ABSTRACT

APPLICATION OF URANIUM ISOTOPES AS A TEMPORAL AND SPATIAL TRACER OF NUCLEAR CONTAMINATION IN THE ENVIRONMENT

by Rebecca Tortorello

The Fernald Feed Materials Production Center (FFMPC) was established in 1951 to process natural uranium ore and recycled recoverable products. This study tests the utility of sediment cores as a proxy for the degree and timing of anthropogenic uranium contamination, using the FFMPC as a test case. An 80 cm long sediment core was extracted from an impoundment located approximately 6.7 km southwest of the FFMPC. The lack of measurable $^{137}$Cs in the deepest sample as well as a natural $^{235}\text{U}/^{238}\text{U}$ signature and no measurable $^{236}\text{U}$, are consistent with pre-FFMPC activity. The timing of elevated U concentrations, non-natural $^{235}\text{U}/^{238}\text{U}$ (0.00645 to 0.00748), and elevated $^{236}\text{U}$ ($^{236}\text{U}/^{238}\text{U} = 2.1 \times 10^{-7}$ to $3.6 \times 10^{-5}$) found in the sediment core coincide with the two largest known U dust releases from the FFMPC. Three local lichen samples were also analyzed, and displayed either EU or DU signatures coupled with elevated $^{236}\text{U}$, recording airborne U contamination.
APPLICATION OF URANIUM ISOTOPES AS A TEMPORAL AND SPATIAL TRACER OF NUCLEAR CONTAMINATION IN THE ENVIRONMENT

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1. Introduction

The improper handling of radioactive waste at industrial or nuclear facilities can introduce non-natural uranium into the environment via the air or groundwater, leading to anthropogenic increases in U concentrations (Sansone et al. 2001; Lloyd et al. 2009). Spatial and temporal variations in the U concentrations in the environment have been studied using sediment cores (Arnason and Fletcher 2003), lichen (Beckett et al. 1982; Jeran et al. 1995; Golubev et al. 2005) and tree rings (Bellis et al. 2001; Bellis and McLeod 2001; Rosamilia et al. 2004). In these studies, samples collected in proximity to industrial or nuclear sites were found to have higher U concentrations than samples collected in areas more distal to the potential sources of anthropogenic influence. However, elevated U concentrations are not necessarily indicative of nuclear contamination. Uranium is relatively mobile under oxidizing conditions, but can be scavenged and concentrated by natural processes in reducing environments (Fleischer, 2008). Therefore, in order to positively attribute elevated U concentrations in the environment to nuclear pollution, it is critical to measure the isotopic signature of the U.

$^{235}$U/$^{238}$U ratios are often used as an indicator of U contamination because the isotopic signature of U products generated by the nuclear industry can vary significantly from the natural ratio ($0.00725\pm0.00001$; Richter et al., 1999), and can be enriched or depleted in $^{235}$U (EU and DU, respectively). In addition, recent advances in mass spectrometry have made it possible to determine isotopic ratios more precisely, including the minor isotopes of U. Recently, $^{236}$U/$^{238}$U ratios have been investigated as a potential tracer of nuclear contamination. Together with $^{235}$U/$^{238}$U, $^{236}$U/$^{238}$U ratios have been employed to investigate U contamination in soils (Hotchkis et al. 2000; Lloyd et al. 2009), tree bark (Ma et al., 2000; Widom and Kuentz 2010), and lichen (Di Lella et al., 2003; Golubev et al. 2005). These studies have suggested that $^{236}$U/$^{238}$U is a far more sensitive tracer of anthropogenic U contamination than $^{235}$U/$^{238}$U (Hotchkis et al., 2000; Boulyga et al., 2002; Widom and Kuentz, 2010).

In this study, lichen samples and a sediment core were collected in the vicinity of the Fernald Feed Materials Production Center (FFMPC) located in southwestern Ohio. Concentrations of uranium and thorium, as well as both major and minor U isotopes were analyzed in order to examine spatial and temporal variations of potential environmental U contamination, and the isotopic profile of the sediment core was compared with the historical record of events associated with the FFMPC. This study serves as a test case to examine the sensitivity of minor U isotopes as tracers of anthropogenic contamination, and to determine the potential use of sediment cores and lichens as an archive for recording temporal and spatial patterns of environmental contamination.

2. Background

2.1 Uranium isotope systematics

The major isotopes of uranium are $^{238}$U and $^{235}$U, which together comprise 99.995% of natural U; the minor isotope $^{234}$U (0.005%) comprises the remainder (Richter et al. 1999). The $^{235}$U/$^{238}$U ratio is essentially constant in nature ($0.00725\pm0.00001$; Richter et al., 1999), but processing of U associated with the nuclear industry can result in materials that have a relative excess or deficit of $^{235}$U. Enriched U (EU) products contain excess $^{235}$U relative to the natural abundance, and are classified as highly-enriched U (HEU) and low-enriched U (LEU) based on the degree of $^{235}$U enrichment. HEU has $^{235}$U/$^{238}$U $>$0.2, and weapons-grade materials can reach $^{235}$U/$^{238}$U ratios as high as 0.8. LEU is characterized by $^{235}$U/$^{238}$U $\leq$0.2, but higher than natural (Forsberg et al., 1998; FEMP-20900-RP-0002, 1998). Depleted U (DU) materials have a deficit
of $^{235}\text{U}$, hence low $^{235}\text{U}/^{238}\text{U}$ ratios relative to natural U (FEMP-20900-RP-0002, 1998), with $^{235}\text{U}/^{238}\text{U}$ as low as 0.002 to 0.004 (Rosamilla et al. 2004).

Uranium-236 is created when a neutron is captured by a $^{235}\text{U}$ atom. $^{236}\text{U}$ can be produced naturally in minute quantities by neutron capture on $^{235}\text{U}$ during spontaneous fission (Sakaguchi et al., 2009), or by cosmic radiation (Hotchkis et al., 2000). This results in an average expected natural $^{236}\text{U}/^{238}\text{U}$ ratio of approximately $10^{-13}$ (Sakaguchi et al., 2009), but these extremely low ratios are generally below detection limits by conventional analytical methods including thermal ionization mass spectrometry (Richter et al. 1999). A much more significant source of $^{236}\text{U}$ is that produced by the neutron flux in nuclear reactors. Approximately 82% of the $^{236}\text{U}$ produced in nuclear reactors undergoes immediate fission, but the remaining 18% is relatively long-lived ($t_{1/2} = 23.4 \text{ Ma}$) and decays by $\alpha$-decay (Firestone et al., 1999). Any significant measured $^{236}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios $>10^{-10}$ in environmental samples can therefore be attributed unequivocally to an anthropogenic source (Boulyga et al., 2006; Widom and Kuentz, 2010).

