters associated with stand productivity (e.g., crown vigor condition), physiological conditions (e.g., average needle mass, foliar nutrient content), soil properties, stand characteristics (e.g., age and site index) and recent management history. Regression methods will be used to relate stand condition (loblolly pine decline) to measured parameters. Early results indicate that south-facing stands on clay loam soils are the healthiest stands, while stand facing south and loamy sand show the greatest decline. However, we did not observe clear effects of slope or aspect, rather loblolly pine decline was influenced by the interaction between slope and soil texture. Effects of management history and nutrient condition on loblolly pine decline will be further evaluated.

SERDP Project Number SI-1474

EFFECTS OF SITE PREPARATION ON NATIVE GROUND LAYER VEGETATION DIMINISH THREE YEARS AFTER APPLICATION ON A HYDRIC SOIL IN NORTH CAROLINA

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Ecological restoration of the longleaf pine (*Pinus palustris*) ecosystem requires successful establishment of longleaf pine seedlings while maintaining the characteristically diverse native ground layer vegetation. This is especially difficult on wet sites where intensive site preparation methods are often used to control competing species. On a poorly drained North Carolina soil, we tested the effects of eight moderate site preparation treatments on the response of ground layer vegetation. We examined effects of the treatments on abundance and species richness of vegetation on 1 m² plots in the following groups: total vegetation, large graminoids, small graminoids, forbs, ferns, shrubs, and vines. We found that after the first growing season (2004), all treatments had significantly reduced total vegetation cover when compared to the untreated check. However, after three growing seasons (2006), only treatments that combined herbicides with an additional mechanical treatment reduced total vegetation cover when compared to the check. There were no significant differences in species richness among the treatments in 2006 ($p = 0.0761$). When 2006 data were analyzed by vegetation group, there were significant treatment differences in fern cover ($p = 0.0363$) and species richness ($p = 0.0412$), shrub cover ($p = 0.0002$) and species richness ($p = 0.0412$), and vine species richness ($p = 0.0379$). Shrubs were significantly reduced by treatments that combined herbicides with either bedding or mounding. Large graminoids, small graminoids, and forbs were not significantly affected by any treatment after three years. The ability to reduce shrubby species while maintaining the desirable herbaceous layer makes moderate site preparations potentially useful tools for restoring the longleaf pine ecosystem on poorly drained sites.

SERDP Project SI-1303

SELECTING PROMISING GRASS GENOTYPES TO LIMIT WEED REINVASION

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Interactions between native and introduced plant species have been extensively studied but little research has examined germination of individual genotypes that co-exist with introduced invasive weed species. Recent research by our group suggests that native species may undergo selection and co-evolve in the presence of exotics. We examine genotypes of *Sporobolus airoides* Torr. (alkali sacaton) and *Hesperostipa comata* (Trin. & Rupr.) Barkworth (needle and thread) obtained from within invaded patches (IN) of *Acroptilon repens* L. (*Centaurea repens*, Russian knapweed) and from outside of invaded patches (OUT). We also conducted germination and growth studies of fingerprinted genotypes to understand variation in phenotype associated with each genotype. We unite results of several experiments with maternal plant seed weight, germination, above- and below-ground growth and competitive response of grasses against *Cirsium arvense* L. Scop. (Canada thistle) and *A. repens*, and performance of weeds against grasses to rank individual genotypes for their potential to compete with invasive weeds. We assign a performance ranking to each genotype within the two grass species based on how each performed in all experiments. We ranked performance on a 1-20 scale within each experiment. To assess promising genotypes, we assigned a performance index to each genotype by totaling the number of experiments where genotypes ranked in the top 10 and totaling the times they ranked below this level. Promising genotypes were determined by superior number of high performance rankings (top 10 finishes). Our performance index allows us to select promising genotypes of *S. airoides* and *H. comata* that may resist reinvasion of *C. arvense* or *A. repens* competition. The notion that populations of native grasses may have evolved to better compete with invasive species may allow for improved success in revegetation in areas subjected to exotic populations. This project (SI-1389) is funded by SERDP.

COMPARING MODEL PROJECTIONS GENERATED BY RSim AND LEAM FOR FORT BENNING

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Land-use practices in the vicinity of military installations influence the military's ability to conduct training and testing, sometimes resulting in the loss of support of assigned missions. Two SERDP projects explored the implications of these influences. Project SI-1257 was conducted by the Army Corps' Engineer Research and Development Center's Construction Engineering Research Laboratory (ERDC-CERL) and resulted in the development of the Land use Evolution and impact Assessment Model (LEAM). Project SI-1259 was conducted by a team through Oak Ridge National Laboratory (ORNL) and created RSim, the Regional Simulation Model. Upon completion of the projects, SERDP also funded the effort reported here to examine what differences there might be in results of LEAM and RSim for the region encompassing Fort Benning and what explanations there may be for the differences. Because a common component of both models is their ability to simulate changes in urban land use, much of the comparison focuses on changes to the urban areas.

Major conclusions of the analysis follow. First, RSim and LEAM address substantially different questions and thus contain different supporting urban growth projection software. Differences in the detail of the model outputs can be associated with these different objectives – resulting in urban pattern outputs that are sufficient for answering the fundamental questions. Second, the application of RSim or LEAM must directly involve the expertise of specialists who can adapt the model to the local changes and impacts. Neither model can be immediately applied to new locations. Thirdly, each application of the models to new locations will likely embody ongoing enhancements that should result in increasingly useful results. Fourth, the urban growth projections of LEAM and RSim rely heavily on supplied run-time parameters. Simple changes to these parameters can generate dramatically different results. Finally, application of both models to a common area, the Fort Benning multi-county region showed differences in forecasted urban patterns due to (1) differences in initial land-use pattern maps, (2) differences in the overall amount of future growth, and (3) differences in the way neighborhoods are generated.

RESTORATION OF STREAM AND RIPARIAN ECOSYSTEMS AT FORT BENNING, GEORGIA

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Mmilitary training activities at Fort Benning, Georgia, have resulted in vegetation loss and severe erosion from upland areas and impacts on the structure and function of riparian and stream ecosystems. To help ameliorate these impacts, we evaluated effects of restoration strategies involving physical stabilization and revegetation of eroded ephemeral drainages and coarse woody debris additions to perennial headwater streams. We selected riparian plots and stream reaches within six to eight 1st- and 2nd-order catchments subject to a range of upland denudation and associated riparian and stream impact. The effects of the extent of upland disturbance on stream and riparian ecosystems were determined in an earlier phase of the project. Ephemeral drainage restorations were performed in three catchments with three additional catchments used as unrestored controls. In-stream restorations (coarse wood additions) were performed in 100-m reaches of four streams, with four additional streams used as unrestored controls. Ephemeral drainage restoration decreased sediment accumulation by about 80% on disturbed riparian plots located downstream from restoration sites. Some disturbed sites showed increased fine root productivity in the upper 10 cm of soil following restoration, and other disturbed plots showed increases in frequency and cover of nonweedy, perennial grasses and native species in the understory. However, there were no clear indications that indices of nutrient cycling have responded to restoration. In-stream restorations showed increased hydraulic complexity and the rate of nutrient uptake relative to control streams. Reach-scale rates of respiration increased, but there is no evidence yet of increases in gross primary production in response to stream restoration. Positive responses of stream biota and habitat variables to wood additions were observed in some restored streams, including increased benthic particulate organic matter and algal biomass and enhancements in several benthic macroinvertebrate measures. Contrary to predictions, restorations had no similar positive effects on increased coarse woody debris accumulation, streambed stability, % *Eunotia* diatoms, and several macroinvertebrate richness measures. These results suggest that such in-stream restoration approaches, although initially beneficial in increasing biotic integrity, may have limited long-term utility unless sediment sources to these highly disturbed streams are significantly reduced. Funding for this project is provided by SERDP – Sustainable Infrastructure Focus Area (SI-1186).

IMPROVED METHODS AND MATERIALS FOR REVEGETATING MILITARY TRAINING LANDS

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The Department of Defense (DoD) must constantly balance its military mission and its commitment to stewardship of millions of acres of training lands. Military training installations are some of the most intensively used lands in the United States, and military vehicular traffic can be very destructive to vegetation. The military mission requires that vegetation be as resilient as possible to training and meet environmental requirements. Damage to vegetation reduces training realism and carrying capacity of the land and causes the loss of valuable topsoil.

Revegetation processes used on DoD lands need to be cost-effective and require low follow-on maintenance because of the large size of military lands. Grasses are usually the species of choice for revegetation because they are inexpensive, readily available, and easy to plant. Only recently, however, have genetically improved grasses and seeding methods been developed for military training lands. Our recent SERDP-funded plant breeding studies are providing improved, more resilient native and introduced plants that establish more rapidly to return the land more quickly to military training. The new cultivars and germplasms have benefits for many non-military land uses and are being demonstrated to federal, state, and regional land managers as well as representatives of seed companies. Under ESTCP funding, large-scale demonstrations are underway at Fort Drum, New York, Yakima Training Center (YTC), Washington, and Camp Guernsey, Wyoming, and the grasses are being tracked at YTC with the DoD's new Stryker vehicle.

Under SERDP and ESTCP funding, we have produced and distributed seed of three of the new germplasms to military facilities in the Intermountain West. Our ecological-bridge concept uses seed mixtures of native and introduced plants sown in one operation to meet the requirements of future land-use goals. Ecological-bridge seed mixtures include a rapidly establishing introduced species to protect the soil environment until the desired natives in the mixture have time to take over. For intensively used lands, rapidly establishing introduced species must often be used alone and the plantings rarely last more than one year. For moderately and lightly used lands, however, native and introduced species can be sown in mixtures with the objective of obtaining a persistent, native plant stand in several years.

INTERGRATING ARCHAEOLOGICAL MODELING IN DOD CULTURAL RESOURCE COMPLIANCE

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Since 2001, the U.S. Air Force, in cooperation with the SRI Foundation and Statistical Research, Inc., has been engaged in validating spatial models that predict archaeological site location and incorporating such models into the compliance programs of individual installations. The groundwork for this effort has been supported by three Legacy grants (01-167, 03-167, and 06-167). In 2007, the project team began a four-year ESTCP project (SI-0720) to complete the validation and integration of archaeological modeling at four installations: Fort Drum, NY; Eglin AFB, FL; Saylor Creek Range, ID; and the Utah Test and Training Range, UT. The four installations pose very different environmental, archaeological, military, and compliance challenges. Upon successful integration of modeling at these installations, the project team will issue DoD-wide guidance and work with the DoD's Federal Preservation Officer on a policy statement. The conclusion of this decade long initiative will be a programmatic approach that allows for military activities with little encumbrance from cultural resources at the same time it improves stewardship and preservation of our nation's heritage.

INTEGRATED MULTI-SENSOR CHARACTERIZATION OF ARCHAEOLOGICAL SITES USING ARCHAEOMAPPER

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Evaluating the eligibility of archaeological sites for the National Register of Historic Places (NRHP) is a major expense for large military installations with active training programs. Traditional methods for site evaluation based on hand excavation are expensive, invasive, time consuming, and potentially unreliable. A recently completed SERDP project (*SI-1263, New Approaches to the Use and Integration of Multi-Sensor Remote Sensing for Historic Resource Identification and Evaluation*) developed methods for fusing (integrating) data from multiple sensors that provide detailed images of diverse subsurface cultural deposits. The field collection of data for relatively large (1-2 ha) areas using multiple instruments can be cost effective. It is the amount of time and levels of expertise, required to process and integrate data from multiple sensors, that currently limits the cost-effectiveness of this approach.

An ESTCP project, “*Streamlined Archaeo-Geophysical Data Processing and Integration for DoD Field Use*” (SI-0611) initiated in 2006 has two objectives: (1) Assemble a user-friendly software (*ArchaeoMapper*) that will allow an integrated multi-sensor approach to site characterization be used effectively by installing CRM personnel with relatively modest levels of expertise and experience, and (2) Demonstrate and validate the cost and performance benefits of the approach and technology infusion tool (*ArchaeoMapper*) to DoD geophysical users; representatives of federal, state, and tribal Historic Preservation offices, federal and state agency resource managers; and other CRM practitioners. The project’s demonstration and validation component will include a multi-sensor survey of a complex archaeological site, processing and integration of the data using *ArchaeoMapper*, predictions about the nature of subsurface features, and an independent evaluation of those predictions by means of carefully targeted excavations.

Currently under development, at the University of Arkansas-Fayetteville, *ArchaeoMapper* will provide a number of new integrative and analytical capabilities that are not currently found in any single existing software package. This poster will illustrate *ArchaeoMapper*’s ability to (1) display and integrate data from multiple sensors in a single, interactive three-dimensional display, (2) manipulate the display of data layers in a GIS-like environment, (3) develop, store and apply series of analytical operations to one or more layers in an “image-chain” approach, and (4) fuse (integrate) multiple layers using a variety of methods.

SONAR PERFORMANCE AGAINST UNDERWATER UXO

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SERDP project MM-1506 strives to identify and understand factors that affect sonar performance against underwater UXO and use this knowledge to develop a simulation tool to optimize sonar design for these targets. This year continues previous SERDP-funded research, leveraging on-going Navy sponsored sonar tests to collect data to update, validate, and refine the Navy's PC SWAT sonar performance software for UXO applications.

A measurement was conducted in the NSWCP Facility 383 test pond to investigate tradeoffs in mono-static vs. bi-static target detection. In the measurement setup, a target was situated on top of a smooth, flat, sand surface by divers approximately 11.6 m from a rail system developed by the Naval Surface Warfare Center – Panama City (NSWCPC) and 10 m from a rail system developed by the Applied Physics Laboratory/University of Washington (APL/UW). The two rails were placed perpendicular to each other and transducers were mounted on each rail system. These were employed to project and receive signals scattered from the target, and the transducers on each rail system stood about 4 m from the sediment bottom. Bistatic images of the UXO targets have been generated by processing the received data using synthetic aperture sonar (SAS) methods.

Progress on speeding up computational times for 3-D finite-element (FE) analyses of acoustic scattering from proud and buried UXO was made by implementing a capability for very fast sweeps over aspect angles and frequencies on a multiprocessor blade-architecture system. They model propagation in the littoral environment surrounding the UXO. When coupled with the FE target scattering models these techniques allow a simulation of the entire propagation, i.e., from source to target (UXO) to receiver over wide frequency ranges. Research into the frequency dependent attenuation and phase speed characteristics of selected muddy sediments at frequencies between 1 and 10 kHz was also initiated by performing laboratory measurements of the compressional wave speed and attenuation to characterize sediment samples for frequencies ranging from 1 to 10 kHz. The technical approach balances laboratory measurements with Boston University's impedance tube and with a prototype probe suitable for testing at the Naval Undersea Warfare Center's Dodge Pond acoustic measurement facility in Newport, RI. The laboratory testing compares measurements made with hydrophones in sediments to determine their ability to measure compressional waves with a known calibration factor.

BROADBAND, MULTI-ASPECT SCATTERING MEASUREMENTS FROM SHELLS, ROCKETS, AND FALSE TARGETS IN THE STRUCTURAL ACOUSTIC DOMAIN

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In order to evaluate the potential for the detection and identification of unexploded ordnance (UXO) in coastal and inland waters by exploiting their structural acoustic response, we have carried out broadband, mono-static scattering measurements over a full 360° on four UXO objects and two false targets. The UXO's included two mortar rounds, an artillery shell, and a rocket warhead while the false targets were a cinder block and a large rock. The measurements cover the band from 1 kHz to 140 kHz and were taken with low and high frequency measurement systems having an overlapping band from 8 to 25 kHz. This band includes a substantial spectral region where the responses are structural acoustic in nature in that the wavelengths in the fluid are comparable to or larger than the target characteristic dimensions. To our knowledge, these data sets represent the first of their kind for actual UXO targets. In general, there are a number of aspects that provide relatively high target strength levels (~ 0 to -15 dB), and based upon our experience this implies that, even though relatively small, the targets would be detectable in this structural acoustics band in most acoustic environments. The rigid body scattering response was also calculated for one of the UXO targets using a parallelized finite element-based scattering code in order to highlight the scattering features in the measured data which involve elastic responses. The various structural acoustic mechanisms observed in the measurements include interior structure and ring resonances and a number of specular highlights. Furthermore, the associated features appear to be exploitable for target identification. In this regard, we carried out a preliminary identification study which used a simple feature set taken to be the energy in each of thirty six equally-spaced sub-bands and a KMP identification algorithm trained on the data from the high frequency system after the addition of noise. Testing was then carried out using noise corrupted data from the low frequency system, and the preliminary results indicate that the data will support feature-based separation of UXO and false targets and various classes of UXO as well. Ultimately, we envision the implementation of an active sonar system designed for the UXO structural acoustics frequency band on an autonomous vehicle, either a surface craft (ASC) for operations near the beach or an underwater vehicle (AUV) for deeper waters. Work sponsored by SERDP as Project MM-1513.

PREDICTING THE MOBILITY AND BURIAL OF UNDERWATER UXO

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This ESCTP-funded project (MM-0417) is demonstrating and validating (DEM/VAL) the UXO Mobility Model, adapted from the VORTEX model used for mine burial prediction. The UXO Mobility Model incorporates specific UXO characteristics (e.g., shape, size, weight, and center of gravity), dynamic coupled processes, and seafloor material properties to predict UXO exposure, mobility, and burial. The resulting data can then be used in risk assessment analyses. The overall architecture couples models to form modules that prescribe boundary conditions, forcing functions, and burial response. The modules form two sets of integrative models, the first being a Littoral Cell Model that computes UXO burial and exposure related to bottom changes associated with farfield sediment balances within the littoral cell. These farfield balances are the only processes that can account for the exposure of previously buried UXO and include river sediment flux, longshore transport, and seasonal beach profile changes. The second integrative model is a Scour and Burial Model that computes UXO burial and mobility due to vortex scour of the local nearfield seabed. Included in the model is the Geomorphic Coastal Classification, an existing classification system that orders world coastal diversity into categories that prescribe the morphology of the littoral cell and determines the calibration parameters and grid scaling for nearfield and farfield events.

This project will validate the model at two geomorphic coastal sites: a Biogenic coastal category with limited cover of carbonate sediments (Kauai, HI) and a trailing edge environment typical of the east coast (e.g., Duck, NC). At each site, a suite of 24 surrogate UXO items will be deployed and their movement tracked.

The field demonstrations involve a model calibration period, during which drag and other empirical coefficients and sediment properties are adjusted for the specific coastal category. Once calibration is complete for a single time period at the site, a broader-based validation of the model will be conducted to enable DoD personnel to apply the model across the range of site variables where UXOs are found and over long windows of time. Target mobility/burial will be checked over a time period selected to capture major forcing events such as intense storm wave action, extreme tides and coastal runoff.

DEEP WATER MUNITIONS DETECTION SYSTEM

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A Deep Water Munitions Detection System is being developed to perform underwater UXO surveys to water depths of 100 feet. This system will utilize a two point towing method consisting of a navigation fish containing a sidescan sonar, doppler velocity log (DVL), an inertial navigation system (INS) along with a video camera and a GPS system. Together with the surface enabled GPS system and the DVL, the INS will have the data to determine in real-time the location of the navigation fish. The navigation fish will have the capability of auto-steering a pre-programmed course while the topside vessel is attempting to maintain the same course. This will provide precise survey area coverage regardless of the topside vessel's course accuracy. The sensor fish will be towed behind the navigation fish and contain a suite of high sensitivity optically pumped Cesium magnetometers. This project, MM-0739, is being funded by ESTCP.

FACTORS AFFECTING LAKE SUBBOTTOM UXO SURVEYS WITH GROUND-PENETRATING RADAR

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Our project is concerned with detecting munitions in lake subbottoms with ground-penetrating radar (GPR). Since February 2006 we have been investigating Joe English Pond (JEP), which is located on the New Boston Air Force Station in New Hampshire. It is ~70 acres with maximum depth of 8.5 m. The pond was a bombing and airborne firing range from 1942-1958 for 20 mm cannon and rockets, to 350 pound depth charges and 1000 pound bombs, many of which did not explode. The quantity, density and placement of these munitions are not known; observations by divers were limited by visibility. JEP has become the main focus of our UX-1440 project, but we utilize data from other lakes we have studied to validate our findings.

This poster is organized around four factors we conclude are responsible for GPR detection of UXO in the subbottom of JEP. The first is the unique phase of the metal target pulse reflection signatures in this environment, which we show occurs regardless of antenna or target orientation. It uniquely identifies UXO because it was unlikely that any other type of metal object would have been dropped and penetrated, and the munitions were mainly high fragmentation, general purpose bombs. The second is the narrow GPR beamwidth across our transect directions, which means our targets were located almost directly beneath our transects. The narrow beamwidth allows us to improve imaging through wave migration. The third factor is the low water conductivity, which allows up to 30 m of penetration with commercially available equipment. The fourth factor appears to be the low clay content of the subbottom sediments, which greatly alleviates the usual high rate of signal attenuation. We show evidence for subbottom penetration into at least 8 m of sediments and even bedrock. Consistently, X-ray diffraction studies reveal no presence of the highly electromagnetically absorbing smectite type clay, and a very high percentage of quartz and feldspar as fine silt. We are trying to verify this exceptional penetration with measurements of complex permittivity. The penetration reveals (1) that the density of munitions can form its own stratigraphic layer within ongoing natural deposition; (2) that the density of munitions can distort ongoing depositional processes, such as by draping of the sediments over the munitions; and (3) isolated cases of perforation, distortion and apparent cratering.

SYNTHETIC APERTURE SONAR FOR DETECTION AND DISCRIMINATION OF UNDERWATER

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We are pursuing a combined simulation and observational study to assess the potential performance of sonar-based discrimination systems for UXO targets in littoral and other shallow water environments. Sonar is a natural candidate for UXO detection due to its wide-area surveillance capability and target sensitivity. Specifically, we are analyzing synthetic aperture sonar (SAS) imagery for both buried and bottom surface targets to determine repeatability of discriminating features, especially given the complex wave propagation characteristics in the water column and sediments. Environment complexity can couple the target response to the detailed variation of the embedding medium (including bulk properties and surface properties such as sediment ripples). To better understand this we intend to apply a high-fidelity wave simulation for modeling of acoustic wave propagation, wave propagation in heterogeneous porous media and wave interaction with targets embedded in that media. The resulting sonar phase histories will then be processed with a SAS image formation processor for image generation. We are using the Biot formulation of the wave equations in the porous medium, derived using the averaging principle in a biphasic system, for the simulations and we are assigning realistic values of Biot propagation parameters using experimental characterizations derived from previous studies. For the acoustic equation of motion, a displacement potential formulation is used, which results in an acoustic-poroelastic coupling based on a non-iterative time scheme. The Spectral Element Method (SEM) is currently being evaluated as the numerical method for the wave solution. In principle, other methods are applicable as well (e.g., finite difference, time domain), but the SEM is a high-order variational method, which allows to compute synthetic seismograms in heterogeneous models with deformed geometry with very high accuracy and low numerical dispersion. To be useful, the numerical method must capture arbitrary target/environment complexity and accurately model all wave phenomena (resonant modes, surface waves, diffractions, specular scattering, target-environment coupling) over the low and high frequency regimes of interest. To support this effort we are in the process of building target and environment models. This activity, along with the results data products, target signatures and features from both simulations and real data collections will provide an outstanding resource for evaluation, design and development of target recognition systems. This work is supported under the Munitions Management (MM) focus area of SERDP as Project MM-1533.

LIDAR AND ORTHOPHOTOS IN UXO WIDE AREA ASSESSMENT SUMMARY OF LESSONS LEARNED

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URS Corporation and Terra Remote Sensing, Inc. were awarded ESTCP funding MM-0534, to investigate cost and performance parameters of high-density lidar and orthophotography as one component of the ESTCP Wide Area Assessment (WAA) Pilot Program. Lidar and orthophotography were collected by the URS team at three sites, near Albuquerque, NM, Victorville, CA and Marysville, CA. Lidar was collected at data densities ranging from 1.5 to 13.8 pts/m². Orthophotos were collected at pixel sizes of 10 and 20 cm, and one site had pre-existing orthophotography at a pixel size of 30 cm. Lidar and orthophoto data were successfully used identify munitions-related features and ambiguous features for further investigation, and to validate and correct the initial CSM, assess the locations of potential Munitions Response Sites and MEC-related features such as craters, and provide data for planning for subsequent phases of the investigation. The performance of each data set was evaluated for its effectiveness in locating calibration objects and MEC-related features.

URS has subsequently been awarded ESTCP funding to investigate the effects of vegetation on feature detection using lidar, and to produce a draft guidance document summarizing lessons learned pertaining to planning, acquisition, processing, analysis and interpretation of lidar and orthophoto data for munitions sites.

This poster will include a general description of lidar and orthophoto technology, results at the three sites investigated by URS, and a summary of lessons learned to date, including for the following topic areas: (1) When in the assessment cycle should lidar and orthophotos be used? (2) What kinds of features can lidar and orthophoto detect – and not detect? (3) What kinds of MEC-related features were detected using magnetometry but not by lidar and orthophotos? (4) What kinds of MEC-related features detected using lidar and orthophotos but not by magnetometry? (5) What should users of lidar and orthophoto data understand about ambiguous features, effects of land use and vegetation cover, noise effects and data artifacts?

These findings will assist Government land managers in the formulation of realistic expectation regarding the capabilities of lidar and orthophotos at future munitions sites.

A COMPARISON OF FILTER STRATEGIES FOR PRECISION GEOLOCATION OF UXO DETECTION INSTRUMENTATION USING INTEGRATED IMU SYSTEMS

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Precision navigation of mobile scientific data acquisition systems with sub-second temporal resolution and operated in potentially harsh local environments typically rely on an external ranging system (e.g., GPS) integrated with inertial measurement units (IMUs). Such integrated geolocation systems are similarly advantageous for such very local applications as UXO detection and discrimination using hand-held and land-mobile geophysical EMI systems. The integration of data from IMUs, distinctively characterized by accumulating positioning errors, with data from an external ranging system whose integrity is often compromised by environmental factors (such as physical blocking of received signals), offers challenges in modeling since the navigation equations are non-linear and the IMU noise characteristics may not be well understood. The (extended) Kalman filter (EKF) is the customary tool to perform an optimal integration of data, and it is successful if the conditions of a “not-too-non-linear” model and of Gaussian noise are satisfied. We test two new types of filter that eliminate these conditions, and apply them to the specific problem of geolocation of EMI systems for UXO detection and discrimination. The new filters are the sigma-point (also “unscented”) Kalman filter (SPKF) and sigma-point particle filter (SPPF). The SPKF eliminates the linearity assumption by propagating samples of the errors directly through the non-linear navigation equations, rather than theoretically through a linear approximation. The SPPF goes one step further by eliminating the Gaussianity assumption in the errors using a Monte Carlo approach to error characterization. We simulate typical scenarios of cart-mounted or hand-held detection systems deployed over larger areas, as well as the latter over very local (say, 1 square meter) patches. Various grades of IMU quality are considered and the analyses show how each filter performs under different durations of ranging signal outage. The simulations demonstrate that the SPKF and SPPF generally yield smaller geolocation errors than the EKF and that this improvement becomes more pronounced as the duration of external ranging outage increases, that is, as the non-linearity of the model grows. We also test the Gaussianity assumption to ascertain the benefit of the much increased computational load of the SPPF over the SPKF and find mixed results. Finally, we include a post-survey RTS smoothing for the case of data acquisition over a very local patch to show that even with 30 s between control updates, a tactical grade IMU yields a precision of 2-4 cm (s.d.) in the horizontal coordinates. Project MM-1565 supports this work.

TESTING AND ANALYSIS OF GEOSTATISTICAL CHARACTERIZATION TECHNIQUES USING FULL-COVERAGE MAGNETOMETER DATA SETS

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Sandia National Laboratories' and Pacific Northwest National Laboratories' ESTCP-funded research in the application of geostatistical techniques to the challenge of UXO site characterization has led to the development of a series of tools for the identification and characterization of target areas at former artillery and bombing ranges. These tools provide comprehensive mapping of probable target areas based on very limited geophysical survey data. Their application typically involves the development of comprehensive magnetic anomaly density maps developed from limited ground-based magnetometer surveys.

The ESTCP-funded Wide Area Assessment (WAA) program has provided a unique opportunity to test the performance of these geostatistical techniques in a real-world environment. The WAA program has collected numerous magnetometer data sets, both airborne and ground-based, from various former munitions ranges across the U.S. These data sets were collected in both full-coverage mode, where the goal is to collect data across the entire site, and in transect mode where only single, isolated transects are collected.

In this work, we make use of the WAA sites transect data sets to identify and characterize probable target areas using our geostatistical techniques. These results include probable target areas, anomaly densities, and total anomaly counts. The results from these analyses are then tested against the comprehensive full-coverage data sets. The results indicate that the developed geostatistical tools provide a reliable identification and characterization of former target areas. Sensitivity analysis results show that these techniques are also robust when presented with differing site sampling scenarios. These investigations also indicate the potential for more rapid site characterization using our geostatistical techniques combined with airborne-based magnetometer transects data.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94-AL-85000.

This effort is funded by ESTCP as MM-0325.

CAMP BEALE WIDE AREA ASSESSMENT TRANSECT DESIGN AND TARGET AREA IDENTIFICATION

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In an effort to demonstrate how several technologies developed under the SERDP and ESTCP programs for wide area assessments can be used to restrict the footprint of UXO remediation requirements and support target area identification and delineation, a major characterization effort was undertaken at Camp Beale near Yuba City, CA. Several technologies were deployed including high altitude lidar and ortho-photography, helicopter-based magnetometry, and ground based electromagnetic transect surveys using both towed array and man portable systems. Using the Visual Sample Plan (VSP) software tool, PNNL and SNL developed the ground-based transect survey design and analyzed the resulting survey data.

Transect surveys were designed to detect three types of munitions target areas in three separate sections of the site. The man portable system (1 m wide transect) covered much of the difficult to access hilly and forested terrain. The 2 meter wide towed array system surveyed the accessible regions of the site. The merging of the data from the different survey systems, varied terrain, and multiple munitions provided a unique challenge and demonstration of the geospatial analysis algorithms in VSP. The final identified and delineated target area results along with the density maps will be presented.

This effort is funded by ESTCP as MM-0325.

HELICOPTER MAGNETOMETRY CHARACTERIZATION: INTEGRATED TECHNOLOGY FOR WIDE AREA ASSESSMENT

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Wide Area Assessment (WAA) is a scaled application of remote sensing and geospatial technologies, designed to efficiently map unexploded ordnance (UXO) and munitions related features of a munitions response area (MRA). WAA mapping technologies can be classified into three types according to acquisition rate, feature resolution and data acquisition cost per unit area: High Airborne, Low Airborne, and Ground Systems.

Helicopter-based magnetometer technology (HeliMag) is a low airborne technology that provides highly efficient digital geophysical mapping for UXO with detection and feature discrimination capabilities approaching ground-based methods. The HeliMag system includes a helicopter-borne array of magnetometers and software designed specifically to process data collected with this system and performs physics-based analyses on identified targets. The helicopter technology utilized by Sky Research, Inc. is based on the Naval Research Laboratory (NRL) MTADS technology, transferred to Sky Research for commercialization via a Cooperative Research and Development Agreement signed in 2005. In addition, Sky Research recently completed updates to the NRL MTADS technology to improve performance and reliability of the technology.

From 2005-2007, Sky Research has demonstrated the use of HeliMag technology at multiple sites as part of WAA as part of ESTCP's WAA Pilot Program, project ESTCP-0535. Integration of the HeliMag datasets with the high airborne and ground system datasets collected as part of the Pilot Program allows for multiple-sensor delineation and cross-confirmation of target and range features and derivation of munitions and explosives of concern spatial distribution patterns. The goal is to establish technically achievable and regulator-acceptable processes for characterizing large MRAs, including the delineation of associated Munitions Response Sites (MRS), and provision of reliable data to support regulatory disposition of non-MRS portions of the MRA and to support risk analysis and cost estimation by site remediation contractors.

This poster will focus on the results of the HeliMag demonstrations at the ESTCP WAA demonstration sites as well as the performance assessment of the technology at those sites.

NEXT GENERATION HELIMAG TECHNOLOGY

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The Airborne Multi-sensor Towed Array Detection System (AMTADS) technology has evolved as an important and significant tool in characterizing former and active military bombing ranges for the presence of contamination from munitions and explosives of concern (MEC). The helicopter-borne AMTADS technology (HeliMag) has been demonstrated and used to detect and map the density and distribution of MEC at more than a dozen sites (nearly 25,000 acres). During the course of these surveys, several areas for improvements in the HeliMag technology have been identified that can result in more efficient surveys, broader applicability, and increased MEC detection capabilities. The objective of project ESTCP MM-0741 is to develop technology innovations that can provide significant benefits for MEC site characterization through increases in data collection/processing efficiency; increases in operational applicability; and increases in detection rates. We illustrate technical innovations that are being developed, including deployment from a MD530F helicopter, a configurable sensor boom design, a state-of-the-art data acquisition system (DAS), real-time data telemetry, and automation through real-time processing of survey data.

The Bell 200 Long Ranger was replaced with the McDonald Douglas MD530F helicopter to provide better power and maneuverability capabilities. For geophysical applications, the MD530F has a smaller magnetic footprint. The five bladed system and higher rotor rpm result in lower noise levels in the recorded data allowing improved detection of smaller targets. The DAS has the flexibility and capability to acquire data at increased sampling rates. Data resolution and sampling rates can be adjusted for various deployment needs. The sensor deployment innovations have three integrated components: (1) creation of adjustable sensor locations in the boom to optimize inter-sensor spacing for detection optimization depending upon the goals of the survey; (2) arrangement of sensors in various vertically offset configurations to mitigate geologic complications in the data; and (3) a flexible processing methodology that allows for arbitrary definition of magnetic gradients in horizontal, vertical and slant directions. The concept of an equivalent layer is being integrated into the data processing to provide a seamless computational framework for dealing with sensor data collected at arbitrary elevations and locations. Integration of a telemetry subsystem with the DAS provides benefits by removing the sensor operator from the helicopter, reducing operator risk and reducing cost. Telemetry of the data stream enables near real-time data QC, reducing potential for data errors, and accelerating production of data products.

INTELLIGENT DATA FUSION FOR WIDE-AREA ASSESSMENT OF UXO CONTAMINATION

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Under the sponsorship of SERDP, MM-1510, data fusion techniques are being developed for use in enhancing wide-area UXO assessment and remediation efforts. Towards this end, a data fusion framework is being created to provide a cohesive data management and decision making utility for site management. Development work to date has focused on data acquired during ESTCP's Wide-Area Assessment Pilot Program for the Pueblo Precision Bombing Range #2 and former Kirtland Bombing Range sites. UXO-related features from helicopter magnetometry and airborne LiDAR surveys are being combined with region-of-interest feature sets developed from manual inspections of LiDAR and orthographic data and other information sources. These latter feature sets include ship targets, target circles, roads, fences, pipelines, and in the case of Kirtland, manually identified craters. Data fusion methods evaluated includes Bayesian, Dempster-Shafer, and heuristic-based frameworks developed specifically for wide-area assessment. Data fusion results obtained for both the Pueblo and Kirtland sites demonstrate a heightened resilience to high false positive rates from algorithmically identified anomaly and crater features derived from the magnetometry and LiDAR data, respectively. Site-wide maps demarking areas of likely UXO contamination are shown for both sites, and indicate the benefits and additional quantifiable information obtained with a data fusion approach to wide-area assessment.

