Depleted Uranium, Natural Uranium and Other Naturally Occurring Radioactive Elements in Hawaiian Environments

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Executive Summary

Fragments from depleted uranium (DU) spotting rounds were recently discovered at two US Army firing ranges in Hawaii. They were M101 rounds fired by in the 1960s by the Davey Crockett weapon system (Figure 1a). The fragments raise questions about the amount of uranium (U) and other radioactive elements in the Hawaiian environments, the mobility of those radioactive elements in the environment, and how U contamination at a particular site is detected. This paper addresses these questions.

U occurs naturally in trace amounts in Hawaiian rocks, soils and waters at or below concentrations of 1 to 3 parts per million (ppm) by weight. Along with thorium (Th) and potassium (K), these three elements contribute significantly to the natural background radioactivity there. The chemical attributes of water and soil (e.g., pH, oxygen content, organic matter, soil age and Fe-rich minerals) affect U mobility in the environment. Most soil types in Hawaii bind U to soil particles generally limiting U mobility.

Studies of natural U in Hawaiian rocks and soils indicate it is only slowly leached from rocks and soils in Hawaii. U generally builds up in soils as they age because of this, and because natural dust particles carried from Asia to Hawaii add small amounts of U to surface soils each year.

General geochemical arguments suggest that metallic DU particles or DU-oxide particles from M101 spotting rounds fired in Hawaii are not highly mobile in local environments. Contamination should be restricted to the immediate area of use. Chemical analysis of environmental samples in the affected areas conducted by US Army contractors thus far show very limited dispersion of DU from the point of use, indicating low mobility of such particles here.

Figure 1a. The Davey Crockett weapon system, which fired M101 spotting rounds

Figure 1b. M101 spotter rounds from the Pahakoloa Training Area (PTA) range.

There is currently no evidence of DU contamination outside of the confines of the US Army firing ranges where it was used in the 1960s. Members of the general public who do suspect DU or other radioactive contamination somewhere should contact a trained radiation safety professional for assistance with a survey and site assessment.

1. Introduction

Recent discovery of depleted Uranium (DU) fragments from M101 spotting rounds at Schofield Barracks' operational range, on the islands of Oahu, and at the Pohakuloa Training Area (PTA), on the island of Hawaii, raise questions about the potential associated hazards.

- How much Uranium (U) occurs naturally in Hawaiian environments?
- Is U mobile in this environment?
- Does U associate with one or more particular natural materials?
- Is local DU contamination an area for concern?
- How much radioactivity was introduced into the local environment from DU?

The US Army conducted training in Hawaii during the mid-1960s using the M101 spotting round of the Davy Crockett Weapon System. Each round contained approximately one half pound D38 U Alloy (92% DU and 8% molybdenum). This paper addresses what is known about natural occurrences of U and other radioactive elements in Hawaiian environments to put the presence of DU from these activities in context of the Hawaiian Islands.

Scientists and the general public are interested in the mobility of U in the environment because weathering of natural and man made materials, particularly those with high U concentrations, can introduce U into surface and ground water systems, soils, air and the ecosystems that rely on them.

U is a naturally occurring heavy metal. Rocks, soil, coral, water, air, plants and animals all contain varying amounts of U. Natural U is a mixture of three types (or isotopes) of U, written as ^{234}U, ^{235}U, and ^{238}U. Although these isotopes are different radioactive materials with differing radioactive properties, they are the same chemically. Because U normally occurs at very low concentration in natural materials at Earth's surface, (less than 5 parts per million by weight, ppm), geochemists refer to it as a "trace element". U ores and U rich minerals do not occur in Hawaii, but U is dispersed at low abundance in normal rock forming minerals.

There are many sources of radioactivity in the environment besides U – some are natural and some are manmade. An environmental assessment typically considers both natural and contaminant sources of radioactivity. There are multiple natural radiation sources that humans come in contact with every day. Those most relevant to this discussion include the chemical elements thorium, radium, radon, potassium and carbon, which have the chemical symbols Th,

Ra, Rn, K and C. Th is a heavy metal like U that occurs in rocks and soils at similar concentration to U. Th has one major isotope (^{232}Th) and several minor ones, all of which are radioactive. Ra is a natural radioactive byproduct from the decay of U (and to a much lesser extent, Th). It is in the same chemical family as the element calcium (Ca), and occurs at low levels in many materials at Earth's surface. Radon is a radioactive gas formed from Ra that continually seeps out of rocks, soils and waters. All of the atoms of U, Th, Ra, and Rn on Earth are radioactive. K and C are slightly different: these two elements are very common in materials found at Earth's surface, including the human body, yet they are only mildly radioactive because just a small fraction of the K and C atoms are radioactive (these radioactive isotopes are written as ^{40}K and ^{14}C). Both elements are mostly made up of stable (non-radioactive) isotopes; some forms of carbon (such as coal and petroleum) have no ^{14}C in them.

The atomic age brought many new sources of radioactivity into our world. For instance, atmospheric atomic bomb tests in the 20th century produced radioactive isotopes of plutonium, strontium, cesium, and iodine (to name just a few) that were previously extremely rare or not found on Earth. Many of these bomb-test isotopes have since decayed away, although the longest-lived isotopes can still be found at shallow depths in soils, lake sediments, and glaciers around the world. Other modern activities also occasionally release artificial radio-isotopes into the environment, including everything from the nuclear power industry to nuclear medicine to the manufacture and disposal of household smoke detectors. A person exposed to high levels of radioactivity close to the source can suffer numerous possible toxic effects that depend on the type of radioactive material. This is why users of radioactive materials follow strict protocols (based on time, distance, and shielding) to minimize negative impacts on themselves or the general public, and why, for instance, highly radioactive patients undergoing nuclear medicine therapy are kept away from the general public.

Natural, Depleted, and Enriched Uranium.

New forms of U with isotopic compositions that differ greatly from natural U are another development of the atomic age. An industrial process called enrichment is used to concentrate ^{234}U and ^{235}U producing enriched uranium (EU) used for nuclear fuel. The material leftover from the enrichment process is called DU because it has lower concentrations of these two isotopes than natural uranium. DU is thus a modified form of U from which these lighter

and more radioactive isotopes have been partially removed, creating a substance that has more ^{238}U than natural U. The resultant change in the isotopic composition makes it possible to distinguish naturally occurring U from enriched and depleted forms, as discussed in section 5 ("isotopic fingerprinting") of this paper.

EU is more radioactive than natural U, with more highly enriched forms being more radioactive than less enriched forms. Depending on the percent enrichment, EU can be used as nuclear fuel for power plants (less enriched, sometimes called "low EU") or atomic weapons (more enriched, sometimes called "high EU"). DU has numerous civilian and military uses that on occasion cause it to be introduced into the environment. Civilian uses include radiation shielding, gyroscopes, and stabilizers in aircraft. Past and present military uses include spotting rounds, munitions and as shielding in armored vehicles.

The M101 spotting round was a small (20mm) low speed (velocity) projectile that weighed approximately 1 pound, a little more than half (6.7 ounces) of which was DU. This spotting round was designed to mirror the flight characteristics of larger caliber rounds and was fired to identify the correct range and bearing for those larger caliber rounds. The M101 body was constructed of D38 U Alloy (92 percent DU and 8 percent molybdenum). These rounds typically broke into large fragments after use.

2. U Chemistry

U is a heavy metal. In fact, U is the heaviest chemical element to occur naturally today on Earth other than ultra trace amounts of transuranic elements such as plutonium. Much like the element Iron (Fe), U does not naturally occur at Earth's surface as a native (pure) metal. U metal is denser than most metals, but like Fe it will "rust" to form U oxides with yellowish to blackish tints if exposed to the atmosphere. "U is present as a uranyl or hydroxyl-uranyl ion (such as UO_2^{2+}) and is mildly soluble in fresh and salt water at natural pH levels under oxidizing conditions". U solubility is greatly enhanced in the presence of carbonate (CO_3^{2-}) or phosphate (PO_4^{3-}) anions, which combine with U to make complex ions. For instance, when U combines with carbonate to make uranyl carbonate complexes, it makes a very stable aqueous ion, such as occurs in sea water. Carbonate comes from the dissolution of carbon dioxide or solids such as calcium carbonate in water, and occurs naturally in water nearly everywhere on Earth. Phosphorous is an important nutrient for plants and many types of animals, and is also found in

some manmade detergents and pesticides. Phosphate occurs naturally in rock and bone, although phosphate levels are typically very low in natural waters because plants and animals tend to absorb whatever is present. Phosphate is often added to soils as a fertilizer, so phosphate concentration can be high in agricultural runoff, which would likely tend then to also contain more U. In reducing environments (i.e., those with limited oxygen, such as groundwater), U is only sparingly soluble, preferring instead to form U minerals, or to adhere to surfaces, particularly minerals rich in iron (Fe) or insoluble organic matter.

