Explosive Chemicals Bio/Phyto Remediation Project

Part of the legacy of Hawaii’s long-standing role as a base of operations for the U.S. military is the existence of chemicals from explosives (energetic compounds) in the soil and groundwater in some areas of the state. Hawaii has been a strategic outpost of the American military since before World War II. Various locations around the islands have been used to train troops in the use of a variety of explosive weapons, including the island of Kahoolawe, Waikoloa on the Big Island, and Makua Valley on Oahu’s west shore.

Obviously if they fail to detonate, the unexploded weapons can remain dangerous, sometimes for many years, and there have been instances of injury and death caused by unsuspecting people digging up munitions in Hawaii. In addition to this obvious, immediate threat to human health, there is the issue that the chemicals released both from unexploded weapons, and indeed exploded ordnance, at many DoD sites has contaminated soil and groundwater. These chemicals may cause negative health effects to those exposed (see sidebar-Energetic Compounds next page) and environmental damage. The military has recognized these risks and has been taking steps to mitigate them. This recognition resulted in the establishment of the Environmental Security Technology Certification Program (ESTCP). ESTCP is a Department of Defense (DoD) program that “promotes innovative, cost-effective environmental technologies through demonstration and validation at DoD sites.” The ESTCP website states the problem of groundwater contamination caused by unexploded ordnance thus; “As the result of past practices, groundwater at many Department of Defense facilities is contaminated with explosives (e.g., TNT and RDX). Because of their chemical characteristics, these contaminants can persist for long periods in groundwater. Conventional treatment (i.e., pump and treat) often lasts for decades and still cannot completely remove these contaminants.” (http://www.estcp.org/about/summary.cfm).

On the specific issue of Makua, the ESTCP website says the following; “Concerns exist about the potential impact to the surrounding environment from release of energetic compounds during live-firing range exercises conducted within military training ranges in Hawaii and elsewhere in the Pacific Region. The Makua Military Reservation (MMR) on Oahu has been in operation since the 1940s and currently contains the only combined-arms live-fire training range available in Hawaii. At MMR, the energetic compounds RDX, HMX, and DNT have been detected in Open Burning/Open Detonation (OB/OD) area soils and vadose zone pore water at concentrations above Environmental Protection Agency Region IX Preliminary Remediation Goals.” They further state that, “The objectives of this demonstration/validation project are to evaluate (1) in situ degradation of energetic compounds within OB/OD soils as a result of natural plant-mediated degradation and (2) in situ enhanced aerobic and anaerobic bioremediation with low-cost additives to promote the degradation of energetic compounds within the shallow vadose zone pore water and tropical soils.” (http://www.estcp.org/Technology/ER-0631-FS.cfm).

History of Military Use of Makua Valley*

1929
The military takes its first parcels of land in Makua Valley and begins to use the Waianae Coast for war games, conducting amphibious landings at Makua Beach.

1941
The U.S. Army takes over the entire Makua-Kaena Point area for military security and training operations with the territory under martial law. Kuleana residents, railroad workers and McCandless Estate ranch workers are asked to leave the valley.

1964
President Lyndon B. Johnson issues an executive order that reserves use of the interior portion of the valley for the federal government. The Board of Land and Natural Resources signs a 65-year lease with the Army. The coastal area, which the state has plans to turn into a public park, is granted to it as a public trust.

*from the Honolulu Star Bulletin, June 7, 1996
Phytoremediation represents a potential preventive treatment for areas receiving new RDX, such as the live-fire training impact area. This project will evaluate the effectiveness of plants at reducing residual energetic contamination in near-surface soils within the root zone. A total of four lined test cells will be constructed within the OB/OD unit and filled with site soils impacted with a known initial concentration of energetic compounds. Some cells will contain Guinea grass (*Panicum maximum*). The concentration of energetic compounds in the soil, leachate, plant root, and plant shoot will be monitored to evaluate the effectiveness of the naturally occurring Guinea grass in reducing residual energetic compound levels in MMR soils.

