



NORTHERN
ARIZONA
UNIVERSITY

November 11, 2010

**INTERIM REPORT: Results for Isotopic Studies of Uranium in Environmental Samples
from the Vicinity of the Nuclear Fuel Services Facility, Erwin, TN**

Prepared by: Michael E. Ketterer, PhD, Professor, Chemistry and Biochemistry, Box 5698,
Northern Arizona University, Flagstaff AZ 86011-5698

Executive Summary: A study is currently being conducted to determine uranium "signatures" in environmental media (water, soil, aquatic sediments, and biota) near the Nuclear Fuel Services (NFS) facility in Erwin, Tennessee. The overall purpose of the work is to determine the extent to which uranium (U) and related contaminants have been dispersed off-site. The study has involved collection of environmental samples from publicly accessible locations near NFS, followed by laboratory analyses of these samples.

The results discussed herein clearly indicate the presence of enriched uranium, originating from the NFS, in water and sediment samples. The NFS-derived U is present in water and sediments relatively far downstream at Davy Crockett Lake and even past the Davy Crockett Dam. It not been possible to accurately estimate the total quantities of enriched U present in Davy Crockett Lake, though these quantities are likely to be very considerable. The results demonstrate that U-contaminated water containing enriched U is being discharged in apparent violation of NPDES Permit No. TN0002038. The results also demonstrate the entry of groundwater discharges of NFS-derived enriched U into the surface waters, and point to serious questions about the scope/extent of groundwater contamination near the NFS facility.

Purpose. A study is being conducted of uranium “signatures” in environmental media (water, soil, aquatic sediments, and biota) near the Nuclear Fuel Services (NFS) facility in Erwin, Tennessee. The overall purpose of the work is to determine the extent to which uranium (U) and related contaminants have been dispersed off-site. The study has involved collection of environmental samples from publicly-accessible locations near NFS, followed by laboratory analyses of these samples. Mass spectrometry, a well-established analytical technique, has been used to measure relative numbers of atoms for different isotopes (nuclear forms) of U. The results from mass spectrometry are used to compare U found in the environment vs. its known/expected isotopic composition in Nature, in order to evaluate whether naturally occurring U is being mixed with U from other sources that are not naturally occurring. This study is ongoing, and complete results are not yet available, given the open-ended scope/magnitude of the question, and the absence of publicly available information regarding environmental contamination and releases from a facility that has been operating for more than 50 years.

Scope: The results presented in this report are intended to be of a *demonstrative* nature, and do not necessarily reflect a complete set of all results that have been obtained to date. This report emphasizes these ratios as “signatures” of the presence of U from the NFS, without attempting to evaluate or interpret the total amounts or concentrations of U present in the environmental media. Though the concentrations of U present in the environment are of interest, and the total quantities of NFS-derived U present in the environment is an important concern, these data and interpretations thereof are beyond the scope of this interim report. These questions will be addressed in the future as part of ongoing work.

Background: Uranium isotopes. Uranium (U) has four different isotopes (nuclear forms) that occur in detectable quantities in Nature. The chemical behavior of these isotopes is essentially identical; the different isotopes are designated by their mass numbers. The mass number (*a*) is the sum of the number of protons (*p*) and neutrons (*n*) present in the nucleus of the U atom, and isotopes are designated by the element symbol with the mass number being written as a superscript on the left side of the element symbol: ^{*a*}U. All U atoms have *p* = 92. The four isotopes that occur in detectable quantities in Nature are ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U. Each of these isotopes has different nuclear properties (half-life, decay energy, and susceptibility to fission).

Uranium occurs in Nature, and is expected to be ubiquitous in water, soil, sediment, and the biosphere. The isotopes ²³⁵U and ²³⁸U are primordial; they have been present since the solar system was accreted. The isotope ²³⁶U is present in very small amounts in Nature as a result of spontaneous fission processes of other U isotopes, followed by neutron capture of ²³⁵U. The isotope ²³⁴U is present in small amounts in Nature as a continuously produced decay product in the ²³⁸U decay series. The relative proportions of ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U present in Nature are fairly constant and predictable. ²³⁸U is the most abundant isotope, and it is convenient to express the isotope composition of U as “ratios” or “isotope ratios”, that is, as ratios of numbers of atoms. Examples of ratios are ²³⁴U/²³⁸U, ²³⁵U/²³⁸U, and ²³⁶U/²³⁸U, discussed in this report.