3. Radioactivity

Radioactivity is the property that causes some unstable atoms to spontaneously emit energetic particles and/or rays from their nucleus. The three main types of ionizing radiation are named with the Greek letters alpha (α), beta (β), and gamma (γ). All of them carry enough energy to ionize (i.e., knock out electrons) from molecules (e.g., water, protein, and DNA) with which they interact. However, these types of radiation have very different energy, mass and charge, which greatly affect their penetrating power through matter (see additional information in the caption to figure 2). We cannot sense "ionizing radiation", so we must use special instruments to measure the level of radiation.

Each radioactive isotope decays with a unique combination of emitted energy and half life. Half life tells how long it will take for half of a radioactive substance to decay away, making it a good measure of how radioactive that substance is. Substances with very long radioactive half lives, such as U, can be measured by standard chemical means or by detecting their emitted radiation.

Figure 2 - Three Types of Ionizing Radiation. Alpha particles are relatively heavy particles that cannot penetrate most solid or liquid materials; however, they can be a hazard if inhaled or ingested. Alpha particles travel the shortest range among the three types of ionizing radiation (up to a foot in the air and being easily stopped by a sheet of paper or a person's outer layer of skin). Beta particles are smaller and more penetrating than alpha particles, traveling up to several feet in the air. Gamma rays and X rays are energetic, short wavelength forms of electromagnetic radiation (the same spectrum that includes visible light and ultraviolet radiation). The very small particles that make up these rays are uncharged but have a much greater penetration power. Dense materials (e.g., lead) are necessary to block them.
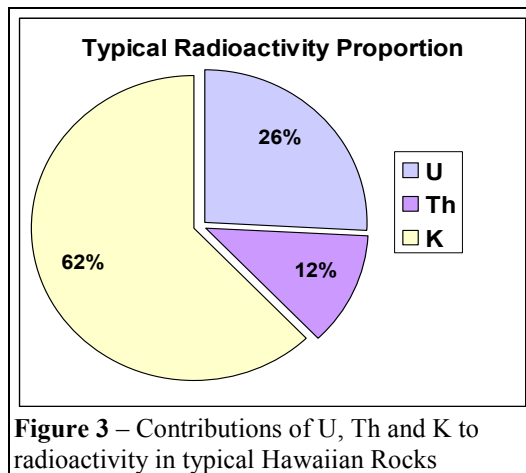
3a. Natural Radioactivity

The elements U, Th and K contribute significantly to radioactivity levels in natural inorganic materials at Earth's surface. All three have isotopes with very long half lives (e.g., ^{238}U half life = 4.47 billion years and ^{235}U half life = 704 million years). The ^{238}U half life is approximately the age of the Earth (4.55 billion years) meaning that roughly half of the U that Earth originally formed with has decayed away. ^{235}U decays roughly six times as fast, so substantially less of Earth's original stock of this isotope is still present. Both isotopes are considered long-lived (i.e., not rapidly decaying). A third, very minor U isotope (^{234}U) comes from the decay of ^{238}U. It typically comprises just over 0.005% of the atoms in a natural U specimen, but being formed from ^{238}U and having a much shorter half life (246 thousand years) means it contributes approximately as much radioactivity as ^{238}U. The radioactivity from all three isotopes of natural U in a material containing 1 ppm U is 1.5 pico-curies per gram (pCi/g)

^{232}Th makes up essentially 100% of natural Th and has a half life of about 14 billion years, which is roughly three times longer than ^{238}U. The natural abundance of Th in most rocks is also three to four times as high as U, so that ^{232}Th and ^{238}U contribute similar amounts to the total radioactivity of those rocks. ^{40}K is a minor isotope of otherwise stable K, making up just over 0.01% of all K currently on Earth and with a half life of 1.3 billion years. ^{238}U, ^{235}U and ^{232}Th all decay initially by alpha particle emission, generally considered the least hazardous decay type for external exposure but considered more hazardous for internal exposure (see the Figure 2 caption). ^{235}U and ^{232}Th also generate gamma rays during some of their decays, as do the immediate decay products of ^{238}U (see appendix 2). ^{40}K decays by beta particle emission and also produces gamma radiation. The importance of these decay pathways is discussed further below.

The amount of radioactivity in a typical sample of Hawaiian basalt or soil is less than 1 to 10 pico-curies per gram (abbreviated as piCi/g). The average 2.6 pCi/g comes mostly from U, Th, and K, in approximate proportions illustrated in figure 3 (average Hawaiian basalt has 1 part per million (abbreviated as ppm) U, 3 ppm Th, and 2000 ppm K, which produce 0.68, 0.32 and 1.65 pCi/g, respectively). Average Hawaiian soil

Figure 3 – Contributions of U, Th and K to radioactivity in typical Hawaiian Rocks

has similar proportions of U, Th and K, at concentrations that are one tenth to ten times those in Hawaiian basalt.

Further enhancing the radioactivity of natural materials containing Th and U is the fact that [238]U, [235]U and [232]Th each are the parents of long radioactive decay chains. This means they each produce radioactive daughters that decay through a series of other radioactive elements before the chains stop at various stable lead (Pb) isotopes. Natural minerals typically contain most of these daughter nuclides, increasing their overall radioactivity. The radioactive gas [222]Rn (radon) is one of many natural by-products of [238]U decay. By some estimates, radon accounts for roughly half of the typical annual ionizing radiation exposure of the average American (figure 4). Refined U metal (depleted, normal, or enriched) usually contains less of these daughter nuclides, so a greater proportion of the radiation it produces comes from decay of U isotopes themselves.

3b. How Much Ionizing Radiation Dose Does a Resident of the Hawaiian Isles Receive?

Many isotopes emitting different particle types and energies, and at different half lives, contribute to the overall public exposure rates to ionizing radiation. The average US exposure level (Figure 4) calculated by the US Nuclear Regulatory Commission (NRC) and the National Council on Radiation Protection and Measurements (NCRP) assumes many things, such as "typical" North American continental rock types for terrestrial sources, typical sealed home construction for radon exposure, typical dietary and medical care practices, etc. In 1987 these groups estimated the average US exposure level to be 360 millirem/year, which is equal to the radiation exposure from one chest x-ray every 10 days. Of the categories in this diagram, Hawaiian residents might expect to receive somewhat less than average exposure from terrestrial sources due to the low Th, U and K abundances of Hawaiian basalts compared to typical North American continental crust, and from and radon gas because homes are generally less well insulated and sealed in Hawaii.
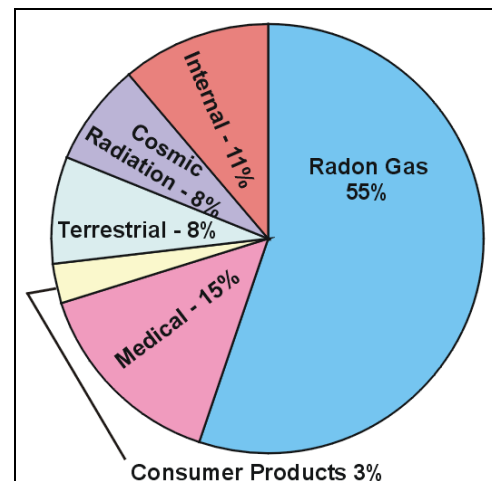
Figure 4. Ionizing Radiation Exposure to the US Public – this figure was simplified by the author from the version that is found on the US NRC website and in NCRP report number 93 (1987). At the time of this estimate, average public exposure was 360 millirem/yr. Roughly 82% of this was from natural radiation sources and 18% was from man-made sources (medical and consumer products). Terrestrial radiation includes sources in rocks, soils, waters and vegetation. Internal sources are ones that have been incorporated into human tissue over the course of a person's life.

3c. Detecting Radiation

There are a variety of devices used to measure the differing types of radiation, or the concentration of the specific isotopes that produce it. The choice of device to use depends strongly on the application. The ultimate in speed and portability come from handheld survey devices, designed for rapid, mobile detection of radioactive contamination at close range to the source. This class of device includes the well-known "Geiger counter", as well as other types designed with different energy ranges, radiation types and accuracies in mind. Appendix 1 discusses considerations about what types of instrument are appropriate for conducting DU surveys. Detection of the alpha particle emission from U and DU requires a device designed for this purpose. Survey meters of this type are generally not able to recognize specific isotopes, so they can not identify contamination as being DU. Although it is possible to deploy survey devices that can identify individual isotopes and activities in the field, issues of cost, durability, and reliability prevent these instruments from being commonly employed.