Bioremediation addresses contamination remaining from OB/OD operations at deeper depths than the root zone. This project will evaluate the effectiveness of in situ enhanced aerobic and anaerobic bioremediation of RDX and HMX dissolved in vadose zone pore water in tropical soils beyond the root zone. Food-grade carbohydrate reagent solution (molasses) at a dilution of 1:20 will be applied with irrigation water to stimulate indigenous soil microbiota and allow enhanced growth of the indigenous microbes on two 25 x 25 foot test plots at the OB/OD area. Concentrations of energetic compounds will be monitored to study the effectiveness of the bioremediation methods.

If proven successful in tropical soils, the phytoremediation and bioremediation technologies will provide low-cost alternatives for remediation of RDX and HMX in shallow soils and vadose zone pore water. Such alternatives will assist the Department of Defense in meeting environmental requirements and sustaining live-firing range exercises at MMR as well as other live-fire training ranges throughout the Pacific Region.

This project will be a collaboration involving personnel and other resources from Environet, the U.S. Army, and the Hawaii Agricultural Research Center (HARC) that will be utilized in experiments to be conducted at MMR and various analyses to be conducted at the University of Hawaii.

The objectives of the UH research are to evaluate in-situ degradation of chemicals found in explosives in tropical soils as a result of natural plant-mediated degradation (phytoremediation) as well as enhanced aerobic and anaerobic bioremediation following the addition of low cost amendments.

Work to be conducted at the University of Hawaii is as follows:

1) **Assist with collection and processing of liquid samples.**

Samples will be collected from field test plots at MMR and greenhouse plants grown at HARC. Liquid samples will include various leachate waters, soil pore waters (vacuum lysimeter leachate), and possibly surface/ground waters. Samples will be analyzed for RDX, DNT and various related explosives and degradation products via EPA Method 8330. Samples will also be analyzed for TOC, nitrogen species (NH4, NO2/NO3), total P, conductivity, DO, pH, and turbidity. UH personnel will conduct all chemical analyses.

2) **Assist with collection and processing of soil and plant tissue samples.**

Samples will be collected from field test plots at MMR and greenhouse plants at HARC. Samples will include composite soil samples and plant roots/shoots. Samples will be extracted using EPA Method 8330. Extracted samples will be analyzed for RDX, DNT and various related explosives and degradation products via EPA Method 8330. UH personnel will conduct all sample extractions and chemical analyses.
Energetic Compounds: Fate and Transport, Health Issues

RDX - Royal Demolition Explosive

RDX is a common synthetic explosive. The military uses RDX as an ingredient in plastic bonded explosives, or plastic explosives which have been used as explosive fill in almost all types of munition compounds. Combinations of RDX and HMX have been the chief ingredients in approximately 75 products.

RDX dissolves in and evaporates from water very slowly, doesn’t bind well to soil particles and can migrate to groundwater. Rate of migration depends on the soil composition. In water RDX is degraded mainly by direct photochemical degradation over several weeks. RDX doesn’t biologically degrade in the presence of oxygen, but anaerobic degradation is possible under certain conditions. RDX’s potential for bioaccumulation is low.

RDX inhalation or ingestion can create nervous system problems, nausea, vomiting, and possibly organ damage. EPA and ATSDR have identified RDX as a possible human carcinogen.

The ecological effects of RDX suggested by laboratory studies include neurological damage including seizures and behavioral changes in wildlife that ingest or inhale it. Wildlife exposure to RDX may also cause damage to the liver and the reproductive system.

DNT - 2,4/2,6-Dinitrotoluene

In addition to being an explosive DNT is used to produce flexible polyurethane foams used in the bedding and furniture industry, to make dyes, and in the air bags of automobiles.