Processes related to the nuclear fuel cycle can produce U of altered isotope composition. “Enriched” U refers to U with a *higher* ²³⁵U/²³⁸U atom ratio than the naturally occurring ratio, and “depleted” refers to U with a *lower* ²³⁵U/²³⁸U atom ratio than the naturally occurring ratio. In the enrichment process, the lighter isotopes are selectively concentrated, with the objective of preparing a material of enhanced ²³⁵U content for use as a nuclear reactor fuel or a fission weapon device. The enrichment process also enhances the ²³⁴U content, and ²³⁴U/²³⁸U is higher

than the typical values found in Nature. Similarly, the enrichment process also produces “tails” from which most of the ^{235}U has been removed (depleted U). Depleted U also has lower $^{234}\text{U}/^{238}\text{U}$ than naturally occurring U.

Some samples of enriched or depleted U also contain readily detectable amounts of ^{236}U ; this isotope usually indicates the presence of U that has been previously irradiated by neutrons in a nuclear reactor. During the Cold War era, the US Government was concerned with an apparent shortage of U, and much of the U introduced into the nuclear fuel cycle had been recovered from plutonium production reactors, referred to as “recycled” U. Most samples of depleted and enriched U contain at least some ^{236}U introduced from previous blending of recycled U.

The following compares the U ratios expected in Nature vs. “enriched” and “depleted” U:

Type of Uranium	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$
Naturally occurring	~ 0.000055 (a)	0.0072527 (b)	< 0.000000001 (c)
Enriched U	> 0.000055	> 0.0072527	Up to ~ 0.01
Depleted U	< 0.000055	< 0.0072527 (d)	~ 0.00003 typical

(a) The ratio between ^{234}U and ^{238}U is variable in Nature due to disequilibria in open systems present in the Earth surface environment. (b) This ratio is essentially constant in Nature, and has only been shown to vary by ~ 1 -2 parts per thousand relative as a result of natural fractionation processes. A few exceptional naturally occurring situations where $^{235}\text{U}/^{238}\text{U}$ differs, such as the Oklo reactor, have also been identified. (c) The highest concentrations of ^{236}U in Nature are found in U ores, with $^{236}\text{U}/^{238}\text{U} \sim 10^{-10}$ being typical. Natural samples of non-ore materials are expected to contain these or lower levels of ^{236}U .

When U of different isotope compositions is mixed, the resulting sample exhibits a ratio that reflects the isotope compositions of the different pure components, and the respective total number of U atoms originating from each source. As a hypothetical example of this, when varying amounts of an enriched U sample having $^{235}\text{U}/^{238}\text{U} = 0.05$ are mixed with naturally occurring U ($^{235}\text{U}/^{238}\text{U} = 0.0072527$), the resulting samples exhibit ratios of $0.0072527 < ^{235}\text{U}/^{238}\text{U} < 0.05$. In this situation, any detectable increase in $^{235}\text{U}/^{238}\text{U}$ above 0.0072527, outside of the ~ 1 -2 part per thousand relative deviation expected in Nature, is clear and incontrovertible evidence for the presence of some U in the sample derived from the enriched source. Analogous mixing behavior occurs for the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios. The detection of *any* measurable $^{236}\text{U}/^{238}\text{U}$ usually indicates the presence of enriched or depleted U, from a recycled U component (previously irradiated in a reactor), though small amounts of ^{236}U have apparently also been produced via nuclear weapons testing.

Owing to their value as tracers of mixing between U from different sources, the ratios $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ are all used herein as probes of mixing between naturally occurring U

and enriched U derived from the NFS facility. Any positive deviation in $^{235}\text{U}/^{238}\text{U}$ vs. Nature, and any detectable $^{236}\text{U}/^{238}\text{U}$ are interpreted in this manner, absent the existence of any other plausible sources of anthropogenic U.