Isotope identification and activity determination is usually done in a laboratory setting using sophisticated but not mobile instrumentation in well controlled analytical environments. Two general types of instruments include radiation counters (i.e., those that directly measure alpha, beta or gamma radioactivity of a sample) and mass spectrometers (i.e., those that analyze the abundance of different isotopes in a sample, rather than their radioactive decay products). Many considerations determine which type of laboratory instrument is used in which case, although in general radiation counters make quicker measurements with large sample throughput rate and are easy to maintain and operate. Mass spectrometers usually provide the ultimate in accuracy, particularly when isotope concentrations are very low or samples are very small, but are of limited availability and they are tie consuming to operate and maintain. Also, they are not practical for examining large numbers of samples in a short amount of time because each sample requires significant chemical processing before it can be introduced into the instrument for analysis.

4. Geochemistry

       Geochemistry is study of the sources and fates of chemicals in the environment, including the rates and mechanisms of a chemical's movement between living and non-living things. Like most heavy metals, U occurs naturally at low levels in most materials you encounter each day.

       The processes that account for the abundances and exchanges of heavy metals in the environment are summarized in figure 5. The diagram illustrates pathways of natural and contaminant forms of a metal, and shows the types of processes a geochemist considers when determining how fast a metal will disperse into a particular environment. Under natural conditions, most metals first enter the environment by the breakdown of rocks to form soils, after which they enter the air and natural waters below and above ground, and the living organisms of the associated ecosystem. Heavy metals such as U occur as trace components of each of the materials shown in the diagram. Many heavy metals bind to natural organic chemicals that occur in both dissolved and particulate forms, with the fate of the metal in the environment strongly linked to the fate of the organic matter. Many metals also bind to soil minerals or water-borne sediment particles in a reversible process know as adsorption. Metals also occur naturally in many types of wind-blown dust particles.
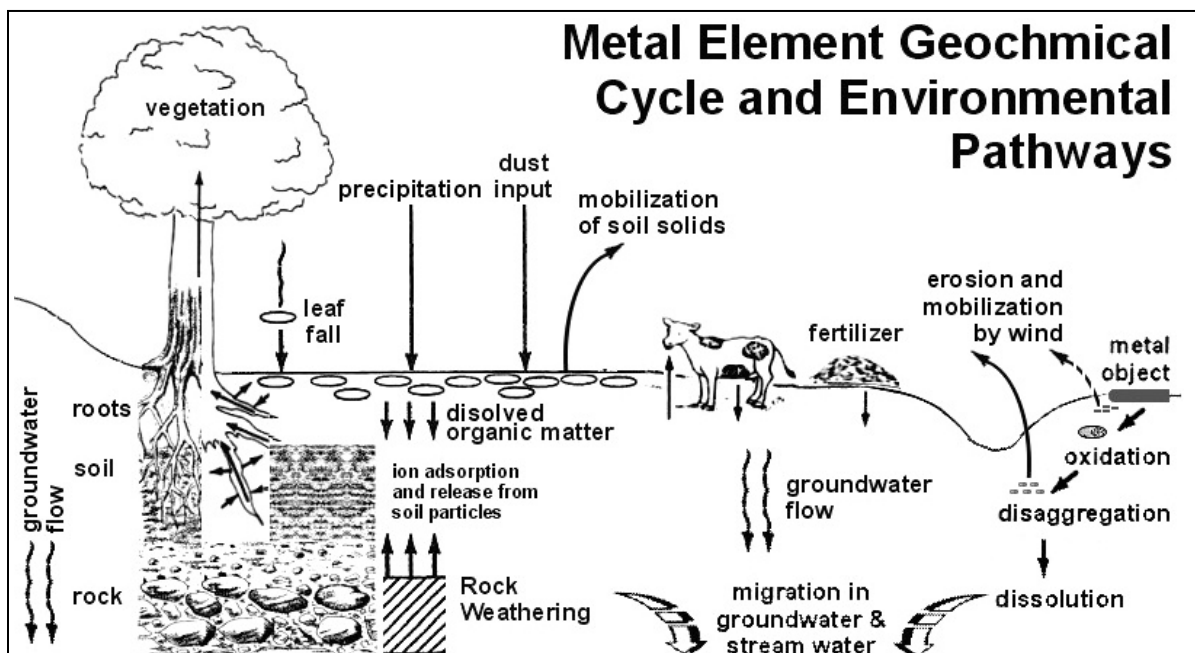
Figure 5. Typical pathways of heavy metal migration in the environment. Natural sources are summarized to the left and some relevant contaminants to the right of the diagram. Often times, excess abundances of heavy metals introduced by human activities behave just like their natural counterparts, and enter the natural cycle of chemical migration in the environment, but at elevated concentration. The concentration and rate of dispersion of a particular chemical like U is determined by its unique chemical behavior during these processes.

Chemicals that are artificially introduced into the environment in a form that differs from their natural forms (e.g., solid metal) are often converted into natural forms over time. The rate of this conversion is often one of the limiting factors on how fast a contaminant will disperse into the environment. Only a few of the many human activities that introduce metals into the environment (e.g., agriculture, industry, mining, energy production and military activity) are shown in figure 5.

Important aspects of U geochemistry as they apply to environments in the Hawaiian Islands are discussed below. Brief mention is also given to Th and K since they also produce natural environmental radioactivity. Table 1 summarizes the amount of U found in many of these materials, as well as in two potential contamination sources (fertilizer and U metal).

Table 1. U Concentrations in Materials found or used in Hawaii

Material	U abundance
"fresh" Hawaiian basalt	0.2 to 2 ppm
Uncontaminated inorganic soil particles, weathered minerals	0.1 to 1 ppm
Uncontaminated soil water or soil organic matter	< 2 ppm
Uncontaminated surface and ground waters	0.00005 to 0.0017 ppm
Sea water, modern (living) corals	2 to 3 ppm
Rock phosphorous fertilizer	20 to 140 ppm[1]
DU metal alloys	>90%

1. Source: National Council on Radiation Protection & Measurements report number 95

Rocks

The element U is rare on Earth, but over geological time has built up in the continental crust (e.g., the rocks one finds on the US mainland) to about of 2 to 5 ppm. These concentrations are equivalent to 1 oz of U in 6 to 16 tons of rock. The situation with Th is similar, although it is three to four times as abundant. These are average values, and particular minerals that are significantly enriched in either Th or U occasionally occur in certain geological settings, but not in Hawaii. The processes that have caused Th and U to accumulate in the continental crust have also stripped Th and U from rocks that make up Earth's underlying mantle, which is the source of the volcanic rocks that make up the Hawaiian and other oceanic volcanic islands. Consequently, U and Th concentrations in Hawaiian lavas are typically 10% to 20% of the values found in continental rocks (0.2 to 1 ppm and 0.6 to 3 ppm, respectively). K is a minor element that behaves similarly to U during many rock formation processes. K typically makes up a few percent of continental rocks and a few tenths of a percent to perhaps 1% in Hawaiian lavas.

Soils

Soils are produced by physical and chemical breakdown of rocks and addition of organic matter from vegetation. Soil character changes slowly over time, such that young and old soils can have very different physical and chemical characteristics. Undisturbed soils (e.g., not plowed) usually form physically, chemically and biologically distinct layers that develop over time as a function of climate, rock type, and local ecosystem. Cultivation of the land dramatically alters these characteristic. All of these factors contribute to soil chemistry variations that are generally much larger than the rocks the soils came from. Hawaiian soils typically have U and Th concentrations that mimic those of the rocks that produced them, with higher concentrations occurring in old soils such as occur on the islands of Oahu and Kauai. This increase is mostly due to the abundant trade winds, which deliver dust particles from continental areas around the Pacific, primarily Asia. These dust particles accumulate slowly and are mixed into the soil by plants, animals, and through-flowing water. Over hundreds of thousands to a million years dust inputs can increase soil heavy metal concentrations by as much as 1000%. K content is more variable in Hawaiian and other soils because of its strong adsorption onto some clay mineral surfaces, and because it is a plant nutrient and common ingredient in fertilizers.