Uranium-234 abundances are also affected by enrichment and depletion of U, and $^{234}\text{U}/^{238}\text{U}$ ratios could potentially also serve as a tracer of environmental U contamination. However, $^{234}\text{U}/^{238}\text{U}$ varies significantly in natural systems due to the “hot atom effect”, which results in preferential leaching of $^{234}\text{U}$ relative to $^{238}\text{U}$ from U-bearing minerals during water-rock interactions (Fleischer 2008). Uranium can be incorporated into the structure of minerals during crystallization, but decay of $^{238}\text{U}$ to $^{234}\text{U}$ (via $\alpha$- and two $\beta$-decays) and the associated $\alpha$-recoil, results in damage to the crystal structure. In general, the daughter $^{234}\text{U}$ is easier to leach from these damaged lattice regions relative to $^{238}\text{U}$, which resides in undisturbed crystal lattice sites (Kigoshi 1971; Fleischer 2008). $^{234}\text{U}/^{238}\text{U}$ activity ratios in natural waters are generally greater than 1.0, reflecting an excess of daughter products due to these processes (Osmond and Cowart, 1976). $^{234}\text{U}/^{238}\text{U}$ activity ratios of uncontaminated sediments can exhibit either a daughter excess or daughter depletion, and have been found to range from 0.5 to 3.3 globally (Szabo et al., 1969). Although sediment $^{234}\text{U}/^{238}\text{U}$ ratios vary significantly on a global scale, $^{234}\text{U}/^{238}\text{U}$ may be substantially less variable in samples from a localized area in which sediment derives from a consistent source (Widom and Kuentz, 2010). In such cases, it is possible that variations in $^{234}\text{U}/^{238}\text{U}$ resulting from environmental contamination may be discernable and useful as an additional contaminant tracer.

2.2 History of the Fernald Feed Materials Production Center (FFMPC)

The FFMPC was a 1,050-acre facility located near Ross, OH and approximately 20 miles from downtown Cincinnati (figure 1). The site was established to process high purity U products from natural U ore and recycled recoverable residues, including EU and DU. Construction of the facility began in May of 1951 and by October 1951, the FFMPC began operations. The site operated from 1951 to 1989, producing over 227 million kilograms of U metal products (FEMP 20900-RP-0001 rev. 0, 1998).

At the FFMPC, U ores and recycled materials were chemically and physically purified and converted to U metal, and often molded into the desired product (FEMP-20900-RP-0002, 1998). The majority of the materials produced at the FFMPC from 1952 to 1971 were shipped to two main facilities: the Hanford site in Washington and the Savannah River site in South Carolina. Both facilities required DU, natural U, and EU products. Production for the Hanford site peaked in 1960, and approximately 50% of the total materials being shipped from the FFMPC were EU products. However, with the closure of Hanford in 1971, total production at the FFMPC decreased significantly (FEMP 20900-RP-0001 rev. 0, 1998).
In 1981, three off-site wells were found to be contaminated with U, suggesting that U had been released into the local groundwater. In 1984, the United States Department of Energy (DOE) reported that nearly 150 kg of uranium oxide was accidentally released into the surrounding environment from one of the facility’s plants. Low production coupled with environmental concerns caused the facility to cease production in 1989. The site was formally closed in June of 1991, and local remediation efforts were initiated (Ohio EPA, 2009).

In 1990, the DOE reevaluated the amount of U that was potentially released to the environment during the operation of the FFMPC. The DOE estimated that the majority of the U was lost during the early years of operation (figure 2). According to DOE records, the largest estimated release of U occurred around 1954 and the second largest around 1963 (Ohio EPA, 2009). In total, the FFMPC is believed to have accidently released 90,000 to 450,000 kilograms of U into the environment between 1951-1985 (Makhijani, 2000).

3. Materials and Methods

3.1 Sediment sample collection and preparation

A sediment core (figure 1) was collected from the lower Timberlake impoundment located in the Miami Whitewater Forest, approximately 6.7 km southwest of the FFMPC site, using a WildCo Gravity Corer. The artificial impoundment was constructed ca. 1945 (Renwick et al, 2005), and thus was in existence throughout the operation of the FFMPC. The extracted core was 80 cm in length, representing 78% of total post-impoundment sediment thickness.

The sediment core was grey-brown in color and fine-grained (clay/mud), with an apparently uniform grain size throughout the core and no visible signs of bioturbation. The core (designated TIM-02) was sectioned into 2 cm intervals, resulting in forty samples representing the entire length of the sediment core. Samples were numbered from the base to the top, such that the lowermost sediment is sample TIM-02-01, and the surface sediment sample TIM-02-40 (samples referred to henceforth only by stratigraphic number, 01 to 40). The edges of the core were removed using a plastic spatula to eliminate any material that may have been smeared during the coring process. The topmost three samples (0 to 6 cm depth) of the core were composed of unconsolidated material and the edges could not be removed. However, contamination from drag along the tube will be minimal for samples at the stratigraphic surface of the core, since the core was extracted from the sampling tube top-first. Sectioned samples were dried in an oven at 80°C, and then crushed manually with a hammer while enclosed in paper.

Approximately 2 to 12 g of each sample was ashed in a porcelain crucible in a furnace at 600°C for 2 to 4 hours. After ashing, the sediment samples remained unconsolidated, but turned a rusty-orange color. Approximately 1g of the ashed sample was leached in 8N HNO₃ overnight on a hot plate at 80°C in sealed 15 mL Savillex PFA Teflon beakers. The samples were centrifuged and the supernatant was drawn from the sediment. The supernatants were stored in Teflon vials and placed on a hotplate at 80°C to dry down. Once evaporated, 5 mL of 1% HNO₃ was added to the sample residue initially. However, fine, yellow particulates remained in the majority of the vials, possibly due to supersaturation of the solution. Samples were therefore re-dried and taken up in 1 mL of 16N HNO₃. The samples were then diluted sequentially from 16N to 8N, 4N, and 2N HNO₃ with 1-hour intervals on the hotplate in sealed vials. Eight of the samples still contained particulates, and these sample solutions were filtered.
3.2. Elemental analysis by ICP-MS

The solutions from the leached sediment samples were then gently evaporated and re-dissolved in 10 mL of 1% HNO₃. The solutions were divided into 5 mL aliquots for ICP-MS analysis, while the remaining 5 mL of each sample solution were stored in tightly sealed 15 mL Savillex PFA Teflon beakers for potential isotopic analysis. All solutions were then analyzed on Miami University on a Varian quadrupole ICP-MS for Th and U concentrations. Samples were standardized using a calibration curve generated by dilutions of an in-house multi-element solution standard.