Samples and Analyses. This interim report discusses U signature results from the following categories of samples: A) surface water from the Nolichucky River and its tributaries in the vicinity of the NFS facility; B) wastewater discharges and solid residue from the NPDES-permitted outfall to the Nolichucky River at Mile 94.6; and C) sediments from the Nolichucky River and its tributaries. Ongoing work will address other types of environmental samples.

Grab samples of water have been collected in 125 mL glass jars or 50 mL polypropylene test tubes. Grab samples of aquatic sediments have been collected using trowels, coring tubes, and plastic pipes. All sampling activities were conducted by the author, his undergraduate student (Kara M. Saaty), and collaborators from the local community.

Samples were prepared by appropriate laboratory procedures, as required, and were analyzed by the technique of inductively coupled plasma mass spectrometry (ICPMS). The facilities at Northern Arizona University were used in this study. The author has 22 years experience in the use of ICPMS in environmental samples and ratio measurements, and has 14 years experience on using ICPMS in studies of U in environmental media. Details on lab procedures will be discussed in future reports.

Results: Surface Water. Results are tabulated below for selected surface water samples collected at the indicated locations. Additional site descriptions will be discussed in future reports. The numbers in parentheses adjacent to the reported ratios are the uncertainties in the measured ratios (\pm one standard deviation); thus, 0.00012(1) should be read as 0.00012 ± 0.00001 .

It is evident that *all* of these samples, with the exception of ER-19, exhibit $^{235}\text{U}/^{238}\text{U}$ ratios exceeding the naturally occurring value of 0.0072527. It is beyond any reasonable doubt that the water in the Old Nolichucky River channel (adjacent to the Erwin Linear Trail) and North Indian Creek contain contributions from “enriched” U, as these samples exhibit $^{235}\text{U}/^{238}\text{U} > 0.01$, a finding that could only be produced via mixing of naturally occurring and “enriched” U. The source of the enriched U is clearly the NFS facility. The enriched U-contaminated water is most likely entering the surface waters through multiple routes, including non-point source surface runoff, and subterranean discharge. One subterranean discharge point, referred to locally as Whaley Spring (ER-4), was located and specifically sampled; this water could be readily identified by its lower temperature vs. surface waters at the time of sampling. The samples exhibiting elevated $^{235}\text{U}/^{238}\text{U} > 0.01$ also exhibit detectable $^{236}\text{U}/^{238}\text{U}$ ratios.

The mixing between naturally occurring and enriched U is also observable in the Nolichucky River, though not at location ER-19 (indistinguishable from Nature). This category of samples includes those from Davy Crockett Lake (DC-11, DC-18, DC-20), the spillway below the Davy Crockett Dam (DC-21), and an additional location (TW-5) several km downstream of Davy Crockett Dam. Note that detectable ^{236}U is also present in some of these samples, though a statement that it is “not detectable” does not indicate absence of ^{236}U (it could not be measured

under the analytical conditions employed, though ^{236}U possibly could still be measured using other conditions). One location in the Nolichucky River (ER-32) also exhibits an enriched U signature. ***The only plausible interpretation for these findings is that the NFS facility is the source of the enriched U component.*** The NFS enriched U is most likely present in the downstream Nolichucky River samples through several entry routes, including the NPDES permitted outfall at River Mile 94.6, and the subterranean discharges. An enriched U signature is also evident in Greeneville tap water (Samples GVL-1w and GVL-7w), from a time series of tap water samples collected between August 26 and September 16, 2010). No evidence to date indicates any U concentrations exceeding 30 $\mu\text{g/L}$ (the drinking water standard set by US EPA) in any surface or tap water samples.