In Hawaii, the basalt substrate of most soils is rather uniform in composition, yet highly variable soil types occur because of the broad range of microclimates and associated plants. These contribute to significant local variations in the concentrations of U, Th and K in local soils. Four main characteristics that affect trace metal migration through soil are texture, permeability (i.e., ability of liquid to flow through the soil), mineralogy and organic matter. All of these characteristics influence the amount of soil moisture and how fast water flows through the soil. The mineral and organic matter content also influence the pH (acidity) of the soil water and influence how long U, Th and other heavy metals will remain in the soil compared to through flowing soil water. Oxygen becomes rapidly depleted in soils that are water saturated for all or part of the year; when this occurs, U changes to a much less soluble chemical form.

Soils in Hawaii are generally slightly acidic and rich in iron (Fe). Under these conditions, U usually binds to Fe rich particles and organic matter in the soil. However, the chemical forms that Fe takes change as a soil gets older, and this change affects how strongly U is bound to the soil substrate. In Hawaii, U has been found to bind least well in young or poorly developed soils, strongly in intermediate age soils (because they contain high-surface-area microcrystalline and

amorphous Fe minerals), and moderately strongly in the oldest soils (where recrystallization produces, larger and less reactive iron mineral grains).

A discussion of soil types where DU rounds have been found in Hawaii and how this affects U behavior in the soil appears in section 6 of this paper.

A final general consideration for U in Hawaiian soil concerns past agricultural practices. Rock phosphate soil amendments (i.e., fertilizers) are commonly employed. Rock phosphates can have 10 to 70 times as much U as natural Hawaiian soils (Table 1). Today mined phosphates are usually purified to remove most U and other heavy metal contaminants, although this was uncommon until the 1930s. Thus, soils in areas where cultivation began in the 1800s, which are common in Hawaii, can exhibit elevated U concentrations that are not related to DU usage.

Corals

Living and fossilized reef building corals are common in Hawaii, both in the near shore environment and on lands currently above sea level. For instance, the Ewa plane of Oahu is built primarily of uplifted coral reef material that is 120,000 to 135,000 years old. Corals contain between 2 and 3 ppm U, with negligible Th and K. Crushed coral fragments have been used in Hawaii for various purposes, such as in road beds and as an agent to neutralize excess acidity in some soils. This explains why one can find bits of coral well removed from the current shoreline. If present, coral fragments will contribute some U to soil, but more importantly, will also be a source of carbonate ions, which strongly increase the solubility of U in soil water.
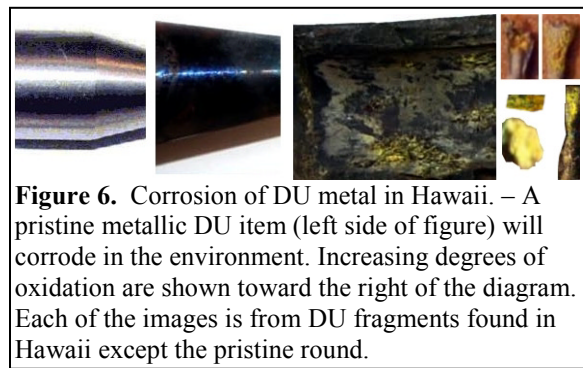

Waters

U abundance in natural waters is a strong function of the acidity (pH), oxygenation level, organic matter content and dissolved carbonate and phosphate concentrations. Oxygenated, very slight acidic (e.g., normal) surface waters in Hawaii generally have less than 0.002 ppm (mg/L) U. Limited oxygen environments such as in deep ground water tend to have lower U concentrations. Sea water has a globally uniform U concentration of roughly 3 ppm.

Rates of U migration in ground water above and below the water table are mostly determined by the water flow rate and the chemical form of the U. How strongly U will bind to different types of mineral surfaces is an important consideration once the U becomes dissolved in water. A recent government study in the United Kingdom of U mobility in ground water looked

at this issue. It calculated the length of time it would take to leach U from a DU fragment into ground water and for this U to show up at a water well 60 feet (20 meters) away. Using a computer model, it considered the full range of likely groundwater flow and solid substrate conditions, and determined that U contamination would show up in the well in as little as 100 years or as much as 30 million years. Groundwater conditions in Hawaii lie somewhere in between the extremes considered in that report, although they more closely match the "slow" case.

Metals

U does not naturally occur as a metal in the environment and will therefore oxidize if left there for any appreciable time. The corrosion of metal to oxide is a multi-step process that is affected by whether it is immersed in air, water, or soil, as well as the acidity and salt content of water it may encounter. In its most

Figure 6. Corrosion of DU metal in Hawaii. – A pristine metallic DU item (left side of figure) will corrode in the environment. Increasing degrees of oxidation are shown toward the right of the diagram. Each of the images is from DU fragments found in Hawaii except the pristine round.

oxidized form, U becomes a friable material that can more easily break into particles. This form is also more soluble in water. Oxidation therefore increases the mobility of metal-derived U by wind and water. However, DU metal and DU oxide particles are 3 to 6 times denser than soil particles, so they are not easily mobilized from soils by wind. U metal in various stages of environmental oxidation are shown in Figure 6. Unpainted DU metal used in some weapon systems will oxidize rapidly during use and a significant fraction of the projectile can be dispersed as microfine particles or aerosols during impact. The M101 spotting round is not this class of projectile, and probably experienced limited to moderate oxidation during firing and subsequent impact. Rupture or fragmentation of the M101 spotting round during impact would have exposed DU fragments to the environment. These fragments would subsequently oxidize and further disaggregate at a rate that depended on the specific environment where they were used. The rate of metal oxidation has been different at sites in Hawaii where M101 spotting rounds have been found, as described in section 6 of this paper.

5. Isotopic Fingerprinting

The proportions of U isotopes in a substance can be used to determine the source of the U it contains. If environmental U contamination is suspected, isotopic tests can determine if the U came from natural U ore or from non-natural DU or EU. Except in extremely rare cases (not found in Hawaii), natural U dispersed in rocks, soils and waters at earth's surface today have the same $^{235}U/^{238}U$ radioactivity ratio, even if the U concentration (by weight) is different between them. This fact provides a fingerprint of natural U isotopic composition. DU has comparatively less ^{235}U and EU

Figure 7. Typical proportions of radioactivity from the decay of ^{234}U, ^{235}U and ^{238}U in natural and manmade U materials. Enriched U in this diagram is nuclear fuel with a 5% ^{235}U atomic abundance ("low EU"). The isotopic differences shown here are easily distinguished with laboratory analysis, as are most mixtures between them.

has more, giving these materials non-natural $^{235}U/^{238}U$ ratios (Figure 7). There have been slight variations in the ^{235}U depletion level in DU manufactured in different places and times, but normally ^{235}U has been reduced by at least 70% from its natural value. There is more variation in EU, depending on how it is made and the intended use of the material; mildly enriched EU for nuclear fuels is shown for comparison in figure 7, although there is no reason to suspect EU contamination in Hawaiian soils.

^{234}U is affected even more by depletion and enrichment than ^{235}U. However, unlike ^{235}U, the amount of ^{234}U in a natural material can vary relative to the amount of ^{238}U due to natural processes, making the $^{234}U/^{238}U$ ratio less precise but still useful for isotopic fingerprinting of U contamination. The reason $^{234}U/^{238}U$ varies in nature and $^{235}U/^{238}U$ does not is that most ^{234}U in a rock has been produced there from decay of ^{238}U and its immediate daughters, causing slight radiation damage to the place in a mineral where it resides. ^{235}U and ^{238}U are not decay products of other isotopes on Earth so there is no radiation damage to their mineral residence sites. The radiation damage from ^{234}U production increases with the age of the rock, causing that ^{234}U atom to be more easily leached from the rock during rock weathering. The water that does the leaching usually ends up with elevated $^{234}U/^{238}U$ and the rock and soil residues usually have lower ratios, although secondary mineral formation can affect rock and water ratios as well. Recoil of ^{234}U atoms as they are produced can also push "extra" ^{234}U into soil water. The changes in $^{234}U/^{238}U$ from natural processes are usually smaller than the changes caused by the
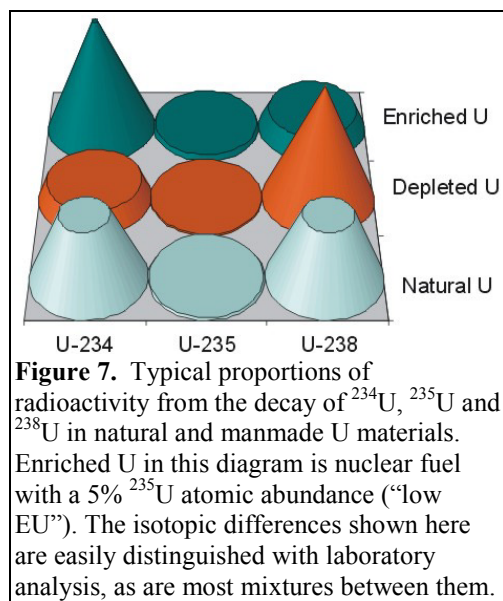
manufacture of DU and EU, so $^{234}U/^{238}U$ is still useful for fingerprinting of U contamination in nature.