3.3 Gamma counting

Approximately 8 to 10g of sediment from fifteen samples spanning the length of the core were chosen for gamma ray spectrometry in order to measure $^{137}\text{Cs}$ activities for sediment age determination. Twelve of the selected samples were analyzed by an EG&G Ortec N-type HPGe detector system at Case Western Reserve University, and three samples were analyzed using a low-background (10-cm Pb shield) Canberra reverse-electrode intrinsic Ge detector system (34% relative efficiency at 1.33 MeV) with a DSA-2000 digital spectrum analyzer interface with a PC Genie-2000 MCA software package at the University of Illinois at Chicago. The detection limits for $^{137}\text{Cs}$ activities (measured at 661.62 keV) by the two instruments are approximately 0.001 Bq g⁻¹ and 0.002 Bq g⁻¹, respectively. A detailed synopsis of the methods used in this study for samples analyzed at Case Western is reported in Bonniwell et al. 1999, although samples in this study were tightly sealed in individual specimen cups using electrical tape instead of polyamine epoxy resin.

3.4 Lichen sample collection and preparation

Three crustose lichen samples were collected approximately 3.2 km southwest, 2.5 km southeast, and 1.1 km south of the FFMPC site (figure 1). The lichens were approximately 7 cm, 11 cm, and 4.5 cm in diameter, respectively. Samples were ashed at 600°C in porcelain crucibles for 2 hours, resulting in 70 to 95% mass loss. Samples were then leached in 8N HNO₃ on a hotplate overnight, centrifuged and the supernatant withdrawn.

3.5 Uranium purification

Nineteen sediment samples and all three lichen samples were selected for U isotopic analysis by thermal ionization mass spectrometry (TIMS). All samples selected for U isotopic analysis were evaporated and re-dissolved in 5 mL of 8N HNO₃. Samples were passed through anion exchange columns using BioRad AG1-X8 anion exchange resin, which has a strong selectivity for U in the presence of 8N HNO₃. After rinsing with additional 8N HNO₃ to remove other metals, the U was eluted from the resin using H₂O. Samples were evaporated, re-dissolved in 1 mL of 8N HNO₃ and passed again through the columns to ensure sufficient purity of the U. The purified U samples were dried down, and then dissolved and dried alternately with a drop of concentrated HNO₃ followed by a mixture of HNO₃ and HCl and then a drop of concentrated HNO₃ again, in order to break down any potential organics.

Total processing blanks for U by isotope dilution were performed along with the sediment and lichen samples during the dissolution steps and chemical separation by ion exchange chromatography.
3.6 Uranium isotopic analysis

Purified samples were loaded in 1N HNO$_3$ onto one filament of a double Re filament assembly for analysis by TIMS. Sediment and lichen leachates were analyzed using a Finnigan Triton multi-collector TIMS equipped with a Retarding Potential Quadrupole (RPQ) energy filter. Due to the extremely low abundances of the minor isotopes ($^{234}$U and $^{236}$U), low energy tails from $^{238}$U and $^{235}$U can interfere with the measurements of the minor isotopes. The RPQ sufficiently improves the abundance sensitivity to eliminate any contribution to $^{234}$U and $^{236}$U from tailing of $^{235}$U or $^{238}$U, thus ensuring that the minor isotopes can be measured accurately (Richter et al. 1999). Measurement accuracy and external reproducibility were determined by replicate analyses of the NBS U005a standard. The 2 standard deviation (2SD) external reproducibilities based on repeat measurements (n=10) of the NBS U005a standard for $^{234}$U/$^{238}$U, $^{235}$U/$^{238}$U, and $^{236}$U/$^{238}$U are $\pm$0.00004 (0.64% relative), $\pm$0.00002 (0.44% relative), and $\pm$0.00002 (0.67% relative), respectively. Average measured values of $^{234}$U/$^{238}$U, $^{235}$U/$^{238}$U, and $^{236}$U/$^{238}$U were 0.00671, 0.00512 and 0.00235, respectively, all within 2SD of the certified values (table 1). Replicate analyses of three sediment samples indicate 2SD external reproducibility slightly higher than those determined by replicate analysis of the NBS005a standard, up to 0.76% and 0.6% for $^{234}$U/$^{238}$U and $^{235}$U/$^{238}$U, respectively. Reported errors for the measured $^{235}$U/$^{238}$U ratios in the sediment and lichen samples are therefore based on the 2SD reproducibility of the replicate sediment samples, resulting in absolute errors of $\pm$0.00004. Reproducibility of $^{236}$U/$^{238}$U was dependent on the measured $^{236}$U/$^{238}$U ratio, and 2SD relative errors ranged from $\pm$1.42% for $^{236}$U/$^{238}$U ratios of $10^{-5}$ to $\pm$10% for $^{236}$U/$^{238}$U ratios of $10^{-6}$. The total procedural blank for U was 22.6 pg, which represents an insignificant contribution to the sample U.

4. Results

4.1 Cesium-137 activities in the sediment core

Measured $^{137}$Cs activities in the sediment core samples range from 0.0012 to 0.466 Bq g$^{-1}$ (figure 3). The $^{137}$Cs activity of sample 01 is below the detection limit. Sample 02, the sample immediately above sample 01, contains measurable $^{137}$Cs with an activity of 0.001±0.001 Bq g$^{-1}$. From the base upwards, the samples show a general increase in $^{137}$Cs activity up to the peak $^{137}$Cs activity of 0.047±0.002 Bq g$^{-1}$, which occurs in sample 08. The peak $^{137}$Cs activity is well defined, with the samples surrounding the peak, samples 09 and 07, exhibiting $^{137}$Cs activities significantly lower than the peak value (0.022 and 0.017 Bq g$^{-1}$, respectively). From sample 08 upwards in the core, $^{137}$Cs activities show a continuous decrease. Sample 40, representing the stratigraphic surface at the time of collection in June 2011, has a $^{137}$Cs activity of 0.0044±0.0009 Bq g$^{-1}$.