WIDE AREA UXO SCREENING WITH THE MINIMUM ALTITUDE REMOTE SENSING (MARS) FIXED WING AIRBORNE SYSTEM

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The capabilities of the Minimum Altitude Remote Sensing (MARS) system are being evaluated under Project ESTCP MM-0607 as an alternative and cost-effective technology for wide area assessment (WAA) of former and active military facilities contaminated with unexploded ordnance (UXO). At sites suitable for deployment of a fixed-wing system, MARS is intended to provide a cost-effective alternative to existing helicopter magnetic systems.

The MARS system was successfully developed, tested and deployed by SeaTerra GmbH in Germany. Sky Research, Inc. has partnered with SeaTerra to certify and demonstrate the system's capabilities for UXO detection and target density in the US. The system's platform is a CT SW Light Sport Aircraft, an all-composite ultralight plane with very little ferrous metal and a low signature footprint. The aircraft deploys six cesium vapor magnetometers using an advanced 200 Hz data acquisition system with 0.1nT resolution. At a survey rate of approximately 35 m/sec (68 knots) at an altitude of 2-3 m above ground level, the system collects data at 0.18 m intervals. Positioning is achieved with RTK GPS, a laser altimeter, and motion compensation via a digital compass and inertial measurement unit.

This technology is being evaluated relative to capabilities of helicopter-based low-altitude mapping technologies. The data collection and analysis approach was developed within this context, and was designed to demonstrate the benefits of a fully functional, multi-sensor MARS technology. The modified CT aircraft was granted the required manufacturer's approval, and a demonstration survey was conducted in May 2007 at the former Kirtland Precision Bombing range in New Mexico.

The Kirtland site was previously surveyed using helicopter magnetometer systems, and the existing data were directly compared with the MARS system results. Additionally, items were emplaced in a test plot and the survey results for these flights allowed a quantitative evaluation of the MARS performance. The statistical and target density analysis results will be presented in this poster (we expect performance results to be available in a September to October time-frame).

DEMONSTRATION OF TWO AIRBORNE VERTICAL MAGNETIC GRADIENT SYSTEMS FOR UXO SURVEYING

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Two new airborne vertical magnetic gradient arrays, designed for operation at 1.5-5m altitude, have recently been tested at an unexploded ordnance (UXO) test site in Ohio and at the Kirtland, NM Wide-Area Demonstration site, under ESTCP Project MM-0633. The arrays consist of 16 and 22 cesium vapor magnetometers respectively, configured as 8 and 11 vertical magnetic gradiometers.

The two new vertical magnetic gradiometer systems are referred to as VG-16 and VG-22. The VG-16 system was designed to maximize sensitivity in wide-area assessment surveys, where data are to be acquired at about 3m altitude or higher. By comparison, the VG-22 system was designed to address the detection of small ordnance items, 81mm and smaller, which typically have detection rates of less than 50% in airborne total field system performance assessments.

A total of 79 individual test items were emplaced at the Ohio site, consisting of fourteen different types of ordnance, generally with three distinct orientations (north-south east-west, and vertical) and three representative depths (ranging from 0.0 to 1.5m). Measured vertical gradient data were acquired with both systems at nominal altitudes of 1.5, 3, 5, and 10m. Assessment of VG-22 data from 1.5m altitude was conducted by automatically picking all analytic signal anomaly peaks, using a 1.0 nT/m threshold. This resulted in a selection of 198 anomalies. Of these 77 were associated with emplaced targets (including surface items). All of the emplaced items were detected (100%) except for the non-ferrous Mk-118 submunitions. The locations based on the dipole inversion had a mean error of 0.3m and a standard deviation of 0.2m.

Airborne data were acquired at two areas within the Kirtland NM Wide-area Assessment sites in April and May 2007. The South Area contained blind-seeded ordnance items, while the North Area contained pre-existing ordnance items. In addition to the data listed above, which were acquired at the lowest safe altitude, we acquired data over the northeastern 500-acre block with the VG-16 system, using a nominal altitude of 5m. Performance in the South Area will be assessed by comparison of anomalies to known locations of seeded items, and will be assessed in the North Area by comparison with ground survey results and validation excavations which will be conducted by an ESTCP contractor.

MM-1414: IMPROVING DETECTION AND DISCRIMINATION OF UXO IN MAGNETIC ENVIRONMENTS

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Geologic environments with magnetic soils and rocks produce significant problems for the successful detection and recovery of unexploded ordnance (UXO). SERDP Project MM-1414 focuses on understanding the origin of magnetic soils and their effects on electromagnetic (EM) and magnetic data, and on developing methods and procedures for identifying and removing these effects from geophysical data in UXO clearance. Over the past three years, we have investigated five separate sites with a wide range of magnetic soils. At each site, we have collected geophysical data as well as soil samples both on the surface and in soil pits. The soil samples were analyzed to study the geologic and mineralogical origin of soil magnetism within the context of geologic history of each site. 3D soil models were also constructed from soil samples and geophysical data and these models enable us to characterize the spatial variation and frequency dependence of magnetic susceptibility. Furthermore, geophysical data were analyzed to gain understanding of various signatures of magnetic soils, and to develop methods for separating the geologic noise from UXO signals in magnetic and EM data. As the project continues towards completion, we have begun to develop a comprehensive comparison among different sites with magnetic soils, gain a systematic understanding of the influence of magnetic soil on UXO geophysics, and formulate a set of practically applicable methods for treating EM and magnetic data acquired in such environments. This poster will summarize the major research results achieved in this project thus far, while presenting the details of latest developments. These will include the analyses of data acquired at Sentinel Plains in Arizona, the simulation of EM data over magnetic soils with 3D variations, statistical approaches to remove the soil response from EM data and a wavelet-based approach to separate geologic and UXO anomalies in magnetic data.

IMPROVING GEOSPATIAL POSITIONING ACCURACY TO SUPPORT UXO DISCRIMINATION

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Reliable and precise navigation technology is essential for robust detection and discrimination of unexploded ordnance (UXO) in a wide variety of field conditions where conventional methods are inadequate. Based on an evaluation of the strengths and weaknesses of current navigation technologies, laser-based robotic total station (RTS) technology has shown great promise in meeting the need for precise, robust, flexible and cost effective UXO navigation and positioning. These needs are being addressed by the research and development activities associated with the SERDP 1441 project UXO Navigation Technology that leverages existing laser navigation technology and improves its technological capabilities for application to the UXO field. This project is developing the technical modifications needed to integrate laser technology with handheld platforms to address geophysical survey needs for precise sensor location and orientation data for both UXO target detection and discrimination needs.

For this project, a detailed assessment of the laser technology was conducted to determine laser accuracy in terms of distance, accuracy and line-of-sight obstructions. The main conclusion drawn from the assessment is that the RTS technology, with its millimeter level accuracy, is highly applicable for targeted applications. The core optical capabilities of the technology provide the precision, update rates, and repeatability needed for accurate positioning.

Furthermore, we have found that the tracking capability of the robotic component of the RTS is highly robust. The functional elements of the active prism and tracking firmware provide all the tools needed to create a reliable prism-tracking application suitable for continuous tracking in visually cluttered environments such as wooded survey scenarios. Based on this functionality, a new multi-gun system has been developed with the capability to provide accurate positioning in wooded environments for UXO applications and integration with orientation sensors to provide further accuracy in sensor positioning. Development of the multi-gun tracking technology is ongoing and includes development of navigation performance and design specifications for a full suite of possible deployment scenarios.

THE MAGNETIC UXO RECOVERY SYSTEM (MURS)

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Liabilities, risks and costs associated with unexploded ordnance (UXO) may be mitigated with the Magnetic UXO Recovery System (MURS), Project #0732. Expected to operate at currently active and formerly used ranges, use of the MURS may lead to faster and more effective transfers of Formerly Used Defense Sites (FUDS), Base Realignment and Closure (BRAC) sites, and installations designated for transfer to public use. The MURS may also reduce the cost for maintenance at active ranges by eliminating many manual operations.

The MURS demonstration will gather data on the effectiveness of automating an excavator fitted with an electromagnet in removing UXO from military ranges. This will be accomplished by adding an electromagnet to the Automated Ordnance Excavator (AOE) whose conceptual design was developed by the Air Force Research Laboratory (AFRL/MLQF) through the National Defense Center for Environmental Excellence (NDCEE). Originally developed with U.S. Army Environmental Command (USAEC) and the Naval Explosive Ordnance Disposal Technology Division to remotely excavate suspected UXO, the AOE will be fitted with a 57-inch Walker Magnetics Scrapmaster[®] D series magnet. After integration, the MURS-equipped AOE will be tested for UXO lifting capabilities from soil surface, shallow water, and limited subsurface scenarios.

At Tyndall AFB, FL, initial testing will use inert ordnance to set multiple scenarios, with ordnance and scrap buried at different depths and orientations in terrestrial and shallow water conditions. Anticipated ordnance types will range from 60mm mortars to aerial bombs. Subsequent testing during the live demonstration will evaluate the AOE-equipped MURS on an active range to determine its ability to pick up different-sized UXO in a variety of physically intact conditions. The demonstration will encompass shallow water and terrestrial scenarios.

During the live demonstration effort (currently at Camp Guernsey, WY), the field operations team will use the same geophysical and location information as supplied to the rest of the UXO removal team. The effectiveness of the MURS will be compared with that of standard UXO clearance operations on a dollar-for-dollar basis within the parameters for which the MURS was designed. Success of the demonstration will be dependent upon the MURS being more cost-effective than standard UXO removal techniques, based upon the amount of UXO removed and the comparison of daily operational costs. Additionally, the effect of MURS on the soils will be evaluated as to whether normal detection techniques can still occur after the MURS has been used at specific setup locations.

ELECTRODEPOSITION AT NANOSCALE: THE PROSPECT FOR MAGNETIC FIELD SENSORS FABRICATION

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The work focusing on design of the solution chemistry (pH) and the pulse current magnitude enabling the incorporation of metal-hydroxide in ferromagnetic nanocontact matrix and simultaneously the formation of the nanocontact single crystal structure is investigated. The conditions leading to the precipitation of metal hydroxide at the electrode surface are defined after fully realizing the transport limitation for hydrogen ions towards the electrochemical interface in nanocoined electrode geometry. This work establishes the relation between the pH of the solution and the resulting vol. % of the metal oxide in the nanocontact matrix while having the other deposition conditions ensuring the growth of single crystal deposit. This provides the experimental approach to study the transport characteristics in ferromagnetic nanocontact as a function of their structure and metal-metal oxide ratio. The additional results are presented with the aim to achieve the metal-metal oxide structure in magnetic nanocontact using the anodic pulse during the electrodeposition. Our goal is to design the anodic pulse resulting in the growth of NiO or FeO barrier layer with 3- 5 nm in thickness resembling the nanocontact with desired amount of oxide in its structure. The formation of the oxide layer is the intermittent stage in the nanocontact deposition producing ~ one third of the nanocontact thickness. The final outcome of this work is anticipated to be completely defined relation between the conditions for electrochemical metal-metal oxide growth at nanoscale and the corresponding magnetoresistance of nanocontacts with metal-metal oxide structure.

This effort is funded by SERDP as MM-1593.

HIGH FIDELITY ELECTROMAGNETIC INDUCTION INSTRUMENTS AND PHYSICALLY COMPLETE MODELS

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We are developing advanced, man portable EMI instruments in both the frequency and time domains intended for queued interrogation of anomalies. The Man Portable Vector (MPV) time domain EMI instrument (MM-1443) has a single 75 cm diameter primary coil and five triaxial cubic receivers that measure the secondary vector magnetic field. Initial testing of the MPV instrument is complete, and we have an extensive data set collected at the ERDC test stand. Using this data set, we have adapted our physically complete high fidelity models, the SEA and the NSMC models, to the MPV. The ArcSecond system will provide geolocationing for the MPV and is expected to provide centimeter level positioning. With its high SNR, high fidelity, high diversity data acquisition capabilities, the MPV provides quality data for UXO discrimination models.

The GEM 3 D + (MM-1537) is a frequency domain EMI instrument adapted from a GEM 3 from Geophex. Transverse receivers were added to the GEM 3 to provide the capability of measuring a vector magnetic field in the frequency domain. Acquiring the transverse components of the magnetic field offers several advantages including data diversity and partial immunity to geological noise. The GEM 3 D + also incorporates an advanced geolocationing system. This positioning system is based on using the instruments own primary field to locate and orient the primary coil of the instrument. Initial testing has suggested an accuracy on the order of a centimeter when the instrument is within the 3 m of the positioning receiver coils. Our physically complete SEA and NSMC models are easily adaptable to new geometries such as the GEM 3 D +. We have successfully adapted these models for the GEM 3 D + geometry, and are ready to take advantage of more extensive data sets.

EMI ARRAY FOR CUED UXO DISCRIMINATION

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With support from ESTCP MM-0601, we are performing a project to design, construct, and demonstrate a vehicle-towed combined magnetometer/EMI sensor array to be used for cued discrimination of UXO from clutter. The array is used as part of a two-step process for identifying and classifying buried metal targets. Step one of the process is detection of possible targets for classification. Step two is to position the array roughly over the anomaly to make magnetometer measurements and EMI measurements sequentially. During both the magnetometer and EMI measurement periods, the position and orientation of the array is determined to high precision by an array of GPS antennas. The two data sets, with near-perfect spatial correlation and no motion-induced noise, are then cooperatively inverted for the desired target parameters. These inversions will be performed “on-the-fly” and the classification decision will be available in the field.

The first step in this project was to select and characterize the EMI sensor. We have selected a time-domain EMI sensor with a 35-cm diameter transmit loop and a 25-cm receive loop. We will deploy 25 transmit/receive pairs in a 5×5 array. We performed a series of characterization measurements with a prototype sensor in January 2007 and received delivery of the array in August 2007.

In this presentation we will include our plans for the system, characterization measurements on the array, and our first tests of the complete system at Blossom Point, MD.

ALLTEM UXO DETECTION SENSITIVITY AND INVERSIONS FOR TARGET PARAMETERS FROM YUMA PROVING GROUND AND TEST STAND DATA

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An advanced multi-axis electromagnetic induction system, ALLTEM, has been specifically designed for detection and discrimination of unexploded ordnance (UXO) with funding from SERDP Project MM-1328. ALLTEM uses a continuous triangle-wave excitation that measures the target step response rather than the more common impulse response. An advantage of using a triangle-wave excitation is that the responses of ferrous and non-ferrous metal objects have opposite polarities. In May 2006, the U.S. Geological Survey operated ALLTEM with a Leica 1200 GPS over the Army's UXO Calibration Grid and Blind Test Grid at the Yuma Proving Ground, Arizona. The system multiplexes through all three orthogonal (H_x , H_y , and H_z axes) transmitting loops and records a total of 19 different transmitting (Tx) and receiving (Rx) loop combinations. The ALLTEM system was in continuous motion with a spatial data sampling interval of 15 cm to 20 cm. ALLTEM records data at a constant 100 kilosamples/s rate with 24-bit precision. The high-density time-series data are then digitally filtered. Using an early-time pick of 275 μ s, late enough that the step response of an analog low-pass filter has settled, amplitude difference data and maps are produced. These data are almost free of ground response and system drift effects while retaining good sensitivity to UXO. The improvement in the signal-to-noise ratio greatly enhances the ability to detect small or deep targets. An inversion algorithm has been developed and applied to data from various sets of the available 19 Tx-Rx combinations over a number of targets. The algorithm is part of a processing and inversion package called GP Workbench and uses a physics-based non-linear inversion method. GPS position errors and additional errors from cart roll, pitch, and yaw were often small enough that the inversions provided good estimates of target position, depth, and orientation, and reasonable and reproducible values for dipole moments of these targets, even though the system was moving. This suggests that it is possible to obtain good multi-axis system target inversions from moving platform data even with some position "noise." A test stand with an automated positioning system has been developed and used to obtain high spatial density data over a number of inert ordnance and clutter items. These data have allowed us to assess effects of spatial data density, position error, and sensor noise on target parameter estimates produced by the inversion algorithm.

SUB-AUDIO MAGNETICS. THE APPLICATION OF A NEW DUAL MODE GEOPHYSICAL SYSTEM TO THE SIMULTANEOUS ACQUISITION OF TOTAL MAGNETIC INTENSITY AND TOTAL FIELD ELECTROMAGNETIC RESPONSES FROM BURIED UXO

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Sub-Audio Magnetics (SAM) is a technique that uses a fast-sampling total field magnetic sensor to simultaneously acquire Total Magnetic Intensity (TMI) and Total Field Electromagnetic Induction (TFEMI) responses from buried unexploded ordnance. SAM offers significant advantages in that it acquires the two data sets in a single pass over the survey area, recording with high spatial resolution and because the same sensor is used for both datasets, they are precisely co-located. The use of a highly portable lightweight sensor measuring the total field implies that the technique is well suited to difficult terrain. Furthermore, measurement of the B-field response from highly conductive targets provides a distinct signal-noise ratio advantage.

The two key components of this fully integrated UXO detection system are the low voltage, high current transmitter (referred to as the MPTX) and the receiver magnetometer (referred to as the TM-6). Both were developed during the course of this project (UX-0322) with funding from ESTCP, Army EQT and ERDC, and support from CEHNC and the Australian companies G-tek/Gap Geophysics. Both the MPTX and TM-6 have been purpose-designed specifically for the UXO application. The performance characteristics of both are presented, highlighting the significant improvement in data quality that has been achieved over the duration of the project.

Numerous field trials in the U.S. and Australia have been conducted enabling the evaluation and improvement of the SAM system, including field operating techniques and many aspects of the data processing. The need to efficiently process data provided the impetus to create appropriate processing and interpretation software.

Results from trials conducted at Aberdeen and Yuma in 2007 (Standardized UXO Technology Demonstration Program) illustrate the system performance and highlight the advantage gained from the purpose-designed transmitter to accurately represent the true SAM capability in the UXO application. A realistic picture of the cost effectiveness of the SAM method will also be highlighted. The discussion will also outline possibilities for commercial application of the method.

MINIATURE TOTAL FIELD MAGNETOMETERS

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Magnetometers are one of the basic instruments used for the detection and discrimination of unexploded ordnance (UXO). Cesium vapor atomic magnetometers are commonly used since their readings are independent of the orientation of the sensor, which eliminates the noise problems due to rotation or even vibration of other types of sensors. In order to better discriminate UXO from clutter or scrap, a high spatial density of readings is desirable. In order to efficiently make such measurements, and to position such measurements accurately, arrays of sensing elements would be highly desirable. However, existing cesium vapor sensors are extremely large and consume a lot of power.

Recently, considerable advances have been made in total field magnetic sensors, as well as towards miniaturizing cesium clock technology using micro-electro-mechanical machining (MEMS) techniques. In this work, we are extending those techniques, and optimizing the design and operating principles used in MEMS clocks for magnetometry. In addition, potential exists for pursuing extremely sensitive devices operating at wide bandwidths. Such sensors could replace inductive coils currently used in EM devices for UXO detection and discrimination. In addition to their small size, measuring the magnetic field instead of its rates of change, as an inductive coil does, has considerable advantages.

The technical objective of this work is to produce a high sensitivity, total field magnetometer of extremely low power, small size, and capable of being mass-produced for low cost. In this paper, we will present extremely exciting results of our work prototyping and testing actual atomic magnetometers no larger than a grain of rice. Measured performance of better than 50 pT per root Hz under actual field conditions will be shown. Power consumption is a small fraction (less than 10%) of that used in existing systems. We will also show results of our work at different cell temperatures, measuring the feasibility of working at higher bandwidths. This work will extend the MEMS technologies, allowing for a single sensor capable of making both a DC magnetic field measurement as well as a high frequency measurement for use in a time domain EM system. Significant progress is also being made towards commercializing these devices. Our design requires straightforward MEMS techniques, which are much less complicated, in fact, than some devices in commercial production today. Geometrics is working with commercial partners to begin producing such devices in the near future.

This effort is funded by SERDP as MM-1512.

METALMAPPER: A MULTI-SENSOR TEM AND MAGNETIC GRADIOMETER SYSTEM FOR UXO DETECTION AND CLASSIFICATION

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The objective of this project is to commercialize advanced technology emerging from recent ESTCP, SERDP, and NAVEODTECHDIV funded EM research. The project draws heavily from *BUDs* (Berkeley UXO Discriminator) technology developed by Lawrence Berkeley National Laboratory (MM-0437), and *AOL* (Advanced Ordnance Locator) technology developed by G&G Sciences with funding from NAVEODTECHDIV. Using this technology, we are assembling an advanced electromagnetic induction (EMI) instrument for detection and characterization of UXO that will perform substantially better than existing commercially available instruments. The instrument will include, as an option, the ability to simultaneously acquire both EMI and magnetic gradient data (*Dual Mode Acquisition*).

The project was funded late in FY06. There was a long startup period that was consumed with developing agreements between Geometrics, Lawrence Berkeley Labs (LBL), and G&G Sciences for the use and further development of various elements of advanced EMI technology that is being incorporated into the MetalMapper. However, we have made substantial progress toward developing key components of the MetalMapper system. Together with LBL, we have updated their low-power high-speed multi-channel data acquisition circuit board. Secondly, we have completed required modifications to the FPGA (Field Programmable Gate Array) that controls data acquisition. We have developed a Windows-based acquisition program that interfaces with the new data acquisition boards. And, on a parallel track, we have also made substantial progress in developing user-friendly interpretation software. DockPanelMetalMapper is based on a robust algorithm for UXO model parameterization developed by T. Smith at LBL. The program includes a data base for storage and retrieval of target parameters generated through the inversion of static multi-gate, multi-channel, multi-transmitter TEM data using an anisotropic dipole model and is able to automatically invert target data from a queued list of data files. A prototype MetalMapper system will be demonstrated at a Standardized UXO Technology Demonstration Site during FY08.

This work was supported by ESTCP under MM-0603.

SUPERIOR DEPTH OF DETECTION AND UXO TARGET CHARACTERIZATION USING AN ARRAY OF FLUXGATE MAGNETIC SENSORS

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We are developing an operational prototype of an EMI system for UXO detection using a single transmitter coil of moment 180 A.m^2 , and three 3-component fluxgate sensors (B-field Electromagnetic Array for Munitions and Ordnance Detection - BEAMOD).

Comparative testing at the Newholme (NSW Australia) UXO Test Range of a commercial single-component instrument (Geonics EM63) and the 9-component BEAMOD provides field data for verification of model studies which predict the BEAMOD system to have a depth of detection of order 40% greater than the EM63 and greatly enhanced resolution of target orientation.

We compare EM63 and BEAMOD profiles over 10 kg practice bombs, and 550lb bombs. The latter provide an example of superior depth of detection of the new system; for the larger bombs at depths 0.6, 1.5, and 2.5 m, we find that the BEAMOD system is capable of profiling the 2.5 m deep target on all components, while the EM63 is unable to detect any signature of that deep target.

For shallow bomb targets, classical dipole models prove insufficient for modeling target responses and we find that the use of conductive-susceptible models of finite size is necessary to fully characterize the EMI response of the target.

The proof-of concept project was supported by SERDP as Project UX-1445, and the current development is supported as Project MM-1598.

REPEATABILITY OF COMMON UXO DETECTION & DISCRIMINATION INSTRUMENTS

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In support of UXO detection and discrimination, considerable effort has been and is being devoted to (1) understanding the operating characteristics of currently deployed EMI sensor systems, (2) characterizing the sensor system response as a function of location of a given ordnance target relative to the system, (3) characterizing the sensor signatures of given EMI systems to a wide variety of ordnance types, and (4) currently an effort to characterize the variation in signatures of given EMI sensors to a statistically significant sampling of representatives of the same ordnance type. Complementary to the fourth item, there has not been a similar effort to characterize and understand the signature variation to a given ordnance item among various geophysical systems of the same type. Production geophysical surveys for UXO detection and discrimination typically use two technologies: electromagnetic induction (EMI) systems and total field magnetometry (TFM). EMI systems are the most versatile of the geophysical methods used for surveys for buried UXO, leading to environmental restoration. The EMI systems are versatile due to the capability of broad bandwidth operation and variable transmitter and receiver configurations. TFM sensors are the most reliable and simplest systems to operate while also having the ability to detect large targets at greater depths than EMI. ESTCP Project MM-0506 was funded to quantify the repeatability and reproducibility of the most commonly used sensors.

Repeated measurements taken with the three most common sensors used in UXO detection (the Geonics EM61 and EM61-MK2, and the Geometrics G-858) show variation in sensor response. This work has characterized these variations by the following methodology. A field data collection was simulated by fixing the sensors at a location and taking repeated measurements of the background and a representative target over a four hour period. The targets used were wire loops for the EM61 series instruments and wire loops with a constant current for the G-858. The loops were toggled open or closed every three minutes over the four hour test. The test was repeated six times consecutively for each instrument. Two variations of the test were used, in one the battery voltage was constant throughout the test and in the other the voltage stepped down to simulate a draining battery. These tests allowed for the quantification of individual instrument repeatability as well as the reproducibility of a group of the same instrument, specifically ten units of the same instrument type. The results of this work have led to suggestions for improving the field performance of these sensors.

AN EM SYSTEM WITH DYNAMIC MULTI-AXIS TRANSMITTER AND TENSOR GRADIOMETER RECEIVER

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Funded by SERDP (Project No. MM-1534), this project seeks to develop an advanced TEM system that exploits the benefits of both multi-axis transmitter loops and multiple receiver differencing measurements. In contrast with other SERDP-funded projects with similar objectives, however, the project will deploy an array small (10cm loops) tri-axial induction receivers to measure field differences over a short baseline in order to approximate the true secondary gradient field in the vicinity of the target. Difference measurements can also reduce the amplitude of ambient electromagnetic noise and, for properly positioned receiver pairs, can substantially reduce the very large signal transient produced by direct inductive coupling between the transmitter loop(s) and the receiver pair thereby improves the ability of these systems to measure the low-level transients induced by buried metallic targets. The purpose of the multi-axis transmitter is to allow the target to be “illuminated” with primary fields having different directions without the need to move the antenna platform. The project exploits advanced ordnance locator (AOL) technology for TEM measurements developed by G&G Sciences and funded by NAVEODTECHDIV. Its objective is to assemble and test a system with 3 orthogonal transmitter loops and an array of small tri-axial receivers configured to provide estimates of the full tensor gradient of the secondary transient magnetic field.

A new start in FY 2006, the project has completed its first task which was to perform a numerical study aimed at establishing design specifications including dimensional and alignment characteristics and to conduct an experimental study with the objective of determining the best way to make the required measurements of the field differences. This poster describes the results of the completed study. During FY 2008, our objective is to implement and test a tri-axial receiver array geometry to measure the gradient tensor of the secondary magnetic field.

THE ACTIVE TENSOR MAGNETIC GRADIOMETER SYSTEM: A DUAL MODE SYSTEM FOR MAPPING AND DISCRIMINATION OF UXO

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Magnetic gradiometry has long been a standard method for locating and mapping UXO. Typically such surveys employ either a single or multiple total-field magnetometers, such as the cesium vapor type. Serious drawbacks to this method, however, limit its usefulness for range cleanup. Whereas magnetic effects from clutter and closely spaced UXO can interfere with and degrade the signature of a UXO target, perhaps the most serious limitation of total-field magnetometry is the inability to discriminate between intact UXO and scrap.

The U.S. Geological Survey in Denver, Colorado, under project UX-1328 MM funded by the Strategic Environmental Research and Development Program (SERDP), has over the past three years developed and field tested a passive tensor magnetic gradiometer system (TMGS) for UXO surveys. This TMGS incorporates four three-axis fluxgate magnetometers to simultaneously measure the vector magnetic gradients at each point in a survey. The main advantage of the TMGS is being able to solve for a target's location and magnetic moment at every measurement point. In this manner, TMGS data can map targets as it goes along, unlike total field data, which have to be analyzed as a two-dimensional dataset, gridded over the survey area. The problem remains, however, of distinguishing between UXO and scrap. It is well known that passive magnetic systems, while having a high probability of detect (Pd), also have a high probability of false alarm (Pf). By combining magnetic data with electromagnetic data, as some current prototype systems do, it may be possible to characterize a target's geometric shape in terms of an induction polarizability matrix. The polarizability matrix may then be used as a discriminator to classify object either as spheroidal (UXO-like) or thin plate (scrap-like).

The active mode of the TMGS, explored under SERDP project MM-1514, approaches the discrimination problem differently. Rather than relying on the polarizability matrix as a discriminator, it splits the total magnetic moment of a ferrous target into separate remanent and induced magnetization components. The remanent component is a function of the metal's history, whereas the induced moment depends on the shape of the target, its magnetic susceptibility, and its orientation in the earth's magnetic field. Recent research has shown that an intact UXO possesses a high induced moment relative to its remanent moment. Conversely, scrap exhibits a high remanent moment relative to the induced moment. The active TMGS empirically derives the remanance-to-induced ratio to use as a sensitive and reliable discriminator.

UNCONVENTIONAL SOURCES OF PERCHLORATE

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While not forming spontaneously perchlorate occurrence has proven to be greater than can be explained by strictly industrial and military activity. Having both industrial (electrochemical) and natural (photochemical) sources, the origin of widespread low level perchlorate remains currently unresolved. Lightning is an energetic electrical event generating ozone, oxides of nitrogen, high voltages (100 million to one billion volts), high amperage (10,000-200,000 amps), and high temperatures up to 30,000 degrees C. Lightning strikes the Earth's surface one hundred times a second or 8.6 million times a day. Lightning striking sandy soils produce a natural glass fulgurite. To determine if lightning could produce perchlorate fulgurite, several samples from several different locations (Africa, Australia, AZ, CO, TX, and FL) were obtained. These samples were prepped and analyzed by Texas Tech University. Perchlorate was detected in concentrations ranging from less than 1 ppb to approximately 5 ppb. Fulgurites are very resistant to weathering and can persist for millions of years under certain circumstances. Can the formation of fulgurites, over geological time, be a significant source of environmental perchlorate, is unknown. Perchlorate also is used as a source of oxygen and found in hypochlorate. Analysis of various paper products (towels, coffee filters, feminine hygiene products, bandages, and sponges) revealed perchlorate up to 60 ppb. No lite charcoal and cigarette papers contain up to 25,000 ppb. This is consistent with their ease of ignition and sustained combustion. Further studies on these paper products, fulgurites, and other natural glass, like tectites, need to be conducted to determine their relevance to human exposure to perchlorate. This project was supported by SERDP Project CP-1435.

OCCURRENCE AND DEPOSITION OF ATMOSPHERICALLY GENERATED PERCHLORATE

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Perchlorate (ClO_4^-) occurrence in groundwater has previously been linked to industrial releases and the historic use of Chilean nitrate fertilizers. However, recently a number of occurrences have been identified for which there is no obvious anthropogenic source. The possibility that ClO_4^- contamination of surface and groundwater may have multiple origins (military, industrial, agricultural, or natural) complicates site characterization and efforts to assign responsibility for remediation. Other complications arise when assessing potential human exposure to ClO_4^- , especially if affected waters are used for drinking, livestock or irrigation of food crops. For example, human exposure to ClO_4^- has been documented in vegetation and in dairy milk. This research effort supported by SERDP (EP-1435) examined the occurrence of ClO_4^- in the vadose zone from undisturbed locations throughout the Southwest as well as its occurrence in wet deposition across the North American continent. Results from this research show that there is a significant reservoir (up to 1kg/ha) of natural ClO_4^- present in the unsaturated zone of semi-arid and arid areas of the Southwest in the United States and potentially the world. The ClO_4^- is most likely of atmospheric origin and concentrations in the subsurface are highly correlated to chloride concentrations which are known to have accumulated throughout the Holocene. This reservoir of ClO_4^- is sufficiently large to have a substantial impact on groundwater where irrigation from agriculture or urbanization is sufficient to flush accumulated salts. Related research indicates that the source of this ClO_4^- is likely atmospheric production and deposition by precipitation events. Sub-samples of precipitation collected through the National Atmospheric Deposition program over a period of 2 years were analyzed for ClO_4^- . Sample locations included sites in 14 continental states, Hawaii, and Puerto Rico. ClO_4^- has been detected in over 70 % of samples from all the locations tested. Concentrations were generally low and quite variable and ranged from ND to 75 ng/L. This relatively unexplored source may help to explain the growing reports of ClO_4^- in produce, milk, and other food items and should be considered when evaluating overall source contributions.

CHARACTERIZING THE MICROBIAL COMMUNITY IN A BIOREACTOR TREATING PERCHLORATE-CONTAMINATED GROUNDWATER

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Biological perchlorate reduction is a promising water treatment option because perchlorate-reducing bacteria (PRB) are common in the environment. PRB reduce perchlorate to chlorate and chlorite via perchlorate reductase (*pcr*). Chlorite is converted to oxygen and chloride by chlorite dismutase (*cld*). The feasibility of biological perchlorate treatment has been demonstrated at the pilot-scale with biologically active carbon (BAC) filters, but little is known about the perchlorate-reducing microbial communities in the filters. Molecular tools might be used to track the expression of perchlorate-reduction genes as a function of water quality conditions, and they have the potential to detect microbial community disturbances before process performance is adversely affected. Sequences for *pcr* and *cld* genes have been reported for several phylogenetic groups (e.g., *Dechloromonas*, *Dechlorosoma*), and associated PCR primers have been designed; however, these primers might not detect all PRBs. For example, while *Azospirillum* PRB have often been found at perchlorate-contaminated sites, they were not considered in the primer design since their perchlorate-reducing genes have not been sequenced.

One objective of our project (ER-1563) is to characterize the microbial community in a BAC filter to determine if some PRBs might not be detected by available primers. BAC samples were collected from a pilot-scale perchlorate bioreactor in California. We established a PRB enrichment culture by seeding medium with BAC, and this culture repeatedly degrades 5 mg/L perchlorate spikes. Twenty isolates from this enrichment are being screened for perchlorate reduction, and the PRB will be phylogenetically identified by 16S rRNA gene sequencing. DNA was isolated from the BAC to examine microbial community diversity (e.g., via terminal restriction fragment length polymorphism). The available *pcr* and *cld* PCR primers will be tested on the BAC, enrichment culture, and PRB isolates. Our data will show if different primers are needed to detect the diversity of perchlorate-reduction genes in BAC filters.