The general principles of isotopic fingerprinting of U in contaminated samples are illustrated in figure 8. Contamination generally results in elevated U concentrations, although if U is leaching from the environment almost as fast as the contaminant is added, the isotopic composition is affected but the overall U concentration may not change as dramatically. If the contamination is from natural U (e.g., some phosphorous fertilizers or U ores) the U concentration will change but the isotopic composition will not. The isotopic composition will change if contamination is from DU or EU. If DU or EU contamination is present, U in environmental samples will be mixtures of natural and contaminant U, with intermediate isotopic composition, except in extremely contaminated cases. Mixing follows predictable trajectories, shown schematically as arrows in the figure. Laboratory measurements of U concentration and isotopic composition are used to determine the type and amount of contamination.
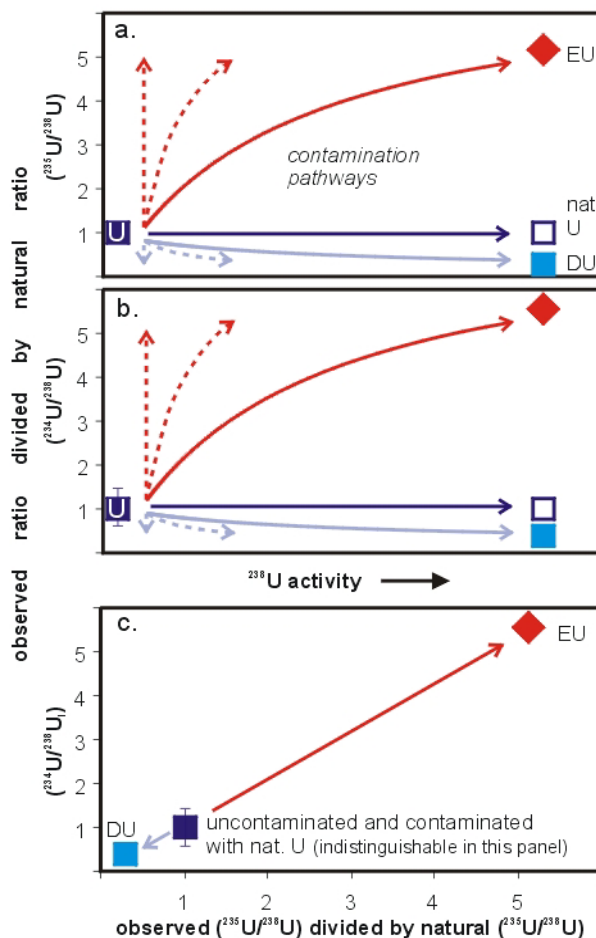

Figure 8. Isotope ratio shifts and radioactivity effects during U contamination. Isotope activity ratios are plotted relative to natural U (i.e., as the ratio of the observed value divided by the natural value). A ratio of 1 means the observed value is natural U; a ratio of 2 means the observed value is double the natural one.

Each panel has symbols representing natural U (dark blue square), DU (light blue square) and EU (red diamond), and their mixtures (as arrows). In panels a and b the dark blue square for uncontaminated, natural materials is also labeled with a white letter "U". The white "U" does not appear in panel c because uncontaminated materials and materials contaminated with natural U lie in the same spot in that diagram.

The colored arrows show changes in composition as contamination is added to a substance with natural U. Greater contamination moves compositions farther along the path of the arrows, leading away from natural U isotopic composition and abundance. Panels a and b depict changes in isotope abundance and U concentration. Solid arrows are for simple contaminant addition. The dashed arrows show what happens if contamination occurs in an environment where U leaching is also occurring (such as leaching to groundwater). Panel c considers only isotopic compositions. The dashed trajectories are not shown because they lie on top of the solid ones.

6. Site Specific Characteristics for U and DU Geochemistry in Hawaii

Each location where U contamination is suspected needs to be evaluated for site specific characteristics that may influence U retention or mobility there. A generalized site model (figure 9) demonstrates the important variables to be considered.
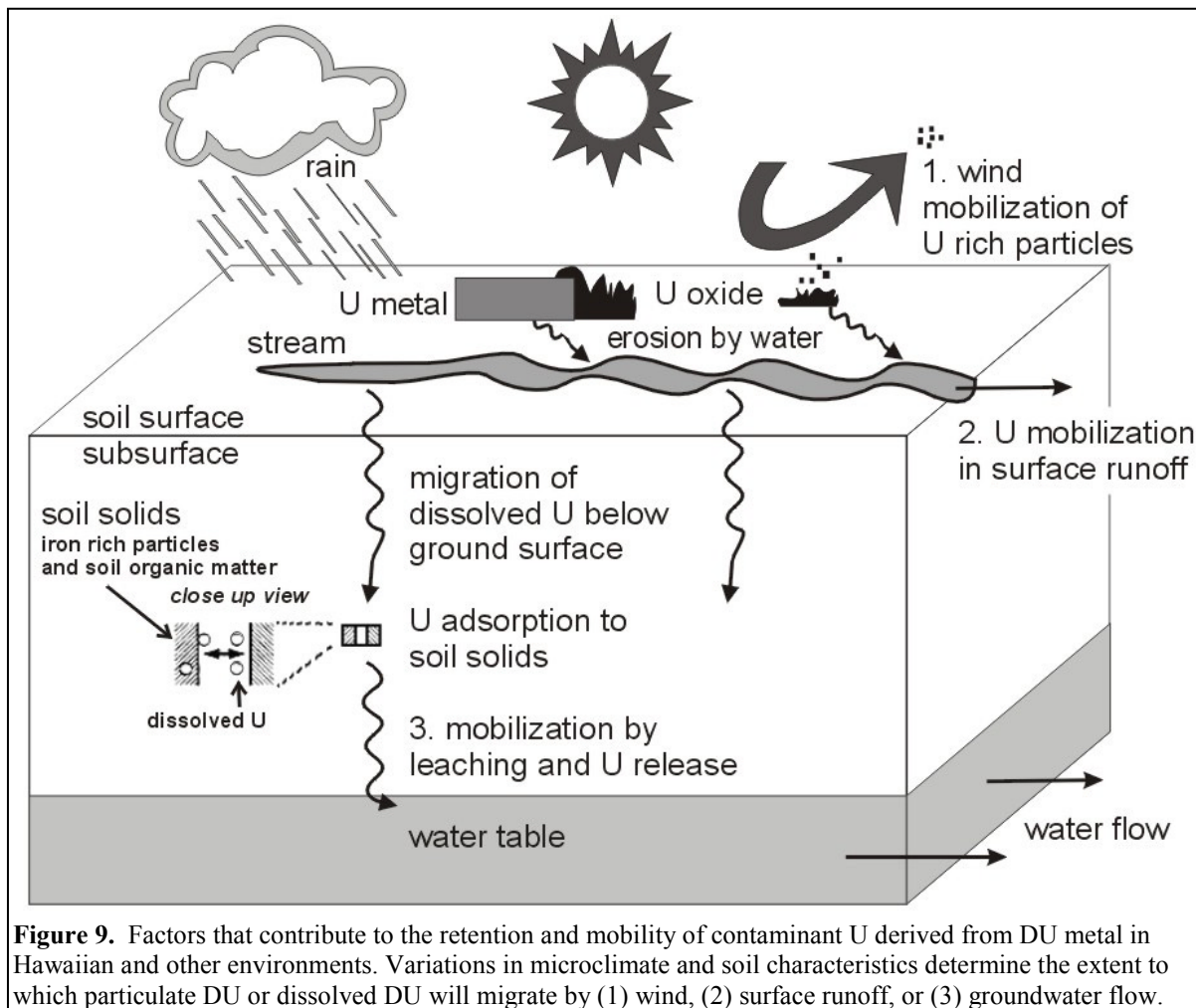
Figure 9. Factors that contribute to the retention and mobility of contaminant U derived from DU metal in Hawaiian and other environments. Variations in microclimate and soil characteristics determine the extent to which particulate DU or dissolved DU will migrate by (1) wind, (2) surface runoff, or (3) groundwater flow.