4.2 Elemental concentrations in the sediment core

Uranium and thorium concentrations in the sediment core range from 0.4 to 1.1 ppm and 2.7 to 6.4 ppm, respectively, and Th/U ratios range from 4.4 to 9.1 (table 1). Uranium and thorium concentrations are generally well correlated (figure 4), and most samples from the sediment core produce a well-defined linear trend ($r^2=0.87$). However, there is a distinct deviation from the trend in seven consecutive core samples (samples 03 to 09). The anomalous samples have an average Th/U ratio of 4.8±1.3 (2SD), while the remaining samples average 7.7±1.4 (2SD). Uranium concentrations exhibit a relative increase near the base of the core, with the highest U concentration found in sample 04, representing a depth of 74 cm (figure 5). The
samples with anomalous Th/U comprise the U concentration peak near the base of the core. These samples have thus been separately demarcated in figure 4 and subsequent figures.

4.3 Uranium isotopic signatures in the sediment core and lichen samples

Sediment samples exhibit $^{235}\text{U}/^{238}\text{U}$ ratios ranging from 0.00645 to 0.00748 (figure 6), which deviate significantly from the natural $^{235}\text{U}/^{238}\text{U}$ ratio of 0.00725±0.00001 (Richter et al., 1999), and indicate the existence of both DU and EU. The $^{235}\text{U}/^{238}\text{U}$ ratios in samples 01 and 02 are within error of the natural ratio. However, six of the seven samples immediately above the basal samples (samples 03 to 09; those with elevated concentrations of U relative to Th) have $^{235}\text{U}/^{238}\text{U}$ ratios that deviate from natural. Samples 03 to 06 have depleted U signatures with $^{235}\text{U}/^{238}\text{U}$ ratios ranging from 0.00645 to 0.00712. In contrast, samples 08 and 09 have enriched U signatures, with $^{235}\text{U}/^{238}\text{U}$ ratios of 0.00748 and 0.00742, respectively. Sample 07 has a $^{235}\text{U}/^{238}\text{U}$ ratio of 0.00722, within error of the natural $^{235}\text{U}/^{238}\text{U}$ ratio. Sample 11 did not show elevated U concentrations, but had a slight DU signature of 0.00718.

With the exception of sample 01, all analyzed samples have detectable $^{236}\text{U}$ (figure 7). Measured $^{234}\text{U}/^{238}\text{U}$ ratios range from 7.98x10$^{-7}$ to 3.57x10$^{-5}$. The highest $^{236}\text{U}/^{238}\text{U}$ ratio was found in sample 09, although the group of samples with elevated U concentrations and non-natural $^{235}\text{U}/^{238}\text{U}$ ratios range in $^{236}\text{U}/^{238}\text{U}$ from 1.79x10$^{-5}$ to 3.57x10$^{-5}$ overall. Aside from sample 01, samples that have $^{235}\text{U}/^{238}\text{U}$ ratios within error of the natural value still display elevated $^{236}\text{U}/^{238}\text{U}$ ranging from 7.98x10$^{-7}$ to 1.86x10$^{-5}$.

Sediment samples display $^{234}\text{U}/^{238}\text{U}$ activity ratios (designated from here forward as $^{234}\text{U}/^{238}\text{U}$) that range from 0.92 to 1.22. However, the samples with natural $^{235}\text{U}/^{238}\text{U}$ exhibit a narrower range in $^{234}\text{U}/^{238}\text{U}$ from 1.09 to 1.22, suggesting that this is the natural background signature for the local environment of the impoundment (figure 8). Samples with $^{235}\text{U}/^{238}\text{U}$ significantly below the natural ratio (i.e. with DU signatures) range in $^{234}\text{U}/^{238}\text{U}$ from 0.922 to 0.926, all lower than the inferred range for the background $^{234}\text{U}/^{238}\text{U}$ signature. The samples with low $^{234}\text{U}/^{238}\text{U}$ relative to background values and DU $^{235}\text{U}/^{238}\text{U}$ signatures comprise the samples with the highest U concentrations (1.33 to 0.836 ppm) and anomalously low Th/U.

Measured $^{235}\text{U}/^{238}\text{U}$ ratios of all three lichen samples are significantly different from the natural $^{235}\text{U}/^{238}\text{U}$ ratio of 0.00725±0.00001 (Richter et al., 1999), and include both EU and DU signatures ranging from 0.00680 to 0.00736 (figure 9a), which is within the $^{235}\text{U}/^{238}\text{U}$ range found in the sediment core. Similarly, all three samples have measurable $^{236}\text{U}$ with $^{236}\text{U}/^{238}\text{U}$ ratios ranging from 5.47x10$^{-6}$ to 8.82x10$^{-5}$ (figure 9b), also within the range found in the sediment core. $^{236}\text{U}/^{238}\text{U}$ ratios decrease systematically from southwest of the FFMPC site towards the southeast, with the highest $^{236}\text{U}/^{238}\text{U}$ corresponding to the sample that deviates the most from natural $^{235}\text{U}/^{238}\text{U}$. The $^{234}\text{U}/^{238}\text{U}$ in the lichen samples range from 0.896 to 1.008, falling outside the estimated range of background values for the region (figure 9c), and exhibiting a strong positive correlation with $^{235}\text{U}/^{238}\text{U}$ ($r^2$=1.0; figure 9d).

5. Discussion

5.1 Sediment core ages

Age constraints for the core samples were obtained by relating measured $^{137}\text{Cs}$ activities to the known timing of atmospheric nuclear testing. The most significant peak in $^{137}\text{Cs}$ activity can be correlated to the culmination of atmospheric nuclear weapons testing in 1963 (Perkins and Thomas, 1980; Wu et al., 2010). Furthermore, samples containing $^{137}\text{Cs}$ activity below detection
limits can be attributed to pre-1953, before the initial global fallout of $^{137}$Cs from high-yield thermonuclear tests that occurred in November of 1952 (Perkins and Thomas, 1980).