Sample Name	Location	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$
ER-2	Wooden bridge area, linear trail	0.00020(1)	0.01256(5)	0.000054(4)
ER-4	Whaley Spring - subterranean seep	0.00021(1)	0.01681(6)	0.000065(2)
ER-10	Old Nolichucky channel	0.00021(1)	0.01505(6)	0.000065(2)
ER-19	Nolichucky River, ~ Mile 94	0.00013(2)	0.00740(15)	Not detectable
ER-28	N. Indian Cr., downstream Martin Cr.	0.00021(1)	0.01329(5)	0.000048(4)
ER-32	Nolichucky River, ~ Mile 90	0.00011(1)	0.00854(13)	Not detectable
DC-11	Davy Crockett Lake, 8/11/2010	0.00012(1)	0.0087(1)	Not detectable
DC-18	Davy Crockett Lake, 9/17/2010	0.00009(1)	0.00821(4)	0.000014(1)
DC-20	Davy Crockett Lake, 9/17/2010	0.00012(1)	0.00762(1)	0.000011(1)
DC-21	DC Lake spillway, 9/17/2010	0.00012(1)	0.00858(11)	0.000017(4)
TW-5	Nolichucky River, ~ Mile 41	.000013(1)	0.000834(19)	Not detectable
GVL-1w	Greeneville tap water	0.00016(3)	0.00857(8)	Not detectable
GVL-7w	Greeneville tap water	0.00023(6)	0.00819(27)	Not detectable
Natural U signatures		~ 0.000055	0.0072527	< 10⁻⁹

Results: Aquatic Sediments. Results are tabulated below for selected aquatic samples collected at the indicated locations. Additional site descriptions will be discussed in future reports. The numbers in parentheses adjacent to the reported ratios are the uncertainties in the measured ratios (\pm one standard deviation); thus, 0.000077(5) should be read as 0.000077 ± 0.000005 .

In a manner similar to discussed above, most of these samples demonstrate, unequivocally and beyond any reasonable doubt, that there is enriched U present in the environment. The various ratios result from mixing between naturally occurring U and enriched U from the NFS facility. Evidence for the presence of enriched U (derived from NFS) has been observed as far downstream as Davy Crockett Lake, using a series of surface grab samples collected at different points within the lake (DC-1 through DC-16 below). The presence of U with a very high $^{235}\text{U}/^{238}\text{U}$ is observed in the Nolichucky River within the immediate vicinity of the NFS NPDES outfall at River Mile 94.6 (Samples ER-12 and ER-13), and in solid material scraped from within the end of the plastic outfall pipe itself (Sample NPDES). The Old Nolichucky River Channel, in the vicinity of the Erwin Linear Trail and close to the boundary of the NFS facility, contains sediments contaminated with enriched U from the NFS facility (Samples ER-3, ER-5, and ER-14). Sediment from North Indian Creek (ER-29) also has an enriched U signature. Notably,

however, sediments collected upstream of the NFS facility, in Martin Creek and in the Nolichucky River, exhibit U signatures that are not significantly different from Nature.