Another objective of our research is to sequence perchlorate-reduction genes that are not detected by the available *pcr* and *cld* primers. Suppression Subtractive Hybridization (SSH) PCR cDNA Subtraction, a technique we recently extended from eukaryotes to prokaryotes, identifies genes that are up-regulated by a bacterium under particular conditions (e.g., perchlorate-reducing conditions). cDNA Subtraction will be applied to several PRBs, such as those with rapid perchlorate-reduction kinetics or those who are distantly related to the PRB for which *pcr* and *cld* have already been sequenced. These data will allow us to improve the current primer sets for perchlorate-reduction gene detection.

ENGINEERED INTRINSIC BIOREMEDIATION OF AMMONIUM PERCHLORATE IN GROUNDWATER

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Perchlorate is a highly water-soluble anion that has been used by the U.S. DoD for more than 50 years as a component in munitions, pyrotechnics, propellants, explosives, and rocket and missile fuels. It is toxic to humans and is highly persistent in groundwater where it has been frequently observed, especially in the western United States. Perchlorate has been detected in public drinking water supplies that serve millions of people. New technologies, particularly *in situ* approaches, are needed to remove perchlorate from groundwater. The primary objective of this project (SERDP ER-1562) is to demonstrate that transformation of natural subsurface biofilms by free DNA encoding constitutively expressible genes for perchlorate degradation (reduction) can be employed to institute a process of *engineered natural attenuation* for *in situ* treatment of perchlorate in groundwater. This is to be accomplished without the addition of genetically engineered microorganisms (GMOs) to the environment and will avoid the requirement to drive contaminated aquifers anaerobic by biostimulation, since this new approach uses indigenous electron donors as a source of electrons for perchlorate reduction. Project tasks are to (a) isolate and characterize novel perchlorate-reducing bacteria, in addition to those available from culture collections and other investigators; (b) identify members of the strain collection that are most effective at perchlorate reduction by use of a genetic algorithm-based optimization; (c) clone and sequence perchlorate reductase (*pcr*) and chlorite dismutase (*cld*) genes from the most efficient strains in our collection; and (d) transform laboratory-based natural subsurface biofilms with free DNA encoding *pcrABCD* and *cld* to foster *engineered natural attenuation* of perchlorate. Numerous perchlorate reducers have been obtained from culture collections or have been newly isolated. These strains include isolates of phylogenetic groups not previously known to reduce perchlorate. PCR has been used to amplify *pcrABCD* and *cld* homologues from the genomic DNA of the several of these strains. Cosmid libraries from the total genomes of selected perchlorate reducers are being prepared, and *pcrABCD*- and *cld*-specific probes are being employed to locate clones (Southern analyses) containing full operons for subcloning as the smallest fragments possible. The cloned genes are being placed within an expression vector (a derivative of plasmid *pSP2* developed in our prior work; Biodegradation [2006] 17:545-557). These new vectors will be examined for aerobic and anaerobic expression of perchlorate reduction enzymes first in transformed pure cultures of common aquifer bacteria and then in biofilms of both mixed and pure cultures.

SUCCESSFUL FIELD-SCALE BIOREMEDIATION OF PERCHLORATE IN GROUNDWATER UTILIZING AN ACTIVE-PASSIVE TREATMENT APPROACH

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Laboratory and field studies have shown that perchlorate-reducing bacteria are indigenous in many groundwater aquifers and that these organisms can utilize a wide variety of organic and inorganic substrates as electron donors for perchlorate reduction. These data suggest that *in situ* treatment of perchlorate in groundwater through electron donor addition will have broad application. There are two primary approaches to deliver electron donor to the subsurface: (1) engineered treatment systems that actively mix soluble electron donors into groundwater, usually via groundwater recirculation; and (2) passive systems with slow-release electron donors that utilize natural groundwater flow for substrate distribution. This presentation will focus on a hybrid “Active-Passive” approach for electron donor addition. This approach employs intermittent groundwater extraction-reinjection to establish a groundwater recirculation zone and mix electron donor within a designed treatment area, then allows natural groundwater flow to further distribute electron donor. The main advantages of the Active-Passive treatment system are that it provides a wide zone of influence and superior mixing of electron donor with perchlorate-contaminated groundwater, while minimizing biofouling often seen in active recirculation systems.

An Active-Passive treatment system was installed at the former Whittaker-Bermite Facility in Santa Clarita, CA. This project utilized a pair of extraction wells installed approximately 20 meters apart and perpendicular to groundwater flow with a single injection well placed in between. The system design was based on extensive hydrogeological characterization and modeling. A network of 11 monitoring wells, including 3 nested wells, was used to assess system performance. Citric acid was added as the electron donor in 5 active treatment phases (6-10 gpm total flow lasting 1-3 weeks each), and the system was shut down between these events (passive mode). Chlorine dioxide was used to mitigate biofouling of the injection well during active operation. Perchlorate concentrations in five of the system monitoring wells (of 8 in the treatment zone) declined from ~ 300 µg/L to < 2.5 µg/L during the 7-month demonstration, and concentrations in two of the three remaining wells declined to < 50 µg/L. Nitrate levels in each of these wells also declined significantly, from > 15 mg/L to < 0.2 mg/L. Iron and manganese levels increased in some of the monitoring wells, but mobilization of arsenic was not observed. The pilot test shows that an Active-Passive system can be used to effectively mix electron donor into groundwater with minimal well biofouling, and that significant reductions in perchlorate can be achieved through this approach.

NOVEL ELECTROCHEMICAL PROCESS FOR TREATMENT OF PERCHLORATE IN WASTE WATER

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The objective of this project is to develop an innovative and cost-effective technology for the treatment of perchlorate from wastewaters generated by treatment processes. The technology is based on electroactive ion exchange technique combined with nanostructured electroactive ion exchange materials. The technology will be sufficiently safe as to be easily extended for the treatment of drinking water because the perchlorate uptake step is essentially an ion exchange at open circuit, thus no pretreatment of drinking waters is required. Since the ion adsorption/desorption is controlled electrically without generating a secondary waste, this electrically active ion exchange process is a green process technology that will greatly reduce the operating costs.

We have developed a direct electrochemical approach to synthesize novel hybrid material composed of a conducting polypyrrole (PPY) matrix on the surface of carbon nanotubes (CNTs). We found that a porous CNT matrix improves the redox switching stability of PPy films greatly. The feasibility and potential applications of PPy/CNT for removing perchlorate from aqueous solutions through electrically switched anion exchange have been demonstrated. The high surface area of carbon nanotubes and ion exchange properties of PPy provide the composite film with a high capacity and stability for anion uptake and elution. The selectivity of PPy films for the perchlorate ion is demonstrated through cyclic voltammetric measurements. Furthermore, the functionality of PPy can be easily achieved by introducing a new functional group; therefore, the selectivity and capacity can be further improved. Such a novel and stable hybrid material promises a new route to develop a practical process for removing perchlorate through electrically switched ion exchange. Recent progress on technology development will be presented.

A COLORIMETRIC BIOASSAY FOR PERCHLORATE

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Recognition of perchlorate (ClO_4^-) as a widespread contaminant across the United States and its potential adverse health effects has motivated the EPA to place perchlorate on its contaminant candidate list for drinking water supplies. While a federal MCL has not yet been set, a recommended public health goal of 1 ppb ($\mu\text{g/L}^{-1}$) was established by EPA in 2002. To date, methods of detection require use of sensitive ion chromatographic equipment that are expensive, time consuming, and require highly trained personnel for use. Our studies are focused on the development of a highly sensitive, simple, and robust colorimetric bioassay based on the primary enzyme involved in microbial perchlorate reduction, the perchlorate reductase (Pcr). Previously, we described a purification protocol for the Pcr from *Dechloromonas agitata* strain CKB which resulted in a final protein product containing two subunits of molecular mass 95 kD and 37 kD representing the PcrA and PcrB subunits respectively. The loosely bound cytochrome containing PcrC was lost during the purification. A 15-fold purification was achieved with a final protein yield of 11% of the initial material. The purified PcrAB displayed Michaelis-Menton kinetics towards perchlorate with a K_m of 128.45 mM, and a V_{max} of 0.355 U mg^{-1} . The enzyme appeared to be very robust and was stable over a range of environmental conditions including a pH tolerance of pH 6-8 with an optimum activity observed at pH 7.5, and a temperature tolerance of 20-60 °C with an optimum of 50 °C. Furthermore, the enzyme was stable over a broad range of salinities (0 to 4M) and 40% of maximum activity was still observed at NaCl saturation (4 M). Although the enzyme was oxygen labile more than 40% activity was still observable after 5 hours incubation in an oxic system in the absence of anti-oxidants. The enzyme also indicated remarkable stability when stored under anoxic conditions and 50% of the activity was still retained after 9 days incubation at room temperature while no significant loss was observed at -20 °C. All of these characteristics render this enzyme an ideal candidate for the development of a field bioassay for perchlorate. An initial colorimetric method for the determination of perchlorate concentration was developed using dithionite as the reductant with 2,6-anthraquinone disulfonate (AQDS) as the dye. This initial assay, although somewhat complex, had a lower detection limit of 9.6 ppb which when combined with the previously developed sample preparation protocol will give an ultimate detection limit in the range of 20 ppt. In an attempt to optimize and standardize the perchlorate assay protocol while reducing its complexity several alternative electron donors and dyes with a range of redox potentials were screened. The results indicated that AQDS was the most efficient electron shuttle and dye for the PcrAB complex. The results of these studies indicate the great potential for the development of a simple, robust, and highly sensitive colorimetric bioassay for perchlorate that can be widely used to screen laboratory and environmental samples.

CONTINUOUS BIOELECTRICAL PERCHLORATE TREATMENT

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Microbial perchlorate reduction has been identified as the most feasible and complete means of remediating this contaminant from groundwaters and waste streams. Previous SERDP-funded investigations have revealed the ubiquity and diversity of dissimilatory perchlorate-reducing bacteria (DPRB), confirmed the dependency of the metabolism on molybdate, and shown that perchlorate reduction is negatively regulated by oxygen and nitrate. These organisms are able to oxidize a wide variety of organic substrates for degradation of perchlorate, but addition of such compounds for in-line treatment can cause overgrowth and biofouling, leading to poor water quality, increased operational cost, and treatment failure. We have developed a novel bioelectrical reactor (BER) for stimulation of DPRB that avoids addition of chemical substrate based on our previous studies with electrochemical stimulation of microbial perchlorate reduction. Initial studies showed successful stimulation of native DPRB populations with graphite electrodes poised at -500 mV vs. an Ag/AgCl reference electrode and the soluble mediator AQDS. A novel organism, strain VDY, was isolated from the cathode surface of this perchlorate-degrading reactor and found to be most closely related to *Dechlorospirillum* strain WD by 16s rRNA sequence analysis. In batch culture, strain VDY was capable of perchlorate reduction in the cathodic chamber of a BER both with and without a mediator, and was therefore used to inoculate novel continuous up-flow BERs for the treatment of perchlorate. These reactors were able to continuously remove 100 mg/L perchlorate over the course of three weeks compared to open-circuit controls, and subsequently shown to be capable of operating without the mediator similarly to the batch system. Abiotic headspace measurements of both the batch and continuous-flow reactors showed the presence of hydrogen, generated via hydrolysis at the cathode, at high enough quantity to provide the necessary reducing equivalents for the observed perchlorate reduction. In the mediatorless configuration, BERs inoculated with VDY were capable of continuous treatment of perchlorate at 100% efficiency with loading capacities of up to 60 mg perchlorate L⁻¹day⁻¹, could operate effectively at low (100 ppb) perchlorate concentrations, and also remediate mixed nitrate/perchlorate influent at 100:1 molar ratio. These results demonstrate the capacity of bioelectrical treatment of perchlorate over a range of influent conditions and suggest a promising novel technology for remediation of this contaminant.

LINES OF EVIDENCE FOR MONITORED NATURAL ATTENUATION OF PERCHLORATE

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The potential for perchlorate to biodegrade under ambient conditions is a powerful alternative to active, and more costly, groundwater remediation approaches. Solutions-IES, funded by the Environmental Security Technology Certification Program (ESTCP), is conducting an in-depth study (ESTCP Project No. ER-0428) to identify conditions required to implement Monitored Natural Attenuation (MNA) as a preferred groundwater remedy. Two demonstration sites are currently in the performance monitoring phase: (1) IR Site 67, Naval Support Facility Indian Head, MD, and (2) a perchlorate/trichloroethene SWMU at Alliant Techsystems, Inc. (ATK), Elkton, MD.

At Indian Head, elevated perchlorate concentrations (~24,000 µg/L) from a former rocket motor hog-out facility gradually decline as the plume migrates toward Mattawoman Creek, a tidal stream 400 feet downgradient. The inter-tidal zone is an extensive wetland with organic rich sediments. Perchlorate in groundwater enters the sediments beneath the inter-tidal zone at concentrations ranging from 4,200 to 21,000 µg/L. Concentrations rapidly decline as the perchlorate-laden groundwater moves upward through the organic-rich near-surface sediments resulting in only 3.4 to 6 µg/L residual perchlorate in the shallow groundwater beneath the creek. The three order-of-magnitude decrease in perchlorate concentration is much more rapid than would be expected based on dilution alone indicating that perchlorate is biodegrading.

At ATK, the source area perchlorate level (~1,500 µg/L) attenuates approximately 10-fold prior to groundwater discharging into Little Elk Creek 3,000 feet downgradient. Biodegradation of remaining perchlorate appears to occur within the riparian buffer surrounding the creek. Anaerobic conditions, elevated methane, low but measurable total organic carbon, and low nitrate support natural attenuation in this zone. Corroborating lines of evidence to support the remedy including chlorite dismutase enzyme assays, bio-geochemical profiles of the impacted groundwater, biodegradation results from in situ columns installed in the riparian buffer, and mass flux calculations will be presented.

EVALUATION OF ALTERNATIVE CAUSES OF WIDE-SPREAD, LOW CONCENTRATION PERCHLORATE IMPACTS TO GROUNDWATER

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The frequency of detection of wide-spread, low concentration perchlorate impacts to groundwater is increasing as regulators nationwide analyze perchlorate as part of regional groundwater monitoring programs. While impacts from natural sources and mechanisms may explain some cases, other cases may result from long-term, non-military-based inputs, potentially including: fertilizer use; environmental release of electrochemically-prepared chlorine products (mainly chlorate) containing perchlorate as an impurity; use of road flares containing perchlorate; blasting explosives and firework displays. Furthermore, EPA Method 314.0 is prone to a variety of false-positive detections and interferences related to common industrial chemicals such as sulfonates, raising the question of whether these low-level detections are perchlorate at all. Given the high cost of groundwater remediation at perchlorate sites (typically \$1M to \$10M per site based on experience), the Department of Defense (DOD) is developing information and tools that can distinguish between military and non-military perchlorate impacts so that remediation responsibility and cost can be accurately defined and limited.

The objective of this research was to identify and ultimately quantify, to the extent possible, the potential impacts of the aforementioned wide-ranging, non-military perchlorate inputs to the environment. This poster will present key findings from experiments with road flares, fireworks, blasting explosives, and bleach. A summary table will be included showing estimated relative contributions of perchlorate from these various sources.

ENHANCING MICROBIAL REDUCTION OF PERCHLORATE IN AMMUNITIONS WASTEWATER BY ZERO-VALENT IRON

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U.S. Army and DoD facilities generate perchlorate (ClO_4^-) from munitions manufacturing and demilitarization processes. Ammonium perchlorate is one of the main constituents in Army's new main charge melt-pour energetic, PAX-21. In addition to ammonium perchlorate, RDX and 2,4-dinitroanisole (DNAN) are the major constituents of PAX-21. Biological treatment of DNAN and RDX is inefficient due to the presence of electron-withdrawing nitro constituents in these energetic compounds, and microbial perchlorate reduction requires a constant supply of electron donors for perchlorate reducing bacteria (PRB). The objective of this study is to develop an innovative treatment process to chemically reduce and biologically remove both perchlorate and energetic compounds from PAX-21 wastewater.

A series of anaerobic batch biodegradation experiments was conducted in order to evaluate whether microbial perchlorate reduction may be a practical option for the removal of perchlorate in PAX-21 wastewater. After an acclimation period, perchlorate was rapidly and completely removed to an undetectable level in control bottles containing only glucose and seed microorganisms. In contrast, negligible amount of perchlorate (less than 2%) was removed in batch reactors containing PAX-21 wastewater. In order to investigate whether the constituents in PAX-21 wastewater were toxic to the perchlorate respiring bacteria, comparable anaerobic batch reduction experiments were conducted with synthetic PAX-21 wastewater. Similar results were obtained with synthetic PAX-21 wastewater, suggesting that the constituents in PAX-21 wastewater may be toxic to perchlorate-reducing bacteria.

In order to identify the toxic constituents in PAX-21 wastewater, a series of batch biodegradation tests was conducted with DNAN and RDX solutions. Microbial perchlorate removal was not observed in wastewater containing 100 mg/L of DNAN during 5 days of incubation, while perchlorate in RDX-laden wastewater (40 mg/L RDX) was completely removed at a rate similar to that observed in the control bottles. These results suggest that DNAN was responsible for inhibiting the activity of perchlorate-respiring bacteria. It was hypothesized that pretreatment of PAX-21 by zero-valent iron granules will transform toxic constituents in PAX-21 wastewater to non-toxic products. We observed complete reduction of DNAN to 2,4-diaminoanisole (DAAN) and RDX to formaldehyde in abiotic iron reduction study. After a 3-day acclimation period, perchlorate in iron-treated PAX-21 wastewater was rapidly decreased to an undetectable level in 2 days. This result showed that iron treatment not only removed energetic compounds but also eliminated the toxic constituents that inhibited the activity of perchlorate respiring bacteria.

A PRELIMINARY LOOK AT CLIMATIC CONTROLS ON LEVELS OF ATMOSPHERICALLY-DERIVED PERCHLORATE IN NATURAL MATERIALS

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Studies during the last 8 to 10 years have shown that perchlorate is ubiquitous in the environment and that much of this perchlorate cannot be linked to anthropogenic sources. A variety of research has demonstrated directly, and indirectly, that perchlorate can be generated in the upper atmosphere, and is widely deposited at the earth's surface by wet and dry precipitation. Extensive background sampling of soils/sediments and plants, supported by SERDP (EP 1435), has shown that climate plays a large role in the concentration of natural perchlorate. Perchlorate contents in plants and soils can vary widely between and within sample areas, plant species, and soil and sediment types. However, recent work indicates that climate, specifically effective moisture, controls the maximum amount of perchlorate that is found in specific locations. Effective moisture can be defined as precipitation minus evaporation; temperature plays a role in determining the degree of evaporation. With higher precipitation or effective moisture, the maximum potential levels of detectable natural perchlorate are relatively low. As effective moisture drops, the maximum potential levels of perchlorate increase leading to a much larger variance in natural perchlorate levels. This inverse relationship between potential maximum perchlorate level and effective moisture is especially strong in plants, although a similar, but weaker pattern is found in soils and sediments. This relationship between perchlorate content and effective moisture is also supported by results from rodent paleomiddens. Higher potential natural perchlorate concentrations related to low effective moisture has implications for human activities and exposure levels in arid and semi-arid climates.

EVALUATION OF PERCHLORATE ORIGIN USING STABLE ISOTOPE ANALYSIS

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The combination of lower detection limits for perchlorate and increased sampling nationwide has revealed that this chemical is much more widely distributed in the environment than previously thought. Mounting evidence suggests that the past application of Chilean nitrate-derived fertilizers and indigenous mineral and soil sources of perchlorate in the U.S. are significant contributors to its apparent ubiquity. The key objective of this ESTCP-funded project (ER-0509) is to apply isotope ratio mass spectrometry (IRMS) to differentiate perchlorate from natural and synthetic sources. Techniques have been developed to collect, purify, and measure the isotopic composition of perchlorate in source materials (e.g., flares, fireworks, chlorine bleach) and in groundwater and soil samples. Consistent and significant differences in $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ have been observed between naturally occurring perchlorate derived from the Atacama Desert of Chile (and fertilizers prepared from this material) and all man-made sources tested to date. The Chilean perchlorate as well as one sample of indigenous perchlorate from the Mojave Desert are also characterized by a unique ^{17}O excess that readily differentiates these natural samples from synthetic perchlorate and indicates an atmospheric origin.

Evaluations of chlorine and oxygen isotopic signatures of perchlorate in groundwater have been conducted at several locations around the U.S., including sites in CA, NV, NJ, NY, MD, TX, and OR. Isotopic signatures similar to those determined for synthetic perchlorate sources have been observed at several of these sites. Isotopic values representative of Chilean perchlorate, including the distinctive ^{17}O enrichment, have also been found at four locations thus far. Interestingly, isotopic ratios of oxygen and chlorine that are unlike those from natural perchlorate (Chilean or Mojave) or synthetic perchlorate have been detected in samples from several wells in West Texas. The isotopic data suggest that either this perchlorate was formed by a different mechanism than natural Chilean evaporites or that the perchlorate was modified by biological, physical, or geochemical processes after deposition, thus altering its original isotopic composition. The existence of this large $\Delta^{17}\text{O}$ anomaly in the Mojave Desert sample but not in the West Texas samples suggests that the origin of these two perchlorates is different. Additional studies are ongoing to explain the genesis of the West Texas perchlorate and to determine if other perchlorate samples with a similar isotopic signature can be identified.

THE EFFECTS OF PERCHLORATE EXPOSURE ON A MODEL VERTEBRATE SPECIES: THE THREESPINE STICKLEBACK

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Perchlorate is an endocrine disrupting toxicant known to interfere with thyroid hormone synthesis. We describe perchlorate-induced behavioral changes among two generations of threespine sticklebacks exposed to environmentally relevant concentrations of perchlorate: two-year-old adult males exposed to one of four treatments between 0 and 18.6ppm during courtship and parental care, and a second generation raised from syngamy through sexual maturity in one of four treatments between 0 and 100ppm perchlorate. The swimming ability of this second generation was tested at sexual maturity.

Dose-response relationships were noted during the swimming and behavioral testing. Treated fish had higher failure rates in the flume and failed at lower flow rates than control fish. Progressively fewer treated fish performed courtship displays, yet those that courted did so with few differences compared to control fish. Behavioral inhibition ultimately led to fewer successful spawnings and reduced fry production among treated fish. The lowest observed adverse effect level was 30ppm perchlorate, and complete inhibition of reproductive behavior was noted among males treated with 100ppm perchlorate. A small number of treated females were isolated and some performed male-typical courtship behaviors in the presence of other females and were found to be functionally hermaphroditic. Additional impacts to life history traits will be presented.

POSSIBLE SEQUESTRATION MECHANISMS FOR NATURALLY-OCCURRING ARSENIC MOBILIZED DURING IN SITU BIOREMEDIATION OF CHLORINATED SOLVENTS (ER-1374)

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A study of the mobilization and fate of naturally-occurring arsenic (As) was conducted at a site where anaerobic bioremediation has been employed to treat a tetrachloroethene plume. Molasses has been injected via a transect of wells oriented perpendicular to groundwater flow, which has resulted in an anaerobic reducing zone that extends approximately 30 m down gradient of the injection transect. At the down gradient edge of the reducing zone, dissolved As and iron (Fe) concentrations have been observed at over 0.7 and 450 mg/L, respectively. However, 60 m down gradient (and outside of the reducing zone), As and Fe concentrations have remained at levels below their detection limits for over 900 days (as compared with a groundwater travel time of approximately 140 days), demonstrating natural attenuation of As.

Laboratory studies were conducted using natural sediment collected down gradient of the reducing zone. Sediments were equilibrated with As(III) or As(V) under deoxygenated conditions in synthetic groundwater. Batch-reacted sediments were examined by X-ray absorption spectroscopy (XAS) at the As, Fe, and Mn K-edges and compared with unreacted composite sediment. X-ray absorption near edge spectroscopy (XANES) was used to determine the arsenic oxidation state in the reacted sediments. Extended X-ray absorption fine structure (EXAFS) spectra were collected for two samples to confirm the sorption mechanism.

The As XANES spectrum of the unreacted sediment showed that all of the native As is present as As(V). Sediments reacted with As(V) solutions retained their As(V) speciation after sorption to sediment minerals, but sediments reacted with As(III) solutions showed evidence for oxidation from As(III) to As(V). With exposure to lower dissolved As(III) concentrations, most sorbed As was oxidized to As(V), but with exposure to higher concentrations most sorbed As remained as As(III). EXAFS results were consistent with adsorption of As as the primary mechanism of retention by sediment minerals. These results indicate that the sediment has a limited sorption and abiotic oxidation capacity for As. For sediments reacted with As(III) showing surface oxidation to As(V), the Mn XANES spectra indicate differences between unreacted sediments and the As(III)-reacted sediments consistent with increases in the proportion of reduced to oxidized Mn in the reacted sediment. Laboratory tests were also conducted in which sediments amended with a synthetic Mn(III, IV) oxide were equilibrated with As(III). These results clearly show an enhancement of the sediment's native capacity for As(III) oxidation.

BIOAVAILABILITY OF LEAD IN SMALL ARMS RANGE SOILS

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An estimated 2,000-3,000 military small arms ranges exist in the continental U.S., ranging in size from a few lanes to hundreds of firing lanes. These ranges are all commonly contaminated with lead (Pb) and copper (Cu) from copper-jacketed lead bullets. Bullets can be entire, fragmented, or oxidized, and risk assessment methods attempt to address the health and environmental effects of these varied forms. Ultimately, the metals are oxidized to compounds of Pb and Cu that interact with the soil particles, forming a potential vehicle for metal ingestion through soil adherence and hand-to-mouth activity. The main tool for human health risk assessment of these sites is the integrated exposure uptake biokinetic model (IEUBK) or adult lead methodology (ALM) (both to be replaced by the All Ages Lead Model) which both require a bioavailability term. The “gold standard” for RBA is the *in vivo* juvenile swine study, where animals are twice-daily-dosed with lead for 14 days and blood and tissue concentrations are used to calculate RBA. The resulting RBA is a comparison of lead absorbed from test soil to that of a similar amount of lead acetate, with the denominator lead acetate being considered 100% bioavailable. An alternative, less expensive method is the *in vitro* bioaccessibility method, which is a simple bench top surrogate for mammalian digestion that extracts lead from soil at pH 1.5 and compares it to the total lead in the sample. Considering the difference in complexity, these methods can agree remarkably well over a range of bioavailabilities. Final results of an ESTCP study entitled Validation of a Rapid and Low-Cost Method for Prediction of the Oral Bioavailability of Lead from Small Arms Range Soils (<http://www.estcp.org/projects/cleanup/200222o.cfm>) are presented. The study compared a well established *in vitro* method with the standard *in vivo* swine method using 8 soil samples from military small arms ranges across the continental United States. The methods agreed well, though an anticipated range of bioavailabilities was not observed, and high bioavailabilities were observed for all sites tested. All samples have been analyzed and the final report has been submitted.

SPECIES SENSITIVITY VARIATIONS IN AMPHIBIANS EXPOSED TO LEAD AND COPPER

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An evaluation of sediment-associated lead and copper toxicity, in the presence of physicochemical factors which have the potential to affect metals bioavailability, was conducted as part of ESTCP-funded project ER-0514 designed to develop standardized amphibian risk assessment protocols. One of the objectives of this program is to derive screening benchmarks for use in ecological risk assessments of wetlands. Lead and copper were selected as the constituents for this study since they are commonly co-located at military sites and ranges, and are often found at elevated concentrations in hydric soils at these sites. Dilution series sediment and hydric soil laboratory toxicity tests were conducted with northern leopard frog tadpoles (*Rana pipiens*). Exposure sediment was spiked with lead, copper, or mixtures of both metals. Relationships between metals concentration(s) and adverse effect were evaluated, and screening values and algorithms were developed to support screening level risk assessments. The predictive ability of the screening values developed through these tests was further evaluated through comparison of the laboratory data to (1) toxicity testing data in aged soils containing lead and copper from two demonstration wetland sites; (2) amphibian field survey data gathered from these demonstration sites. In order to better understand potential species sensitivity variation, toxicity tests using spiked soils were conducted on additional species including: *Rana palustris*, *Rana sylvaticus*, *Rana clamitans*, *Hyla chrysoscyllis*, *Ambystoma maculatum*, *Rana catesbeiana*, *Xenopus laevis*, *Xenopus tropicalis*, and *Rana utricularia*.

REACTIVE CAPPING MAT DEVELOPMENT

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The Navy is evaluating reactive core mat technology to sequester metals and organic contaminants in sediments as part of SERDP project ER-1493. The phased approach involves laboratory amendments evaluation, site selection, geotextile evaluation and composite mat evaluation.

Lab studies utilizing dilute solutions of metals and organics and various mixtures of organoclay, activated carbon and apatite in batch and flow through column experiments have been performed. Thirteen identified potential sites were narrowed to two primary sites based on chemical, physical, biological and logistical factors. These two primary sites are Cottonwood Bay in Dallas, Texas and Pearl Harbor in Honolulu, Hawaii. A primary site comparison was performed between each of these locations in terms of nature and extent of sediment contamination, groundwater flow parameters, management planning, logistics and ongoing remediation. A series of mat designs for field testing of geotextile behavior were selected and 14 small scale test mats have been constructed and deployed using various amendment combinations of apatite, activated carbon, organoclay and Ottawa sand. Modeling of cap performance based on variable permissivity characteristics was completed. Site surveys for specific mat placement areas were performed including bathymetry, sidescan, subbottom profiling, sediment profile imaging and vibracoring. A follow-up ground water monitoring study using a Trident probe is underway to determine specific placement of large scale mats. Results of these lab and field studies will be discussed in light of the design of large scale mats to be tested in the third year of the study.

THE EFFECT OF SOIL PROPERTIES ON TOXIC METAL BIOAVAILABILITY

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ESTCP-funded project ER-0517 capitalizes on the work of two previously funded SERDP projects to demonstrate the applicability of modeling based on soil properties and *in vitro* studies to make adjustments to bioavailability assumptions at metals contaminated soil sites. In order to demonstrate these principles, *in vivo* swine studies, *in vivo* ecological assays, *in vitro* studies, and soil properties modeling are being done. A workshop was held for scientists, regulators, and end users to discuss the state of the science of soil metal bioavailability and the needs of the regulatory and user community for making site decisions. Soils have been collected from 12 DoD sites. Collected soils are from various regions of the country and are contaminated with Pb, Cr, Cd, and/or As. Contaminated and control soils from each site have been homogenized and distributed to the various laboratories for testing. Mechanisms of enhanced metal sequestration and solid-phase metal speciation will be quantified using a variety of high-resolution surface spectroscopy techniques. Metal availability will be measured in site soils using several wet chemical methods and compared to modeled predictions. Bioassays of earthworms and plants are being done to determine metal bioavailability and toxicity. The immature swine model will be used to assess *in vivo* metal bioavailability. Finally, all of the data will be cross correlated and model validation will be undertaken based on both the results of this study and data from the supporting SERDP studies.

GRENADE RANGE MANAGEMENT USING LIME FOR DUAL ROLE OF METALS IMMOBILIZATION AND EXPLOSIVES TRANSFORMATION

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Currently, there is not an accepted technology available for management of explosives and metals in active grenade range soils using non-invasive techniques. The grenade range management project is based on the premises that increased alkalinity, caused by lime addition to the range soil, will result in: (1) significantly decreased water solubility of heavy metals present in the soils, and (2) base-catalyzed transformation of explosives that will eliminate migration of RDX- and TNT-based explosives from the range area. The effects of continued hand grenade range use and precipitation events will be addressed during in-situ lime treatment through surface and leachate water monitoring. Pre- and post-treatment assessments will consist of chemical analysis, soil characterization, contaminant leachability testing, and toxicity assessments at the demonstration site.

Treatability studies indicate that, at a pH of 11.5, the RDX- and TNT-based explosives are quickly transformed. The degradation of these base-induced transformation products continues via biotic and abiotic reactions, mineralization of greater than 75% can be achieved within a few weeks. Mesoscale lysimeter studies, where hydrated lime was applied to hand grenade range soils, were used to evaluate the technology prior to application in the field. The field demonstration is currently being conducted at the Fort Jackson, SC, Hand Grenade Range.

This poster will describe the research performed to date that is attempting to validate the long-term degradation of explosive contaminants and the immobilization of metals in the soil through the use of the in-situ application of lime on hand grenade ranges. A compilation of over 20 months of field data and preliminary results will be presented along with suggested comments for range managers on how to incorporate the grenade range management strategy.

Proactive management of grenade ranges will help to mitigate potential range closures that could significantly impair military training and mission readiness. The potential DoD cost for soil remediation also is reduced via in-situ treatment and through an elimination of explosives contaminant migration to water sources. This project is funded through ESTCP Project ER-0216.

MASS BALANCE EVALUATION OF MECHANO-CHEMICAL DESTRUCTION OF PCBs

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A supplemental treatability study (STS) was performed by Shaw Environmental, Inc. for the U.S. Navy BRAC Program Management Office to further evaluate Mechano-Chemical Destruction (MCD) treatment of PCB contaminants with post-MCD metals stabilization in soil from Hunters Point Shipyard (HPS). MCD treatment utilizes the high energy collisions of a ball mill to fracture soil constituents and produce reactive species on fresh mineral surfaces. The radicals generated react with PCBs and other organic molecules yielding amorphous carbon and inorganic salts.

An initial MCD treatability study was performed in 2006 which proved the technology successful in reducing Arochlor 1260 concentrations from over 100 mg/kg to less than 1 mg/kg in less than 15 minutes of treatment. The concentrations of pesticides DDT and dieldrin were also reduced by more than 99%. However accounting for the complete destruction to amorphous carbon and salts could not be confirmed with the analytical data. Furthermore the post-MCD metals stabilization with Apatite II was only moderately successful, passing TCLP but not STLC procedures for lead.

The focus of the STS was to obtain additional data required to more completely evaluate the effectiveness of the MCD technology. The additional data included:

- Mass balance for the organic chemicals of concern
- Evaluation of potential organic compound volatilization during the MCD process
- Evaluation of transformation products potentially generated during the MCD process
- Stabilization of metals in the MCD-treated soils

Seven separate samples were run through the MCD reactor with extensive analytical data taken on the soil before and after treatment, and analysis of the off-gas during system operation. The analyses performed included: TOC, TOX, total chloride, chlorine and HCl vapor, pesticides, PCB congeners, dioxins and furans (total and isomer-specific), VOCs, SVOCs, TIC, TPH, and metals. Wipe sampling was performed on the reactor internals after one of the trials for additional mass balance data. Post-MCD stabilization of lead using Portland cement at three weight ratios was evaluated by TCLP and STLC.