The $^{137}$Cs activity of sample 01 was below detection limit, thus dating to pre-1953. Furthermore, sample 01 contained natural $^{235}$U/$^{238}$U and no measurable $^{236}$U, indicating that this sediment does not contain any significant component of non-natural U, consistent with an age prior to the initiation of U processing at FFMPC. These factors, coupled with the $^{137}$Cs age of pre-1953, strongly suggest that the base of the core pre-dates activity at the FFMPC site. In contrast, the measurable $^{137}$Cs in sample 02, immediately above sample 01, indicates that this sample dates to 1953 or younger. The non-natural $^{235}$U/$^{238}$U and elevated $^{236}$U/$^{238}$U in sample 02 indicates contamination at that level, further consistent with sample 02 post-dating the initiation of activity at the FFMPC. Sample 08 contains the highest $^{137}$Cs activity (0.047±2 Bq g$^{-1}$) and can thus be correlated to 1963 (Perkins and Thomas, 1980).

5.2 Sources and degree of uranium contamination in the sediment core

5.2.1 Sediment uranium concentrations and Th/U systematics

The well-defined correlation of U vs. Th concentrations ($r^2 = 0.87$; figure 4) for most of the sediment core samples suggests that the Th and U budgets are linked to one or more sources that have resulted in fairly constant relative background inputs. This trend is similar to a well-defined correlation of Th vs. U seen in surface soil collected from the Nagarjuna Dam near a proposed U mining site in Andhra Pradesh, India ($r^2 = 0.73$; Sartandel et al., 2009). Variation from the otherwise consistent Th/U ratio reflects increased U input relative to Th that can be recognized despite varying local Th and U concentrations. Th/U ratios measured in the sediment core range from 4.4 to 9.1, and the samples with anomalously elevated U concentration fall at the low end of this range with an average of 4.8±1.3 (2 SD) compared to 7.7±1.4 (2 SD) for the remaining samples. Although these Th/U ratios are higher than average upper continental crust (3.89; Rudnick and Gao, 2003), they are similar to the range of average Th/U ratios for shale and pelagic sediment (3.4 – 7.6; Taylor and McLennan, 1985) and all are within the wide range of natural Th/U ratios found in various types of sedimentary rocks (0.02 to 21; Adams and Weaver, 1958). The lower Th/U ratios and elevated U concentrations in the anomalous sample group could result from changing environmental conditions, such as more reducing conditions that concentrate U relative to Th in the sediment, or an additional source of U to the sediment, either natural or anthropogenic.

Uranium concentrations in the sediment core range from 0.4 to 1.1 ppm (table 1). Sample 01, which predates FFMPC activity, has a concentration of 0.7 ppm, suggesting that background U concentrations are at least this high. Furthermore, samples that fall within the well-defined Th-U trend (figure 4) reach concentrations of 0.8 ppm U, which may also represent background sediment U concentrations. In contrast, the group of anomalous samples in Th-U space (figure 4) range from 0.8 – 1.1 ppm U, reflecting an additional input of U to these sediment samples, either natural or anthropogenic. Nevertheless, the U concentrations in the sediment core are all below the average upper crustal concentration of 2.7 ppm (Rudnick and Gao, 2003), suggesting that there is no significant U contamination above typical crustal levels at the Timberlake impoundment. For comparison, soil collected during the Lee and Marsh study (1992) onsite near FFMPC Plant 2/3 contained U concentrations as high as 200 ppm, significantly higher than concentrations recorded in the sediment core (this study) and offsite soil (0.01 and 0.40 ppm collected 1.5 and 1 miles west of the FFMPC, respectively; Lee and Marsh, 1992). The relatively low U concentrations in the sediment cores and offsite soil samples compared to the onsite soil
suggest that most of the U released from the FFMPC was not transported far offsite.

Relatively low U concentrations (<1 ppm) found in tree bark >5 km northwest of the FFMPC site, and higher concentrations (1-6.5 ppm) in more proximal tree bark (Widom and Kuentz, 2010) are consistent with the interpretation that airborne transport of U from the FFMPC site was relatively localized. Similar dispersal distances have been reported near the Agnew Lake mine-uranium recovery plant complex and Quirke uranium mill in Canada (Beckett et al., 1982) as well as near a uranium processing plant in Colonie, NY (Lloyd et al., 2009). Uranium concentrations in lichen and moss samples collected in transects from the Agnew Lake mine-uranium recovery plant complex and the Quirke uranium mill reached as high as 8 to 12 ppm, respectively, but decreased to 2 ppm or less at sites >3 km from the site. Uranium concentrations in surface soils collected at the Colonie processing plant were found to be >12 ppm, but decreased to estimated background concentrations (0.7 to 2.2 ppm) approximately 4 km from the site. Sediment >5 km from FFMPC, including that in the sediment core analyzed in this study, is therefore likely to have experienced significantly lower exposure to contaminant U than sediment located <5 km from the site.

5.2.2 $^{235}$U/$^{238}$U systematics and mixing models

The samples that display anomalously elevated U relative to Th concentrations all have non-natural U signatures including DU or EU $^{235}$U/$^{238}$U signatures and/or elevated $^{236}$U/$^{238}$U, providing unequivocal evidence for an anthropogenic source of U in these samples. Anomalous Th/U ratios may therefore serve as an indicator of the possible presence of anthropogenic U in some cases. Furthermore, the $^{137}$Cs data for these anomalous samples provide evidence that the non-natural U signatures were imparted to the sediment during the early years of the FFMPC operation. The lack of measurable $^{137}$Cs in sample 01, and the peak $^{137}$Cs activity in sample 08 (representing pre-1953 and 1963, respectively), constrain the age of the anomalous samples to approximately 1954 to 1964. This time range coincides with the DOE’s estimates (1955 and 1961) for the two largest releases of U from the FFMPC (Killough et al., 1999). During this time span, a shift from DU signatures (0.00645 to 0.00715; Samples 03 to 06) to EU signatures (0.00748 to 0.00732; Samples 08 to 09) is recorded in the sediment core. The first EU signature is recorded in sample 08, which is correlated to 1963 based on the $^{137}$Cs peak. This is generally consistent with the timing of the peak production for the Hanford site in 1960, which was primarily EU materials (FEMP 20900-RP-0001 rev. 0, 1998). No known previous studies have documented such a shift in $^{235}$U/$^{238}$U from a single locality. This documented change over time from DU to EU signatures in the sediment core, which corresponds to historically documented activities at a uranium processing facility, demonstrates the strength of $^{235}$U/$^{238}$U in sediment as a proxy for tracing the nature and source of U contamination from the nuclear industry.