6a. Schofield Barracks Firing Range

Schofield Barracks sits in central Oahu on a gently sloping plane between the extinct Waianae and Koolau volcanoes (Figure 10). The area receives about 50 inches of rain a year in a humid tropical climate. Soils range from rust colored (Fe-rich) oxisols to saprolites (heavily weathered rock, in this case basalt, containing essentially no particulate organic matter). There are two small streams that run through the Schofield firing range and drain towards the Wahiawa reservoir to the east. The area is underlain by the Schofield High Level aquifer that drains towards Pearl Harbor in the south.

Fragments from DU spotting rounds were discovered on a Schofield Barracks operational range in 2005. The site is in the extreme western portion of the range, in the hilly terrain of Waianae volcano (Figure 11). Subsequent walkover surveys in 2007 identified DU fragments at a second, nearby site and delineated the exact location and quantity of DU contamination in surface soils at both sites (which the US Army refers to as areas Alpha and Bravo).
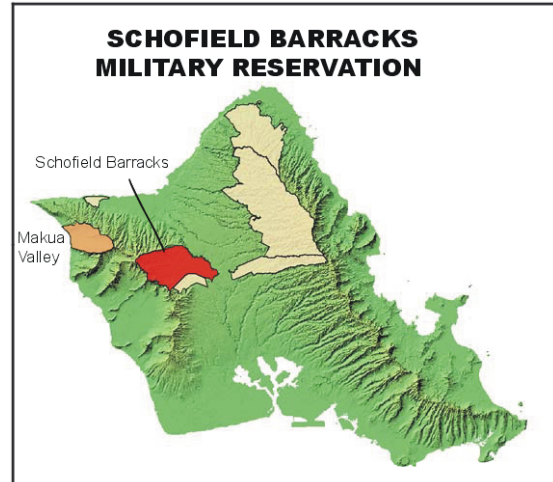

Figure 9. Schofield installations on Oahu

Vegetated slopes surround the Schofield operational range, including areas Alpha and Bravo, isolating them from the general populace. Both oxisols and saprolites occur in this area of the range. In Hawaii, these soil types are generally oxidized, mildly acidic and Fe-rich, conditions that should favor U binding to soil particles if U is in a natural, oxidized form (i.e., not U metal). Moderately high rainfall, warm air temperatures, and oxidized surface soils promote the oxidation of DU fragments, which accounts for the yellow corrosion seen on some rounds collected in the region, as well as the occurrence of yellow U oxide particles in soils near the rounds. U will also typically bind to soil humus if present (such as on slopes around the range). Because U is likely bound to soil particles, the primary means for U mobilization on the range appears to be by wind action or water flushing of U-rich particles, particularly during storms. Through flowing rain water will likely slowly leach U that is adsorbed to surface soil solids into the groundwater. U leaching from natural Hawaiian
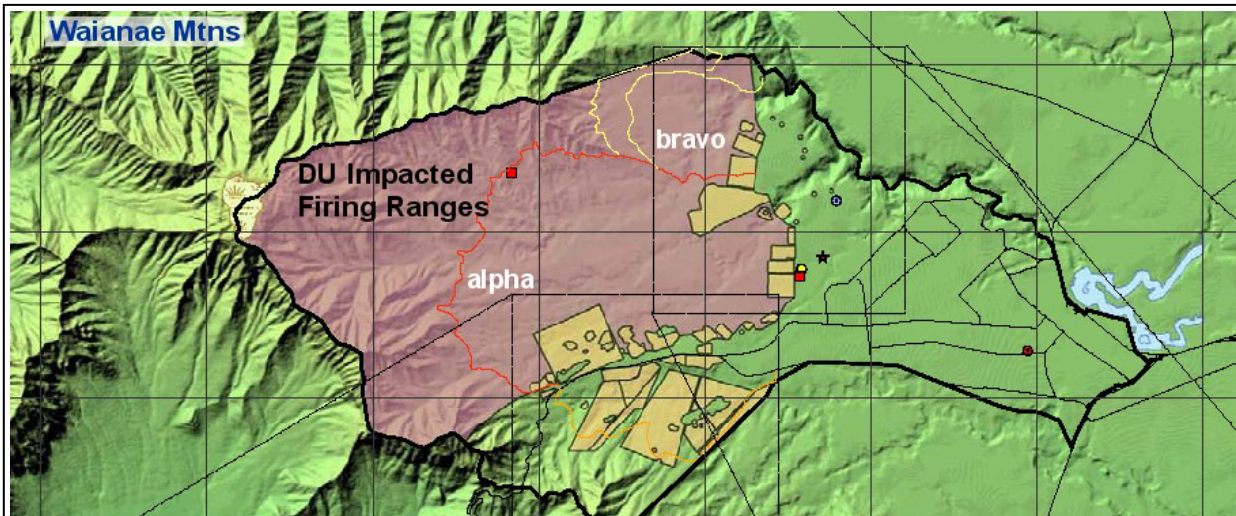

Figure 11. Location map of the Schofield firing range where DU rounds were found. The base is well isolated within the confines of Schofield Barracks.

soils is generally very slow, but it is not possible to predict how fast or extensive this might be in this specific environment without detailed soil and soil water analysis.

Analysis of surface soil samples collected during detailed surveys conducted for the Army by an environmental contractor confirmed the presence of DU at a number of subsites within areas Alpha and Bravo. Limited sampling of subsurface soils (to a few cm depth) indicates significant contamination at depth beneath surface contaminated sites, although lower maximum U activities imply that U has not been thoroughly mixed downward into the soil column over the 40 years since the M101 spotting rounds were fired on the range.

The question of DU mobility on the site was evaluated by the contractor using various forms of environmental sampling. For instance, air filtration sampling of particulate matter downwind of a particle plume generated during a test burn procedure on the range did not find DU contaminated particles, indicating limited DU mobility as dry aerosol or micro-fine particles during the test. Limited testing of surface waters on the range and soils within nearby gullies for U abundance and isotopic fingerprinting did not show evidence of DU contamination, suggesting limited U mobility by through flowing water. Such results are encouraging, although more systematic sampling would be required to conclusively demonstrate DU immobility by surface water runoff or groundwater percolation.

6b. Makua Military Reservation (MMR), Makua Valley.

Makua Valley lies westwards of Schofield Barracks on the drier, leeward side of the Waianae range (Figure 10). As of this writing, DU has not been found on the MMR operational range, but the US Army contracted for scoping survey work there because documentary evidence suggested that the M101 may have been used there. Heavy vegetation and the presence of explosive hazards have prevented extensive ground surveys for DU on the range. Ten soil samples were collected from sites where sediment had collected from past runoff/erosion events around the perimeter of the MMR. Radiometric analysis of those samples found only natural U abundances and ^{234}U/^{238}U isotopic composition. Were presently unidentified DU contamination to exist somewhere on the range, its mobility in soils and waters at Makua Military Reservation are expected to be generally similar to somewhat less than at the Schofield firing range because of lower average rainfall at otherwise similar environmental

conditions. Additional soil and water sampling conducted after such a discovery would demonstrate the actual extent of DU mobility on the range.

6c. Pohakoloa Training Area (PTA)

PTA sits in the saddle between Mauna Loa and Mauna Kea volcanoes on the Island of Hawaii (see Figure 12). The volcanic terrain is dominated by young lava flows from Mauna Loa Volcano. In fact much of PTA has exposed, bare rock surfaces (Figure 13). Annual rainfall is light (about 15 inches per year). Soils are not well studied in the region, but are generally poorly developed, rocky, and well drained. Vegetation is sparse. U content in lavas of the region is less the 0.5 ppm; where present, soils should have similar concentrations.

The US Army discovered one almost intact M101 spotting round

Figure 12. Location of Pohakuloa Training Area and firing range

during a screening survey of the remote Impact Area at PTA. The recovered fragment is nearly completely unoxidized metal found lying on a bare rock lava surface. Subsequent surveys uncovered aluminum firing tubes for the spotting round, but no additional spotting rounds themselves. Ten soil samples were collected from sites where sediment had collected from past runoff/erosion events around the perimeter at the PTA. Radiometric analysis of those samples found only natural U abundances and $^{234}U/^{238}U$ isotopic composition.