CHARACTERIZATION AND TREATABILITY OF Pb, Cu AND Zn IN BACKSTOPS SOILS OF FOUR CANADIAN SMALL ARM SHOOTING RANGES

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There are more than 250 small arm shooting ranges on Canadian Force Bases across Canada. The purpose of this study is to assess the environmental impacts of the small arm firing ranges on soil and groundwater. Backstop soils in small arm shooting ranges at four Canadian Forces Bases located in Alberta, Manitoba, New-Brunswick, and Québec were sampled and characterized. Embankments soils were characterized in order to establish their grain size distribution, and the Pb, Cu and Zn concentrations in 9 size fractions (SF). The results showed that at every bases, all 9 SF were contaminated in Pb, in many cases in Cu and to a lesser extent, in Zn over the acceptable maximal concentration level guidelines given by the Canadian Council of Ministers of the Environment (CCME) for commercial and industrial uses (Pb: 600 mg/kg; Cu: 91 mg/kg; Zn: 360 mg/kg), and the commercial «C» criterion of the Québec Ministry of Environment (Pb: 1000 mg/kg; Cu: 500 mg/kg; Zn: 1500 mg/kg). The 9 SF were then combined in 4 SF (>2000 µm, 500-2000 µm, 53-500 µm, and <53 µm) in order to test the effectiveness of three different soil treatment apparatus, the Jig, the Wilfley table and the Multi Gravimetric Separator (MGS). Preliminary results obtained with the Wilfley table treatment assays on the 53-500 µm SF showed that 74% to 93% of the original Pb concentration was removed, indicating that gravimetric separation methods can remediate these soils. Hazardous character of the soils was established with the TCLP (Toxicity Characteristic Leaching Procedure), SPLP (Synthetic Precipitation Leaching Procedure), and the GJST (Gastric Juice Simulation Test) lixiviation tests. TCLP and SPLP simulate buffered landfill and unbuffered acid rain leachates respectively, and GJST estimates the amount of Pb transferred to the human organism if Pb-contaminated soils were ingested. Results showed that the TCLP mobilized more than 100 times Pb than the acceptable concentration limit of 5 mg/L. SPLP and GJST mobilized 0,58 to 12 mg/L Pb, and 282 to 2090 mg/L Pb, respectively. This indicates that these soils are potentially dangerous. Scanning electron microscope (SEM) investigation showed that metals are mostly present in the form of altered free particles in the soils. Principle alterations of Pb, Cu or Zn particles are carbonation, oxidation and to a lesser extent silicification. Detailed soil sampling of a backstop showed that 6% of the total soil volume is contaminated in Pb.

PRECIPITATION OF ARSENIC UNDER SULFATE REDUCING CONDITIONS AND SUBSEQUENT LEACHING UNDER AEROBIC CONDITIONS

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The precipitation of dissolved metals in groundwater under anaerobic conditions has been the subject of numerous studies, but there has been very limited research on the mineralogy and the stability of these precipitates under variable geochemical conditions. Examining the mineralogy and establishing the rate of dissolution of these precipitates under aerobic conditions is the subject of this SERDP (Project # ER-1373) supported research. A field research site was established at Site No. ST-65, a former refueling area at the AvonPark Air Force Range in Florida. Sediment and groundwater were collected from the area with the highest concentration of As in groundwater (1,800 ppb) and were used to construct four flow-through columns. In these experiments indigenous sulfate reducing bacteria were stimulated with injections of lactate, ethanol, ferrous iron and sulfate over a period of several months under strictly anaerobic conditions. Arsenate, lactate, ethanol, ferrous iron and sulfate concentrations diminished and sulfide was produced during these injections. Examination of the sediment from a sacrificed column revealed a mixture of iron sulfides, iron hydroxides, sulfur and phosphate as well as As concentrations that were 10x greater than in the original sediment. Speciation by XANES spectroscopy of column sediments detected primarily As-bearing sulfides, including orpiment, arsenopyrite and realgar. Aerobic natural and artificial water was then passed through one of these columns for a period of five months. The results of the column studies demonstrated that we can successfully sequester As under anaerobic, sulfate-reducing conditions, and that the precipitated As sulfide is resistant to dissolution under aerobic conditions. Both a mass balance approach and a modeling approach were used to calculate the percentage of As liberated with the introduction of fully aerated groundwater. By the mass balance approach only 3% of the sequestered As was dissolved, whereas the modeling results indicated approximately 2% was liberated after 116 pore volumes of aerobic groundwater had passed through the column. For many subsurface environments the groundwater is naturally anaerobic and sulfidic and for these environments the sequestration of As would be an effective and permanent solution. For aquifers that are naturally aerobic or where the anaerobic conditions are temporary due to a high organic load, the transition to fully aerobic conditions will be gradual and not expected to cause a significant amount of As release in the presence of sulfate. A small-scale field pilot demonstration is currently being planned for this technology at ST-65.

DEMONSTRATION AND VALIDATION OF A REGENERATED CELLULOSE DIALYSIS MEMBRANE DIFFUSION SAMPLER FOR MONITORING GROUND-WATER QUALITY AND REMEDIATION PROGRESS AT DOD SITES

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Dialysis membrane diffusion samplers are a promising alternative type of diffusion sampler. These samplers are made of regenerated-cellulose dialysis membrane material and have an advantage over Polyethylene diffusion bag (PDB) samplers in that they can be used for both dissolved inorganic and dissolved organic chemicals (volatile/nonvolatile) sampling in ground water. PDB samplers have been validated for the measurement of most volatile organic compounds (VOCs). However, PDBs are limited in sampling all VOCs or any common soluble inorganic constituents. Recently developed in-well dialysis membrane diffusion samplers show promise for greatly reducing monitoring costs by eliminating much of the time needed at the well head and by minimizing the production/treatment of purge water.

The objectives of this project are to demonstrate and validate in coordination with the Interstate Technology and Regulatory Council (ITRC) how long it takes for dialysis membrane diffusion samplers to equilibrate with ground-water concentrations of a range of inorganic and organic constituents and to compare the results of field samples collected using these samplers with samples collected using the standard low-flow purging technique. Bench-scale testing has shown that dialysis samplers equilibrated within 3-7 days for most cations and trace metals and within 1-3 days for anions, silica, methane, dissolved organic carbon, and all VOCs (including MTBE). Dialysis samplers equilibrated in essentially the same time period at lower concentrations as they did at higher concentrations. Lower temperatures were found to have a small affect in lengthening equilibrium times for several inorganic constituents from 3 days to 7 days. Ground-water temperatures across the continental U.S. vary within the boundaries of the temperatures tested so these findings should have transfer value to most sampling locations. Field-comparison testing has shown high correlations between the concentrations of most inorganic and organic parameters collected with dialysis samplers and the concentrations of these same constituents collected with low-flow purging. Comparability is best when the dialysis sampler is positioned at the depth of the highest mass flux of a contaminant into the screened or open interval of a well. The ITRC Diffusion Sampling Team is currently publishing a new Tech Reg document, which will include the protocols of using Dialysis membrane diffusion samplers. The project has recently expanded to include testing the Dialysis membrane diffusion sampler on Perchlorate and Ordnance compounds. Currently bench scale testing and field comparison sampling are underway.

BIORED: BIOMARKERS AND TOOLS FOR REDUCTIVE DECHLORINATION SITE ASSESSMENT, MONITORING, AND MANAGEMENT

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Reductive dechlorination plays a major role in the transformation and detoxification of chloroorganic pollutants, including chlorinated ethenes. Biostimulation alone or in combination with bioaugmentation have emerged as viable plume and source zone bioremediation strategies. Crucial for the success of bioremediation are prognostic tools for site assessment prior to technology implementation and diagnostic tools for process performance monitoring. The value of molecular biological tools (MBTs) for remediation applications has been demonstrated but the current tools provide only a snapshot of the microbial community contributing to contaminant detoxification. To address the current MBT limitations, SERDP ER-1586 aims at identifying novel reductive dechlorination biomarker genes and developing MBTs that improve our understanding of target gene diversity, presence, abundance, and expression, and thus, contaminant detoxification. Three complementary microarray approaches, including *Dehalococcoides* whole genome arrays, KB-1 shotgun arrays, and the RDase array, which contains oligonucleotide probes targeting all currently known bacterial reductive dehalogenase (RDase) genes, are being used to identify genes that respond to contaminant exposure. Following biomarker gene identification and assignment of function to RDase genes, quantitative real-time PCR (qPCR) assays will be designed, and multiplex (mqPCR) applications will allow for simultaneous detection of multiple biomarker targets to reduce the cost of the analysis. DNA-based MBTs provide information about the presence and abundance of biomarker genes but this analysis cannot provide activity (i.e., rate) information. Hence, we are applying fluorescence in situ hybridization techniques (FISH) for visualization and quantification of active target bacteria, and we are developing approaches that correlate quantitative DNA (i.e., gene) and quantitative RNA (i.e., transcript) data with measured dechlorination rate information. This comprehensive approach will be developed in laboratory systems and subsequently validated with samples from field sites undergoing bioremediation treatment. Ultimately, the information provided by the new tools will allow site management decisions based on predictable science rather than empirical practice.

EX SITU SOIL REMEDIATION OF BOTH ARSENIC AND CYANIDE CONTAMINATION

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Activities at Montenay Power Corporation site in Miami, Florida resulted in high concentrations of cyanide and arsenate compounds. Our unique method of soil remediation utilizes a novel, nontoxic aluminum complex which both oxidizes and reduces contaminants, decomposing them into their elemental components. This occurs, by adjusting pH and temperature at the time of addition to the soil, resulting in a reaction releasing large amounts of charged complex. Remediation Approach The approach taken was to demonstrate effective reduction in levels of cyanide and arsenate on the bench top then adapt a system to treat the entire 14 acre site by ex situ methods to guarantee complete treatment to a 4 foot depth. Soil was excavated and placed on a conveyor belt. While the conveyor was moving at a very slow speed our proprietary decontaminating liquid was allowed to soak into the soil via controlled drip method. The soil moved over a 4 hour period on the conveyor after which it was placed on the ground to dry. All effected areas of the property were excavated and treated using this method regardless of the degree of contamination. One thousand four hundred (1,400) gallons of decontaminating liquid were used to treat the 14 acre site. Results Effective and dramatic reductions to levels below detectable by reference laboratory in both cyanide and arsenate levels. Conclusion Case study proving a safe nontoxic method of soil remediation of organic and nonorganic compounds. Method may be adapted to both insitu and exsitu approaches to soil remediation.

OSCILLATORY PRESSURE WAVES AS ENERGY SOURCE FOR HYDRAULIC TOMOGRAPHY

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Oscillatory pressure waves have been generated in the field and used as an energy source for tomographic investigation of the hydraulic conductivity distribution between source and receiver wells. A mathematical and numerical framework is needed to interpret this field data. Theory for a homogeneous aquifer predicts that the amplitude should decay exponentially with radial distance and the phase shift should increase linearly with radial distance. Both the exponential decay coefficient and the phase shift should vary inversely with the square root of the hydraulic conductivity. A logical extension of this simple theory to heterogeneous aquifer systems suggests the hydraulic conductivity should be replaced with the spatially averaged value over the ray path of interest. Since analytical solutions are not available, modeling studies have been applied to test this hypothesis. Plotting numerical model results and the straight ray path approximation for heterogeneous situations indicates very good agreement. There is some difference but it is generally small except near the upper and lower model boundaries which are assumed to be impermeable by the numerical model. The straight ray approximation is for an infinite aquifer; so, differences at these boundaries are to be expected. Image theory could probably be used to correct the ray path approximation for the presence of finite boundaries. The validity of the straight ray approximation makes the inversion of data much easier, since no nonlinear iterative methods must be used. The least squares fitting of the data to the hydraulic conductivity distribution can be reduced to a set of linear equations, if the region between the source and receiver is described by a pixilation of nodes and elements. The Singular Value Decomposition (SVD) method is used to solve these equations efficiently. Theoretical results indicate that layers and blocks of differing hydraulic conductivity with dimensions of about one meter (3 feet) or more should be resolvable. We are currently processing field data using these techniques and will present preliminary results of that work. At this point, the use of oscillatory pressure waves for hydraulic tomographic reconstruction of hydraulic conductivity distributions looks promising. This work funded by the Strategic Environmental Research and Development Program (SERDP) as project ER-1367.

TOOLS FOR LONG-TERM GROUNDWATER MONITORING OPTIMIZATION: IMPROVING GTS

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Because long-term groundwater monitoring (LTM) is required across DoD and government sites, yet very costly (the Air Force alone spent almost \$25 million in 2005), AFCEE is upgrading and improving its software implementation of the Geostatistical Temporal-Spatial (GTS) LTM optimization scheme under ESTCP Project ER-0714. By enhancing the current beta GTS interface into a fully-featured software technology, AFCEE will (a) promote widespread adoption of statistically-based LTM optimization efforts across DoD and government facilities; (b) accelerate and promote transfer of GTS as a free, public domain software technology to analysts, site managers, and consultants; (c) incorporate site-specific flow regime information into the GTS mapping capability; and (d) demonstrate the applicability, usability, and effectiveness of an enhanced GTS software interface at sites representing multiple branches of DoD. GTS is a statistical and geostatistical decision-logic groundwater monitoring optimization algorithm. It uses a novel combination of statistical techniques to answer two questions given an existing LTM network: (1) what is the optimum number and placement of wells in that network (i.e., is there spatial redundancy and/or is there lack of coverage within the spatial network)?; and (2) what is the optimal sampling frequency for wells in the network (i.e., is there temporal redundancy)? GTS is designed to balance some of the practical and scientific difficulties inherent in optimization schemes, namely, how to perform a scientifically defensible optimization analysis without requiring substantial involvement from hydrogeologic and/or statistical or mathematical experts. The software has several state-of-the-art statistical and geostatistical analytical routines built-in, all tailored to LTM optimization, yet woven into a user-interface designed to smartly guide the user through a complex series of analyses. Because the GTS software is designed to be used without site-specific coding or specialized programming, the updated user interface and software is being tested at a variety of sites and hydrogeological environments. The improved GTS software will allow development of more resource-effective LTM programs: (1) reduced sampling frequency and minimized spatial redundancy in existing networks, (2) statistically defensible addition of new wells to better characterize contaminant plumes, and (3) trend mapping and trend flagging to better monitor changes over time in site conditions and to identify new anomalies or unexpected sampling results. Projected annualized and life-of-project cost savings from implementation of a GTS-optimized program at a given site can be significant, in the range of 30%-60%. (ESTCP Project ER-0714)

THE ARSENIC IN GROUNDWATER AND ARSENIASIS FROM THE HETAO AREA, INNER MONGOLIA

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In Hetao Area, Inner Mongolia, China, Quarternary alluvial aquifers used for public water supply are contaminated by naturally occurring arsenic, which is heavily affecting the health of the 300,000 people there and is the area of heaviest poisoning and most people effected in China arseniasis. A lot of efforts to improve drink water have been carried out since 1990s. But the arsenic effects for resident health cannot be avoided effectively. This indicates that the cognition, which the arsenic is derived from rich arsenic aquifers formed under the anoxic conditions, for arsenic contamination in the groundwater in Hetao Area may not be right. Our study shows that the contaminant derives from the upper reaches where groundwater is high in arsenic. The concentration of As in the water reduces from 0.251 ml/L to 0.005 ml/L along the working line by 44 km. Arsenic concentration in the soil varies gradually at the working lines along the flow direction as follows: from 22.0 mg/kg to 9.6 mg/kg, from 20.0 mg/kg to 7.9 mg/kg', and from 18.0 mg/kg to 9.9 mg/kg at work lines by 52, 68, and 40 km respectively. Strontium isotope data of well water, which is used for drinking by residents, and the variation of arsenic levels in resident people hair suggest that mobilization of the arsenic from the upper reaches, front Yin Mountains, to the alluvial aquifers of the lower reaches may be responsible for the current health crisis of resident arseniasis. Potential solutions should be: the treatment of mining water before drainage in upper reaches, finding groundwater in too depth to be reached by rich arsenic water from mining and weathering in upper reaches or the groundwater under aquifuge stratum, and treatment of groundwater as drinking water at the point of use or in the water supply plant.

Key Words: Arsenic poisoning; Groundwater; The Hetao Area, Inner Mongolia

KINETICS OF REDUCTIVE DECHLORINATION OF PCDD/FS BY A DEHALOCOCCOIDES-CONTAINING CULTURE

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Kinetics of dechlorination of PCDD/FS by a mixed culture containing *Dehalococcoides* *ethenogenes* strain 195 was investigated. Microcosms were spiked with 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TeCDD) at 62 μM , 31 μM , 3.1 μM and 0.31 μM , a concentration range across 3 orders of magnitude. 1,2,3,4,7,8-hexachlorodibenzofuran (1,2,3,4,7,8-HxCDF) was added at 5 μM .

Dechlorination of 1,2,3,4-TeCDD occurred at all concentrations, and the rate varied according to the 1,2,3,4-TeCDD concentration. The culture transformed 68-79% of the 1,2,3,4-TeCDD at all concentrations except 0.31 μM . The transformation rate was proportional to the substrate concentrations, and exhibited first order characteristics. At 0.31 μM , only 4% of the 1,2,3,4-TeCDD was dechlorinated in four months. The first order reaction rate constants were 0.0024 ± 0.0003 , 0.0019 ± 0.0001 , 0.0023 ± 0.0006 , $0.00019 \pm 0.00004 \text{ day}^{-1}$ for initial concentrations of 62 μM , 31 μM , 3.1 μM and 0.31 μM , respectively. 1,2,3,4-TeCDD was transformed to 1,2,4-trichlorodibenzo-*p*-dioxin (1,2,4-TrCDD) then to 1,3-dichlorodibenzo-*p*-dioxin (1,3-DCDD). The 1,2,4-TrCDD and 1,3-DCDD were detected in the cultures amended with 62 μM , 31 μM , and 3.1 μM 1,2,3,4-TeCDD. However the dechlorination of 1,2,3,4-TeCDD did not proceed beyond 1,2,4-TrCDD when the concentration of 1,2,3,4-TeCDD was 0.31 μM .

The culture dechlorinated 1,2,3,4,7,8-HxCDF to 1,3,4,7,8-pentachlorodibenzofuran (PeCDF) and 1,2,4,7,8-(PeCDF), and, when co-amended with 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), further to two tetrachlorodibenzofuran (TeCDF) congeners, identified as 1,3,7,8-TeCDF and 1,2,4,8-TeCDF. After 195 days, the treatment amended with 1,2,3,4-TeCB contained $57.6 \pm 1.5 \text{ mol } \%$ 1,2,3,4,7,8-HxCDF; $32.2 \pm 0.7 \text{ mol } \%$ PeCDFs; and $5.8 \pm 0.4 \text{ mol } \%$ 1,3,7,8-TeCDF and $4.4 \pm 0.4 \text{ mol } \%$ 1,2,4,8-TeCDF. In the bottles spiked only with 1,2,3,4,7,8-HxCDF, the mole percents at day 195 were $87.2 \pm 0.7\%$, $12.1 \pm 0.4\%$, and $0.3 \pm 0.2\%$ and $0.3 \pm 0.1\%$, for 1,2,3,4,7,8-HxCDF, the PeCDF congeners and the two TeCDF congeners, respectively. Similarly, the final mole percents in the treatment amended with PCE were $84.1 \pm 4.4\%$, $15.5 \pm 4.2\%$, $0.3 \pm 0.1\%$, and $0.2 \pm 0.0\%$ for the parent compound, intermediates and final products. In cultures amended with 1,2,3,4,7,8-HxCDF alone, the first order rate constant was 0.0031 ± 0.0012 , for 1,2,3,4,7,8-HxCDF plus PCE the rate was 0.0028 ± 0.0006 , and the rate for 1,2,3,4,7,8-HxCDF plus 1,2,3,4-tetrachlorobenzene was $0.0047 \pm 0.0010 \text{ day}^{-1}$. Addition of 1,2,3,4-TeCB enhanced both the rate and the extent of dechlorination of 1,2,3,4,7,8-HxCDF.

ADAPTIVE LONG-TERM MONITORING AT ENVIRONMENTAL RESTORATION SITES

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The objective of this project is to demonstrate and validate the use of the recently developed Summit monitoring tools for reducing costs and improving effectiveness of long-term monitoring (LTM) through adaptive assessment while achieving remediation goals. These tools will allow performance assessment relative to site-wide remediation targets (e.g., assessing plume stability), reduce redundancy in LTM data, and identify where and when additional data may be most beneficial to reducing uncertainties regarding performance. A secondary objective is to compare the results with the Monitoring and Remediation Optimization Software (MAROS), which is currently available for monitoring optimization.

This ESTCP project (ER-0629) was started by Naval Facilities Engineering Service Center and partners in FY 06. The project includes Dem/Val at three DoD sites. The first dem/val is at the Camp Allen Landfill, Norfolk Naval Base, and the findings are presented in this poster session.

There are three components that comprise the Summit monitoring tools. The first, Model Builder, creates geostatistical or statistical models of spatial and temporal data. The second, Sampling Optimizer, identifies redundant sampling locations and frequencies in historical data, and also highlights areas of significant data uncertainty that may benefit from additional sampling. The third, Data Tracker, enables users to create time-dependent site-wide remediation targets (e.g., reductions in mass) or well-specific targets (e.g., concentration trends) and evaluate new data relative to those targets, providing automated alerts of unexpected deviations.

At the Camp Allen Landfill, two aquifer systems are impacted by contamination: the shallow aquifer and the underlying deep aquifer. The optimization for selection of sampling locations and/or frequency was performed simultaneously for three COCs (cis-1,2-DCE, TCE, and VC). The optimization results are in the form of “tradeoff curves” associated with two competing objectives: (1) minimize the number of sampling locations; and (2) minimize the maximum concentrations errors at the “plume boundary sampling points” that result from removing specific sampling locations. Constraints limit the maximum error in the core portion of plume. For comparison purpose, MAROS was also applied at Camp Allen Landfill, to compare results where such comparisons can be made, and to establish where comparison of results is not possible because of differences in the software applicability or functionality.

DEMONSTRATION OF THE SNAP SAMPLER PASSIVE GROUND WATER SAMPLING DEVICE FOR INORGANIC ANALYTES

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Passive (no-purge) sampling techniques have been gaining acceptance by the scientific and regulatory community for many ground water sampling applications. Where the use of this sampling technology is appropriate, data-quality improvements and cost reductions can be achieved. However, most passive diffusion samplers have limitations. For example, the PDB sampler can be used only for selected VOCs, and the dialysis membrane sampler cannot be used for long deployments because the membrane can undergo biodegradation.

In contrast, grab-type passive samplers, such as the Snap Sampler, can be used to sample for a wide spectrum of analyte types and, unlike diffusion-based passive samplers, can provide a sample in real time. The Snap Sampler collects a whole water sample from the screened portion of the well that is under *in-situ* conditions.

The objectives of this ESTCP-sponsored project were to demonstrate that passive sampling, and especially the Snap Sampler, can provide technically defensible analytical data for a wide spectrum of analytes, and to demonstrate the utility and potential cost savings of this technology.

The research plan for this demonstration was to collect samples at five sites with (1) the Snap Sampler, (2) low-flow purging and sampling, and (3) other passive diffusion samplers (as appropriate). Analytes of interest at these sites include VOCs, explosives, perchlorate, metals, and natural attenuation parameters.

This poster presents the results from our first test site, Pease Air Force Base (AFB) near Portsmouth, New Hampshire. The analytes of interest at this site were several inorganic analytes including metals. Eight 4-inch-diameter wells were selected for this study. Prior to this demonstration, the flow in each of the wells was characterized and the presence of possible vertical stratification of the analytes was determined.

For this demonstration, there were ten sampling events. For each sampling event, the following samples were collected from each well: two Snap Sampler samples (filtered and unfiltered), two low-flow samples (filtered and unfiltered), and a dialysis membrane sample. The Snap Samplers and the dialysis membrane samplers were deployed at a depth that matched the depth of the pump intake (as closely as possible). Collecting both filtered and unfiltered samples allowed us to compare colloidal-borne and dissolved metal species.

MASS FLUX DISTRIBUTION USING THE HIGH-RESOLUTION PIEZOCONE AND GMS

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Understanding ground water flow pathways, gradients, and contaminant mass flux distribution is essential for proper remedial design, risk determination, and evaluation of remediation effectiveness. Conventional long-screened wells are not adequate for determining ground water and contaminant flow pathways in three dimensions. Therefore, flux distribution estimates resulting from non-discreet well measurements can be flawed. The objective of this project is to demonstrate the use of the high-resolution piezocone direct push sensor probe to determine direction and rate of ground water flow in three dimensions. Field measured hydraulic conductivity, head, effective porosity and calculated seepage velocity distributions can be estimated through interpolation methods recently incorporated into Groundwater Modeling System. Following chemical concentration data collection, these innovative data processing approaches allow for the determination of flux distributions at resolutions and spatial configurations never before available. Under the aegis of ER-0421, field scale data collection, interpolation, and modeling results from deployment at a site in Port Hueneme, California, will be presented and discussed.

OPTIMIZED ENHANCED BIOREMEDIATION THROUGH 4D GEOPHYSICAL MONITORING AND AUTONOMOUS DATA COLLECTION, PROCESSING AND ANALYSIS

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Under ESTCP Project ER-0717, a demonstration/validation of a Hydrogeophysical Performance Monitoring System (HPMS) will be conducted to provide timely, actionable information to site managers on the processes associated with enhanced bioremediation. This system will allow for the near real-time monitoring of amendments, such as vegetable oil, molasses, etc., injected into an existing groundwater contamination plume (e.g., TCE, DCE, etc.). The HPMS system utilizes autonomous and automated acquired hydrological and electrical geophysical datasets. These datasets are automatically QA/QCed and imported in a relational database. Subsequently web accessible tools allow for automated data processing and result delivery, both on demand and automatically. The latter are constructed as modular distributed software components (e.g., for data retrieval, data validation and graphing) which are executed by configurable workflows which chain these elements together.

The demonstration/validation of the HPMS system will be done at the Andrews AFB Brandywine DRMO site, in the context of a large ongoing enhanced bioremediation effort. While deployment of this system at the selected test site is in the early stages (full system operability is expected in November 2007), several important components of this system are already operational and will be discussed in out poster. These include:

- A suite of formal QA rules for the automated validation of autonomously and automatically collected time series data, coupled with a software backend for the QC implementation. These rules build upon prior work by NOAA, USGS, and other federal agencies, but extend this work by taking in to account the existence of multisensor data
- An integrated database structure which can accommodate relevant site data including weather data, soil and aqueous chemistry data and geophysical and hydrological data. Associated with this are tools for data import and export to 3rd party applications
- Web based analysis tools for electrical geophysical data which provide for near real time analysis of novel data
- A parallelized 3D electrical geophysical inverse code which will allow for rapid, near real time inversion of novel electrical geophysical data

IMPROVED MANAGEMENT OF GROUNDWATER CONTAMINANT RISKS USING DYNAMIC, MODEL-BASED FUSION OF HYDROLOGIC PROCESSES AND ELECTRICAL RESISTIVITY SURVEYS

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Electrical resistivity imaging (ERI) holds great promise for managing groundwater contaminant risk and improving remediation efforts. This potential has previously been demonstrated at sites where ERI successfully identified spatially distributed source zones and complex geologic heterogeneities affecting flow and transport. This static approach to imaging is limited, however, given that the transport of contaminants is critically dependent on dynamic multi-scale processes that lead to the chemical and physical evolution of a plume through time. We are pioneering innovative new technologies for the collection and analysis of electrical resistivity data that adaptively couples hydrogeologic processes to geophysical observations in an effort to produce the next generation of in-situ contaminant characterization and management tools.

Static ERI inversion techniques require thousands of individual resistivity measurements to yield ‘fuzzy’ pictures of the subsurface that are notoriously difficult to use for quantitative hydrogeologic interpretation. In contrast, a single resistivity measurement may contain a significant amount of information about changes in the state of a contaminated aquifer through time. We take advantage of the transport constraints imposed by physics through coupling of real-time hydrogeologic modeling with the adaptive acquisition of electrical resistivity measurements. Our approach is revolutionary in its ability to (i) improve accuracy in the characterization of contaminant distribution and migration by constraining geophysical interpretation by the physics of groundwater flow and transport, (ii) monitor highly transient processes because the volume of data acquired is minimized, and (iii) assess predictive uncertainty in contaminant behavior by directly linking hydrologic process and parameters to geophysical data. We demonstrate the power of our new integrated data fusion approach by presenting a simple synthetic case study of a saline tracer test. The results indicate that our approach can yield more accurate estimates of the evolution of a contaminant in a homogeneous aquifer using orders of magnitude fewer resistivity measurements compared to traditional time-lapse imaging by static ERI. Our approach also goes beyond the current capabilities of ERI by automatically providing estimates of transport properties (e.g., hydraulic conductivity and dispersivity) that are required for the design of contaminant management strategies.

CONTAMINANT MASS TRANSFER DURING BOILING IN FRACTURED GEOLOGIC MEDIA

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Many sites contaminated with chlorinated volatile organic compounds (CVOCs) are underlain by fractured rocks or soils with significant matrix porosity. Remediation options for treating these sites are limited because low matrix permeability and unknown fracture locations make the delivery or recovery of fluids a challenge. Thermal methods hold promise because the mechanisms of thermal conduction and electrical resistance heating can efficiently transfer heat without any fluid flow. Once a fractured rock or soil is heated above the water boiling point, subsequent depressurization of the fracture network by vacuum extraction may induce boiling in the matrix, leading to large gas-phase pressure gradients and a steam stripping effect that can remove volatile contaminants from the matrix.

Preliminary simulations were conducted using T2VOC to evaluate the combination of heating and depressurization as a mechanism for TCE removal from an idealized fracture/matrix system. Three different sets of gas-liquid relative permeability curves were considered in the simulations, and the results depend strongly on the details of these curves. When gas is immobile compared to liquid water, boiling in the rock matrix results in a volume change that pushes the liquid water out of the matrix and into the fracture where it boils. This mode of boiling results in essentially no removal of the TCE from the matrix, even after 60 days. In contrast, when the liquid water is assumed to be nearly immobile but the gas is mobile, boiling occurs in the rock matrix and creates a strong steam stripping effect that removes all of the TCE from the matrix in roughly 3 days. When realistic Brooks-Corey type gas and liquid phase relative permeability curves are used, TCE concentrations are predicted to fall by 3 to 4 orders of magnitude during several weeks of boiling.

The results of the analyses are encouraging, and they show that multiphase fluid flows have a major influence on the boiling process and subsequent contaminant mass transfer. To better understand these processes, we have recently initiated a project funded through SERDP (ER-1553) that involves conducting a series of laboratory experiments, where contaminated cores of different materials are heated and depressurized while detailed monitoring is taking place. The results of the experiments will be evaluated with theoretical analyses, which will then be used to evaluate field-scale implementation at contaminated sites.

EFFECTS OF BIOGEOCHEMICAL FACTORS ON THE PERFORMANCE OF IN SITU ACTIVATED CARBON SEDIMENT CAPS FOR PCB SEQUESTRATION

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Activated carbon (AC) amended geotextiles have been proposed as an in situ capping material for PCB-contaminated sediments due to their high adsorption capacity and ability to be easily installed in natural systems. In this research effort, we address critical research gaps in the development and application of this technology.

PCB-AC capacities and competing solutes (i.e., dissolved organic matter (DOM) and biofilms) may affect the lifetime of the cap. In this laboratory study, equilibrium adsorption capacities of 9 PCB congeners were determined on virgin, DOM- and biofilm-loaded AC using a previously developed solid-phase partitioning technique with polyoxymethylene. PCBs showed extremely high equilibrium adsorption capacities on AC and fit the Freundlich equation over the environmentally relevant range of aqueous concentrations studied (0.1- to 1,000-ng/L). Planarity effects were evident at low aqueous concentrations (<10 ng/L), where adsorption of three PCB congeners with similar hydrophobicities decreased with increasing number of ortho-chlorines, indicating steric hindrances attenuated adsorption. Despite that DOM and biofilm loadings on AC decreased PCB equilibrium adsorption capacities by an average of one order of magnitude, the Freundlich parameters remained large enough to suggest that AC would still be an effective material to sequester PCBs in sediment caps. As such, the comparatively time consuming task of evaluating PCB-AC reaction kinetics under the low flow conditions typical in sediment caps became a worthwhile endeavor.

Fixed-bed PCB-AC column studies were performed with organic-free and synthetic Suwannee River water to illustrate the potential importance of reaction kinetics under sediment capping conditions. Ongoing rapid small-scale column tests (RSSCTs) with organic-free water indicate that PCB effluent concentrations are adhering to breakthrough profiles predicted based on the equilibrium isotherm parameters even at very high approach velocities (equivalent to 500 cm/day in full-scale systems). However, RSSCTs with synthetic Suwannee River DOM at these high approach velocities show incipient breakthrough of all 9 PCB congeners, indicating kinetic limitations for PCB adsorption could compromise cap integrity under in situ conditions where DOM is present. This poster will also include results from upcoming RSSCTs at lower (more realistic) approach velocities with DOM-laden water and a preliminary assessment of the technical feasibility of AC-amended sediment caps under in situ conditions.

PAH TRANSPORT THROUGH SEDIMENT CAPS WITH AND WITHOUT SORBENT AMENDMENTS

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Sediment capping is a common remediation strategy for contaminated sediments. Many contaminated marine sediment sites reside in shallow, coastal areas that are often impacted by advective processes such as groundwater flow, tidal pumping, and wave pumping. These processes can contribute to the total flux of contaminants through sediments and ultimately through a sediment cap. In this research, experimental column studies were combined with novel analytical techniques and numerical modeling to build on the current knowledge of contaminant transport through caps.

Glass columns (44 inches long, 2 inches inner diameter) were constructed with six equally spaced sampling ports. Approximately six inches of sediment, contaminated with creosote from a former wood treatment facility in Eagle Harbor, WA, was placed at the base of the columns. The experimental cap was constructed with a 2 ft layer of clean capping material obtained from an existing cap at Eagle Harbor.

Small volume (1.5 ml) pore water samples were collected from the six ports and ten polycyclic aromatic hydrocarbons (PAHs) were measured using solid phase micro-extraction (SPME) followed by gas chromatography and mass spectrometry. With a flow rate of approximately 25 ml/hour through the columns, breakthrough of PAHs was observed after 5 days (3 bed volumes) of column operation with the native cap. After 76 days of operation (47 Bed Volumes), low molecular weight PAHs were depleted in the sediment pore water. The dissolution of high molecular weight PAHs increased with time as their mole fraction increased in the creosote phase. The performance of the standard cap was compared with similar columns constructed with capping material that was amended with activated carbon or natural organic matter in the form of peat moss. With 2% (wt.) granular activated carbon (GAC) added to the capping material, the column did not show breakthrough even after 2 months of operation (42 bed volumes). Experimental results from the amended and unamended column studies will be presented in this poster. Results from this investigation are being used to enhance the scientific and engineering principles of capping and establishing design criteria that account for processes governing vertical contaminant migration through sediment caps. This research is being conducted as part of a larger SERDP-funded research project titled: Characterization of Contaminant Transport Potential Through In-Place Sediment Caps (ER-1370).