Relative contributions of U from natural and anthropogenic sources can be calculated using a two-component mixing model for mixtures of natural U with end-member EU or DU compositions. The DOE has stated that the FFMPC never processed highly enriched materials or any products used for nuclear weapons or reactors (FEMP 20900-RP-0001 rev. 0, 1998); rather only LEU ($^{235}$U/$^{238}$U ≤ 0.2) material was processed at the FFMPC (FEMP-20900-RP-0002, 1998). An end-member value of $^{235}$U/$^{238}$U = 0.2 is therefore best representative of the most enriched material processed the FFMPC (Forsberg et al., 1998). DU, on the other hand, is estimated to reach $^{235}$U/$^{238}$U ratios as low as 0.002 in some nuclear products; therefore, this value best represents the $^{235}$U/$^{238}$U ratio for end-member DU that may have been processed at FFMPC (Magnoni, 2001). Using end-member isotopic compositions for the LEU and DU contaminants
ensures that the calculated contributions of anthropogenic U to the environmental samples are minimum estimates. Furthermore, because the FFMPC handled both EU and DU materials, the measured $^{235}\text{U}/^{238}\text{U}$ ratios in the environmental samples may be mixtures of DU and EU. In this case, the calculated contribution of anthropogenic U is also a minimum estimate of the anthropogenic input into the environment, and the actual contribution may be significantly higher.

The respective inputs of $^{235}\text{U}/^{238}\text{U}$ from each source are determined by the following equation:

$$R = R_A f_A + R_B (1-f_A)$$

where R is the measured $^{235}\text{U}/^{238}\text{U}$ in the sample, $R_{A,B}$ are the $^{235}\text{U}/^{238}\text{U}$ ratios of the respective mixing components, and $f_A$ is the fraction of U contributed by component A. Assuming component A represents end-member EU or DU, and component B represents the natural $^{235}\text{U}/^{238}\text{U}$ ratio of 0.00725, one can calculate the minimum amount of EU or DU that contributed to a sample that is a mixture of natural and anthropogenic U (Magnoni, 2001).

The range of $^{235}\text{U}/^{238}\text{U}$ ratios measured in the sediment core (0.00645 to 0.00748) indicates the existence of both DU and EU contamination from the nuclear industry (figure 6). Samples 03 to 06 and sample 11 have DU signatures ranging from 0.00645 to 0.00718. Assuming mixing between natural U and DU with a $^{235}\text{U}/^{238}\text{U} = 0.002$ (Magnoni, 2001), two-component mixing calculations suggest a minimum addition of 15.2 to 1.2% of DU, respectively. Sample 08 and 09 display EU signatures of 0.00748 and 0.00732, respectively. Mixing calculations, assuming EU with $^{235}\text{U}/^{238}\text{U} = 0.2$ (Forsberg et al., 1998), indicate a minimum addition of 0.12 to 0.09% of EU, respectively. However, if the contaminants are mixtures of DU and EU or have signatures less extreme than the modeled end-member DU and EU isotopic compositions, then a significantly higher fraction of the U in the sediment may be anthropogenic.

5.3 Minor isotopes as tracers of uranium contamination

5.3.1 $^{236}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios

The natural $^{235}\text{U}/^{238}\text{U}$ signatures found in the majority of the samples in the sediment core are consistent with no contribution of non-natural U from FFMPC. However, the presence of measurable $^{236}\text{U}$ and elevated $^{236}\text{U}/^{238}\text{U}$ in all samples except sample 01, despite natural $^{235}\text{U}/^{238}\text{U}$ signatures in many of these samples (samples 20 to 40), provides indisputable evidence for contamination from an anthropogenic source. Previous studies have found similar results. Soil and sediment samples collected near the Malvési COMURHEX uranium-plant in France exhibited natural $^{235}\text{U}/^{238}\text{U}$ signatures, but elevated $^{236}\text{U}/^{238}\text{U}$ ratios that ranged from 0.5 x $10^{-6}$ to 1.5 x $10^{-5}$ (Pourcelot et al., 2011). Similarly, soil samples collected from Belarus, northwest of the Chernobyl nuclear power plant, have natural $^{235}\text{U}/^{238}\text{U}$, but $^{236}\text{U}/^{238}\text{U}$ ratios on the order of $10^{-7}$ (Mironov et al., 2002). Collectively, our results as well as these studies demonstrate the sensitivity of $^{236}\text{U}$ as a tracer of anthropogenic sources in environmental samples that have either minor contamination or contamination from mixed DU and EU sources that result in apparently natural $^{235}\text{U}/^{238}\text{U}$.

5.3.2 $^{234}\text{U}/^{238}\text{U}$ activity ratios

The production of EU and DU will either enrich or deplete the U, respectively, in all of the isotopes that are light with respect to $^{238}\text{U}$; therefore, one would expect a correlation between
(\textsuperscript{234}U/\textsuperscript{238}U) and \textsuperscript{235}U/\textsuperscript{238}U in U products associated with the nuclear industry. This is complicated in environmental samples by the substantial natural variations in (\textsuperscript{234}U/\textsuperscript{238}U) that result from the “hot atom effect” described previously. The large natural variations in sediment (\textsuperscript{234}U/\textsuperscript{238}U) have been argued by some to preclude the use of (\textsuperscript{234}U/\textsuperscript{238}U) as a tracer of environmental U contamination from nuclear sources (e.g. Minteer et al., 2007; Fleisher et al., 2008), although if variation in background signatures is relatively limited and well constrained, this may not be prohibitive (Widom and Kuentz, 2010).