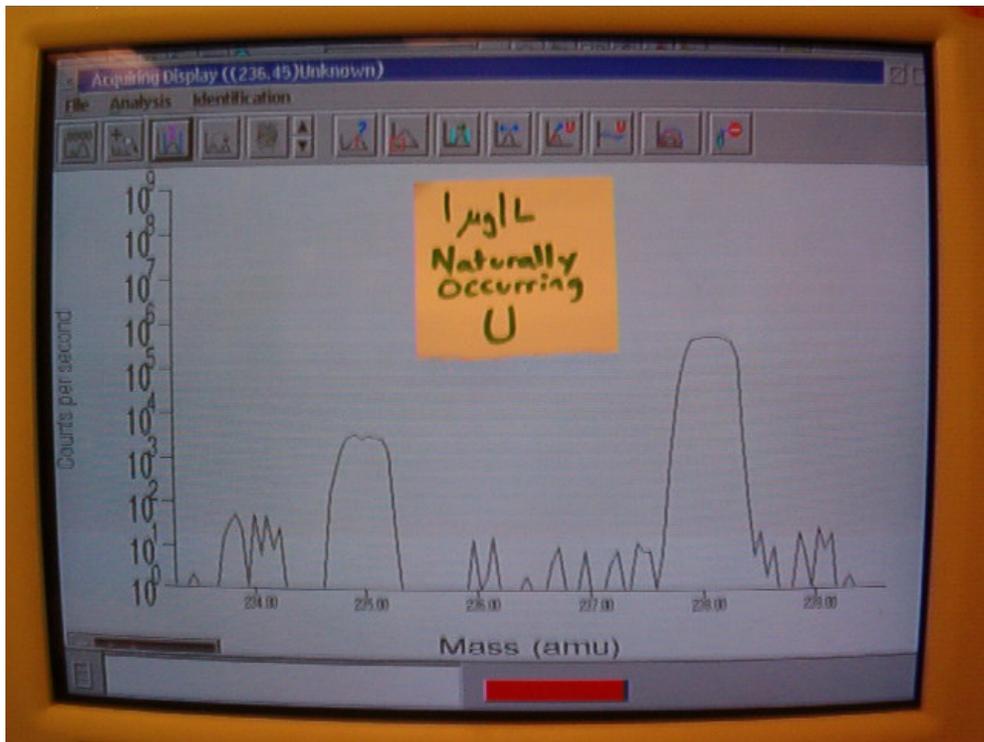
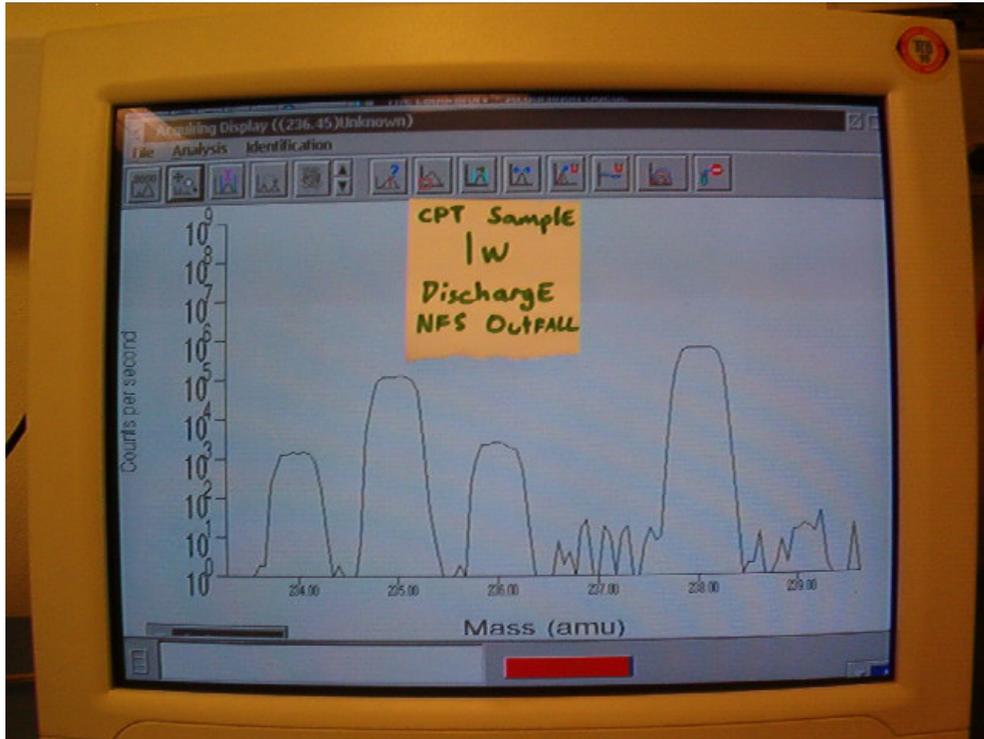
In many of the samples containing enriched U (as evidenced by $^{235}\text{U}/^{238}\text{U} > 0.0072527$), correlated changes in $^{234}\text{U}/^{238}\text{U}$ and detectable $^{236}\text{U}/^{238}\text{U}$ ratios are evident. The inability to measure $^{236}\text{U}/^{238}\text{U}$ (under the analytical conditions employed) *does not* imply that NFS-derived ^{236}U is absent in Davy Crockett Lake; the possible presence of NFS-derived ^{236}U therein is currently being addressed by additional analytical work in progress.