IN SITU REMEDIATION OF METAL AND ORGANIC POLLUTANTS IN SEDIMENTS USING SORBENT AMENDMENTS

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Impacted sediments often contain a mixture of organic and heavy metal contaminants that pose a threat to the ecosystem and human health. The bioavailability of these toxic chemicals in sediments depends on sediment geochemistry and binding characteristics that are specific for a particular site and contaminant. Contaminant bioavailability can be reduced if the pore water concentrations are lowered. This can be achieved by increased binding or assimilation into the organic or inorganic sediment matrices. Previous research has evaluated the addition of single amendments to sediments to stabilize distinct classes of contaminants and reduce their bioavailability, either by chemical breakdown or physical binding. The overall objective of this research is to advance in-situ remediation of contaminated sediments by developing sorbent mixtures and composites that can stabilize combinations of organic and metal contaminants in sediments.

A primary list of 75 potential sediment amendments were identified from existing industrial sorbents used for other matrices such as water and gas-phase treatments. Initial screening was based on literature information on sorptive/degradative capacity, potential ecological effects in the sediment environment, and potential complications during deployment such as material density, erodability, decay or transformation in freshwater and saltwater environments. The screening yielded a list of 11 sorbents that were used for detailed sorption testing of metals and organics. Selected sorbent materials were used as sediment amendments to evaluate organic and heavy metal bioavailability reductions in a freshwater oligochaete. Using the right selection of sorbents, the bioaccumulation of PCBs, cadmium, methyl mercury, and total mercury could be reduced by nearly an order of magnitude. The amendments were also tested for toxicity to a range of benthic organisms.

Techniques to create and to administer the sorbents have also been developed that are less energy-intensive, less expensive, and less disruptive to the environment than conventional technologies. This poster will present the approach for selecting and testing amendments that can reduce the bioavailability of multiple contaminants of concern and will show results of the effectiveness of those amendments in laboratory-scale microcosms.

This research has been supported by funding from SERDP (ER-1491) and EPA SBIR program.

GUIDANCE FOR MONITORED NATURAL RECOVERY AT CONTAMINATED SEDIMENT SITES

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Environmental restoration of active and abandoned military installations poses a major challenge for the United States Department of Defense (DoD) due to the sheer number and diversity of facilities and past activities that have released contaminants into the environment. Contaminated sediment issues can be significant for DoD installations located near ecologically-sensitive aquatic environments, with costs totaling over one-billion dollars for remedies that utilize traditional dredging and capping techniques. A multi-disciplinary team of experts from industry, DoD, including U.S. Navy, U.S. Army Corps of Engineers, and U.S. Environmental Protection Agency have drafted a guidance to facilitate the understanding and application of monitored natural recovery (MNR) at DoD sites with contaminated sediments. MNR involves leaving contaminated sediments in place while monitoring the performance of the natural physical, chemical, and biological processes that physically isolate, transform, and/or reduce the bioavailability and mobility of the contaminants. Although MNR usually requires a much more intensive monitoring program than capping or dredging, MNR avoids construction costs while retaining the potential to achieve remedial action objective at many sites, resulting in potential DoD cost savings of hundreds of millions of dollars. This presentation will provide a brief overview of each of the MNR guidance topics, including: (1) key definitions, processes, objectives, and considerations for MNR; (2) conceptual site models that highlight natural recovery processes; (3) lines of evidence used to investigate the feasibility of MNR as a potential remedy during the remedial investigation/feasibility study process; (4) the application of quantitative modeling to predict natural recovery performance and interpret natural recovery monitoring results; and (5) goal-focused frameworks for long-term MNR monitoring designs. The technical and strategic topics of the guidance are presented to assist site managers and remedial project managers in assessing the feasibility of MNR as a remedy and implementing successful MNR monitoring plans.

EVALUATION OF BIOPOLYMER COATED SANDS AS CAPPING MATERIALS

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Capping technology is one of the few in-situ technologies available to environmental scientists and engineers to remediate polluted sediments. While capping technology has been applied successfully in some sites, conventional capping technology employs simply sand as a cap. This may provide inadequate risk reduction at some sites. This poster will explore novel biopolymer materials that might significantly enhance the capabilities of a simple sand cap. The objective is to prepare and test the ability of these materials to significantly reduce the migration of contaminants from sediment to above water body and to evaluate their suitability as capping materials based on their physical properties. The biopolymers evaluated included different combinations of xanthan gum, guar gum, alginate, and chitosan. The focus was on biopolymers coated on sand to produce an easily placed cap material and on cross-linked biopolymers to insure long-term stability of the biopolymer coating. The properties of the coated sand mixtures were assessed to characterize their active capping capability: organic carbon content; bulk density; porosity; permeability; resistance to erosion; solubility; sorption; and longevity. Two biopolymer coatings were found to be the most promising, a mixture of guar gum, chitosan and borax and a mixture of xanthum, chitosan and calcium chloride. The poster will summarize the physical and chemical properties of these biopolymer coated sands and provide an initial assessment of their feasibility and appropriateness as capping material. This research was conducted with the support of SERDP Project ER-1501.

EVALUATION OF THE APPLICABILITY AND EFFECTIVENESS OF ORGANOCLAYS AS ACTIVE CAPPING MATERIALS

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Organommodified clays are among the most promising amendments for a cap to improve organic contaminant sequestering capabilities. This poster will summarize the results of a variety of experiments on the chemical and physical characteristics of commercially available organoclays and show how these characteristics have proven useful in the design and application of organoclays as permeable absorptive barriers for the remediation of sediments.

Organoclay sorption capacity for both dissolved and separate phase organic contaminants was measured. The effect of sorption on the physical properties of the organoclay, including permeability, were assessed. The influence of organoclay on benthic organisms was also assessed including measurements of the reduction of contaminant availability as indicated by bioaccumulation in deposit feeding oligochaetes.

Organoclay sorption capacities for dissolved contaminants are similar to those of activated carbon and the physical properties of organoclay are more amenable to bulk placement in the subaqueous environment. Separate phase capacities are of the order of 1 g nonaqueous phase liquid per g of dry organoclay, which is far higher than other sorbents. The high sorption capacity also opens up the opportunity of placing organoclay in a thin layer as in a reactive core mat and some applications have seen placement in this manner.

These experimental results were used to identify particularly promising capping configurations using organoclay and in numerical simulations of the capabilities of an organoclay cap to effectively contain contaminants. The implications of these results for current field demonstrations and full scale implementations of organoclay caps will be summarized. Evaluations of organoclay up to 2 years after placement at the McCormick and Baxter creosote site in Portland Oregon will also be included to indicate long term viability of the approach in the field. This research is partially supported by SERDP Project ER-1501.

EVALUATION OF THE POTENTIAL SIDE-EFFECTS OF SEQUESTERING AGENTS USED FOR THE DEVELOPMENT OF ACTIVE CAPS FOR CONTAMINATED SEDIMENTS

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Under project ER-1501, several sequestering agents have been identified as cost-effective materials for making active caps that remediate organic and inorganic contaminants under a broad range of environmental conditions. However, these amendments should be tested for adverse impacts before they are used in field applications. Therefore, the objective of this paper is to determine if these amendments have side-effects that could harm aquatic environments; thereby providing crucial input data needed to determine the composition of active caps.

Sediment toxicity tests were conducted on an uncontaminated sediment, playground sand, rock phosphate, organ clay, and sand coated with the biopolymers xanthan/chitosan cross-linked with calcium chloride. The uncontaminated sediment served as a control. Sand is widely used in passive caps; therefore, playground sand was compared with the active cap components. The materials were evaluated individually and mixed with sand or coated sand the tests involved exposures of laboratory cultured amphipods *Hyalella azteca* to the tested materials in aquatic tests chambers. All treatments were conducted for 10 days, utilized eight replicates, and followed EPA protocols. Survival in coated sand and rock phosphate did not significantly differ from survival in reference sediments. The playground sand and organ clay were associated with significant reductions in survival. Survival in the mixture of rock phosphate and playground sand (50/50 by dry weight) did not differ from survival in the reference sediments, however; the mixture of organ clay and sand depressed survival. Reasons for depressed survival in some treatments will be discussed in the paper.

The EPA toxicity characteristic leaching procedure (TCLP) was used to assess the potential toxicity of leachates from amendments that have high potential for use in active caps. Contaminants extracted by the TCLP procedure have the potential to be bio-available and toxic to aquatic organisms. The TCLP extracts were analyzed for metals by ICP-MS, and the concentrations of the metals were compared with ecological screening values and ambient water quality criteria for surface waters. Metal concentrations that exceed these benchmark values were conservatively assumed to have the potential for deleterious effects. The data from the toxicity tests and TCLP procedure will help to design an active cap that remediate contaminants without causing harm to aquatic organisms. Such caps can protect biota from sediment contaminants, improve ecological and human health, and be readily accepted by regulators and public.

ACTIVE CAPS FOR REMEDIATION OF MIXTURES OF CONTAMINANTS AND RESISTANCE TO EROSION – A COMPREHENSIVE EVALUATION

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This paper reports on the first year of a project that investigates the use of combinations of sequestering agents to develop in situ active sediment caps that stabilize mixtures of contaminants under a broad range of the environmental conditions and create a barrier that resists mechanical disturbance. Initial efforts focused on the selection of the best sequestering agents for use in active caps, active cap composition, and the effects of active cap components on metal bioavailability, retention, and toxicity. Materials for active caps were selected on the basis of sorption/desorption, retention, and toxicity studies. Eight step sequential extractions were used to evaluate the bioavailability/mobility and retention of metals. Metal fractions recovered in early extraction steps were termed the Potentially Mobile (Bioavailable) Fraction (PMF) because they are less strongly bound than fractions collected in later extraction steps. Fractions collected in later extraction steps were termed the Recalcitrant Factor (RF) because they are likely to include strongly bound metals that will be retained by the treated sediment.

Retention of organic contaminants was based on kinetic studies. The penetration time was calculated for 15 and 2.5 cm layers of organoclays or apatite. The results showed that organoclay (OCB 750 and PM-199) can effectively contain organic contaminants.

Biopolymer products for inclusion in active caps were evaluated on the basis of resistance to biodegradation, sorption capacity for organic and inorganic contaminants, and potential for erosion control. Promising materials included chitosan/guar gum cross-linked with borax and xanthan/chitosan cross-linked with calcium chloride. Methods were developed for coating sand with biopolymers to produce a barrier that resists mechanical disturbance.

Organoclay, rock phosphate, and cross linked biopolymers have high potential for remediating mixtures of organic and inorganic contaminants in sediments under a broad range of environmental conditions while controlling erosion. Future efforts will focus on the use of these materials to produce active sediment caps that achieve remedial objectives with minimal environmental disturbance.

This research work was sponsored by the DoD Strategic Environmental Research and Development Program (SERDP) under project ER 1501.

APPLICATION OF TOOLS TO MEASURE PCB MICROBIAL DECHLORINATION AND FLUX INTO WATER DURING IN-SITU TREATMENT OF SEDIMENTS

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This SERDP-funded research (ER-1502) is quantifying the two most important long-term loss processes of PCBs in sediments: (1) microbial degradation and (2) diffusive and resuspension-related losses to the water column. These mechanisms depend upon the ease with which PCBs can partition between solid and porewater phases, which may be impacted by in-situ remediation. Amending aquatic sediment with activated carbon greatly reduces PCB bioaccumulation. This research asks (1) how is PCB microbial dechlorination activity in sediment affected by the addition of activated carbon and (2) how is PCB mobility altered by the addition of activated carbon? Our experimental strategy includes (1) characterizing the microbial community and dehalogenating activity in treated and untreated sediments, and (2) measuring how activated carbon additions alter phase partitioning and sediment-water exchange rates of PCB congeners.

The factors affecting the reductive dechlorination of PCBs in the three historically impacted sediments (Grasse and Buffalo Rivers, NY and Anacostia River, DC) have been characterized. In Grasse River sediment an in situ enriched population consisting of *Dehalococcoides* phylotypes was abundant in high numbers together with a high dechlorination potential and a high concentration of congeners containing unflanked chlorine substitutions. In contrast, microbial communities in Anacostia and Buffalo River sediments consisted of similar total numbers of dechlorinating bacteria, but the populations consisted of more diverse dechlorinating phylotypes and were associated with low dechlorination potentials and high concentrations of flanked congeners. Ongoing experiments are also evaluating the effects of activated carbon addition on the aerobic degradation of PCBs in the Grasse River sediment.

The impact of activated carbon on the erodibility of the sediments and the PCB desorption rates is being explored with microcosms and a sediment-water exchange model. Size-specific PCB partitioning to particles and activated carbon suspended in the water and in surficial sediments is modeled. A unique feature of this model is that the particles form aggregates and diffusion-controlled exchange of PCBs from these flocs to the surrounding water is simulated. This poster presents results from the first 1.5 years of this 3-year study, which includes the initial sediment characterization, initiation of microbial dehalogenation incubations, and model development.

BAYESIAN MODELING OF POLYCHLORINATED BIPHENYL DECHLORINATION IN SEDIMENT FOR REMEDIATION DECISION SUPPORT

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Natural anaerobic degradation of polychlorinated biphenyls (PCB) is preferentially carried out by largely unidentified populations of microorganisms. Microbial specificity is believed to be governed by the nature of the microbial populations, the physical and chemical characteristics of the site, and the structure and concentration of PCBs. Current dechlorination models incorporate neither this specificity nor the biogeochemical parameters that affect it. Inclusion of these parameters in a novel Bayesian-belief network (BBN)-based model can significantly improve the accuracy of anaerobic PCB dechlorination predictions. This model exploits congener relationships established during the Aroclor manufacturing process: particular congener pairs accepted chlorine atoms at constant rates such that selected pairs of congeners maintain the same relative concentrations across all Aroclor mixtures. Inclusion of tracker pairs in the BBN-based model is useful because knowledge of the source contaminating Aroclors and the degrading microorganisms is not necessary.

The route taken from a higher-chlorinated to a lesser-chlorinated congener is termed a pathway. Eight groups of dechlorination pathways, called processes, have been identified via trend analysis of laboratory and field data. They contain 96 of the 837 theoretically possible pathways. A preliminary construction of the BBN revealed that dechlorination predictions using only these 96 pathways were inadequate. Thus, a thorough and systematic investigation of pathways grouped by processes was undertaken to reveal trends as to why some dechlorination pathways are grouped into processes. Logistic regression is used to identify discriminating congener properties from over 400 quantitative structure-property relationships for each of the 209 PCB congeners. Discriminating properties are used to identify additional pathways belonging to degradation processes that were not previously identified due to limited data and the inability to distinguish coeluting congeners in gas chromatograph analyses. The amended processes, will be included in the BBN. Because degradation processes have been linked to biogeochemical parameters, this model is expected to lead to more accurate site-specific predictions of PCB dechlorination. Further, it will provide decision makers with insight into the relationships among PCB congener distributions, sediment geochemistry, and populations of microorganisms in a sediment system. This model may offer an alternative remediation option where there was none before. In cases where monitored natural recovery or cap-and-treat technologies are chosen over dredging, use of the model will have resulted in a reduction in costs, and human health and environmental risks.

BIOAVAILABILITY OF SEDIMENT-BOUND METALS FOR MARINE POLYCHAETES

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To evaluate the bioavailability of metals from contaminated sediments to benthic animals, we used gamma-emitting radioisotopes to determine the uptake of Cd, Cr, and As from pore water and surficial sediments collected in the Chesapeake Estuary in the polychaete *Nereis succinea*. We compared two locations in the Chesapeake, the Elizabeth River site near Norfolk VA, and Baltimore Harbor. These sites differed in geochemical properties, including the salinity of the water, the organic carbon content and the sulfide concentrations of the sediments. For the Elizabeth River site, the assimilation efficiency (AE) of ingested Cd ranged from 43.7% for freshly labeled sediment to 26.7% for 1.5 months to 15.7% for 3-month aged sediment; the assimilation of Cr and As also declined similarly in aged sediment. The AEs of As and Cr in *N. succinea* correlated well with the fraction lost from sediment into simulated gut fluid, consistent with the idea that these metals must be in a dissolved form before they can assimilate into tissues. The metal AEs also matched their trophic transfer from sediment to worm. For example, As concentrations in surface sediment averaged $15.5 \mu\text{g g}^{-1}$ dry weight while in field-collected polychaetes they ranged from 3-5 $\mu\text{g g}^{-1}$ dry weight (or 19-32% of the sediment value), compared to the measured AE for As (27.9% in 1.5-month aged sediment). We also assessed the assimilation of ingested metals as a function of their speciation in surficial sediment. Metal accumulation in *N. succinea* from pore water was generally found to be low relative to accumulation from ingested sediment, suggesting that bioaccumulation of these metals results primarily from ingestion of sediment. Parallel experiments are ongoing with the Baltimore Harbor site and results of these experiments will be presented. These and other experimental results will provide a mechanistic understanding of how sediment-bound metals bioaccumulate in benthic organisms. [SERDP Project ER-1494]

SEDIMENT ECOSYSTEM ASSESSMENT PROTOCOL (SEAP): AN ACCURATE AND INTEGRATED WEIGHT-OF-EVIDENCE BASED SYSTEM

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The purpose of this research is to develop an efficient, accurate and integrated approach for the assessment of ecosystem risk and recovery at sites where contaminated sediments exist, or previously existed. The integrated system (Sediment Ecosystem Assessment Protocol – SEAP) incorporates rapid *in situ* hydrological, chemical, biological and toxicological measurements to provide concise, decision-oriented scientific and ecological information to improve the overall management of contaminated sediment sites. By integrating multiple tools/assays simultaneously there can be better linkages of exposure and effects measures. This includes placing *in situ* toxicity and bioaccumulation test systems into the existing Trident and UltraSeep Systems. The Trident is a multi-sensor sediment probe device that is designed to rapidly identify groundwater-surface water (GSI) discharge zones, and to sample pore water from these areas. The UltraSeep System provides the ability to directly and continuously quantify GSI discharge rates and collect flow proportional samples to quantify both water and chemical flux. During this first year of the project we have selected candidate assays for further evaluations that will be used for short-term screening and *in situ* testing. These assays include: Mussel embryo-larval development, *Eohaustorius* (amphipod) survival, *Leptocheirus* (amphipod) survival, *Neanthes* (polychaete) feeding rate, *Brachionus plicatilis* (Rotifer) survival, QwikLite (two species: *Ceratocorys* & *Pyrocystis*), sea urchin fertilization, and biomimetic devices (SMPEs, DGTs). Fate and transport of migrating sediment and groundwater contaminants will be assessed with the tools on-board and adjacent to the current Trident and UltraSeep Systems, while effects (bioresponses) from surficial sediments, upwelling groundwater and sediment porewater contaminants, from mobilization of sediment-bound contaminants, or from overlying surface waters, will be assessed concurrently with *in situ* toxicity and bioaccumulation tests (live organisms and passive sampling devices (PSDs)). The resulting data from these multiple lines-of-evidence will then be integrated into a Weight-of-Evidence based Geographic Information System, providing statistically based rankings of the likely dominant physical and chemical stressors at each station and across the site. SERDP Project No. EER-1550.

IN SITU MEASUREMENT OF PAH ACTIVITIES IN SUBMERGED MARINE SEDIMENTS USING LOW DENSITY POLYETHYLENE PASSIVE SAMPLER

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Building on previous work showing that low density polyethylene (PE) can be used as a passive sampling medium for assessing hydrophobic organic compounds (HOCs) in contaminated sediments (SERDP Project Number ER-1496), we have designed, built, and tested a vehicle for deploying PE strips at field sites. The vehicle was deployed in the Boston Harbor, in conjunction with sampling being performed by the Massachusetts Water Resource Authority (MWRA), at a site where PAHs have previously been measured in the sediments. The vehicle was retrieved and analysis of the PE was performed to obtain chemical activity profiles for a suite of PAHs across the sediment-water interface and into the bed to a depth of 15 cm. Such data indicate (a) the fluxes of PAHs from the bed, and (b) the extent of PAH contamination that may require clean up.

To make this passive sampling methodology useful for a wider range of HOCs (e.g., PCBs, alkylated PAHs), we have worked to extend the method so as to allow quantification of chemical activities of compounds for which PE-impregnated standards were not utilized. This requires use of chemical structure-based estimates of diffusivities (D_{PE} or D_{sediment}) and partition constants (K_{PEW} or K_d), so we have examined our ability to estimate the PE-related parameters versus new observations of D_{PE} and K_{PEW} . Further, using a numerical model, we have assessed the accuracy of correcting any under-equilibrated HOC accumulations in the passive samplers to obtain estimates of the corresponding chemical activities in the sediment bed. The extended method was evaluated using HOC data from previous field exercises, and limitations for the use of PE passive sampling are delineated in the absence of using impregnated standards that match the HOCs of interest.

TECHNICAL OBJECTIVE 1 EXPERIMENTAL INVESTIGATION OF A WALL SHEAR STRESS IN A PULSATING CHANNEL FLOW WITH STRONG BULK FLOW REVERSAL

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ER-1497 research goal is to develop laboratory methods to reliably measure and predict erosion of contaminated fine-grained sediment field under bottom shear stress conditions that represent combined wave and current action. These methods will utilize the USACE SEAWOLF flume. The shear stress conditions for erosion measurements in the flume will replicate those for non-breaking waves in estuarine, harbor, and coastal environments. The first specific objective of the project is to directly measure the shear stress time histories that occur in the SEAWOLF flume so that flume pumps and pistons can be programmed to represent prescribed wave/current-induced bottom shear stress time history. The second objective is to develop an erosion database for various sediment and hydrodynamic conditions and correlate erosion to these conditions.

Wave/current bottom shear stress time history is well known. Methods for replicating this in the laboratory must be developed. Therefore, a novel high-magnification particle-based velocimetry system has been developed and applied to measure shear stress time history in SEAWOLF. Particle Image Velocimetry (PIV) is used to measure the overall velocity profiles throughout the SEAWOLF oscillating flow cycle. Particle Tracking Velocimetry (PTV) is used to measure near-wall velocity profiles to within 7 mm of the wall throughout the cycle. Velocity profiles from time histories constructed from PIV and PTV data are used to estimate bottom shear stress time histories. Instantaneous PIV realizations at low magnification clearly display relaminarization of the flow during periods of strong acceleration which is followed by transition back to turbulence during weakly accelerating and decelerating portions of the forcing cycle. The phase-evolution of the streamwise velocity profiles, wall shear stress and turbulence quantities are extracted from the PIV recordings.

Simultaneously, a relatively new high-sensitivity a floating element sensor (FES) was modified for application within the flume. This sensor, if properly applied, provides direct physical shear stress measurement. Demonstration of this floating element sensor application permits substitution for the more reliable, but more costly PIV/PTV system. PIV and PTV results are in good agreement with FES results to date indicating that shear stress time histories can be directly measured and pump/piston programming is possible.

BACTERIAL AND BENTHIC COMMUNITY RESPONSE TO INORGANIC AND ORGANIC SEDIMENT AMENDMENTS

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Copper, zinc, cadmium, lead, and chromium are typical pollutant metals common to many Department of Defense (DoD) sites. Amendments are currently being added to sediments to sorb, degrade, transform or immobilize toxins and metals and some amendments are added to stimulate growth of indigenous microorganisms to contribute to these processes. Our proposal is in its first year of funding; the goal of this proposal is to evaluate the toxicity of sediments without and with amendments intended to remediate mixed heavy metal contamination.

Our first year project involves exposing surrogate benthic community members to clean sediments amended with inorganic and organic additions that are currently being field tested for sediment remediation. Later years will involve contaminated sediment sites. We will examine 10 different amendment mixture scenarios on four benthic community members. The four community members used will include two benthic organisms (amphipods, polychaetes), and two epi-benthic organisms (sea urchin, sheepshead minnow); all of which have life stages intimately associated with surficial sediment. The amendments examined will be: control sediment, raw geotextile mat, geotextile mat + apatite; geotextile mat + apatite + developed organoclay, rock apatite only, chitin only, acetate only, developed organoclay only, raw apatite + raw chitin, and raw apatite + raw organoclay. The geotextiles will be cut to fit the beakers and sewn to prevent release of the inside material.

The microbiological component will examine potential microbial pathways present in different depth horizons (0 to 3 cm) in sediments to evaluate for iron- and sulfate- reducers (FeRB and SRB) and phosphate solubilizing bacteria (PSB). The most probable number (MPN) technique will be used to analyze major microbial members and succession under varying amendment conditions. The presence of bioavailable metals will be examined by graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled plasma optical emission spectrometry (ICP-OES). The EPA will perform the X-ray absorption spectroscopy (XAS) to determine metal speciation, including oxidation state, coordination environment, interatomic bond distances, and identity of nearest neighboring atoms. Mössbauer spectroscopy may be used to facilitate iron (Fe) speciation research.

EX SITU DECHLORINATION OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS IN KYMIJOKI RIVER SEDIMENT, FINLAND

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Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are unwanted byproducts from various industrial processes. They are of major concern due to their extreme toxicity and high resistance to microbial degradation, in particular the historical PCDD/F contaminants in the sediment. Micro- and mesocosms were established to assess the reductive dechlorination of aged PCDD/Fs in contaminated sediment from Kymijoki River, Finland. In 30-liter anaerobic mesocosms we detected the dechlorination from octa-CDF to hepta- and hexa-CDF congeners, as well as production of penta-, tetra-CDFs from hexa-CDFs after 3 years incubation. Whether the dechlorination of PCDD/Fs could be stimulated by different amendments was examined in 200 ml microcosms. The effects of spiked 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TeCDD), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB) and 1,2,3,4,5-pentachloronitrobenzene (1,2,3,4,5-PeCN) as “haloprimers” in the presence of combined electron donors were examined. Vegetable oil was tested for the effect on enhancing dechlorination of historical PCDD/F congeners in the sediments with and without bioaugmentation of *Dehalococcoides ethenogenes* strain 195. Extensive reductive dechlorination of spiked 1, 2, 3, 4-tetrachlorodibenzo-*p*-dioxin and 1, 2, 3, 4-tetrachlorodibenzofuran indicated that the sediments contained active populations of native dechlorinating bacteria. Native *Dehalococcoides* species were detected by molecular community analysis. The results suggest ways to enhance dechlorination of historical PCDD/Fs contaminants by indigenous microbial populations and can be used for identification of potential dechlorinating microbes for in situ biotechnology and bioremediation of PCDD/F contaminated sediments

PERSISTENCE OF HIGH EXPLOSIVES FROM LOW-ORDER DETONATIONS WITHIN A SALT MARSH IMPACT AREA

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The accumulation or persistence of energetic compounds resulting from live-fire training with howitzers and mortars has been investigated at various locations on Alaskan training ranges since 2000. Several studies have shown that high explosive ordnance detonations of mortar and artillery projectiles normally leave very little energetic residue in the impact area. Occasionally, a malfunction will produce either unexploded or partially (low order) detonated ordnance that consists of pieces of the projectile body and chunks of the HE (high explosive) filler that may be scattered up to tens of meters from the impact point. Within an Alaskan salt marsh impact area, we have studied the spatial distribution and persistence of the high explosives TNT (2,4,6-trinitrotoluene), RDX (1,3,5-hexahydro-1,3,5-trinitrotriazine) and HMX (1,3,5,7-octahydro-1,3,5,7-tetrazocine) that were deposited from low order detonations of 120-mm mortar projectiles. The scatter areas of the solid pieces of high explosives filler were measured and the number of macroscopic pieces determined for three low order detonations. A subset of chunks was monitored using photography within two of the scatter areas (SERDP ER-1482). All of the chunks were collected within another scatter area to determine mass of the macroscopic residue, and mean HE concentration in the surface sediment was estimated from multi-increment sediment samples collected within the scatter area for three consecutive summers. Distributional heterogeneity was examined at several scales by analyzing discrete sediment samples collected at 0.1-m, 1-m, 3-m, 5-m, 10-m, and 30-m intervals. The HE chunks have diminished in size by dissolution and disaggregation. Only the largest chunks were still present 1.5 years after deposition. HE concentrations in discrete surface sediment varied by several orders of magnitude. The multi-increment sediment sample data showed that the concentrations of all three analytes declined where the macroscopic HE chunks were removed and if there is no new input. Rate of decline is the least for HMX and the greatest for TNT. The water-saturated, anaerobic conditions of the salt marsh are likely to result in biotransformation following the dissolution of the solid high explosives.

STUDY OF PROPELLANT RESIDUES AND GASES EMITTED DURING 105-MM HOWITZER LIVE FIRING AT THE MUFFLER INSTALLATION IN NICOLET, LAC ST-PIERRE, CANADA

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For years, the Defence Research and Development Valcartier (DRDC Valcartier) has studied environmental impacts of munitions at target positions. More recently, investigations have addressed propellant residues, i.e., NG and 2-4 DNT at anti-tank, artillery, and mortar firing positions. In addition to environmental impacts, there are health concerns for artillery gunners, headache being one symptom often experienced by the gunners. DRDC Valcartier and DRDC Toronto collaborated in this study to assess the gaseous emissions and the particles size distribution during live-firing of a 105-mm Howitzer gun. Studies were performed both in the open atmosphere and inside a muffler installation in Nicolet. The trials inside the muffler enhanced the collection of emitted particles and gases. Furthermore, to better understand the combustion processes, firings at full and partial charges were performed using both settings. Sampling of the gases revealed that sub-micron particles were produced as well as contaminants of concern such as: cyanhydric acid, aromatic hydrocarbons, etc. That deserves more attention to evaluate the potential health risk to the users. Different concentrations of the gases were observed at Charge 6 and at Charge 4. Firing at Charge 4 in the muffler spread 2,4-DNT ranging from 0.29 to 0.39% while firing with 6 bags spread 0.19 to 0.23%. Atmospheric firings confirmed those results. Results also indicate that the gunners positions are exposed to high concentrations of 2,4-DNT when firing the Howitzer gun. This potential health risk will have to be evaluated in further study. This work was supported by the Sustain Thrust of DRDC, Canada and the Strategic Environmental Research and Development Program (SERDP ER-1481), Washington D.C., USA.

ENERGETIC RESIDUES DEPOSITION FROM 84-MM CARL GUSTAV ANTITANK LIVE FIRING

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The potential environmental contamination as a result of live fire military training has to be assessed in order to train our troops in a sustainable manner. Recently, propellant residues were detected around artillery, antitank and small arms firing positions during field characterization. However, the source term per round have not been defined yet for antitank shoulder weapons. In February 2007, DRDC Valcartier teamed with the Canadian Infantry School to sample the residues generated by the firing of thirty nine 84 mm Carl Gustav shoulder weapons. Samples were collected using sixteen rows of particle traps up to 50 m in front and behind the weapons. This allowed the calculation of an estimate of the percentage of unreacted nitroglycerine (NG) that is expelled on the surface soil, in the area where our traps were installed. As much as 781 g (14% w/w) of NG was expelled on the soil surface, with 98% of the residues being deposited rearwards of the firing positions, mostly within the first 15 m. There is a high uncertainty in the calculated estimate, but this trial clearly demonstrated that 84 mm Carl Gustav firing is not efficient and lead to the rapid buildup of propellant residues in the surface soils. Our results are in agreement with the high levels of NG that were detected in many antitank ranges, and demonstrate that these weapons have the highest environmental impact measured up to now. Other similar trials should be conducted to confirm these results, and research is needed to develop better propelling charges that will reduce this adverse impact. This work was supported by the Sustain Thrust of DRDC, Canada and the Strategic Environmental Research and Development Program (SERDP ER-1481), Washington D.C., USA.

METABOLITE DISTRIBUTION AS INFLUENCED BY ABIOTIC, BIOTIC, AND MIXED (BIOTIC-ABIOTIC) PATHWAYS, pH AND BIOAVAILABLE Fe(III) IN ELECTRON SHUTTLE-MEDIATED BIOTRANSFORMATION OF RDX

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Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are toxic compounds that contaminate subsurface aquifers at firing ranges and explosives test sites. Current bioremediation technologies rely on specific cyclic nitramine-metabolizing microorganisms, which vary in their activity. The SERDP-supported study (ER-1377) presented here describes a novel approach for cyclic nitramine-contaminated environments using humic substances and microbially-mediated electron shuttling.

Recent research focused on the distribution of RDX metabolites generated due to the biological pathway versus the abiotic pathway, and when both were functioning simultaneously. Buffered suspensions (pH 6.8/7.9/9.2) were performed with cell-free AH₂QDS as the sole electron donor, cells (*Geobacter metallireducens*) alone, or cells+AQDS (as the electron shuttle). RDX degradation rates and metabolite distribution were influenced by the pH. Cells alone reduced RDX faster at the lowest pH (6.8). However, at all pH values the rates of the electron shuttle-mediated pathways were consistently the fastest, and the proportion of carbon present as formaldehyde, which is the precursor to mineralization, was highest in the presence of electron shuttle. Formaldehyde accounted for 45/51/54 % of the carbon in electron shuttle-amended cell suspensions as opposed to 13/42/45 % of carbon without electron shuttle at the pH 6.8/7.9/9.2, respectively. About 7 - 20% of RDX was mineralized to CO₂ in the presence of cells at all pH tested; mineralization was most complete in electron shuttle-amended suspensions. Nitroso metabolites were insignificant, and MEDINA accumulated most at the high pH (9.2), but its concentration was lower at 6.8 and 7.2. Nitrous oxide and nitrite were dead end products in the strictly abiotic pathway, but nitrite was reduced to ammonium in the presence of cells. In the presence of bioavailable Fe(III), the rate and extent of RDX degradation decreased in cell-free AH₂QDS incubations at all pH tested, but increased in cells+AQDS incubations at the lower pH (6.8 and 7.9). The increased RDX degradation rates were due to magnetite formation. Formaldehyde concentration was highest in the presence of magnetite as well. These results suggest that electron shuttles stimulate RDX ring cleavage and mineralization in both Fe(III)-rich and Fe(III)-poor environments. A final product of this work is the novel isolate MJ-1, which is an RDX degrading, Fe(III)-reducing bacterium that was enriched from sediment with RDX as the sole electron acceptor.

FIELD DEMONSTRATION OF IN SITU BIOREMEDIATION OF ENERGETIC COMPOUNDS IN GROUNDWATER

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Energetic compounds, including 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) have been identified in soils and groundwater at a number of military installations. Laboratory research suggests that bacteria capable of degrading these compounds are widely distributed in nature but that an organic or inorganic co-substrate is usually required to stimulate degradative activity. Several approaches have been tested to promote energetics bioremediation in soils, but there have been comparatively few field tests of similar technologies for groundwater.

The objective of this ESTCP-funded project (ER-1425) was to demonstrate *in situ* bioremediation of energetic compounds in a contaminated aquifer using co-substrate addition. The project was conducted at a former explosives packing facility (Area 157) at the Picatinny Arsenal, Dover, NJ. Laboratory microcosm and column studies showed that energetics-degrading bacteria are indigenous to this aquifer, and that these bacteria can be stimulated to biodegrade explosives using cheese whey or yeast extract as co-substrates. Many other organic and inorganic substrates, including lactate, acetate, benzoic acid, hydrogen gas, and ethanol were ineffective. A groundwater recirculation system was installed to distribute and mix cheese whey with the energetics-contaminated groundwater. The system was operated in cycles, pumping at 10 gallons-per-minute for 3-5 days during injection of cheese whey, then remaining passive for 2-4 weeks once adequate mixing and distribution of the whey was achieved in the aquifer. Within one month after the first injection of the whey, significant reductions in RDX, TNT, and 1,3,5-trinitrobenzene were observed in several wells, with concomitant increases in some common degradation intermediates, particularly MNX and TNX (from RDX degradation) and 2,4-diamino-6-nitrotoluene from reduction of TNT. The field study is ongoing. The system design, modeling, and compiled analytical data from the field investigation will be presented. This treatment approach is anticipated to be widely applicable and cost-effective for *in situ* remediation of energetic compounds in groundwater at DoD facilities.