In this study, sediment samples with natural \textsuperscript{235}U/\textsuperscript{238}U range in (\textsuperscript{234}U/\textsuperscript{238}U) from 1.09 to 1.22, which may represent the local natural background range (figure 8). Samples that deviate significantly from natural \textsuperscript{235}U/\textsuperscript{238}U also deviate from this background range of (\textsuperscript{234}U/\textsuperscript{238}U), reaching (\textsuperscript{234}U/\textsuperscript{238}U) values as low as 0.92. When compared to \textsuperscript{235}U/\textsuperscript{238}U (figure 9), an apparent mixing trend can be observed between the samples with the strongest DU signatures and those with natural background signatures, consistent with the correlation of (\textsuperscript{234}U/\textsuperscript{238}U) and \textsuperscript{235}U/\textsuperscript{238}U in material altered by nuclear processing. This trend is also consistent with the DU mixing trend observed in isotopic signatures of tree bark collected near the FFMP, in which \textsuperscript{234}U/\textsuperscript{238}U values as low as 0.69 were observed, much lower than the inferred natural background ratio of \textasciitilde 1.14; Widom and Kuentz, 2010). Similarly, (\textsuperscript{234}U/\textsuperscript{238}U) in soils collected from the Dundrennan Firing Range in Dumfries and Galloway (SW Scotland), and the Eskmeals Firing Range in Cumbria (NW England) reached values as low as 0.24, substantially lower than the estimated local natural background ratios of 0.8 to 1.2 (Oliver et al., 2007). In addition, (\textsuperscript{234}U/\textsuperscript{238}U) and \textsuperscript{235}U/\textsuperscript{238}U signatures measured in pine needles collected at the Oak Ridge K-25 site exhibit a mixing trend between natural and EU signatures, with (\textsuperscript{234}U/\textsuperscript{238}U) ratios in the most EU-rich samples extending to values as high as 2.45 (Hembree et al., 1995).

Collectively, our results coupled with the results from these previous studies suggest that (\textsuperscript{234}U/\textsuperscript{238}U) can, in some cases, be used as an effective tracer of U contamination in environmental samples that have been impacted by EU or DU sources, or both. However, the large range in background (\textsuperscript{234}U/\textsuperscript{238}U) ratios in sediment is likely to make (\textsuperscript{234}U/\textsuperscript{238}U) a less sensitive tracer than \textsuperscript{235}U/\textsuperscript{238}U. Despite having significant EU or DU \textsuperscript{235}U/\textsuperscript{238}U signatures, three samples from this study were still in the range of background values for (\textsuperscript{234}U/\textsuperscript{238}U). In this case, (\textsuperscript{234}U/\textsuperscript{238}U) cannot distinguish the small anthropogenic contributions in these samples that were clearly exhibited in the respective EU or DU \textsuperscript{235}U/\textsuperscript{238}U signatures. These observations are consistent with the results from Magnoni et al (2001), which suggest that an addition of 20% end-member DU (\textsuperscript{235}U/\textsuperscript{238}U = 0.002) is needed to detect non-natural (\textsuperscript{234}U/\textsuperscript{238}U). A similar situation applies to EU materials, although the minimum addition needed to produce non-natural (\textsuperscript{234}U/\textsuperscript{238}U) will vary based on the EU end member. Ultimately, (\textsuperscript{234}U/\textsuperscript{238}U) can potentially be used as a tracer of anthropogenic U contamination in environmental samples, but typically it will be less sensitive than \textsuperscript{235}U/\textsuperscript{238}U and \textsuperscript{236}U/\textsuperscript{238}U.

5.4 Uranium contamination in lichen

Lichens act as passive bio-monitors of atmospheric pollution because they are long-living organisms that lack a root system. Thus, they mainly derive necessary nutrients from the air and do not incorporate significant amounts of metals from their substrate environment (Nash and Egan, 1988; Nash, 1996). Measured \textsuperscript{235}U/\textsuperscript{238}U signatures of all three lichen samples (0.00736, 0.00714, and 0.00680) deviate significantly from natural (figure 9). The range of \textsuperscript{235}U/\textsuperscript{238}U signatures found in the lichen samples are within the range of those in the TIM-02 sediment core (0.00645 to 0.00748) and overlap the range found in tree bark samples from the vicinity of
FFMPC (0.00725 to 0.0051; Widom and Kuentz, 2010). All three lichen samples have measurable $^{236}\text{U}/^{238}\text{U}$ ratios ranging from $8.82 \times 10^{-5}$ to $5.47 \times 10^{-6}$. The elevated $^{234}\text{U}/^{238}\text{U}$ ratios as well as the non-natural $^{235}\text{U}/^{238}\text{U}$ signatures in the lichen require an airborne contribution of anthropogenic U from the nuclear industry.

Fahselt et al. (1995) investigated the longevity of contaminant U in lichen from the Agnew Lake mine-uranium recovery plant complex and Quirke uranium mill in Canada by comparing U concentrations in lichen to those measured in lichen in the earlier Beckett et al. (1982) study from the same location. Fahselt et al. (1995) suggest that U can be present in fruticose lichens for several years; however, due to differing lichen U concentrations between the two studies, Fahselt et al. (1995) conclude that significant U loss from the thallus can occur in only a few years. However, it is possible that U retention in lichen may be species-dependent. The Fahselt et al. (1995) and Beckett et al. (1982) studies both analyzed fruticose lichen, which have large surface exposure area compared to the crustose lichen samples investigated in the present study.

Reduced surface area might minimize loss of U from the thallus, or there may be other species-dependent retention controls such that crustose lichens may preserve contaminant U for a longer time period.

The non-natural $^{235}\text{U}/^{238}\text{U}$ signatures and the presence of $^{236}\text{U}$ in the lichen samples analyzed in the present study could indicate that the lichens are retaining U isotopic signatures of contaminant U dating to the early 1950s to late-1960s, when non-natural $^{235}\text{U}/^{238}\text{U}$ signatures were recorded in the sediment core. Alternatively, airborne U contamination from FFMPC may have continued to more recent times, during operation up to 1989 and potentially during more recent cleanup activities. The latter interpretation is consistent with the presence of $^{236}\text{U}$ throughout the sediment core including the surface sediment, as well as with the estimates of the longevity of contaminant U in fruticose lichen, but further studies would be necessary to constrain the longevity of the contaminant archive in the crustose lichens.