Limited U metal oxidation and the intact nature of the round suggest that metallic U does not oxidize quickly in PTA's environment. Oxide particles that do form would likely be washed into crevices between exposed lava flows, and eventually interact with cinders or soil particle
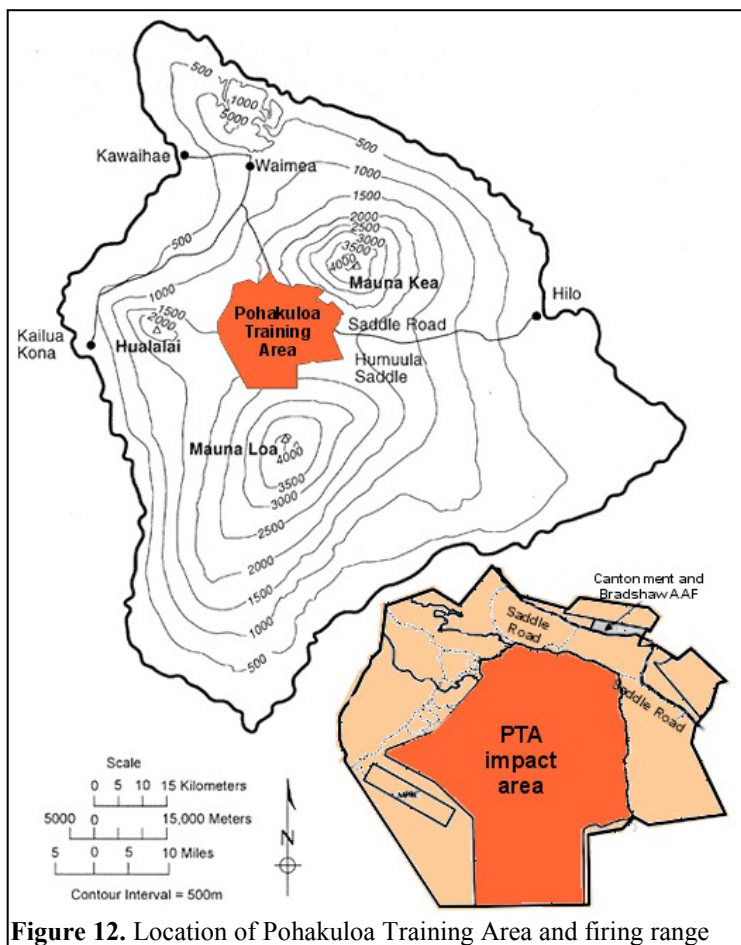
surfaces in the area, where adhesion of dissolved U to Fe-rich particles is a likely outcome. The young, poorly developed soil at the site is not anticipated to bind U as strongly as the sites on Oahu, because of low organic matter content, high porosity, and lesser degree of high surface area Fe oxide particles. The general ground slope of PTA is downward gently to the northwest (figure 13), which indicates the likely direction of waterborne particle migration should it occur.
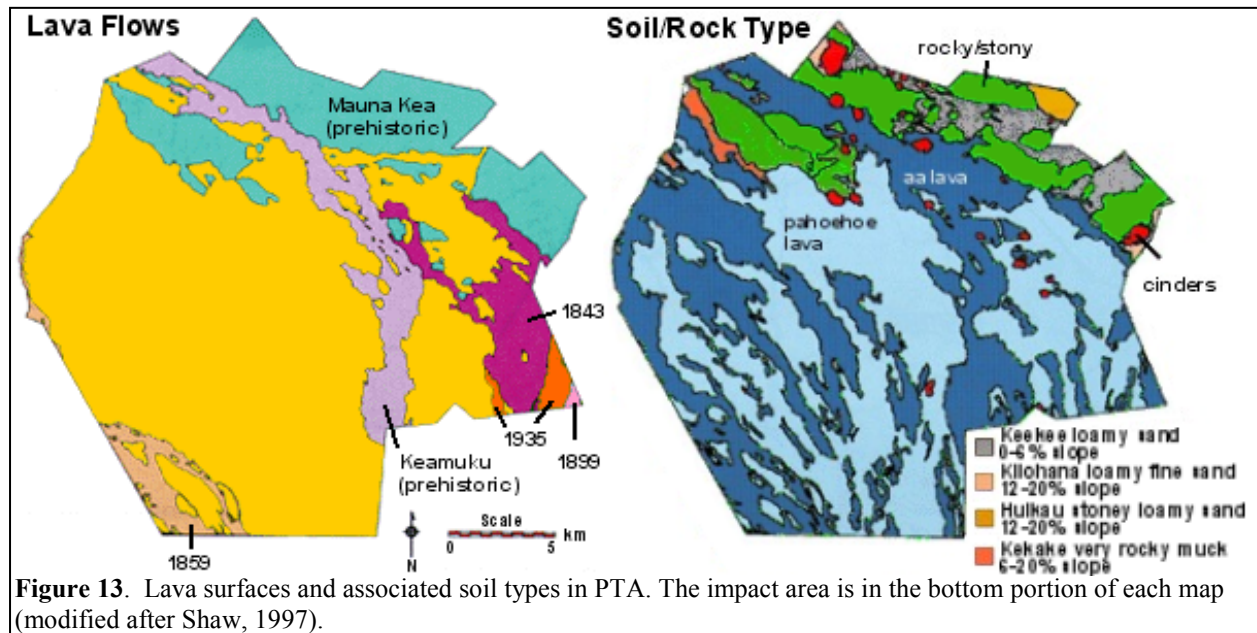
Figure 13. Lava surfaces and associated soil types in PTA. The impact area is in the bottom portion of each map (modified after Shaw, 1997).

7. Public Concerns

Media reports in Hawaii and associated Internet traffic indicate the general public is concerned about the past use of DU in Hawaii and the potential impact of the presence of DU on both their health and the environment. The below points should help allay these concerns.

- Large U oxide particles are dense (not easy to mobilize with wind) and dissolve slowly into water in semi-arid environments.
- U has a high binding affinity for Fe-rich particulates found in Hawaii soils, which should help immobilize DU and U that has been dissolved into groundwater (i.e., DU particles) near the point of impact. Limited surface water sampling at Schofield has not detected radioactivity from DU; surface water monitoring will continue on site.
- The M101 spotting rounds were used in Hawaii (and elsewhere) to mimic the flight trajectory of the Davy Crockett warhead and to mark the point of impact. The spotting rounds would have mostly produced large DU fragments with limited dispersal. They did not produce sub-micron DU particles. This is different from DU penetrators in use today as kinetic energy munitions, which may generate a cloud of DU-rich dust particles (in amounts that depend on the munition, the target, and the type of impact).
- Air sampling conducted by the US Army within Schofield Barracks and around Pohakuloa Training Area has not found airborne radioactivity in excess of natural levels at either of those sites.

Public comments indicate that some people remained concerned about DU contamination and mobility in the environment after release of the Schofield Barracks Site Characterization and Baseline Human Health Risk Assessment studies in April 2008, which show no elevated risks from DU at that site. Many comments arose from the Big Island of Hawaii, where site assessment of PTA is ongoing (as of this writing). The main concerns are aerial dispersal of microfine DU particles from past or present activities at active US Army ranges in Hawaii, or during brush fires there. Oxidized DU should not be a hazard for grass or brush fires (and air sampling during a test burn at Schofield did not find DU in the smoke). Microfine DU aerosols ("nano-particles") should not exist in Hawaii from M101 spotting rounds used there (and air sampling at contaminated sites has not found any). Continued monitoring would likely assure the public that there is no current risk from microfine DU particles in Hawaii.

Concerns about potential DU contamination from Army use of the M101 spotting round have prompted some individuals to purchase and deploy radiation survey devices in public access areas they suspect are contaminated (such as down wind of PTA) and to report readings they attribute to DU contamination. Because of this, it is important the public be made aware of what they might be measuring, what the measurements mean to them and their families, and how and why their measurements might differ from those being made by official monitoring efforts of Federal and Hawaii State agencies. The State of Hawaii Department of Health (DOH) reports that in their recent experience, many of the devices being used by lay persons are not designed to measure the type and energy radiation emitted by DU. DOH also recently established a training program since many users were not properly aware of how to properly use, maintain and calibrate their device, or how to interpret the results of their measurements.

The following general points should be considered by members of the public who wish to conduct their own DU contamination surveys:

- Natural U radiation from soils and rocks in Hawaii can not be measured accurately or at all by most field survey devices.
- The type of radiation to be measured dictates the type survey device required.
- Many portable radiation survey devices will not detect alpha particle radiation such as that generated by DU, nor can they identify the specific radioactive isotopes present.
- Measurements of alpha particle radiation should be done close to the source (within 1 foot), unless beta or gamma radiation is too high to approach the area of suspected contamination.
- To generate meaningful results, survey meters must be carefully calibrated and should be used by trained personnel.
- Materials with significantly elevated activity detected with a properly maintained, calibrated and deployed field survey device must be subsequently analyzed in a qualified laboratory to determine if DU is present.