MONITORED NATURAL ATTENUATION OF EXPLOSIVES IN GROUNDWATER USING STABLE ISOTOPE RATIO ANALYSIS

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Past monitored natural attenuation (MNA) efforts at explosives-contaminated sites have been characterized by a lack of strong tertiary lines of evidence. The chief reason for this lack of evidence is the difficulty encountered in identifying and quantifying the short-lived transformation products of explosives. Consequently, establishing a mass balance between explosives and their transformation products in the field is considered to be virtually impossible. The objective of this work (ESTCP Project Number 0706) is to establish a strong tertiary line of evidence for explosives contaminant transformation by utilizing methodology that focuses on the analysis of reactants rather than the products. This line of evidence will involve the application of a specific analytical method, namely gas chromatography-isotope ratio mass spectrometry (GC-IRMS), to spatially characterize stable isotope enrichment effects in groundwater plumes of explosives contamination. In this FY07 project, (a) the evaluation of field-scale ^{13}C and ^{15}N stable isotope enrichment effects will be extended to a list of aqueous munition constituents; (b) enrichment effects will be correlated with site environmental conditions by evaluating primary and secondary MNA lines of evidence, derived chiefly from historical site data; (c) the effectiveness of any existing in-place remedies, especially remedies that lead to enhanced bioremediation, will be assessed by evaluating the stable isotope enrichment effects in the vicinity of such remedies relative to background enrichment effects; and finally (d) findings of steps (a) through (c) and the key steps from the ESTCP Protocol for the MNA of Explosives will be codified into a managerial software decision tool to support the identification of sites where MNA is likely to be a successful remedy by itself, or as part of a combination of remedies. The poster presentation will cover the first six months of work accomplished for the project, including the selection of target analytes and their detection goals for the GCIRMS analytical method, and a preliminary database of candidate sites for the field demonstration.

OUTDOOR DISSOLUTION OF COMPOSITION B, TNT, AND TRITONAL

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We aim to measure how quickly cm-sizes detonation residues of TNT, Comp B, and Tritonal dissolve under natural weather conditions. Dissolution is the rate-limiting step preceding aqueous transport of HE into groundwater. Our experiment mimics field conditions on training ranges, where spatially isolated particles of high explosives (HE) on the soil surface are dissolved by rainfall. In May 2006, we placed pieces of TNT, Comp B and Tritonal outdoors in funnels. Approximately every two weeks, we measure the volume and analyze the explosives concentration of the precipitation passing through the funnel and thereby record HE dissolution with time. Our outdoor tests also allow us to see how quickly HE pieces fracture and disaggregate by weathering. Understanding how explosive residues weather and break apart on ranges is critical because particle size strongly influences dissolution rate. This poster presents the first year of dissolution results for 11 TNT, 5 Tritonal, and 12 Comp B pieces. The shapes of the cumulative mass-loss curves for all pieces are similar, but mass loss differs by up to a factor of eight among pieces of the same explosive. The largest pieces have lost the most mass and the smallest pieces the least. However, small HE pieces lost a larger percentage of their initial mass. This finding is expected because dissolution rate depends on surface area and smaller particles have proportionally more surface area per unit mass than larger particles. Observations of the HE pieces show that the TNT in all three HE compounds becomes red when exposed to sunlight. The TNT particles have become smoother with time whereas both the Comp B and Tritonal have become rougher due to the loss of surface TNT. In the case of Comp B, loss of TNT exposes RDX crystals whereas for Tritonal loss of TNT exposes aluminum grains. Cracks have appeared in three of the TNT, one of the Tritonal and two of the Comp B pieces. Most of the pieces have lost flakes and, in some cases, mm-sizes particles. Lever et al. (this conference) used our mass-loss and weather data to validate dissolution models for TNT and Tritonal chunks. Their results indicate that annual total rainfall is the key parameter governing annual dissolution for a given particle size. Their results are very encouraging as they imply that climatic data can be used to estimate the dissolution rate of explosives on training ranges across the US.

MOLECULAR STRUCTURE DETERMINES TRENDS BETWEEN CHEMICAL AND PHYSICAL PROPERTIES OF NITRAMINES, CAGE NITRAMINES, AND NITROAROMATIC ENERGETICS

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Because of its widespread presence and toxicity in the environment, as well as its mutagenic and potentially carcinogenic nature, the prediction of the chemical and physical properties of trinitrotoluene (TNT) and certain products of its environmental degradation are of high interest to DoD research. The hypothesis that *the environmental fate and effects of energetic materials can be predicted from their molecular structures* (in regard to the nitroaromatic, TNT; cyclic nitramines, RDX, HMX; and cage nitramine, CL-20) was extended to include new emerging compounds of military interest, such as dinitroanisole (DNAN), trinitrotriaminobenzene (TATB), n-methyl-p-nitroaniline (MNA), dinitro pyroazole (DNP), nitro triazolene (NTO), and m-trinitro imidazole (MTNI).

Our theoretical study involved MOPAC and DFT quantum mechanical and classical force field mechanics to predict most likely bond lengths and angles, heat of formation, ionization potential, steric energy, dipole moments, solvent accessibility and electrostatic potential surfaces, partial charges, and HOMO/LUMO energies. Vapor pressure, Henry's law constants, water solubility, and octanol-water partition coefficients are important physicochemical properties that are essential for environmental modeling of the transport and fate of chemical contaminants. These physical characteristics are also important to our understanding of the behavior of toxicants. Correlations between the compound's chemical/physical properties and their molecular structure were then studied to discover possible trends.

Comparison of the aforementioned compounds results in identifying fast forming intermediates, predicting potential or probable reactivity with media, and prioritizing compounds of greatest concern. To develop a predictive framework and computational chemistry (CC) protocols to assess energetic reactivity, nitramine, cage nitramine, and nitroaromatic energetic compounds are being compared as to structure, sites and modes of transformation and transformation products and therefore, their reaction with environmental media. Thus, study of CL-20 and its reactivity relationships is providing the nucleus for transitioning to other MUCs. This study is expected to come full circle in providing basic understanding of nitramine and nitroaromatic MUCs and their reactivity in the environment, as well as the development of a predictive framework and CC protocols practical for basic research into new compounds and for application specific to environmental sites.

A STUDY OF MOLECULAR STRUCTURE AND REACTIVITY OF TNT AND SELECTED DERIVATIVES

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This study focuses on the structure and reactivity of the nitroaromatics, TNT and selected derivatives, within their environmental context for the purpose of demonstrating possible trends for enhancing the study of transformation mechanisms, particularly those with toxic potential. Computational chemistry is used to evaluate these compounds in terms of TNT molecular structure, reactivity, and comparison with related analogues. Emphasis is placed on the link between substituent position and the resulting reactivity associated with their change in location. Significant correlations relating structural changes to energy variations are obtained using both Semi-empirical (AM1) and DFT computational approaches.

Both AM1 and DFT show substituting an amine for the TNT nitro group results in the following: (i) HOMO energy values are always lower when the amine is substituted on the ortho C₂ rather than on the para C₄ position with respect to the methyl group, because amines activate the aromatic ring by adding electrons. This lowering of energy to the methyl group ortho position is due to both inductive and steric effects. (ii) For both mono- and di- substituted amino and hydroxyl groups, formation energy and HOMO are always lowest when the substitution is on the ortho rather than the para position. (iii) The same trend pertains to diamino and dihydroxy substitutions on TNT. That is, 2,6-diamino and 2,6-dihydroxy are always lower than 2,4-diamino and 2,4-dihydroxy substitutions. (iv) The opposite effect is observed for the nitro groups due to their electron withdrawing nature. For example, 2,6-dinitrotoluene has higher steric energy, heat of formation, and HOMO energy than 2,4-dinitrotoluene. Also, substituting amines in the ortho position is effective in further preventing complexation. Therefore, this substitution might impact toxicity, making the amino substituted derivatives more available in the media.

HOMO/LUMO energies will increase and the heat of formation will decrease with subsequent nitro group replacement by amino or hydroxyl groups. The lowest heat of formation occurs with greatest hydroxyl group substitution. HOMO energy is lower when amines or hydroxyl groups are substituted at the ortho (2-,6-) rather than the para (4-) position. This is true for both mono- and di- substitutions. For example, 2,6-diamino-nitrotoluene and 2,6-hydroxyl-nitrotoluene are always of lower HOMO/LUMO energies than 2,4-dinitro-nitrotoluene and 2,4-dihydroxyl-nitrotoluene. In contrast, due to the electron withdrawing nitro groups, this trend is reversed in the dinitrotoluenes, with 2,4-dinitrotoluene always having lower HOMO/LUMO and formation energies than 2,6-dinitrotoluene.

PILOT-SCALE EVALUATION OF ZERO-VALENT IRON TECHNOLOGY: TREATMENT OF RDX WASTEWATER

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Over the last decade, zero-valent iron (ZVI) has been increasingly used as a reducing agent in subsurface permeable reactive barriers (PRBs) for remediation of subsurface environment. Recently, U.S. Army ERDC-CERL and University of Delaware has examined the feasibility of ZVI for treating ammunitions wastewaters containing energetic compounds such as heterocyclic nitramines (e.g., RDX and HMX), nitro-aromatics (e.g., TNT and DNT), and nitrate esters (e.g., nitroglycerin, NG). These studies have shown that these nitro explosives can be rapidly degraded by ZVI through chemical reduction, and that the reduction products are less toxic and/or more degradable by chemical or biological oxidation.

The logical next step in the investigation and development of this innovative technology is to evaluate the pilot-scale system to determine the scale-up potential of the iron pretreatment technology. This is a necessary and critical step in obtaining interests and, more importantly, investments from ammunition plants for large-scale testing. The objectives of this demonstration are (1) To demonstrate and validate the zero-valent iron (ZVI) wastewater treatment system with RDX-containing wastewater (50 gallons per hour) and compare the results with the bench-scale tests, (2) To evaluate the degradation kinetics with treatment goal of < 10 ppb (detection limit) and to analyze the effects of detention time on the performance of zero-valent iron reactors, (3) To characterize effluent quality (final and intermediate by-products) and recommend subsequent treatment methods (i.e. biological treatment or Fenton's oxidation).

In order to demonstrate and validate the zero-valent iron (ZVI) technology, we constructed a continuous flow 50 gallons per hour pilot plant in a of 8 ft (W) × 9 ft (L) × 29 ft (L) mobile trailer. The ZVI demonstration unit consists of a pre-column and main ZVI reactors. RDX-containing water (10 mg/L RDX) was continuously pumped at 50 gallon/hour to the pre-column (25% iron and 75% sand) to eliminate suspended particles and dissolved oxygen prior to the main ZVI reactors. The deoxygenated RDX-containing wastewater was then be treated in the two PVC columns (50 gallons each) in series. ZVI reactors have iron-to-sand ratio of 50:50.

The successful demonstration of this study is an important step in the development of an efficient and cost-effective option to treat energetic compounds in the wastewater and convert them into products that are either innocuous or more easily degradable through chemical or biological oxidation in the overall treatment of wastewater streams from ammunition plants.

SUBSURFACE SEDIMENT TREATMENTS FOR MINERALIZATION OF RDX, HMX, AND TNT

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In situ remediation of energetics RDX, HMX, and TNT by different combinations of abiotic and biotic processes of subsurface sediments was investigated in this SERDP-funded (ER-1376) laboratory scale project using sediments that are biostimulated (addition of carbon/trace nutrients) and abiotically treated to create a reducing environment (chemical reduction or zero valent iron addition). Results show that there are different aquifer sediment treatments for RDX/HMX and for TNT that maximize degradation and mineralization rates. Optimal sediment treatment for RDX and HMX, which have similar degradation pathways, is mainly chemical reduction of sediment, which increased mineralization rates 100 to 150 times (relative to untreated sediment), with additional carbon or trace nutrient addition slightly increasing rates an additional 3 to 4 times. The rate-limiting step for RDX and HMX appears to be formate mineralization. Formate mineralization was quite slow in untreated sediment (7,400 h half-life) with similarity to RDX mineralization (31,000 h half-life), and rapid in reduced sediment (60 h half-life) again with similarity to RDX mineralization (315 h half-life). Formate mineralization is a coupled abiotic/biotic reaction, as the presence of a bactericide stopped formate mineralization, and increasing amounts of sediment reduction greatly increased the formate mineralization rate (i.e., abiotic component of the reaction). Methylene dinitramine (MDNA), another RDX and HMX degradation intermediate, was degraded in oxic and reduced sediments at similar rates as its degradation was dominated by acid hydrolysis. It may be a second rate-limiting step for RDX/HMX mineralization at high sediment/water ratios in aquifers that are somewhat alkaline. In contrast to RDX and HMX, the optimal aquifer sediment treatment for TNT involves mainly biostimulation (glucose addition), which stimulates a glucose/TNT cometabolic degradation pathway (7 times more rapid than untreated sediment), with secondary treatment of chemical reduction (13 times additional rate increase). TNT is transformed to triaminotoluene, which irreversibly sorbs in reduced systems, but is rapidly degraded in oxic systems. Although the TNT degradation pathway is biotically dominated, the iron-reducing conditions created by abiotic reduction of sediment promote more rapid abiotic degradation of amino-intermediates than biodegradation of these intermediates. This mechanistic information is needed for the proper application of this technology to differing field sites.

DISSOLUTION AND TRANSPORT OF M9 AND M30 PROPELLANTS IN SOIL COLUMNS

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Presented work was funded under SERDP project ER-1481 “Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges”, Task 2. Release and transport. The objective of the task was to define transport process descriptors for several common propellants in dissolved form and as components in propellant formulations. Propellant constituents and solid phase propellant formulations were tested under different flow regimes and in different soils.

In a second year of the project, laboratory column studies were conducted to evaluate dissolution and transport of nitroglycerin (NG), nitroguanidine (NQ), and ethyl centralite (EC) from intact solid propellant formulations M9 (58% nitrocellulose, 40% NG, 1.5% potassium nitrate, 0.75% EC, and up to 0.4% graphite) and M30 (28% nitrocellulose, 22.5% NG, 47.7% NQ, 1.5 % EC, and 0.3% cryolite). M9 is manufactured in a form of small flakes, while M30 as larger perforated cylinders coated in graphite. Transport parameters for propellants were determined from breakthrough curves using HYDRUS-1D code. Paused flow experiments, along with a conservative tracer (3H), were used to distinguish between physical and chemical nonequilibrium processes.

It was observed that propellant constituents originating from the solid propellant formulations behaved similarly to solution phase propellants that were studied under the same project last year. Nitroguanidine adsorption was not statistically different from zero. Nitroglycerin was retained to a greater extent than NQ but still exhibited less preference for soil than water, while ethyl centralite had the greatest adsorption.

Dissolution rates of propellant constituents were different for the two formulations as indicated by 14 to 80 times greater NG outflow concentrations in M9 experiments than in M30. Differences were explained by smaller particle size of M9 propellant and larger surface area available for dissolution; and by graphite coating of M30 propellant. For both formulations, dissolution rate was the highest initially but decreased with time, approaching a steady-state condition.

Transport parameters obtained in this study are suitable for use in environmental transport models and/or in environmental and human health risk assessments.

DEVELOPMENT OF TOXICITY DATA FOR MUNITION COMPOUNDS TO SUPPORT TOXICITY REFERENCE VALUE DERIVATIONS FOR WILDLIFE

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The DoD is the steward of extensive land holdings, many of which encompass land uses such as training (e.g., firing ranges), munition manufacturing, and demilitarization operations. Due to the large size of these areas, their relative habitat value, and the occurrence of munition compounds found in the soil, sediment, and surface water at these installations, it is important that the DoD can address issues associated with wildlife exposures to these substances particularly in regard to threatened and endangered species. Currently, few toxicity data for wildlife are available for munition compounds. This work (ER1420) represents a tiered approach to provide those data, where needed for the most prevalent munition compounds and constituents for wildlife that would be useful in a risk assessment context. Wildlife laboratory models were developed and exposed to various munition compounds in a controlled regime and investigated for adverse effects. From these data, safe thresholds for exposure are determined for RDX, TNT, DNT, and amino-dinitotoluenes for birds, mammals, reptiles and amphibians.

EFFECT OF SOIL PROPERTIES ON PARTITIONING OF RDX AMONG SOIL, INTERSTITIAL WATER, AND EARTHWORM TISSUE

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Earlier studies showed that RDX can accumulate in aquatic organisms and in soil invertebrates, suggesting an ecotoxicological risk for food chain transfer of this energetic material. The present study was undertaken to determine RDX partitioning among soil, water, and earthworms. We hypothesized that RDX accumulation follows the Equilibrium Partitioning Theory (EqP), which states that the dissolved fraction of a compound in soil interstitial water diffuses passively into the organism. We tested this hypothesis using three single-compartment model systems: soil-interstitial water (24-h incubation), soil-earthworm (7-d exposure), and distilled water-earthworm *Eisenia andrei* (48-h exposure). Four different soils, including a sandy soil from Quebec (DRDC), Teller sandy loam (TSL), Kirkland clay loam (KCL), and Webster clay loam (WCL), were first amended with nominal concentrations of RDX ranging from 1 to 10,000 mg/kg soil, then incubated under controlled laboratory conditions. In the soil-interstitial water system, the RDX concentration in interstitial water was greatest in DRDC, followed by TSL, KCL, and WCL soils. In the soil-earthworm system, RDX accumulated in the earthworm in proportion to RDX concentrations in the soil. The bioaccumulation factors (BAF; calculated as the tissue/soil concentration ratio), obtained in the DRDC soil-earthworm system, decreased from 13 to 0.2 as the concentrations of RDX in this soil increased from 1 to 10,000 mg/kg. Similar results were determined in the remaining soils tested in these studies. In the distilled water-earthworm system, the greatest tissue RDX concentration of 350 mg/kg was determined at the 25 mg/L treatment (the greatest concentration of RDX tested in distilled water). The bioconcentration factor (BCF calculated as tissue/water concentration ratio) of 14 determined in this treatment was similar to BCFs of the remaining treatments, thus suggesting that the BCF is independent of media concentrations of the water-earthworm system. This finding contrasted with the BAF values, which depended on the exposure media concentration. These preliminary results indicate that using interstitial water concentrations may offer a more accurate approach for quantifying bioaccumulation risk at RDX-contaminated sites than the currently used BAF approach, which is based on bulk soil concentrations. This project (ER-1416) was funded by SERDP.

2D QSAR ANALYSIS OF NITROAROMATIC TOXICITY OF THE TETRAHYMENA PYRIFORMIS

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The present study applies the Hierarchical Technology for Quantitative Structure - Activity Relationships (HiT QSAR) (i) to evaluate the influence of the structure of 95 various nitroaromatic compounds (including some widely known explosives) on their toxicity to the ciliate *Tetrahymena pyriformis*; (ii) for virtual screening of toxicity of new nitroaromatic derivatives; (iii) analysis of the characteristics of the substituents in nitroaromatic compounds as to their influence on toxicity. The 50% inhibition growth concentration (IGC₅₀) was used to develop QSAR models based on Simplex representation of molecular structure. During the second part of the work the whole initial set of compounds was divided into 3 interpenetrating sets depending on the possible mechanism of action.

Obtained 2D QSAR PLS models are quite satisfactory ($R^2=0.86-0.98$; $Q^2=0.71-0.95$). The predictive ability of QSAR models was confirmed through usage of three different test sets (maximal similarity with training set, also minimal and random choice, taking into account toxicity range only) for any obtained model ($R^2_{\text{test}}=0.54-0.97$). Molecular fragments that promote and interfere with toxicity were defined. The initial division into different sets was confirmed by developed QSAR analysis, i.e., the models developed for structures with one mechanism (e.g., redox cyclers) cannot satisfactorily predict the others (e.g., participating in nucleophilic attack, etc.). However, the reliable predictive model can be obtained for all the compounds, regardless of mechanism, when structures of different action modes are sufficiently represented in the training set.

Virtual screening of toxicity for new nitroaromatics has been carried out. It was shown that substituent interference in the benzene ring plays the determining role for toxicity.

ENHANCING RHIZOSPHERE BACTERIAL DEGRADATION OF RDX

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The focus of our research is on understanding the relationship between rhizosphere bacteria and their host plants in environments exposed to munitions compounds. Our overall goals are to identify RDX-degrading bacteria in plant rhizospheres, discover the factors that control their population levels, and develop probes that can be used in the field to detect them.

We have enriched communities of RDX degraders from explosive contaminated soils. We report here the diversity of these community populations including the identification and partial characterization of isolated bacteria capable of using RDX as a sole nitrogen source. Also, we explore the possibility of additional bacteria present in the community which may utilize RDX as a sole nitrogen source but have yet to be isolated. Methods to separate ^{15}N and ^{14}N DNA will be described.

We describe development of group-specific capture probes for 16S rRNA that will be used for quantitative community characterization by hybridization with nested probe sets. Exudate profiles of *Arabidopsis* roots will be described and experiments with colonization by RDX-degrading *Rhodococcus* 11Y.

This research is funded by SERDP Project ER-1504.

ENGINEERING TRANSGENIC PLANTS FOR IN SITU TREATMENT OF RDX

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Decades of military activity on live fire training ranges has resulted in severe contamination of land and groundwater by recalcitrant high explosives. The explosive RDX is a major concern, because of its high mobility through soils and subsequent contamination of ground water. The objective of this SERDP funded project is to engineer plants to contain and degrade TNT and RDX in the root zone of explosives contaminated soil. To achieve this goal we are investigating the expression in plants of novel microbial explosives degrading enzymes.

Our studies on the biodegradation of explosives resulted in the isolation of a strain of *Rhodococcus rhodochrous* that is capable of metabolizing RDX. The gene, *xplA*, responsible for RDX degradation in *R. rhodochrous* strain 11Y was cloned and identified as encoding a cytochrome P450. XplA is of unique structural organization in that it was found to possess a flavodoxin domain fused to the N-terminus of the P450 domain. Recombinant XplA, with its partnering reductase XplB, was shown to efficiently degrade RDX to the metabolites nitrite, formaldehyde and 4-nitro-2,4-diazabutanol. We have demonstrated that expression of the rhodococcal gene *xplA* in the plant system *Arabidopsis* confers the ability to degrade high concentrations of RDX. Transgenic *Arabidopsis* expressing both XplA and XplB were observed to efficiently remove RDX from liquid media. As a model system for RDX phytoremediation in the field, *Arabidopsis* expressing XplA/B were grown in RDX contaminated soil and found to be resistant to RDX phytotoxicity, producing shoot and root biomasses higher than wild type plants. Soil leachate experiments were also conducted on plants grown in pots containing uncontaminated soil which was then flooded with an aqueous solution of RDX, left for seven days then flushed through with water. The results demonstrated that *xplA/B*-expressing plants rapidly removed RDX from soil leachate. Transgenic *Arabidopsis* expressing *xplA* and the bacterial nitroreductase *nfsI* were shown to efficiently remove RDX and TNT from liquid media.

Our primary goal is to introduce the genes discovered for RDX degradation and TNT phytotoxicity resistance into grasses that can be used on training ranges. Transformation of creeping bentgrass with our targeted genes through *Agro*-mediated transformation is currently underway.

This research was funded wholly or in part by SERDP Projects ER-1498 and ER-1318.

THE ROLE OF GLYCOSYLTRANSFERASES IN THE PHYTODETOXIFICATION OF TNT

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The explosive 2,4,6-trinitrotoluene (TNT) is a highly persistent, organic pollutant introduced into the environment by human activities. Contamination results predominantly from the manufacture, use and decommissioning of explosives, and the scale of the pollution is now causing significant international concern. Phytoremediation has emerged as a technology with the capability to remediate this problem. Recently, plants have been successfully engineered with bacterial genes, including a nitroreductase gene (*nfsI*) from *Enterobacter cloacae* that confer enhanced TNT detoxification. However, to effectively use plants to remediate this pollutant, it is vital to understand the genetics and biochemistry behind TNT detoxification. Previous studies have shown that, following uptake by the plant, TNT is reduced to hydroxylamino- (HADNT), then amino- dinitrotoluenes (ADNT). Using *Arabidopsis thaliana* as a model system, we have conducted microarray experiments and identified seven uridine diphosphate (UDP) glycosyltransferases (UGTs) involved in the conjugation of these reduced TNT derivatives. There are over 100 UGTs in *Arabidopsis*, which catalyse the transfer of glycosyl residues from activated nucleotide sugars to acceptor molecules, altering the bioactivity, solubility and/or transport properties of the acceptor molecule. *In vitro* characterisation shows that six of the seven UGTs conjugate glucose to predominantly HADNT, exhibiting marked differences in stereospecificity, favouring either the 2-HADNT or 4-HADNT isomer. In addition to monoglucosides, diglucosides were also produced.

To investigate the role of these UGTs *in vivo*, *Arabidopsis* plants over-expressing these UGTs were produced alone and together with *nfsI*. In liquid culture grown plants, we detected increases in TNT metabolites in these lines compared to wild-type plants. Subsequent HPLC-Mass spectroscopy revealed the presence of glucosides with masses corresponding to those seen *in vitro*. UGT over-expressing lines also exhibited increased root lengths when grown on agar plates containing TNT.

This research was funded in part by SERDP Project ER-1498.

PHYTOREMEDIATION FOR THE CONTAINMENT AND TREATMENT OF ENERGETIC AND PROPELLANT MATERIAL RELEASES ON TESTING AND TRAINING RANGES

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The three current focus areas of this research (SERDP Project ER-1499) are phytodegradation, phytoavailability and phytotoxicity. These focus areas combine to give a holistic understanding of the uses of phytoremediation in the containment and treatment of TNT, RDX and HMX on military ranges.

Part 1: Phytodegradation microcosm studies were performed using potted plants, a grass mixture of bahiagrass (*Paspalum notatum* Pensacola) and switchgrass (*Panicum virgatum* Alamo) and hybrid poplar cuttings (*Populus deltoides* × *nigra* 34), and using two different soils collected from Eglin Air Force Base, Dorovan Muck and Lakeland Soil, spiked with 2,4,6-trinitrotoluene (TNT). The purpose of the microcosm study is to evaluate the performance of the planted systems in removing TNT from contaminated soils. Soils were freshly contaminated with 100 mg/kg TNT and 5 µCi/kg [U-14C]TNT in the laboratory.

Part 2: A new protocol has been developed for measuring the phytoavailability of TNT and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) in soil systems in this project. Solid-phase micro-extraction with negligible depletion (nd-SPME) extracts TNT and RDX from the aqueous phase in a non-exhaustive manner, and will be used for bioavailability assessment of TNT and RDX compounds in aged soils. Preliminary experiments have determined that this method is reliable and measuring bioavailability of RDX and TNT in aged soils is still ongoing.

Part 3: *Populus deltoides* × *nigra* DN34 cuttings were exposed to 5mg/L TNT, a pre-determined threshold concentration for phytotoxicity for up to 48 hours. Triplicate plants were sacrificed at 0, 8, 24, and 48 hours and RNA was extracted from the roots. Using the extracted RNA, the University of Iowa DNA Core then prepared the RNA to be hybridized to the Affymetrix® *Populus* Genechip®. The large quantity of genetic data collected from the triplicates at the four time points (12 microarrays) is being processed using the biostatistical programs R and ArrayAssist® in conjunction with the Affymetrix® gene library and the online JGI poplar tree databases. Preliminary results of a significance analysis of the time course experiment indicate that the genetic areas most affected are carbohydrate transport and metabolism, transcription, posttranslational modification and protein turnover, and lipid transport and metabolism.

IN-SITU EVALUATION OF RELEASE OF EXPLOSIVES COMPOUNDS FROM A CRACKED UXO ITEM

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At the Massachusetts Military Reservation (MMR) particulate residues of explosive filler and broken open unexploded ordnance (UXO) have been observed. Field investigations confirm that releases of explosive compounds such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) have resulted in groundwater plumes. Characterizing the release of RDX and other MEC-related compounds is critical in evaluating future impacts to groundwater and the need for soil/UXO remediation.

Several field and laboratory studies have addressed explosives released from particulates (Lever et al 2005, Lynch et al 2002), however, few have addressed cracked or broken UXO. Thus, a pan lysimeter system containing native soil was placed on the ground surface and a cracked 155-mm munition was placed in it and exposed to the natural precipitation and environmental conditions at MMR. Soil porewater was collected from this apparatus periodically (the frequency dictated by precipitation events) and analyzed for RDX, 2,4,6-trinitrotoluene (TNT), and other explosives compounds. In addition, measurements of precipitation, volume of porewater collected, filler surface area exposed, and other environmental parameters were recorded.

More than 20 porewater samples have been collected and analyzed over a study period of one year. Observed RDX concentrations ranged from 0.4 to 8.9 ppm and TNT concentrations ranged from 0.13 to 11 ppm. Results suggest that: (1) the volume of porewater collected is typically more than 60% of precipitation (indicating <40% evaporation/specific retention), (2) the compounds principally being released are RDX and TNT consistent with the Comp B formulation, (3) the cumulative mass released correlates to surface area of exposed filler and “weathering” of the surface, and (4) the ratio of RDX to TNT also correlates to the degree of weathering, indicating the more soluble TNT is depleted from weathered explosive filler. Observed release rates are compared to theoretical estimates of explosives release from perforated UXO (Praxis, 2004, Lever et al. 2005) and particulates of known surface area. This experiment is intended to provide a baseline methodology for future UXO-based studies and, ultimately, should contribute to an improvement in the ability to predict potential future release of RDX to the environment and thereby assist in defining any required remedial actions.

DISTRIBUTION AND FATE OF PROPELLANT RESIDUES ON MILITARY TRAINING RANGES

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Over the past two years, the U.S. Army Engineer Research and Development Center and the Defence R&D Canada–Valcartier have partnered to develop an improved understanding of the distribution and fate of propellant residues on military training ranges in SERDP Project ER-1481. As a portion of this work, field studies have been conducted to estimate the mass of propellant residues deposited per round fired from various munitions. This research included artillery, mortars, small arms, shoulder-fired rockets, and several large missiles. Particles of the propellant residues deposited have been collected and studied, and initial experiments conducted to measure the rate of release of nitroglycerin (NG) and 2,4-dinitrotoluene (DNT) after deposition. Field studies have been conducted at a number of U.S. and Canadian installations to determine the mass and distribution of residue accumulation from different types of munitions. Depth profiling has been accomplished to document the depth to which these residues have penetrated the shallow subsoil. Lysimeters have been installed at several firing point areas to help assess whether these propellant constituents are migrating downward toward underlying groundwater aquifers. Laboratory column studies have been conducted with NG, nitroguanidine, and diphenylamine to document transport rates for solution phase propellant constituents and develop process descriptors for use in mathematical models to enable prediction of fate and transport for these constituents. Subsequent column studies have utilized intact propellants. A summary of the major accomplishments from these field and laboratory studies will be presented.

ACCUMULATION OF PROPELLANT RESIDUES AT SMALL ARMS FIRING POINTS

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Soil samples were collected at three types of small arms ranges at five U.S. and Canadian installations to determine the concentrations of propellant-related residues that have accumulated in near-surface soils. The ranges included several M-16 rifle ranges where 5.56-mm rounds are fired, 9-mm pistol ranges, and multi-purpose machine gun and rifle ranges (0.50 cal, 0.338 cal, 7.62-mm, 5.56-mm). The small arms rounds fired at these ranges contain nitrocellulose (NC), nitroglycerin (NG), and lesser amounts of 2,4-dinitrotoluene (2,4-DNT). No analyses were conducted for NC, but detectable amounts of NG and two dinitroglycerol compounds were found in near surface soil at all three range types. 2,4-DNT was also detected in many cases, but it was always present at much lower concentrations. Maximum concentrations of NG in surface soils near the firing points ranged from 30.0 to 528 mg/kg for the 5.56-mm rifle ranges, 28.8 to 124 mg/kg for 9-mm pistol ranges, and 10.7 to 576 mg/kg for machine gun ranges. The major accumulation of propellant residues was within 20 m of the firing line for these small arms ranges. Depth profile samples indicate that only small concentrations of propellant-related residues are present at depths below 10 cm, and thus it does not appear that significant amounts of these residues are leaching to groundwater aquifers from small arms ranges. These studies have been funded under SERDP-ER-1481, U.S. Army Garrison Alaska, the Canadian Department of National Defence, and the U.S. Army Corps of Engineers Distributed Source Program.

DISPLACEMENT IMMUNOASSAY OF TNT BASED ON ELECTROACTIVE SILICA NANOPARTICLE LABEL

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We present a novel electrochemical competitive displacement immunosensor for detecting TNT based on the functionalized silica nanoparticle (NP) label. The analogs modified with poly(guanine)-functionalized NPs are attached onto the anti-TNT antibody-coated magnetic beads and then displaced into solution by TNT through competitive immunoreaction. The resulting solution was separated from the immunocomplex coated magnetic beads and transferred to the electrode surface for electrochemical measurements. The sensitive assay of TNT is realized by dual signal amplifications: (1) a large amount of guanine residues is introduced into the solution by displacement and by a poly(guanine)-functionalized silica NP label, and (2) guanine is catalytically oxidized with a $\text{Ru}(\text{bpy})_3^{2+}$ -induced reaction, which results in great enhancement of anodic current. The performance of the electrochemical immunosensor was evaluated, and some experimental parameters were investigated. The method was found to be very sensitive, and the detection limit for TNT is 0.05 ng mL^{-1} . The immunosensor based on the poly[guanine]-functionalized silica NP label offers great promise for simple, rapid, cost-effective detection of explosives.

BIODEGRADATION OF 1,4-DIOXANE

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During SERDP project ER-1422 we evaluate biological degradation of 1,4-dioxane and studied the molecular biology of 1,4-dioxane degrading bacteria. Although several organisms were shown to degrade 1,4-dioxane via cometabolism during growth on propane or THF, 1,4-dioxane was not degraded by indigenous organisms in microcosms created with samples from two different aquifers regardless of the redox conditions employed. Likewise, 1,4-dioxane was not degraded in samples from 2 different treatment systems that had been exposed to 1,4-dioxane for extended periods. No bacteria that could grow on 1,4-dioxane were enriched or isolated from the 4 systems tested. Therefore, results of this study demonstrate that biological treatment and natural biological attenuation are unlikely to be successful remedial alternatives for 1,4-dioxane contaminated sites.