Sample Name	Location	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$
DC-1	Davy Crockett Lake sediment	0.000077(5)	0.00839(13)	Not detectable
DC-2	Davy Crockett Lake sediment	0.000075(1)	0.00919(4)	Not detectable
DC-4	Davy Crockett Lake sediment	0.000076(6)	0.00861(3)	Not detectable
DC-5	Davy Crockett Lake sediment	0.000077(3)	0.00841(2)	Not detectable
DC-8	Davy Crockett Lake sediment	0.000063(1)	0.00842(3)	Not detectable
DC-9	Davy Crockett Lake sediment	0.000076(3)	0.00880(5)	Not detectable
DC-10	Davy Crockett Lake sediment	0.000092(6)	0.00990(27)	Not detectable
DC-15	Davy Crockett Lake sediment	0.000070(2)	0.00797(1)	Not detectable
DC-16	Davy Crockett Lake sediment	0.000088(4)	0.00921(4)	Not detectable
ER-3	Sediment, Old Nolichucky River channel	0.000194(4)	0.0176(1)	0.000069(7)
ER-5	Sediment, Old Nolichucky River channel	0.000122(8)	0.0136(1)	0.000024(3)
ER-12	Bank sediment, near NPDES outfall	0.000319(5)	0.0255(1)	0.000094(7)
ER-13	Bank sediment, near NPDES outfall	0.000335(2)	0.0273(2)	0.000981(2)
ER-14	Sediment, Old Nolichucky River channel	0.000976(31)	0.092(4)	0.000228(10)
ER-29	Sediment, Indian Creek	0.000134(4)	0.0115(1)	0.000026(1)
NPDES	Sediment from inside NPDES outfall	0.00373(4)	0.2742(2)	0.00684(31)
ER-38	Martin Creek sediment, upstream	0.000067(2)	0.00716(10)	Not detectable
Noli-Up	Nolichucky River sediment, upstream	0.000057(2)	0.00710(6)	Not detectable
Natural U signatures		~ 0.000055	0.0072527	< 10-9

Results: NPDES Outfall. Water from the NPDES outfall was collected at several points in time, and all of these samples exhibit U with very high $^{235}\text{U}/^{238}\text{U} \gg 0.0072527$. As an example, water collected on July 13, 2010 exhibited $^{235}\text{U}/^{238}\text{U}$ of 0.60 and grossly elevated $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios as well. These results indicate that the waters being discharged from the outfall are in clear violation of NPDES Permit No. TN0002038, which specifically regulates and permits releases of “Uranium, Natural, Total”. The U being discharged from this outfall is not naturally occurring U as is required by the Permit. The sediment obtained from within the discharge pipe itself (labeled “NPDES” in the tabulated sediment results) and from the Nolichucky River near the outfall (ER-12, ER-13) demonstrate cumulative releases of similar material in the past, though the timeframe is undefined.

The contrast between U from the NPDES outfall (water sample of May 28, 2010) and naturally occurring U is immediately obvious in the mass spectra depicted below. These plots show (on a logarithmic vertical scale) the relative numbers of atoms of each mass. Note that the naturally occurring U has no detectable ^{236}U , and relative amounts of ^{234}U and ^{235}U vs. ^{238}U are congruent

with the natural signatures. In contrast, the signatures for the NPDES outfall are vastly different and clearly underscore the presence of enriched U.



Summary. The results discussed herein clearly indicate the presence of enriched uranium, originating from the NFS, in environmental media. The NFS-derived U is present in water and sediments relatively far downstream at Davy Crockett Lake and even past the Davy Crockett Dam. It has not been possible to accurately estimate the total quantities of enriched U present in Davy Crockett Lake, though it is considered important to address this, using an appropriate series of piston cores. The results demonstrate that U-contaminated water containing enriched U is being discharged in apparent violation of NPDES Permit No. TN0002038. The results also demonstrate the entry of groundwater discharges of NFS-derived enriched U into the surface waters, and point to serious questions about the scope/extent of groundwater contamination near the NFS facility.

This work is ongoing and additional results will be presented as interim reports and a final report in the future.

Submitted by:

A handwritten signature in black ink, appearing to read "Michael E. Ketterer", with a stylized flourish at the end.

Michael E. Ketterer, PhD

Disclosure: This work has been conducted as a scientific research and community service project by Northern Arizona University. Neither NAU, nor the principal investigator, have received any external funds to conduct this work (other than reimbursement of airfare for a sampling trip). NAU undergraduate students Kara Saaty and Alixandria Ruechel contributed to the analytical results reported herein.