In water, DNT can be broken down by sunlight. Under conditions without oxygen or without light, DNT may be broken down by biological degradation, whereby microbes utilize the chemical as a source of energy. DNT in water can result from releases of waste water from trinitrotoluene (TNT) manufacturing plants and from buried munition wastes.

DNT has been found in the soil, surface water, and groundwater of at least 122 hazardous waste sites that contain buried ammunition wastes and wastes from manufacturing facilities. DNT does not usually remain in the environment long because it is broken down by sunlight and bacteria. Increases in death rate due to heart disease have been seen in workers exposed to 2,4-DNT. 2,4- and 2,6-DNT may also affect the nervous system and the blood of exposed workers. One study showed that male workers exposed to 2,4/2,6-DNT had reduced levels of sperm, but later studies did not confirm this. The International Agency for Research on Cancer has determined that 2,4- and 2,6-DNT are possibly carcinogenic to humans.

Exposure to high levels of DNT compounds in animals regularly causes lowered numbers of sperm and reduced fertility. Studies of animals have also shown that nervous system disorders, liver damage, and kidney damage can occur, as well as a reduction in the numbers of red blood cells. Both 2,4- and 2,6-DNT can cause liver cancer in laboratory rats and may produce the same effect in humans.

HMX - High Melting eXplosive

HMX is used exclusively for military purposes to implode fissionable material in nuclear devices, as a component of plastic-bonded explosives, as a component of rocket propellant, and as a high explosive burster charge.

In surface water, HMX does not evaporate or bind to sediments to any large extent. Sunlight breaks down most of the HMX in surface water, usually in a matter of days to weeks. The amount of time HMX remains in surface water depends on how much light-absorbing material is present. A small amount of HMX may also be broken down by bacteria in the water. Some of the breakdown products of HMX are also harmful to human health, although the amounts one may be exposed to as a result of HMX in drinking water are not expected to be above trace levels.

Studies show that HMX is likely to move from soil into groundwater, particularly in sandy soils. For most soils, however, the movement of HMX to groundwater is expected to be slow. Bacteria in the soil are not expected to break down HMX to any large extent. Exactly how long HMX will remain in the environment is not known; however, HMX in soil and groundwater is expected to persist for a long time. It is not known if plants, fish, or animals living in areas contaminated with HMX build up high levels of the chemical in their tissues.

“Information on the adverse health effects of HMX is limited. Studies in rats, mice, and rabbits indicate that HMX may be harmful to the liver and central nervous system if it is swallowed or gets on the skin. The mechanism by which HMX causes adverse effects on the liver and nervous system is not understood.”

1Agency for Toxic Substances and Disease Registry website: http://www.atsdr.cdc.gov/toxprofiles/phs78.html - ATSDR Public Health Statement for RDX
2http://www.globalsecurity.org/military/systems/munitions/explosives-nitramines.htm
After passage, some municipalities with POTWs that discharged into marine waters argued that this requirement might be unnecessary because marine currents, which allow for greater dilution and dispersion than their freshwater counterparts. As a result, Congress added section 301(h) to the Clean Water Act in 1977, allowing for a case-by-case review of treatment requirements for marine discharges that applied by September 13, 1979. Eligible POTW applicants that met the set of environmentally stringent criteria in section 301(h) to the Clean Water Act in 1977, allowing for a case-by-case review of treatment requirements for marine dischargers that applied by September 13, 1979. Eligible POTW applicants that met the set of environmentally stringent criteria in section 301(h) would receive a modified National Pollutant Discharge Elimination System (NPDES) permit waiving dischargers that applied by September 13, 1979. Eligible POTW applicants that met the set of environmentally stringent criteria in section 301(h) to the Clean Water Act in 1977, allowing for a case-by-case review of treatment requirements for marine discharges that applied by September 13, 1979. Eligible POTW applicants that met the set of environmentally stringent criteria in section 301(h) would receive a modified National Pollutant Discharge Elimination System (NPDES) permit waiving dischargers that applied by September 13, 1979. Eligible POTW applicants that met the set of environmentally stringent criteria in section 301(h) would receive a modified National Pollutant Discharge Elimination System (NPDES) permit waiving dischargers that applied by September 13, 1979.