During this project we did complete the first elucidation of a bacterial biodegradation pathway for 1,4-dioxane. Co-metabolic 1,4-dioxane degradation resulted in the production of 2-hydroxyethoxyacetic acid (2HEAA) that was not further oxidized by the strains tested. 2HEAA was degraded by other isolated organisms and in environmental samples. From these studies we conclude that the inability to metabolize 2HEAA, and thereby generate energy to support prolonged oxidation of 1,4-dioxane, is likely a significant contributing factor preventing biological degradation of 1,4-dioxane. Likewise, the inability of 1,4-dioxane to induce propane and THF monooxygenase genes may also contribute to the recalcitrance of 1,4-dioxane.

Extensive molecular biological analysis of 1,4-dioxane degrading bacteria revealed that each of them produced multiple and diverse monooxygenase enzymes, many of which are induced during growth on their primary substrates. Although none of the cloned genes could be functionally expressed in heterologous hosts strains, evidence generated suggested that broad substrate soluble diiron monooxygenase enzymes are the most likely catalysts of co-metabolic 1,4-dioxane degradation.

CHARACTERIZATION OF MICROBES CAPABLE OF USING VINYL CHLORIDE AS A SOLE CARBON AND ENERGY SOURCE BY ANAEROBIC OXIDATION

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At numerous field sites, anaerobic oxidation of vinyl chloride (VC) has been suspected based on attenuation in anaerobic zones. However, the lack of readily detectable daughter products (i.e., CO₂ and Cl⁻) above background levels makes it almost impossible to document this process without an extensive microcosm study, typically involving custom-synthesized [¹⁴C]VC. A better understanding of the microbes that mediate this process is needed before more efficient methods can be developed to detect anaerobic oxidation in situ and possibly enhance this process. In a previous project, we documented the occurrence of anaerobic VC oxidation at a contaminated site in southern California, using laboratory microcosms. We were then able to develop low-sediment enrichment cultures that repeatedly consumed VC at increasing rates under anaerobic conditions without accumulation of ethene or other nonchlorinated volatile products, including methane, and demonstrated that ca. 70% of [¹⁴C]VC could be accounted for as ¹⁴CO₂.

The overall objective of this research project is to culture and ultimately isolate and characterize a microbe that is capable of using VC as a sole source of carbon and energy by anaerobic oxidation. Efforts are underway to revive activity in the original enrichments. However, these were developed several years ago and it may not be feasible to reestablish them. An effort is underway to recover the same type of activity by preparing new microcosms with samples from the same contaminated site. Treatments include no amendments added and ones supplemented with amorphous Fe(III); EDTA-Fe(III); amorphous Mn(IV); anthraquinone 2,6-disulfonate; and sulfate. The first set of microcosms was prepared with first flush groundwater from two wells. A second set was prepared using groundwater plus soil (which became available at a later date). Microcosms with first flush groundwater from a second site have also been prepared.

Following several months of incubation, decreases in VC have been observed in many of the microcosms, although in most cases as a consequence of reductive dechlorination. In a subset of the microcosms, decreases in VC have been noted without a significant increase in ethene. Samples from these microcosms have been transferred to groundwater and [¹⁴C]VC has been added, to determine if the VC is being mineralized. A third set of microcosms will be prepared soon with first flush groundwater from another site, to further increase the chances of developing an enrichment culture that grows anaerobically using VC as a sole source of carbon and energy.

CHARACTERIZATION OF DEGRADATION OF CHLORINATED ETHENES AND REDOX-SENSITIVE CONSTITUENTS IN COLUMN REACTORS SIMULATING CONSTRUCTED WETLAND CONDITIONS

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Constructed wetland is one of treatment technologies that use natural biogeochemical processes to remove organic and inorganic contaminants from the wastewater. Our ongoing investigations have shown that the constructed wetland can be effective for the treatment of the groundwater contaminated with chlorinated organics (e.g. tetrachloroethylene). Six upward-flowing column reactors (mesocosms) were designed (PVC Columns, 15 cm in diameter and 5 ft in height with hydric soil in fall 2005) to simulate the conditions of an upward-flowing constructed wetland located at Wright Patterson Air Force Base in Dayton, Ohio. All upward-flowing mesocosms were filled with the wetland soil and each species of wetland plants (*Scirpus atrovirens* and *Carex comosa*) were planted in duplicate and remaining two mesocosms did not include vegetation, which was treated as a control reactor.

In this study, degradation of chlorinated ethenes and the distribution of electron acceptors were characterized for six column reactors. Water samples were frequently collected from 7 different sampling ports of reactors and chlorinated ethenes and its daughter products (PCE, TCE, DCE isomers, VC, and methane) were analyzed by gas chromatography. Inorganic species (ferrous iron, nitrate, nitrite, ammonium, and sulfate) were analyzed by spectrophotometer and ion chromatograph. The data analysis will show the degradation profile of PCE and daughter products with the soil depth in the column reactor. Also, the results of redox-sensitive constituents will contribute to the understanding of the biogeochemical processes along with the degradation of chlorinated ethens in the same soil zone.

LOADING RATES AND IMPACTS OF SUBSTRATE DELIVERY FOR ENHANCED IN SITU ANAEROBIC BIOREMEDIATION

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Effective application of enhanced *in situ* anaerobic bioremediation of chlorinated solvents in groundwater depends on the delivery of appropriate levels of substrate amendments in the subsurface and the development of optimal geochemical conditions for anaerobic biodegradation processes to occur. An inadequate substrate loading rate (i.e., the volume, concentration, and frequency of injection) may result in reducing conditions that are insufficient to support complete dechlorination of chlorinated solvents, thereby increasing the potential for accumulation of regulated intermediate dechlorination products. Conversely, excessive levels of organic substrate may lead to inefficient utilization of substrate for anaerobic dechlorination and the potential for long-term adverse impacts to secondary groundwater quality. Therefore, determining an appropriate substrate loading rate and delivery method are critical design and operational objectives for successful implementation of enhanced anaerobic bioremediation.

The objectives of this study are to (1) better understand the effects that substrate loading rates have on substrate distribution and persistence, (2) determine how control of loading rates affects amendment reactivity and development of optimal geochemical conditions, (3) identify loading rates that have adverse impacts on secondary water quality, (4) evaluate the effect that differing substrates or loading rates have on hydraulic conductivity, and (5) develop practical guidelines for designing and optimizing loading rates and injection scenarios for differing substrate types and for differing geochemical and hydrogeologic conditions.

Practitioners of enhanced *in situ* anaerobic bioremediation of chlorinated solvents use differing methods (e.g., stoichiometric mass calculations or empirical estimates) to determine substrate requirements. Determining substrate loading rates is not an exact science, with considerable uncertainty in the methods currently employed. To account for this shortcoming, a substantial design factor is frequently applied, casting some doubt on the value of the calculation. Given these observations, many applications fail to achieve performance expectations or develop unanticipated long-term compliance problems. A comparative review of the methods currently used to determine substrate loading rates is provided. Case studies of substrate determinations and subsequent field modifications provide practical insight into the utility of theoretical substrate calculations or empirical methods. Results of this study will be used to develop guidance for designing appropriate substrate loading rates and implementing effective amendment strategies, with recommendations for the appropriate use of substrate demand calculations and site-specific design factors.

DETERMINING INTRINSIC TCE DEGRADATION AT DOE EM SITES: ENZYME PROBES

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Chlorinated solvents are the most common and widespread contaminants in soil and groundwater at DOE Environmental Management (EM) sites. The majority of the groundwater plumes at DOE facilities are typically aerobic; thus, degradation mechanisms commonly relied on for biological degradation of TCE, reductive biological and abiotic degradation, are not effective at these sites. Field demonstrations over the past five years have shown that aerobic cometabolic degradation of TCE can play an important role in the attenuation of TCE in groundwater systems; enzyme probes are molecular tools that can be used to identify the activity of cometabolic organisms in situ. More recently, enzyme probes have been combined with laboratory microcosms to estimate TCE degradation rates and determine realistic rates of TCE biological degradation under field conditions.

This emerging science has the potential to fundamentally transform the DOE EM Program and to facilitate the transition of the clean-up activities to monitored natural attenuation or enhanced attenuation remedies. Thus, under direction of the DOE EM Program, a demonstration to determine whether sustainable TCE biodegradation is occurring within the regional gravel aquifer (RGA) of the Northwest Plume at the Paducah Gaseous Diffusion Plant was performed. The purpose of this demonstration was to use enzyme probes and carbon isotopic fractionation tests to determine whether bacteria capable of aerobically biodegrading TCE were present and actively contributing to the attenuation of TCE in groundwater at this site.

The groundwater plume in this study originates from a DNAPL source area located in subsurface soil and groundwater, created by suspected historic leaks and spills of solvents; this particular TCE plume extends to areas off DOE property. Results of an initial enzyme probe sampling detected the presence and activity of enzymes capable of TCE cometabolism (aromatic and methane oxygenases) across the plume. In addition, enzyme presence and activity was detected in surface water samples, and within monitoring wells outside the plume boundaries. Microcosm studies to determine TCE degradation rates for multiple locations within this plume are currently being planned. The immediate goals of this study include the determination of realistic rates of TCE cometabolic degradation for the varying field conditions within the RGA of the Northwest Plume at the PGDP; the ultimate goal of these studies is to provide multiple lines of evidence to support cometabolic degradation potential within this and other contaminated groundwater plumes at this site. This work is currently supported by ESTCP, Project ER-0708.

KINETICS OF DCE AND VC MINERALIZATION UNDER ANOXIC CONDITIONS

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Data on the kinetic character of anoxic microbial chloroethene mineralization is presently limited to a single study on anoxic DCE and VC mineralization in surface-water sediments under methanogenic and Fe(III)-reducing conditions. The results of this single study indicated that VC mineralization followed Michaelis-Menten kinetics and that the kinetic parameters of the process varied substantially according to the indigenous redox conditions. In contrast, anoxic DCE mineralization demonstrated first-order kinetics and the kinetic parameters of this process were not sensitive to redox conditions. In light of the apparent differences in the kinetics of anoxic microbial mineralization of DCE compared to VC, the lack of information on the kinetics of anoxic microbial mineralization of either compound in groundwater systems and the fact that information on the kinetics of anoxic chloroethene mineralization in surface water systems is limited to a single study, a more comprehensive evaluation of the kinetic characteristics of anoxic chloroethene mineralization is required for a range of redox conditions and hydrologic environments, if reasonable estimates of the contribution of the process to overall chloroethene biodegradation are to be made. SERDP Project ER-1558 is investigating the kinetic characteristics of anoxic DCE and VC mineralization under a range of redox conditions in surface-water and groundwater sediments collected from several DoD sites, in order to provide further insight into the type of kinetics and the magnitude and variability of the kinetic parameters that are associated with anoxic DCE and VC mineralization in the environment. The results of this study will be interpreted with respect to the range of redox conditions and chloroethene concentrations reported at DoD facilities in order to provide a better understanding of the circumstances under which anoxic microbial degradation of DCE and VC to non-diagnostic products may be a significant component of in situ chloroethene biodegradation.

SUBSTRATE RANGE AND MICROBIAL DIVERSITY OF SDC-9

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During our ESTCP-funded project (CU-0515) we evaluated the ability of an enriched dechlorinating culture, SDC-9, to degrade chlorinated ethenes, chlorinated alkanes, and mixtures thereof. In addition, a recent preliminary evaluation of SDC-9's ability to dechlorinate Arochlor 1260 suggested that the culture may have some activity against PCBs, but longer incubations are needed to confirm this activity. We also evaluated the culture's ability to degrade Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane). This compound was rapidly degraded by SDC-9, and 1,1-dichloro-1,2,2-trifluoroethane, trifluoroethene, and difluoroethene were identified as potential degradation products.

Molecular analysis of SDC-9 revealed that the consortium's microbial population changes during growth on different substrates, suggesting that different members of the consortium are involved in degradation of the many pollutants degraded by the culture. For example, after growth on PCE, DGGE analysis showed the presence of four significant bands on the resulting gel, revealing the existence of two *Dehalococcoides*-type sequences, a sequence for a *Desulfovibrio*-type organism, and a fourth band representing a spirocheate. After prolonged growth in a fermentor with 1,1,1-TCA as the electron acceptor, the DGGE gel contained 6 prominent bands. These bands represented five *Desulfovibrio*-related sequences and one *Desulfobacterium* sequence. After growth on carbon tetrachloride, DGGE analysis identified at least three additional sequences that were not previously detected in the consortium. These sequences were homologous to two sequences identified in an anaerobic PCB-degrading consortium, and a sequence from a uranium reducing culture. These results demonstrate that common molecular biological tools like DGGE may underestimate the microbial diversity of microbial consortia if the culture is analyzed only after growth on a single or few substrates. Furthermore, they suggest that highly enriched cultures like SDC-9 that had been grown for several years with PCE or TCE as the primary electron acceptor may contain persistent microbial populations that can respond to the presence of other pollutants, thereby increasing the substrate range of the consortium.

STANDARDIZED PROCEDURES FOR USE OF NUCLEIC ACID-BASED TOOLS FOR MICROBIAL MONITORING

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The use of molecular biological tools (MBTs) for the detection and quantification of biomarkers (i.e., specific nucleic acid sequences, peptides, proteins, and lipids) in environmental samples is rapidly increasing as remedial practitioners seek to improve the design, field performance, and monitoring of biologically-based remediation technologies. While academic research facilities and several commercial entities have emerged in recent years to provide MBT analyses, often targeting *Dehalococcoides* organisms, there are currently no standardized methods for collection, preservation, transport, storage or processing of environmental samples. These factors all have the potential to significantly influence the analytical results because biomarker integrity during the entire analytical process has not been established.

SERDP ER-1561 performs a systematic evaluation of the factors affecting MBT data to improve the accuracy and reproducibility of these analyses. This will include the development of standardized sample collection and processing procedures to establish user confidence and widespread implementation of these powerful tools for enhanced site management. MBT standardization methods from the medical, forensics, biodefense, and other sectors will be reviewed to bring the current state-of-the-art to site remediation applications.

Molecular techniques for analysis of environmental samples currently do not include surrogate standards or matrix spikes to quantify the efficiency of each analytical step. Experiments are underway to identify and test suitable surrogate standards that will be subsequently used to conduct a systematic evaluation of the efficiencies of each step of the analytical procedure, from sample collection to reporting biomarker concentrations. A standard reference culture containing *Dehalococcoides* organisms along with the surrogate standard(s) will be used to systematically test factors that affect the quantification of *Dehalococcoides* (e.g., holding times, sampling methods, storage temperatures, matrix interferences, preservation methods). The standard *Dehalococcoides* culture(s)/surrogate(s) will also be required to address the relationship between true soil densities of *Dehalococcoides* and the corresponding biomarker concentrations in groundwater samples.

POLYELECTROLYTE-MODIFIED NANOSCALE ZEROVALENT IRON: CHARACTERISTICS OF THE ADSORBED POLYELECTROLYTE LAYER AND THEIR EFFECTS ON DISPERSION STABILITY AND TCE DECHLORINATION

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Nanoscale zerovalent iron (NZVI) are 20nm- to 70nm-sized Fe⁰/Fe-oxide particles used to reduce or immobilize many environmental contaminants. NZVI emplacement requires surface modification, typically by adsorbed polyelectrolytes to minimize aggregation and deposition onto aquifer media. These adsorbed layers, however, can decrease NZVI reactivity. This study (1) examines the ability of surface modification by poly(styrene sulfonate) with a MW of 70k g/mol (PSS70K), carboxymethyl cellulose with MW's of 90k and 700k g/mole (CMC90K and CMC700K), and polyaspartate with MW's of 2.5k and 10k g/mole (PAP2.5K and 10K) to limit NZVI aggregation, and (2) to systematically evaluate the effect of surface modification on TCE dechlorination, by product formation, and H₂ evolution.

Polyelectrolyte adsorption onto NZVI is determined by solution depletion, and Ohshima's soft particle theory is applied to characterize the adsorbed layer thickness, softness parameter, and surface potential. Based on DLS measurements, PSS70K, PAP2.5K, PAP10K, and CMC700K modifiers stabilize 82 vol%, 73 vol%, 82 vol%, and 52 vol% of RNIP particles against aggregation. After seven hours of sedimentation, 40 wt%, 32 wt%, 34 wt%, 5 wt%, and 20 wt% of the particles remain suspended. The enhanced stability correlates with the surface excess and thickness of the adsorbed polyelectrolyte layers.

The TCE dechlorinate rate and reaction products are measured as a function of adsorbed polyelectrolyte. Scheutjens-Fleer theory, for polymer adsorption, is applied to distinguish between reactive site blocking by trains (polymers attached to the surface) and mass transfer resistance due to loops and tails (unattached layer brushes on the surface) on the dechlorination rate and products formed. The layer thickness of the sorbed polyelectrolytes and the TCE partitioning coefficient both affect the diffusion of TCE through the sorbed polyelectrolyte layer and, thus, reactions are mass transfer limited. This approach and conceptual model should be applicable to other high molecular weight polymeric surface modifiers adsorbed to nanoparticles.

CONTINUOUS-FLOW COLUMN STUDIES TO EVALUATE THE EFFECTS OF DIFFERENT PCE AND TCE CONCENTRATIONS AND LACTATE ADDITION ON REDUCTIVE DEHALOGENATION

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A continuous-flow column experiment was conducted to evaluate the reductive dehalogenation of tetrachloroethene (PCE) and trichloroethene (TCE) in Hanford aquifer material after bioaugmentation with the Evanite (EV) mixed culture. The study evaluated reductive dehalogenation at different injection concentrations of PCE (0.09 to 0.27 mM) and trichloroethene (TCE) (0.38 to 1.52 mM) under flow conditions more representative of in-situ remediation. Lactate was added as a fermenting electron donor, and its concentration was increased during the course of the experiment from 0.67 to 1.42 mM to compensate for the increasing PCE and TCE concentrations. The study was conducted as a series of transient tests, with pseudo-steady-state conditions established at each injection concentration. The aquifer material was chemically pre-treated using a 5 mM Na₂S solution to reduce some of the Fe(III) present. Shortly after adding lactate and the EV culture to the column, cis-dichloroethene (c-DCE) concentrations exceeded the influent PCE concentration, indicating enhanced PCE desorption and transformation. Approximately 95% of PCE was transformed to ethene (ETH) at concentrations of 0.09 and 0.27 mM within a hydraulic residence time of 3.6 days. Lactate was fermented to acetate and propionate, and upon the increase in PCE or TCE injection concentration the transient consumption of acetate and propionate was observed. The complete utilization of propionate, but with acetate in excess, resulted in incomplete transformation of PCE to ETH, with pseudo-steady-state concentrations of vinyl chloride (VC) and c-DCE observed in the column effluent. The recovery of essentially complete PCE or TCE transformation to ETH was achieved upon increasing the injection concentration of lactate, which resulted in the increase in acetate and propionate in the column effluent. The detection of excess propionate coincided with effective transformation of PCE and TCE to ETH. Immediately after switching from PCE to TCE addition (0.38 mM), 94% transformation to ETH was observed. At a TCE injection concentration of 1.52 mM (20% of the TCE solubility in water), transformation was essentially complete to ETH. ETH concentrations then exceeded its solubility in water, resulting in bubble formation and incomplete mass balances. Electron donor and acceptor mass balances showed the electron transfer efficiency towards dehalogenation reactions increased from 13% at low PCE concentrations to 39% at the highest TCE concentration. Iron reduction was found to be a competing electron acceptor reaction. The study demonstrated that controlled column studies can be performed to evaluate the association of PCE and TCE dehalogenation reactions to lactate fermentation reactions.

IMPACT OF pH ADJUSTMENT AND BIOAUGMENTATION ON ENHANCED REDUCTIVE DECHLORINATION OF TRICHLOROETHENE

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Dechlorinating bacteria are pH sensitive and dechlorination rates decline below a pH of 6. At many sites the pH is naturally low and can inhibit reductive dechlorination. However, the pH issue is further complicated by geochemical changes that occur during anaerobic bioremediation. Reduction of iron and manganese oxides and sulfate will consume H⁺ causing an increase in pH, while CO₂ production and/or fatty acid accumulation during fermentation of complex substrates can cause a decline in pH.

In a pilot study funded by the ESTCP (ER-0221), Solutions-IES injected emulsified oil substrate (EOS[®]) into a trichloroethene (TCE)-contaminated aquifer beneath SWMU 17 at the Charleston Naval Weapons Station in Charleston, SC. The substrate was distributed via a grid of temporary injection/recirculation wells across a 20 × 20 ft. test area to evaluate the effectiveness of the approach for source area treatment in a shallow, but relatively tight, silty clay formation. The average starting concentration of TCE was 18,000 µg/L in three monitor wells centrally located in the treatment grid. Shortly after EOS[®] injection, TCE began to decline with concurrent production of cis-DCE. However within a few months, TCE biodegradation stalled.

Groundwater monitoring data indicated that the groundwater remained strongly reducing and was not carbon limited. However, the groundwater pH varied from 4.6 to 5.9. Laboratory microcosm studies showed that adjustment of the pH to above 6 stimulated reductive dechlorination of TCE to cis-DCE, but bioaugmentation with BAC-9 dechlorinating consortium was necessary to complete the transformation to ethene.

Approximately 860 days after the initial injection of EOS[®], a pH-buffered EOS[®] formulation called AquaBupH[™] was injected through a direct-push injection tools into the pilot test area. Almost 4,200 lbs of AquaBupH[™] were introduced to the aquifer. Within one month of injection, the pH increased to 6.4 to 7.7. Rapid biodegradation of TCE and cis-DCE resumed with TCE reduced to below the analytical detection limit in most wells. However, further metabolic conversion to vinyl chloride and ethene remained slow, indicating bioaugmentation may be required to meet regulatory targets. The study also evaluated the impact on mass flux through the treatment zone and its usefulness as a measure of source area treatment.

DEVELOPING A DESIGN TOOL FOR PLANNING EMULSIFIED OIL INJECTION PROJECTS

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Emulsified edible oils have been injected at hundreds of sites throughout the world to stimulate anaerobic biodegradation of chlorinated solvents and other anaerobically biodegradable contaminants. However to be effective, the oil droplets must be brought into close contact with the contaminant to be treated. This can be difficult in heterogeneous aquifers where large spatial variations in hydraulic conductivity make it difficult to uniformly distribute the oil droplets. In the emulsified oil process, a specified volume of emulsified oil and water are injected into the aquifer through an array of temporary or permanent wells. The oil droplets are transported through out the aquifer by the ambient or induced groundwater flow until they attach to sediment surfaces. Once attached, the oil is gradually fermented to hydrogen and low molecular weight fatty acids that drive anaerobic biodegradation of chlorinated solvents and other anaerobically biodegradable contaminants. In general, there are only a limited number of approaches that can be used to improve the oil distribution: (a) injecting more oil; (b) injecting more water; (c) using more closely spaced wells; and (d) varying the location and/or timing of the injection. All of these approaches can potentially be effective. However, there is no available information on the effect of these different approaches on the injection system performance.

In ESTCP supported Project ER-200626, the numerical models MODFLOW and RT3D were used to simulate emulsion transport and distribution in spatially heterogeneous aquifers using a rate limited Langmuir sorption approach. The hydraulic conductivity field was generated using the Turning Bands Method with three different levels of heterogeneity: low, medium and high. Injection approaches included simultaneous and sequential injection of wells arranged in grids and barriers. Injection performance was evaluated by calculating the volume-weighted and flow-weighted contact efficiencies. Performance curves were then generated illustrating the effect different design variables on contact efficiency. A spreadsheet based tool was developed to assist designers in planning efficient, lower cost injection systems. Information on aquifer parameters and costs for labor, material and well installation are entered first. Results from the MODFLOW/RT3D model simulations are incorporated as a series of performance curves illustrating the effect of different design variables (e.g., amount of oil, amount of water, injection well spacing, injection pattern) on oil distribution. The designer can then easily evaluate the effect of different injection approaches on oil distribution, initial capital cost and 30-yr life cycle costs.

PERFORMANCE ASSESSMENT DURING REMEDIATION OF CHLORINATED SOLVENT CONTAMINATED SITES: POTENTIAL FOR AND METHODS TO MITIGATE ERRORS BASED ON SAMPLING USING DIRECT-PUSH CORES AND GROUNDWATER WELLS

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The effective in situ remediation of sites contaminated with chlorinated solvents and DNAPL source zones continues to be extremely difficult and even where ‘success’ has been claimed, questions often remain regarding the validity of the monitoring data that are used to judge a remediation as successful. Standard practices for performance assessment, which commonly rely on sampling of subsurface soil and groundwater, can be error-prone due to loss of volatile contaminants during sample collection and handling as well as the unaccounted-for effects that in situ remediation can have on DNAPL contaminant behavior. A SERDP project is ongoing at the Colorado School of Mines (CSM) to enhance the fundamental understanding of current practices and develop improved methods for obtaining and utilizing data from groundwater samples and direct-push cores. The project involves laboratory studies using pervasive organic contaminants with contrasting properties along with modeling to determine: (1) the effects of remediation agents on the ability to infer DNAPL mass levels from groundwater data, and (2) the effects that soil sampling methods can have on the accuracy of measurements made for DNAPL organics in direct-push cores. The results of the CSM project will be used to delineate the limitations of current standard practices and develop improved monitoring and assessment methods. Two primary series of experiments are currently being conducted. The first is focused on investigating the effects that remedial amendments can have on the fraction of organic carbon (*foc*) and the nature of contaminant-organic carbon partitioning (*Koc*). Zero headspace reactors are being used with soils of varied grain size and natural *foc*, with either aqueous or pure phase TCE present. The remediation agents include oxidants (potassium permanganate, activated persulfate), surfactants (DowFax 8390, Tween 80), and heating (varied temperatures). A second series of experiments involves sampling of intact soil cores containing known quantities of PCE, TCE, and 1,1,1-TCA, at varied concentrations with media temperatures of 5, 25, 40, 60, or 80°C. Five different methods of sample collection are being evaluated that are representative of common field methods as determined through a survey of practitioners. These methods have very low to relatively higher degrees of sample disruption and atmospheric exposure. This poster presentation will present the methods and results obtained to date from this research along with their implications for monitoring and performance assessment during in situ remediation.

DEVELOPMENT OF TREATABILITY STUDY PROTOCOL FOR THE REMEDICATION OF CONTAMINATED GROUNDWATER BY IN SITU CHEMICAL OXIDATION (ISCO)

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The contamination of groundwater with biorefractory organic chemicals continues to be a significant problem. However, recent advances in the use of activated peroxygens (hydrogen peroxide and persulfate) for in situ chemical oxidation (ISCO) hold promise for the rapid remediation of dissolved, sorbed, and dense nonaqueous phase liquid (DNAPL) contaminants. Activated persulfate is the use of persulfate anion ($S_2O_8^{2-}$) and an activator, such as iron or hydroxide, to generate a mixture of reactive oxygen species. Activated persulfate has similar reactivity to catalyzed H_2O_2 propagations (CHP, i.e., modified Fenton's reagent) and can destroy a wide range of contaminants. Persulfate is more stable than hydrogen peroxide, with a half-life of 10 to 50 days. Peroxygen chemistry is highly complex, but most ISCO peroxygen vendors use one set of process conditions, not based on fundamental chemistry, for all sites.

Treatability studies for the design of ISCO systems have not been given the same emphasis as those used in the design of industrial waste treatment systems. Depending on the contractor or consultant, treatability studies may range from none at all to batch and column studies. In general, however, treatability studies tend to be more simple than elaborate. Many treatability design issues are not resolved and no protocols have been established. The purpose of this segment of peroxygen demonstration/validation under ER-0632 is to design an effective ISCO treatability study and demonstrate the feasibility of peroxygen ISCO in the field. The treatability study is being conducted in three tiered stages: (1) initial screening focused on the rate of oxidant depletion and demand, (2) detailed peroxygen decomposition rates using a range of activators for persulfate and stabilizers for hydrogen peroxide, and (3) contaminant destruction studies using conditions that provide maximum peroxygen stability. Peroxygen chemistry is strongly influenced by the geochemistry of the subsurface; for example, iron and manganese oxides greatly affect hydrogen peroxide decomposition rates, and soil organic matter influences persulfate decomposition rates. Therefore, heterogeneity and stratigraphy are first being assessed; if heterogeneity is high, treatability studies will be conducted on the varied subsurface materials at the site. The treatability study is a comprehensive effort that will include a range of peroxygen concentrations and concentrations of stabilizers and activators. After the treatability studies are complete, the optimum dosage of peroxygen and stabilizer/activator will be determined and used in field demonstration/validation.

FIELD APPLICATIONS OF ZVI-CLAY TECHNOLOGY FOR CHLORINATED SOLVENT SOURCE ZONES

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ZVI-Clay uses conventional soil mixing equipment to admix reactive media (e.g., zero valent iron) and stabilizing agents (e.g., clay) with contaminated soil. Through mixing, heterogeneous subsurface source zones are transformed into uniform bodies of soils, contaminants, reactive media, and stabilizing agents. Within the treated interval, reactive media drives contaminant degradation while stabilizing agents reduce the hydraulic conductivity. In addition, soil mixing overcomes the challenge of delivering reactive media through complex geologic media. The overall benefit is a dramatic reduction in contaminant flux from the treated interval.

Appropriate reactive media can be selected to treat site-specific contaminants of concern. A common application uses zero valent iron (ZVI) to treat chlorinated solvents. Corrosion of the iron drives degradation of the solvents (Gillham and O'Hannesin, 1994). Reaction rates generally follow pseudo first-order kinetics. In soils treated by ZVI-Clay, observed half-lives for many chlorinated solvents range from 10 to 1,000 hours (Olson, 2005). With these conditions, remaining contaminant mass is reduced by 90 percent every few days to few months. Degradation rates are primarily a function of the contaminant and the amount and type of iron used.

Stabilizing agents (typically clay) provide multiple benefits in the ZVI-Clay process. First, admixing clay and soil reduces hydraulic conductivity to values similar to bentonite slurry walls ($<10^{-7}$ cm/s). This provides source containment. As such, ZVI-Clay is a "belt and suspenders" technology achieving both source depletion and containment. Inclusion of stabilizing agents also: (1) facilitates drilling, (2) provides a high viscosity delivery fluid (necessary for suspension of the reactive media), (3) improves the uniformity of subsurface mixing, (4) reduces inflow of competing electron acceptors (e.g., dissolved oxygen and nitrate), (5) increases residence time for the reaction to proceed, (6) enhances capillary rise precluding air entry into treated material above the water table, and (7) constrains adverse migration of dense non-aqueous phase liquids. To date, ZVI-Clay has been used as a full-scale remedy for chlorinated solvent source zones at eight sites. These include sites at three industrial sites and five DoD facilities. Our poster will present ZVI-Clay cost and performance data for each of these sites. Results indicate that the technology has the potential to be faster, less costly, and more effective than competing technologies for a significant set of sites.

DNAPL REMEDIATION AT CAMP LEJEUNE USING SOIL MIXING WITH ZVI-CLAY

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Site 88 at Marine Corps Base Camp Lejeune, NC, is the former Base dry cleaners. The dry cleaner was about 60 years old and located in a densely developed area. Historical activities resulted in a release of solvents, especially tetrachloroethene (PCE). The volume of contaminated soil was about 7,000 cubic yards, containing an estimated 14 tons (~2,100 gallons) of PCE. Prior to implementation, groundwater concentrations of PCE and daughter products totaled 145,000 $\mu\text{g/L}$ and product was observed in several monitoring wells. Soil mixing with zero valent iron (ZVI) and clay addition was the selected for remediation because the patented technology is robust, can overcome subsurface heterogeneity, and reduces the soil conductivity thus reducing contaminant mobility. The ZVI-clay and soil mixture was injected using a 10-ft auger mounted on a crane to mix 146 overlapping columns to a depth of 20 feet below ground surface. After preparing the site by removing all monitoring wells, subsurface utilities and the former building slab, treatment occurred over 17 days with 200 tons of ZVI and 100 tons of bentonite mixed into the soil. Post-treatment monitoring of the site has included soil, groundwater, soil vapor sampling and analyses, and qualitative analysis using membrane interface probe (MIP) technology. The remedial action has worked well as PCE concentrations in soil have been reduced from 1,100 mg/kg to less than 1 mg/kg across most of the treatment area. Soil gas results have shown 99% reduction in PCE. In addition the hydraulic conductivity of the soil has been reduced by an order of magnitude, thus reducing future contaminant migration. After treatment was completed, the site was stabilized using concrete and a parking lot has been constructed over the entire area.

COUPLED TECHNIQUES FOR MORE EFFICIENT GROUNDWATER REMEDATION: POLYMER FLOODS AND OXIDATION TREATMENT

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The coupling of polymer floods with traditional in situ groundwater remediation techniques holds promise for increased efficiency of treatment. The viscosity of a polymer flood should encourage flow between layers of differing permeability, thus enhancing the overall delivery of treatment agents throughout an aquifer. One promising polymer-enhanced treatment combination involves the use of chemical oxidants, which have been applied previously with some success at sites contaminated with chlorinated compounds. The results of 72-hour compatibility experiments utilizing two non-toxic polymers (hydrolyzed polyacrylamide and xanthan) and two chemical oxidants (sodium persulfate and potassium permanganate) are presented, as part of SERDP Project ER-1486 research. Monitoring of oxidant/polymer mixtures provides information on the amount of excess oxidant consumption as well as the stability of the solutions' viscosity through time. While oxidant demand remains generally low in these batch experiments (ranging from 10-30%), solution viscosities differ widely depending on the choice of oxidant. Sodium persulfate appears to cause a drastic reduction in the viscosity of batch mixtures, but certain polymers can apparently retain some portion of their viscous properties when combined with potassium permanganate. Infrared spectroscopy of the polymer/oxidant mixtures offers additional insight into the chemical structures of each polymer which may be most susceptible to oxidative damage. These combined data reveal that xanthan polymer and potassium permanganate is the most compatible polymer/oxidant pair of those mixtures tested. This combination is further investigated to determine if the xanthan biopolymer inhibits the degradative capabilities of the oxidant, using tetrachloroethene (PCE) and trichloroethene (TCE) as test contaminants. Preliminary findings suggest that the presence of polymer does not significantly slow the rate of oxidation of these chlorinated compounds. Further experiments to determine the possible utility of this polymer/oxidant mixture in field situations include column experiments to determine the relative transport of oxidant within a polymer flood. Both clean sands and natural soils are utilized to determine the possible effects of sorption and natural organic matter on the stability of the polymer/oxidant mixture.

WATER-SOLUBLE POLYMERS TO ENHANCE THE SWEEP-EFFICIENCY OF IN SITU REMEDIATION AGENTS

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A key challenge to subsurface remediation effectiveness is achieving an efficient sweep of the contaminated zone during treatment. This is true of forced-injection strategies that rely on direct contact between the amendment and the target contaminant, as well as for strategies that rely on uniform placement of amendments and subsequent dissolution of the amendment. Subsurface permeability heterogeneities can often limit the sweep efficiency of injected remediation agents due to by-passing of lower permeability media (LPM) during treatment. If sufficient contamination exists within this LPM, remediation fluid by-passing during initial treatment can lead to rebounding of contaminant concentrations within the treatment zone. Methods designed to mitigate the potential for preferential flow and by-passing effects would therefore be highly desirable to the Department of Defense to increase remediation efficiencies and reduce the costs of environmental restoration efforts.