Appendix 1 - Detecting radioactivity from U and other naturally isotopes

The following considerations are important for field surveys intended to detect DU or U contamination. The author does not recommend members of the general public conduct their own environmental radiation surveys. However, determined individuals can consult one of the many web sites that offer information about purchasing, using and ensuring the proper calibration of radiation survey devices. Radioactivity is extremely dangerous at high radiation dose rates and a person should not approach any bona fide radiation source with out proper training and shielding. Radiation at low count rates is tricky to measure and interpret. If attempting a radiation survey:

- Choose a survey device that measures the type of radiation and intensity range you intend to monitor. The most basic varieties usually only detect beta and gamma radiation above 100 kev. Thin window Geiger-Mueller (GM) probes are generally better suited to detect beta radiation above 70 keV while sodium iodide (NaI) scintillators are used specifically for gamma radiation. Special probes (such as zinc sulfide scintillators) are used to detect alpha particles while gas flow proportional probes will detect alpha and beta particles. Pancake probes will detect alpha particles at close range, but with low efficiency.
- Choose a detector that has specificity for the isotope of interest.
- Calibrate the device for the isotopes of interest
- Know the true range of background count rates for the device by frequently measuring in non-contaminated areas. In general, for outdoor conditions:

GM Survey Meter Readings	Assessment of Measurements
0-200 cpm / 0-0.05 mR/hr	Typical Background readings
200-400 cpm / 0.05-0.1 mR/hr	Suspected contamination
>400 cpm / >0.1 mR/hr	Contamination

- Know how to use the device and proper survey methods for each type of radiation
- Approach sources of radiation carefully and follow the time-distance-shielding protocol to minimize possible exposure. For instance, less time, greater distance, or more shielding lowers your exposure to a radioactive source. At the same time, the greater the distance from a source, the less radiation will be detected. Particularly alpha particles are generally not detectable unless the survey device is within 1ft. of the radiation source.
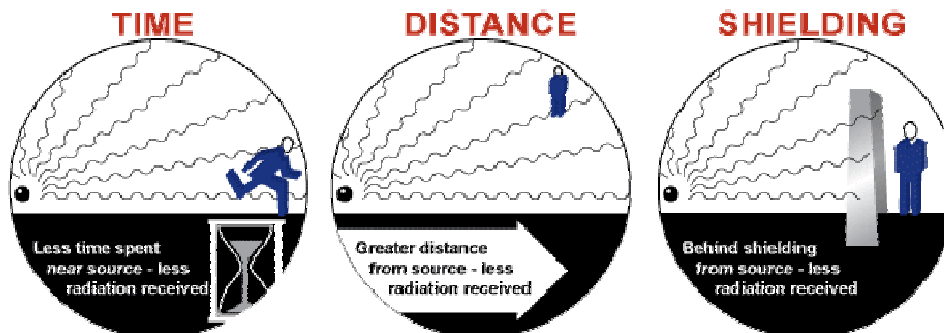

figure source: http://www.ndt-ed.org/

Detecting DU in the presence of natural radioactivity from Th, U, K, C and Ra

U is particularly difficult to detect with a typical survey meter because the 3 main U isotopes (234, 235 and 238) emit high energy but poorly penetrating alpha particles with little associated gamma radiation. On an equal mass basis, DU is generally more difficult to detect than natural U because the lighter, more radioactive isotopes are lower in abundance. At low count rate, the contribution of background radiation becomes an important component (maybe even all) of the detected radiation. The table below lists the types of ionizing radiation produced in uncontaminated rocks and soils by common radioactive isotopes. If you detect elevated count rates with a survey device, the material needs to be analyzed in a laboratory to determine what isotope(s) is causing them. Do not attempt to make such measurements by yourself. Instead, contact the Hawaii State Dept. of Health, Noise, Radiation and IAQ Branch for assistance.

Table 1. Particle types, energies and intensities from common natural radioactive isotopes.

Isotope	half-life	Alpha energy (MeV)	Beta energy (Mev)	gamma energies (MeV)
C-14	5700 years		0.1565	
K-40	1.29×10^9 years		1.3	1.46 (11%)
Th-232	1.41×10^{10} years	4.007 (76%) 3.952 (24%)		0.0638 (0.27%)
U-235	7.04×10^8 years	4.391 (57%) 4.361(18%)		0.1857 (57%) 0.1438 (11%) 0.163 (5%) 0.2053 (5%)
U-238	4.47×10^9 years	4.195 (77%) 4.147 (23%)		0.0130 (7.3%) 0.0496(0.06%)
Immediate U-238 daughters[2]				
Th-234	24.1 days		0.199 (70%) 0.104 (19%) 0.103 (7.6%)	0.0633 (4.5%) 0.0924 (2.6%) 0.0928 (2.6%)
Pa-234m	1.17 minutes		2.29 (98%) 1.22 (1%)	1.001(50.7%) 0.766(17.8%) 0.743 (4.8%) 0.258 (4.4%) 0.786 (2.9%)
Pa-234	6.75 hours		0.47 (29%) 0.64 (17%) 0.47 (11%) 0.41 (7.1%) 0.50 (6.2%)	0.13 (8.5%) 0.95 (6.3%) 0.88 (4.5%) 0.57 (3.9%) 0.93 (3.7%)
Longer-lived U-238 daughters[2]				
U-234	2.452×10^5 years	4.768 (72%) 4.717 (28%)		0.0532 (0.1%)
Th-230	7.569×10^4 years	4.621 (23.4%) 4.687 (76.3%)		0.0123 (7.7%) 0.0677 (0.38%)
Ra-226	1600 years	4.784 (94.4%) 4.601 (5.5%)		0.186 (3.5%)

1. Quantities in parenthesis are percentages of decays at this energy. Minor percentage particles are not shown. Only the top 5 gamma energies are shown for some nuclides. For complete listing see http://www.nndc.bnl.gov/ or http://atom.kaeri.re.kr/
2. These short-lived daughters contribute to gamma radiation detected from [238]U.

Appendix 2 - U concentration and isotopic compositions in natural and contaminated materials

The data in the following two tables show the isotopic compositions of various forms of U at natural concentrations and in pure U metal. This information was used to make the isotope fingerprinting figures in this paper, and to illustrate in more detail the activities and activity ratios expected in materials contaminated by natural U or DU.

U abundances and Isotopic Compositions of Various Materials

Material	U abundance[1]	$^{235}U/^{238}U$[2]	$^{234}U/^{238}U$[3]
Uncontaminated			
"fresh" Hawaiian basalt	0.2 to 2 ppm	0.047	1
Uncontaminated inorganic soil particles, weathered minerals	0.1 to 1 ppm	0.047	0.7 - 1
Uncontaminated soil water or soil organic matter	< 2 ppm	0.047	1 - 2
Uncontaminated surface and ground waters	0.00005 to 0.0017 [4]	0.047	1 - 2
Sea water, modern (living) corals	2 to 3 ppm	0.047	1.14
Rock phosphorous fertilizer	22-140 ppm	0.047	1
DU	>90%	0.013[5]	0.17[5]
Contaminated[6]			
Rock phosphorous contaminated soil	elevated	0.047	1
Rock phosphorous contaminated water	elevated	0.047	1
DU contaminated soil	elevated	0.013 - 0.047	0.17 to 1
DU contaminated water	elevated	0.013 - 0.047	0.17 to 1

1. Abundances are given in ppm except the DU entry, which is in percent.
2. Activity ratio. "Natural" $^{235}U/^{238}U$ has an activity ratio of 0.047
3. Most fresh, unaltered rocks on Earth have $^{234}U/^{238}U$ activity ratio of 1. Weathering can change this ratio.
4. Source: Hawaii State DOH
5. typical DU value
6. "Contaminated" materials are mixtures of one or more contaminant sources and the natural U at the site. Abundances and activity ratios depend on the degree of contamination

Isotopic composition in pure U metal‡

Material	Weight percent				Relative to natural U	
	U-234	U-235	U-236	U-238	235/238	234/238
Natural Uranium	0.0053%†	0.71%		99.28%	1	1
DU produced from natural uranium	0.0009%	0.20%		99.80%	0.28	0.17
DU produced from recycled spent fuel	0.0019%	0.20%	0.20%	99.57%	0.28	0.37
	Activity percent					
Natural Uranium	48.9%	2.2%		48.9%	1	1
DU from natural uranium	14.2%	1.1%		84.7%	0.29	0.17
DU from recycled spent fuel	20%	0.71%	24%	55.2%	0.29	0.36

‡ Typical contamination source.
† varies in nature by ±100% *i.e., 0.001% to 0.02%)