The Water Center continues its long term work evaluating the marine communities around Honolulu’s ocean sewer outfalls. This work has been ongoing since the early 1980s and consists of censuses of fish, corals, mollusks, worms, and crustaceans found around the City’s outfall pipes at Sand Island, Barbers Point, Waianae, and Mokapu on the island of Oahu. Sub-projects involve sorting through sediment/sand samples taken from the sea floor to count benthic organisms, inventorying of sessile macro-organisms, censuses of fish captured on videotape at greater depths, and examination of liver tissue taken from fish caught near the outfalls. The overall goal of the work is to determine if there are any changes occurring in natural populations around the outfalls that could be attributed to the wastewater discharge. This program is performed in part to help the City’s Environmental Services Department comply with the conditions of the waivers Honolulu has been granted from secondary wastewater treatment requirements. The issue of Honolulu not performing full secondary treatment is one that reemerges periodically in the press and the public consciousness.

“In 1972, Congress passed the Federal Water Pollution Control Act Amendments which required Publicly Owned Treatment Works (POTWs) to achieve secondary treatment capability by 1977. After passage, some municipalities with POTWs that discharged into marine waters argued that this requirement might be unnecessary on the grounds that marine POTWs usually discharge into deeper waters with large tides and substantial currents, which allow for greater dilution and dispersion than their freshwater counterparts. As a result, Congress added section 301(h) to the Clean Water Act in 1977, allowing for a case-by-case review of treatment requirements for marine dischargers that applied by September 13, 1979. Eligible POTW applicants that met the set of environmentally stringent criteria in section 301(h) would receive a modified National Pollutant Discharge Elimination System (NPDES) permit waiving the secondary treatment requirements for the conventional pollutants, biochemical oxygen demand

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Estimating Hydraulic Properties for Volcanic Aquifers Using Wave Setup

Hydraulic parameters, such as hydraulic conductivity and storage parameters, are essential elements for models used to manage groundwater availability and quality. Uncertainty in these parameters is reflected in erroneous model estimates, which can result in mismanagement of drinking-water supplies. The traditional approach to evaluating aquifer parameters is through aquifer pumping tests. Another approach is to use naturally occurring phenomena such as tides, which impact the movement of water in aquifers, to estimate hydraulic properties.

The amplitude damping and time lag of aquifer responses induced by changes in sea level due to tides can be used to calculate aquifer parameters. Wave setup, another variable of sea state, has not been previously used in such a manner. Wave setup is associated with the momentum transfer of breaking waves to the water column, which results in an elevated mean sea level at the coast with a duration of several days. Setup is linearly correlated with the wave height outside the breaker zone. Utilization of wave setup in aquifer parameter estimation has an advantage over traditional aquifer pump tests in that it can cover greater areas at a lower cost with simpler logistics. Data for wave height, barometric pressure, and observation well levels are often readily available. Dr. Aly I. El-Kadi and graduate research assistant Kolja Rotzoll are working on a project examining groundwater responses to wave setup in a coastal aquifer in central Maui, Hawaii. The applicability of using the propagating setup signal in hydraulic parameter estimation is being investigated.

Two approaches that are appropriate for the study area were used to estimate setup from wave height in the absence of measurements in Kahului Harbor. The approaches use an empirical relationship of wave height and observed setup and yield similar results with maximum setup values below 20 cm. A multivariable regression analysis showed the effect of setup pulses on low-frequency groundwater fluctuations to be greater than that caused by changes in barometric pressure at times of energetic swell events. The influence of setup can be detected as far as 5 km inland.