The overall focus of this research (SERDP ER-1486) is to explore the utility and efficacy of adding water-soluble polymers to remediation fluids to promote heterogeneity control and mitigate by-passing of LPM during in situ treatment. This presentation will highlight important mechanisms governing the transport of xanthan gum biopolymer within environmental porous media, as well as mechanisms specific to xanthan gum solutions and their ability to enhance sweep efficiencies. Additionally, the results of 2-D tank experiments and numerical simulations will be presented which center on assessing percentage sweep-efficiency improvements within a layered/oriented lens heterogeneous permeability structure. Finally, correlations between observed sweep-efficiencies and xanthan gum formulation parameters (e.g., concentration, viscosity) and operational parameters (e.g., flow rates, pulse durations) will be presented. Testing of additional field-relevant permeability structures are planned for this work with the objective of developing relationships between heterogeneity structure and sweep efficiency improvement to allow site managers a means of readily assessing whether including polymer within remediation amendment formulations would be advantageous at a given site.

DNAPL DISSOLUTION IN FRACTURES AND FRACTURE NETWORKS

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Processes impacting the dissolution of dense non-aqueous phase liquids (DNAPLs) in fractured bedrock are not well understood, thereby limiting efforts to predict the longevity of DNAPL sources, select the appropriate remedial technologies, effectively design and implement the selected *in situ* technologies, evaluate remedial performance, and estimate the time needed to remediate a DNAPL source zone. The rate of DNAPL dissolution is typically controlled by interfacial mass transfer between the DNAPL and surrounding groundwater, especially during implementation of *in situ* remedial technologies such as chemical oxidation and bioaugmentation. Thus, changes in the effective DNAPL-water interfacial area in bedrock fractures due to dissolution of the DNAPL source will have a substantial impact on the overall remedial process. The presence of oxidation precipitates, biofilm growth, and dead-end fractures can also impact overall DNAPL dissolution rates. However, comprehensive studies have hitherto not been performed to evaluate and quantify these phenomena in fractured bedrock systems.

The overall goal of this research is to evaluate DNAPL dissolution in fractured geological settings during implementation of *in situ* chemical oxidation and bioaugmentation, and to investigate the subsequent impact of incremental DNAPL removal on groundwater quality. Specific objectives include: (1) developing functional relationships among DNAPL saturation, interfacial area, and dissolution kinetics, (2) identifying potential limitations of chemical oxidation and bioaugmentation in fractures, (3) evaluating the impact of partial DNAPL removal on groundwater quality, and (4) developing fracture-scale and aquifer-scale models to describe and predict DNAPL dissolution in bedrock fracture systems. DNAPL dissolution experiments will be performed in discrete fractures before, during, and after *in situ* chemical oxidation and bioaugmentation treatments. Both DNAPL dissolution rates and DNAPL-water interfacial areas will be measured. The discrete fracture-scale experiments will be repeated at the fracture network scale to evaluate issues related to fracture connectivity during DNAPL dissolution processes. Based on these data, a validated model that includes dissolution kinetics during *in situ* chemical oxidation and bioaugmentation, will be developed to describe and predict DNAPL dissolution in bedrock fractures.

This project was initiated in the Spring of 2007. Accomplishments to date include the design and construction of both the discrete fracture and fracture network systems, evaluation of the dispersion characteristics within the fractures, and preliminary assessment of DNAPL retention, dissolution, and interfacial area within the fracture systems. Implementation of bioaugmentation was shown to enhance the DNAPL dissolution rate.

FIRST THINGS FIRST--INVESTIGATING DNAPL CONTAMINATED FRACTURED ROCK AQUIFERS

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First things first! Understand the framework. Create detailed maps and sections of the geology and then the hydrogeology, contamination flow paths, and site characterization will be easier to understand for scientific researchers, site administrators, and environmental regulators.

US Navy, USGS, and SERDP (ER-1555) collectively work at remediation and investigation of a CVOC DNAPL contamination site in fractured mudstone in the unglaciated part of the Newark Basin in New Jersey as a research site typical of many contaminated bedrock areas in the U.S.

Two thirds of the US is covered with sedimentary rocks, 2/3rd's of sedimentary rocks are mudstones, and 2/3rd's of the US has not been glaciated. The NAWC site mimics the hydrogeologic framework of hundreds of military-industrial contamination sites in the US. Maps and sections of the geology display the gently dipping cyclically deposited mudstone. However understanding the diagenesis, tectonics, off-loading and weathering of the deposits helps researchers interpret their data, site administrator make economic remediation decisions and environmental regulators oversee cleanup.

Bedrock at the Naval Air Warfare Center in West Trenton NJ was deposited in Van Houten cycles a result of Milancovitch cyclicity. Bioturbation and desiccation converted some soft strata to massive strata while deeper water deposits remained laminated. Diagenesis and lithification set the framework for the gamma-ray logs, caused dissolution and cementation, and variably indurated the strata. Tectonics created the fractures within and crosscutting the strata, based on it variable rheology and created the near vertical fault zone. Off-loading preferentially opened the tectonically induced fractures to create primal groundwater and contaminant flow pathways and dead end fractures. Weathering expanded or sealed the pathways.

The heterogeneous nature of the site's framework is simplified by creating and understanding the geology first. The geologic framework prepares the palate to paint the ground water flow model, and architectural drawing to present contaminant location, fate, ground-water flow, remediation efficacy, and regulatory predicaments.

DELIVERY OF REACTIVE IRON PARTICLES FOR TREATMENT OF DNAPL SOURCE ZONES

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The application of reactive iron particles is a promising technology for treatment of dense non-aqueous phase liquid (DNAPL) source zones. Although the success of iron-based technologies depends on both delivery and reactivity in the subsurface, few studies have rigorously investigated the transport of iron-laden suspensions in DNAPL source zones. In such zones, groundwater velocity and chemistry must be controlled to prevent unintended DNAPL mobilization or adverse changes in contaminant accessibility. Under SERDP Project ER-1487, researchers at Tufts University and Georgia Institute of Technology are developing and evaluating delivery systems for application of iron-based technologies within source zones.

Efforts to assess the transport behavior of iron-laden suspensions have focused on obtaining baseline transport parameters for two commercial products: RNIP (Toda America) and Z-Loy (On Materials). Results from one-dimensional (1-D) column experiments indicate that the transport of uncoated RNIP in coarse-grained sand is severely limited unless site hydraulics are designed to provide a groundwater velocity greater than 85 m/d. The relatively high velocities required to transport uncoated RNIP are likely to present significant challenges at field sites. Greater transport of the Z-Loy product was observed in the same porous medium at a significantly lower groundwater velocity (~2 m/d). A total trapping number analysis of the Z-Loy suspension suggests that introducing Z-Loy at pore water velocities similar to those used in the column experiments will not result in substantial mobilization of entrapped TCE-DNAPL.

Encapsulation of the reactive particles within an oil-in-water emulsion is a novel approach which may provide the ability to target DNAPL during the delivery of iron particles. Iron-laden oil-in-water emulsions were developed by first coating commercially-available iron particles with surfactants that promote particle stability within the non-polar phase. Using a phase inversion technique, 10% wt. iron-laden soybean oil was dispersed within a continuous aqueous phase containing different proportions of nonionic emulsifiers. Oil-in-water emulsions were imaged with light microscopy. Analysis of these images suggests that the average diameter of the oil droplets is approximately 1.1 micrometers. The presence of iron within oil droplets was confirmed in the images and supported by an absence of iron agglomeration within the continuous phase; a property that often hinders the injection of aqueous-based iron-laden suspensions. Future research efforts will address the transport and reactivity of iron delivery formulations in porous media systems containing entrapped DNAPL.

INVESTIGATING THE BENEFITS OF DNAPL SOURCE ZONE TREATMENT: SOURCE ZONE ARCHITECTURE, PARTIAL MASS REMOVAL, AND CONTAMINANT FLUX REDUCTION

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Despite documented successes of chlorinated solvent source zone mass reduction, no current technology (e.g., air sparging, chemical flushing) can be expected to remove all DNAPL contamination, even under favorable conditions. DNAPL contamination remaining after aggressive mass removal may lead to persistent elution of dissolved-phase contaminants that pose risks to human health and the environment. SERDP Project ER-1293, a collaboration between researchers at Tufts University, the Georgia Institute of Technology, and the U.S. Air Force Academy, has integrated bench-scale experiments, multiphase numerical modeling, and field investigations to assess and enhance the realized benefits of partial mass removal from DNAPL source zones. This poster summarizes important project findings.

Potential benefits of in situ treatment include reductions in source longevity, reductions in source zone concentrations, reductions in downstream mass flux, and improvements in the amenability to successful follow-on treatment. Two-dimensional bench scale experiments, supported by field-scale numerical modeling, demonstrate that subsurface heterogeneity will lead directly to nonuniform DNAPL saturation distributions. The efficiency of treatments which rely upon dissolution or solubilization was found to be closely linked to DNAPL architecture, with achievement of greater removal efficiencies associated with higher ganglia-to-pool (GTP) ratios. Predictive modeling was found to require incorporation of site-specific NAPL architecture and pre-treatment plume concentrations. Field-tested modeling tools were developed to quantify mass flux and its associated uncertainty. Study results indicate that a high spatial sampling frequency or a staged sampling approach is needed to provide accurate estimates of mass flux.

Performance of coupled source zone treatments, such as surfactant flushing followed by microbial reductive dechlorination, was investigated through batch and column experiments. Batch experiments demonstrated microbial activity in the presence of DNAPL, when dechlorination kinetics exceeded the rate of PCE-DNAPL dissolution, despite inhibition at elevated PCE (>90 mg/L) concentrations, and 1-D column cell experiments confirmed significant enhancements in dissolution (~4.5x) due to microbial activity. On-going research is extending this work to two-dimensional aquifer cell experiments and simulated field settings.

IMPLEMENTATION OF THERMAL TREATMENT TECHNOLOGY USING INNOVATIVE DECISION MAKING TOOLS FOR THE TREATMENT OF DNAPL

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Thermal Treatment Technology consisting of *in situ* soil mixing combined with the injection of steam, hot air, and zero valent iron (ZVI) is an innovative method for the treatment of soil and groundwater contaminated with high concentrations of VOCs and DNAPL. The technology implemented at Cape Canaveral Air Force Station, FL uses a triad approach that supports real-time decision making for effective treatment.

The technology consists of three major elements: soil mixing, injection, and collection system; VOC treatment system; and the Supervisory Control and Data Acquisition System (SCADA). The mixing system consists of an 8 feet diameter auger that shears and mixes the soil as the auger advances below the ground surface while simultaneously injecting steam and hot air. This action causes volatilization of the VOCs from soil particles and interstitial spaces and is transported to the soil surface where it is collected in a 16 foot diameter shroud maintained under negative pressure. The off-gas stream consisting of steam, air, and volatilized contaminants then travel to the vapor conditioning system to remove particulates and moisture from the vapor stream before being collected and treated by a flameless thermal oxidizer. Thermal treatment is supplemented by placement of ZVI to enhance reductive dechlorination of residual VOCs. The SCADA system integrated with analytical instruments including gas chromatographs and flame ionization detectors allow effective coordination and control of various process parameters in the treatment train along with collection of analytical data for instant analysis and reporting. The real-time data collected during treatment allowed onsite managers to develop, evaluate, and execute strategies for additional treatment depth, increased treatment time, and expanding the treatment area beyond the designed treatment area to optimize removal of VOC mass.

This innovative technology was successfully implemented at two sites at Cape Canaveral Air Force Station, FL. The treatment in the source areas at Facility 18003 and Facility 1381, defined as the TCE concentrations in groundwater greater than 10 mg/L, was completed in June 2007. Field management decisions using real-time data resulted in the removal of approximately 389 pounds of total VOC's from 157 cells at the SPCC source area. At Facility 1381, total VOC mass removed consisted of 11,478 pounds from 799 cells. The effective VOC mass removal was directly the result of a well engineered and sophisticated real-time data collection and supervisory control system that enabled field management decisions to most effectively and efficiently remove DNAPL mass at the sites.

UTCHEM MODEL SIMULATIONS OF VARIOUS TREATMENT TECHNOLOGIES FOR CHLOROBENZENES-DDT-DNA

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Thermal, in-situ chemical oxidation, and hydraulic displacement are treatment technologies being considered to remove dense, non-aqueous phase liquid (DNAPL) composed of chlorobenzenes and dichlorodiphenyltrichloroethane (DDT) at a former chemical manufacturing plant. The DNAPL plume, occupying an area of approximately 3.7 acres and 95 feet below surface, is confined below the water table primarily in the saturated zone of the upper aquitard composed of interbedded sands, silty sands, silts, with small amounts of clayey sand and silts. Below the main source area of the site, a 6-inch thick zone of pooled DNAPL covering an area of approximately 805 ft² exists in the lower permeability layers of silt and silt/clay lenses. The presence of substantial quantities of potentially mobile distributions of pooled DNAPL distinguishes this site from many other DNAPL sites where the majority of the DNAPL occurs as disconnected blobs and ganglia of non-mobile organic liquid referred to as residual saturation.

Computer simulations were performed to study alternative strategies and approaches for remediation that address the heterogeneous lithology, complex DNAPL architecture, and the presence of pooled DNAPL. Mass removal of chlorobenzene-DDT, by thermal treatment (steam and hot water injection), and hydraulic displacement (primary pumping) with and without bioremediation, were simulated using UTCHEM, a three dimensional multiphase flow and transport model. The mass distribution and removal rates of chlorobenzene-DDT in heterogeneous porous media were modeled under residual saturation and pooled scenarios. Simulations were run for 30 years. The performance of thermal treatment was studied by varying steam and hot water injection rates, temperatures/pressures, and location and number of injection points. The performance of hydrodynamic displacement was studied by varying extraction rates, and location and number of recovery wells. The results of model simulations will be presented, along with a comparative analysis of each treatment technology. Conclusions and recommendations for thermal treatment and hydraulic displacement for the removal of DNAPL under residual saturation and pooled conditions will be discussed.

IMPROVED UNDERSTANDING OF THERMAL MECHANISMS OBTAINED DURING METER-SCALE EXPERIMENTS SIMULATING DNAPL SOURCES IN AQUIFERS

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At the core of a three-year SERDP-funded research project, two meter-scale (75m³ and 150m³) 3D remediation experiments are being conducted with controlled release of DNAPL into a lower-permeability layer beneath the water table. Their purpose is to better understand the principal mechanisms controlling the performance of thermal conduction heating (TCH) and vapor recovery of DNAPL in the saturated zone, at field-relevant scales and under well-controlled conditions. A numerical model was optimized based on earlier experiments, enabling it to be used to design the remediation experiments. The progression of heating to 100°C and accompanying desaturation are monitored using 300 temperature sensors and 35 time domain reflectometry probes, respectively, allowing comparisons of the physical conditions and numerical simulations. In addition, solution and vapor samplers enable monitoring of contaminant concentrations at numerous locations within the containers. The extracted vapors collected via Soil Vapor Extraction are also monitored continuously.

Prior to the release of a known mass of tetrachloroethene, heat-transfer experiments were conducted in each of the two containers. The smaller container is 6 m × 3 m × 4.5 m high, with a 1.5-m thick intermediate silty layer, $K_s = 10^{-5}$ cm/s between upper and lower fine sand layers each 1.5-m thick, 10^{-3} cm/s, and four 1.5 kW heaters in a square pattern. The larger container is 6 m × 6 m × 4.5 m high, with a 1.5-m thick intermediate very fine sand layer, $K_s = 10^{-4}$ cm/s between upper and lower coarse sand layers each 1.5-m thick, 10^{-1} cm/s, and four 1.5 kW heaters again in a square pattern. Both intermediate layers are initially saturated. The groundwater flux imposed upon the lower sandy aquifer is varied in steps including 0.5, 1.0 and 2.0 m³/d, allowing the effect of heat losses on temperature distribution and steam convection to be examined.

The heat-transfer experimentation has confirmed the ability to heat the targeted treatment zone to 100°C within the lower permeability layer inside the array of heaters. Numerical simulations suggest that rapid removal of 99.99% of the contaminant from any 3D container with these relatively small dimensions will occur only when the water flux in the underlying aquifer is such that undesired migration of the steam front into the aquifer is prevented. Validation of this finding in the physical containers will improve the ability to model both the 3D remediation experiments and field projects implemented under similar or contrasting sets of conditions.

HONEYWELL TECHNOLOGIES TO ADDRESS DNAPL DETECTION/REMEDICATION

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Honeywell will present and describe two highly advanced technologies suitable to the task of DNAPL (dense non-aqueous phase liquid) detection at concentrations suitable for remediation. The first technology consists of a ruggedized and compact Cavity Ring-Down Spectrometer based upon over 40 years of development of our optical resonator cavity for the Honeywell ring-laser gyro navigation product. The CRDS unit is capable of measurements of the major water contaminating DNAPLs, at ppb levels, as required to be below the carcinogenic threshold for long time exposure.

The second technology is our initial version of a MEMS GC-MS system funded by DARPA's Micro-Gas-Analyzer program. The MEMS-MS hasn't yet been fully developed; however, live-agent tests of the MEMS preconcentrator (PC) and MEMS gas-chromatograph (GC) stages coupled with a Micro-Discharge Device (MDD) at the Army's Edgewood Chemical Biological Center (ECBC) have shown sub 10ppB detection of live chemical agent in the presence of interferents. Moreover, initial experimentation in the laboratory with TCE has also shown 40ppB separation and detection of TCE with an expected LOD of 500ppt! These MEMS component technologies offer SERDP a clear path to a miniaturized, cost effective, and highly sensitive/specific detection system for monitoring of DNAPLs and other environmentally significant TICs and TIMs.

A PRELIMINARY ASSESSMENT TOOL FOR USE OF IN-SITU THERMAL TECHNOLOGIES AT DNAPL-IMPACTED SITES

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Management of DNAPL and LNAPL contamination in soils and groundwater is of continuing concern. Recently, innovative and more aggressive in-situ remedial treatment technologies for source zone treatment have been tested, one of which is in-situ thermal. In-situ thermal technologies include electrical resistive heating, steam and hot water injection, conductive heating, radio frequency heating, and in situ soil mixing with steam. These technologies are of interest in the groundwater remediation industry because of their rapid development in recent years. Through empirical analysis of field data and post-treatment field sampling at select sites, the objective of this study is to develop a tool that will enable practitioners, regulators, and site owners to anticipate the likely performance efficiency of thermal-based technologies for generalized geologic site scenarios.

The final product envisioned for this ESTCP-funded project (CU-0314) is a spreadsheet-based tool where performance experience and theoretical bounds on performance expectations are linked to generalized geologic site scenarios. Based on the scenario that most closely resembles their site, users can quickly assess what technologies have been used, design and operational parameters, and performance data to evaluate treatment efficiency.

To date, the study has identified 168 thermal-based applications: Documents from the majority of these have been collected and captured in the spreadsheet-based tool. While the quality of data for each site is variable, some provide sufficient information to perform an evaluation of technology treatment efficiency including post-treatment mass flux calculations.

To aid in linking field data with generalized geologic scenarios, select sites with full-scale applications, pre/post-treatment groundwater data, and a complete performance assessment were identified for additional field investigations. To date, post-treatment investigations have been completed at one LNAPL and three DNAPL sites, all of which employed electrical resistive heating. At each site, field investigations included physical and chemical characterization including groundwater sampling at multiple temporary discrete-depth sampling intervals along a transect downgradient of the source zone and perpendicular to groundwater flow. Additionally, a fifth site has had on-going groundwater sampling and analysis throughout the electrical resistance heating application and is currently being monitored through the cool-down stage.

CRYOGENIC COLLECTION OF COMPLETE SUBSURFACE SAMPLES FOR MOLECULAR BIOLOGICAL ANALYSIS

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The collection of core samples for genomics and proteomics analyses presents a number of challenges, including minimizing contamination and fluids redistribution during core retrieval. In addition, there is strong interest in characterizing interfaces at the centimeter scale. As part of a new SERDP project (ER-1559) we are developing a new direct-push coring system in which the core is frozen in situ using liquid nitrogen. The new sampler is based on the Geoprobe® Dual Tube sampler, where the sample sheath has been replaced with a coolant coil that connects directly to a liquid nitrogen supply at the surface. Freezing requires only a few minutes, after which the sample is retrieved to ground surface for subsequent processing and/or shipment in an already-frozen state.

To ensure that the samples collected in this manner are not biased by the freezing process, we are conducting an extensive analysis of laboratory, mesocosm and field cores using a suite of microbiological and molecular tools. Laboratory cores involve sand/groundwater/microbial samples that are prepared to test the effect of freezing and storage, and to evaluate decontamination procedures. Mesocosm cores allow us to examine fluids redistribution during sampling and to evaluate techniques for sampling subsurface interfaces. Field sampling will help to demonstrate the robustness of the technique under “real world” conditions. The goal is to produce a robust, simple system for core collection that allows improved genomics and proteomics analysis of subsurface samples.

DIAGNOSTIC TOOLS FOR PERFORMANCE EVALUATION OF INNOVATIVE IN-SITU REMEDIATION TECHNOLOGIES AT CHLORINATED SOLVENT CONTAMINATED SITES

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Historically, the performance of remediation systems at chlorinated solvent contaminated sites has been evaluated using point measurements of dissolved contaminant concentrations in aquifers (e.g., changes in maximum concentrations, plume extent, etc.). Such an approach has significant limitations that may greatly impact the evaluation of technology effectiveness at contaminated sites. First, detailed monitoring of contaminant plumes in granular geologic media conducted by a number of researchers has shown that the distribution of dissolved contaminants is often spatially complex due to several factors including spatial variability of contaminant distribution in the subsurface source zone, variability of groundwater flow rate and direction, and variation in water level. This means that it may often be difficult to impossible for typical groundwater monitoring efforts, especially those relying on sparse networks of long-screened wells, to determine where the majority of the contaminant mass is migrating and thus whether or not remediation systems are effective in reducing that migration. Second, at sites with complex geologies such as fractured rock sites, the evaluation of in-situ technology performance is even more complicated by contaminant migration through discrete fractures.

To better evaluate the success of in-situ remedial systems at chlorinated solvent contaminated sites, a set of diagnostic tools is being used for application at three hydrogeologically distinct sites employing in-situ chemical and biological treatment technologies. Within this ESTCP-funded project (ER-0318), the proposed diagnostic tools include technology- and geology-specific tools, as well as those that can be used widely irrespective of the type of technology or site conditions. Mass flux measurement is used as a technology-wide metric of overall system performance since it can clearly demonstrate a reduction in the rate of contaminant mass release from the treated zone. Innovative technology-specific tools (e.g., molecular tools for in-situ bioremediation) and geology-specific tools (e.g., rock crushing at fractured bedrock sites) are also being tested, and are useful for a real-time diagnosis of remedial technology success. Technology- and geology-specific tools include rock core sampling, isotopic fractionation, molecular tools and integrated conventional techniques.

NZVI TREATABILITY STUDY FOR A TCE SOURCE AREA AT ALAMEDA POINT, CA

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Several nanoscale zero-valent iron (NZVI) products for in situ remediation are commercially available. Each is different and many also have proprietary surface coatings to enhance mobility for emplacement. Site geochemistry (e.g., pH and competing oxidants) can affect NZVI reactivity, however, the fundamental reasons for these effects are not fully understood so treatability studies are conducted to determine the suitability of NZVI for that site's geochemical conditions. This laboratory study compares six types of NZVI (for source zone treatment) and four types of other ZVI-based materials (for plume interception) for the ability to degrade trichloroethylene (TCE) in aquifer material and groundwater from the former Naval Air Station Alameda (now Alameda Point, CA). NZVI products included Toda RNIP, surface-modified RNIP (MRNIP), RNIP-R which is RNIP with a catalyst, Z-Loy™, and Polyflon™. ZVI-based materials included EHC, which is an integrated ZVI and organic carbon, H-200 and HC-15 which are micron-sized ZVI products, and EZVI which is an NZVI-containing emulsion. The study objectives are to determine the rate of TCE degradation, the mass of TCE degraded per mass of ZVI added, the propensity to form chlorinated intermediates, and the impact on site geochemistry.

The observed TCE dechlorination rates for NZVI were all faster than their micron-sized counterparts. At 2g/L, TCE half-life time ranged from 1.2 hr to 89 hours for NZVI, and ranged from 200 hrs to 2000 hours for ZVI. The reactive lifetime of NZVI ranged from 3 days to >30 days. Generally, the fastest reacting material had the shortest reactive lifetime. Acetylene, ethene and ethane were the dominant reaction products, but low levels of chlorinated intermediate compounds (c-DCE and 1,1-DCE) formed and degraded. Vinyl chloride was not detected. Chlorinated intermediates persisted in reactors where NZVI had fully reacted, accounting for as much as 5% of the TCE degraded in one case, but typically less than 1-2%. No chlorinated intermediates were observed using the ZVI products evaluated for plume interception. The mass of TCE reduced to iron added measured at the end of particle reactive lifetime ranged from 1:17 to 1:120. NZVI or ZVI addition increased the pH from 7.3 to 7.8, but the high alkalinity of the site groundwater limited the pH increase. NZVI addition did not decrease microbial diversity in the samples. Based on the treatability study results, two NZVI products and two ZVI products for plume treatment were recommended as the most promising for application at this site.

EFFECT OF pH, PORE WATER VELOCITY, GRAIN SIZE, AND CLAY CONTENT ON THE TRANSPORTABILITY OF SURFACE-MODIFIED NZVI IN SATURATED SAND COLUMNS

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The transport and placement of nanoscale zero valent iron (NZVI) is affected by many hydrogeologic and geochemical factors such as injection velocity, pH, and pore/grain size of the soil. A fundamental understanding of how these factors affect NZVI behavior will aid in planning an injection or placement scheme for a given site to achieve a desired NZVI distribution and treatment effectiveness. The effects of pH (5 to 8), injection velocity (10 to 100 cm/hr), grain size (300 μ m to 110 μ m), and the presence of silica sand fines (<45 μ m) and clay fines (<45 μ m) on the mobility of modified nanoiron were evaluated in water-saturated sand columns. Modifiers included a high MW (125 kg/mol) tri-block co-polymer (PMAA-PMMA-PSS) and polyaspartate (MRNIP) which is a low MW (2 to 3 kg/mol) biopolymer.

A change in solution pH from 5 to 8 did not affect the mobility of surface modified NZVI. Decreasing the injection velocity from 100 cm/hr (fast injection) to 10 cm/hr (slow injection) reduced the elution of MRNIP from 90% to 10%, but the mobility of triblock copolymer modified nanoiron was unaffected. Silica sand grain size (diameter from 300 to 110 μ m) reduced MRNIP mobility to half of that observed at the larger grain size, but had little or no effect on triblock copolymer modified nanoiron. The presence of fine silica sand reduced the mobility of MRNIP to 10%, but had no effect on transport of triblock copolymer modified nanoiron up to 15% wt/wt fines. Clay fines had a greater impact on mobility of the surface modified nanoiron. Only 5% wt/wt clay reduced the elution of MRNIP to 25% and at 15% wt/wt clay MRNIP was immobile. For triblock copolymer-modified nanoiron, elution was only reduced to 90% in the presence of 15% wt/wt clay. The larger impact of clay fines is attributed to the charge heterogeneity on clay mineral surfaces which is sensitive to pH. A heteroaggregation and column transport study with kaolinite and nanoiron over the pH range 5 to 8 confirmed the attachment of modified NZVI to kaolinite at pH<8. The high mobility of triblock copolymer modified nanoiron and its low sensitivity to velocity, grain size and fines and clay are attributed to the electrosteric stabilization afforded by the triblock copolymer. These results indicate that the hydrogeochemical conditions of an aquifer must be considered when selecting surface modifiers.

DECISION & MANAGEMENT TOOLS FOR DNAPL SITES: OPTIMIZATION OF CHLORINATED SOLVENT SOURCE AND PLUME REMEDIATION CONSIDERING UNCERTAINTY

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Defining the benefits of DNAPL source remediation is still an extremely difficult engineering challenge. Uncertainties in the cost and performance of source and plume remediation technologies make decision making difficult. Predicting the impact of the source remediation efforts on plume response is hindered by the lack of tools that explicitly relate source remediation to the downgradient plume over time and space. Our ESTCP project (ER-0704) is leveraging several recent SERDP and ESTCP research efforts to develop an integrated modeling tool to help site managers address these issues.

A recently developed analytical model called REMChlor (for Remediation Evaluation Model for Chlorinated solvents) is used as the technical foundation for this project. This model, produced as part of SERDP CU-1295, is a significant improvement on existing chlorinated solvent transport models such as BIOCHLOR, because it can simultaneously account for both source and plume remediation. We are greatly expanding the functionality of REMChlor by:

- Building a probabilistic framework around the REMChlor source/plume remediation code, so that uncertainty in hydrogeologic variables, remediation performance, source loading, plume response, risk factors, and cost can be accounted for and visualized by users of the new software;
- Providing tools so users can express key process data as probability density functions, and therefore access the probabilistic nature of the new tool;
- Compiling and presenting results of recent research projects regarding cost and performance of source remediation (such as the SERDP Project CU-1293) in the form of probability density functions as background information for users of the new tool;
- Incorporating a vapor transport module, so the critical indoor air pathway can be evaluated. This module will include key research results from ESTCP Project ER-0423 so that users will have the option of including mass flux limitations and radon-based dilution attenuation factors.

The new software will give users a single platform where cost, source treatment, plume management, monitored natural attenuation, and risk assessment can all be evaluated together, and where uncertainty can be incorporated into the site decision making process.

MULCH BIOWALL USED FOR CHLORINATED SOLVENT REMEDIATION

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The Defense Supply Center Richmond (DSCR) is performing a large-scale treatability study for two groundwater cleanup sites (OU6 and OU7) to evaluate the feasibility of innovative bioremediation technologies for cost effective treatment of contaminants. Both sites primarily consist of chlorinated solvents VOCs including TCE and its daughter products. DSCR evaluated biowall technology for OU-7 and Edible Oil Injection for OU-6. The reducing conditions of the groundwater suggest that the sites are both good candidates for anaerobic bioremediation. Furthermore, the groundwater at DSCR exhibit signs of natural attenuation. Pre-design sampling began in early February 2007 and the biowalls were installed in July. Enhancing the dissolution rate of DNAPL will decrease source zone cleanup times with a faster dissolution rate. In addition, it will cost less to contain from a long-term operation and maintenance (O&M) perspective. Remedy of the contaminants is performed in situ with minimal above ground impact, minimal waste generation, and a small footprint at a given site. This technology has relatively low capital costs compared to other ex situ remedial options such as pump-and-treat because the primary capital expenditure is related to injection well installation or direct-push points.

IMPROVING EFFECTIVENESS OF BIOREMEDIATION AT DNAPL SOURCE ZONE SITES BY APPLYING PARTITIONING ELECTRON DONORS (PEDS)

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A recent protocol points out that typical electron donor applications have only 1 to 10% efficiency (i.e., electron donor applications typically use a 5 to 10 times safety factor to account for loss of reducing equivalents) (AFCEE, et al., 2004). Soluble donors (e.g., lactate, vegetable oils, and HRC™) are consumed as they migrate towards source zones and their concentration rapidly diminishes near DNAPLs. Partitioning Electron Donors (PEDs) are electron donors that partition directly into the DNAPL. This promotes the growth of dechlorinating biomass close to the DNAPL and enhances DNAPL dissolution rates.

The advantages offered by partitioning electron donors are that they: (1) are water-soluble; (2) partition readily into DNAPLs; (3) repartition following Roullet's Law such that donor released meets the electron acceptor demand (i.e., chlorinated solvent concentration) as it dissolves from the DNAPL; (4) have predictable impact on DNAPL density or viscosity to evaluate the potential effects on DNAPL mobilization; (5) are non-toxic or generally regarded as safe for use in food products; (6) are inexpensive; and (7) serve as a source of reducing equivalents for the dechlorinating biomass.

The objective of this FY07-New-Start project is to demonstrate/validate (DEM/VAL) the application of a partitioning electron donor (PED) to improve the biologically enhanced dissolution rate of DNAPLs and ultimately to reduce costs associated with the application of electron donors in source zones. The DEM/VAL will focus on two PEDs, for which a laboratory evaluation has already been completed: n-butyl acetate and n-hexanol.

The project involves both laboratory and field evaluations. The laboratory assessment is required in order to screen the suitability of the candidate PEDs, and to collect key data that will be used to design PED field application. The field application will involve loading a DNAPL area with a PED by injecting and intermittently re-circulating the PED through the source area. The re-circulation system will allow efficient loading of the DNAPL with the PED and give the operator control over achieving the desired target loading. We will assess the degree of PED loading into the DNAPL by measuring the change in aqueous phase concentration of the PED. The properties of the PEDs allow for short-duration application (less than their degradation rate) and periodic re-circulation.

OPTIMIZING THE PERFORMANCE OF INJECTABLE ZERO VALENT METALS

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Zero valent metals are powerful electrochemical reductants that react with and eliminate several common groundwater contaminants. Successful *in-situ* remediation is predicated on delivering the metal particles to the contaminant phase and then realizing the desired electrochemical reaction. Zero valent metal remediation is particularly effective when the product is delivered to the aqueous phase contaminant by injecting an aqueous metal particle suspension through wells. Traditional metals, with a particle size of tens to hundreds of micrometers, are generally unsuitable as an injectable product because the particles cannot fit within the ground's interconnected pore volume. When injected large particles instead accumulate and clog the injection well.

Delivery problems can be alleviated by reducing the metal particle size to the micrometer regime. However, small metal particles provide challenges that can limit their applicability for *in-situ* remediation. A fundamental problem is propensity of the small individual particles to aggregate into much larger multi-particle clusters that provide little mobility advantage compared to larger metal products. Another potential problem with small metal particles is rapid reactivity that shortens the product's effective sub-surface lifetime.

This poster will highlight OnMaterials' research and development efforts and field studies that have been undertaken to understand and overcome problems associated with performance of small zero valent metal particles. Our Z-Loy™ products contain an iron/aluminum alloy with a small amount of palladium added as a hydrogenation catalyst. Unlike other small zero valent metal products that are synthesized and/or stored in water, Z-Loy™ is instead synthesized and stored in propylene glycol. Propylene glycol is non-toxic, biodegradable, and does not induce the formation of large multi-particle aggregates that are inherent in waterborne zero valent metal products. Before injection the Z-Loy™ concentrate is mixed with a dispersant that helps maintain an aqueous suspension with small discrete particles. This suspension provides excellent mobility and product transport through common sub-surface lithologies. Z-Loy™ promotes rapid and complete reactivity with common groundwater contaminants. The hydrogenation catalyst greatly increases reaction rates and also promotes reaction pathways that minimize the formation of similarly toxic and sometimes recalcitrant daughter products. Reaction rates can be modified by adjusting composition and particle size; iron-rich and larger particle size products offer the prolonged reactivity that is beneficial for treating DNAPL and source zone contaminants.