Propagation of the wave setup signal through the aquifer is similar to that observed using ocean tides, with exponentially decaying amplitudes and linearly increasing time lags between setup and observed groundwater responses. Hydraulic diffusivity values were estimated from amplitude attenuation of the setup pulse and very closely agreed with parameters estimated using aquifer tests and ocean tides in the same study area. A one-dimensional numerical model verified the results of the analytical solution and confirmed that setup attenuation is suitable to estimate hydraulic parameters. On the other hand, setup phase lags are not suitable for such an endeavor. The approach is expected to be beneficial to many high-permeability coastal environments, such as volcanic islands and atolls. The technique will provide a practical approach for aquifer parameter estimation.

Ocean outfalls continued...

(BOD), suspended solids (SS), and pH. EPA issued regulations and a technical support document for the 301(h) program in 1979.” (http://www.earthscape.org/p1/epa01/301-factsheet.html). Honolulu met (and continues to meet) these stringent requirements and thus was granted 301(h) waivers for the Sand Island and Honolulu outfalls by the EPA. One of the conditions of the waivers is that biomonitoring be performed.

To date the research team working on the outfall biomonitoring project has been unable to find any definitive indication that the outfalls are affecting the ecosystems around the outfalls. It indeed seems to be the case that the great dilution and active currents that local marine conditions provide, are dispersing the effluent efficiently. The absence of heavy industry on Oahu is also working in our favor inasmuch as the sewage being processed by the City’s treatment works is almost entirely from households and storm water runoff. This type of sewage is relatively benign and non-toxic. The receiving waters into which the effluent is released doesn’t serve as anyone’s drinking water supply as is often the case in other states. Some, however, find it difficult to overlook the fact that Honolulu doesn’t treat all of its sewage to the nationwide standard prescribed by the EPA. Some feel duty-bound to lobby (or indeed, sue) for Honolulu to follow the national standard in spite of the fact that doing so would cost the ratepayers on the island hundreds of millions of dollars and produce no appreciable improvement in water quality.
Civil & Environmental Engineering professor and WRRC researcher Dr. Roger Babcock is collaborating with Dr. Morton Barlaz at North Carolina State University on a study regarding the Waimanalo Gulch Landfill on Oahu. The objectives of the research are to simulate/reproduce the production of hydrogen at the Waimanalo Gulch Landfill in laboratory microcosms, to characterize microbial populations responsible for hydrogen production, and to recommend strategies to control hydrogen production and excessive temperatures at the Waimanalo Gulch Landfill.

This research will be a collaboration involving personnel and other resources from North Carolina State University that will be utilized in experiments to be conducted at the University of Hawaii. The scope of work to be conducted by UH is as follows:

1. Assist with Set-up of Landfill Microcosm Experiments.

   Approximately 14 2-liter reactor columns will be set-up in WRRC’s laboratory at UH. Reactor columns will be placed in a temperature controlled water bath. Reactor columns will be sealed and have ports for adding humidified air and collecting evolved gases. Evolved gas will be collected in Tedlar bags for analyses. Eight reactors will contain material excavated from the Waimanalo Gulch Landfill. Another six reactor columns will contain fresh refuse entering the landfill. UH personnel will assist with obtaining landfill contents/fresh refuse, column/waterbath set-up, gas handling system set-up, and other necessary experimental apparatus.

2. Assist with operation and monitoring of landfill microcosm experiments.

   Reactor columns will require daily maintenance and regular sampling. Gas volume will be measured via water displacement. Gas composition (CH4, CO2, N2, O2, H2, CO) will be measured via gas chromatography at UH. Liquid samples from the refuse/landfill contents will be analyzed for pH, carboxylic acids (acetate, propionate and butyrate), and solvents (acetone, ethanol) via gas chromatography at UH. UH personnel will assist with operation, maintenance, sampling, sample extraction/analyses, and other activities as necessary to complete the project.

   Graduate Research Assistant Ahmad Sadri, visiting from North Carolina State University, will be working here in Hawaii with Dr. Babcock on this project.