Measured ($^{234}\text{U}/^{238}\text{U}$) in the lichen samples range from 0.896 to 1.008 (figure 9c), overlapping with the range observed in the sediment core ($\geq 0.92$) but extending to slightly lower values, and significantly lower than the inferred sediment background values (1.09 to 1.22). In the sediment record, the U contribution from weathered bedrock as well as the fresh water in which it is transported and deposited, both with large natural ranges of ($^{234}\text{U}/^{238}\text{U}$), can mask the signature of any contaminant U. Lichens, on the other hand, have minimal influence from the local soil or bedrock, and reflect exclusively airborne U, consistent with the lichens recording slightly more extreme (lower) ($^{234}\text{U}/^{238}\text{U}$) signatures. The lichens in this study may nevertheless have incorporated natural U from a variety of sources, including U ore processed at the FFMPC (FEMP-20900-RP-0002, 1998), fly ash from local coal-burning (Gough and Erdman, 1977), or air-suspended particles such as dust and pollen (Rosamilla et al., 2004). However, the lichen samples exhibit a strong positive correlation of ($^{234}\text{U}/^{238}\text{U}$) with $^{235}\text{U}/^{238}\text{U}$ ($r^2 = 1.0$; figure 9d) that spans both DU and EU signatures, suggesting that ($^{234}\text{U}/^{238}\text{U}$) may be a substantially better proxy for U contamination in lichen than in sediment. Analysis of additional lichen samples in future work will allow this possibility to be investigated in more detail.

5.5 Assessment of sediment cores and lichen as temporal and spatial tracers of environmental uranium contamination

Few studies have employed sediment cores to investigate temporal variations in the nature and magnitude of U contamination from local sources. Previous studies have examined variations in U concentrations through time in sediment cores (e.g. Hardesty, 1991; Waugh et al.,
but elevated U concentrations cannot be definitively linked to an anthropogenic source. Ketterer et al. (2000) investigated U isotopes in dated sediment cores from the Ashtabula River near the RMI Titanium facility in Ohio. Enriched $^{235}\text{U}/^{238}\text{U}$ signatures (0.00781 to 0.00746) with elevated $^{236}\text{U}$ (<0.008%) were found throughout the sediment cores (Ketterer et al., 2000), and suggested that a 1.5 km area of the river was contaminated from two distinct sources after 1964. Our study and the Ketterer et al. (2000) study provide evidence that sediment cores can be effectively utilized to trace the temporal history of U contamination from anthropogenic sources, and to determine the extent of the contamination. The present study is unique in that it is the only known study to have documented a change from predominantly DU to EU contamination in the sedimentary record, the timing of which is consistent with the known history of the FFMPC.

The apparent correspondence between the known releases of uranium dust from the FFMPC through time, and variations in the sediment core U concentration, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios are explored in figure 10, utilizing temporal constraints on the core samples from this study. Three points in time can be specifically defined in the core: 1953 falls between samples 01 and 02, 1963 at sample 08, and 2011 at sample 40. These data are consistent with a constant average sedimentation rate of ~1.5 cm/year both pre- and post-1963, hence a linear depth-time relationship is depicted in figure 10. However, a previous study suggested that the sedimentation rate in the Timberlake impoundment may have been declining since 1989 (Renwick et al., 2005), thus the time-depth relationship in the uppermost section of the core may not be precise. Nevertheless, the appearance of elevated U concentrations and DU and EU signatures fall close to the 1953-1963 time period, which is quite well defined. These results suggest that the main peak in U concentration corresponds to the largest estimated release of U dust from the FFMPC in the early-mid 1950s. Elevated U concentrations in the core continue into the mid-1960s, during the time of the second largest estimated release of U dust from the FFMPC. The sediment core $^{235}\text{U}/^{238}\text{U}$ profile shows a similar correspondence with the timing of estimated releases from the FFMPC, and further indicates that the early release was dominated by DU, while the latter was dominated by EU. Although the variation in $^{235}\text{U}/^{238}\text{U}$ could be ascribed to a single prolonged release with continuous emission of uranium that changed progressively from DU to EU, the $^{236}\text{U}/^{238}\text{U}$ systematics argue against this interpretation. The existence of two distinct peaks in $^{236}\text{U}/^{238}\text{U}$ that correspond to the timing of the estimated releases indicate that the progressive change from DU to EU $^{235}\text{U}/^{238}\text{U}$ signatures is not primarily the result of mixing of DU and EU, but rather of a diminishing contribution of DU contamination from the earliest release, followed by a second distinct release of predominantly EU. The calculated minimum contributions of DU and EU to the sediment core (section 5.2.2) of >15.2% DU and >0.12% EU are qualitatively consistent with the relative magnitudes of the two respective estimated U releases. These data taken together demonstrate the utility of sediment cores as temporal archives of environmental U contamination from the nuclear industry, and further highlight the power of combined major and minor isotopes in documenting the nature and timing of distinct contamination events.

Lichen samples cannot preserve a temporal record of U contamination, but rather preserve a time-averaged record. However, because lichens are nearly ubiquitous in their occurrence, and can be much more easily sampled than sediment cores, they are important proxies for studies of the nature and aerial extant of environmental U contamination. In addition, because lichens have minimal influence from the local soil or bedrock, signatures from non-natural contaminant U are less likely to be masked by natural sources. Furthermore, anthropogenic $^{235}\text{U}/^{238}\text{U}$ signatures measured in lichen can be attributed entirely to airborne dust, whereas anthropogenic U found in
sediment cores may represent a mixture of U introduced by a variety of transport mechanisms, including airborne, waterborne, and soil/sediment-hosted contaminant U. Although the time period represented by the lichen is difficult to determine, and would require both dating (such as that based on inferred growth rates; Roof and Werner, 2011) as well as an understanding of U retention timescales, we propose that the combined use of lichens and sediment cores together can best monitor the aerial and temporal extent of atmospheric U pollution.

6. Conclusions

This study demonstrates clear evidence for environmental U contamination from the Fernald site. Sediment samples were successfully dated using $^{137}$Cs activities, enabling temporal constraints on anthropogenic U contamination in the core. The lowermost sample contains no measurable $^{137}$Cs, indicating that the sample dates to pre-1953. Furthermore, this sample has natural $^{235}\text{U}/^{238}\text{U}$ and no measurable $^{236}\text{U}$, consistent with the bottom of the core pre-dating activity at the FFMPC site.

Uranium and Th concentrations exhibit a strong correlation throughout most of the sediment core ($r^2 = 0.87$). Seven samples immediately above the two basal samples deviate from the linear trend towards higher U concentrations, suggesting an additional source of U. This excursion correlates temporally with DOE’s two largest estimated releases of U from the FFMPC in 1955 and 1964 (Ohio EPA, 2009). Six of those seven samples display non-natural $^{235}\text{U}/^{238}\text{U}$ ratios and all exhibit elevated $^{236}\text{U}/^{238}\text{U}$, providing additional evidence for U contamination originating from the FFMPC. Of these samples, the lower four display DU signatures, followed by a sample with a natural $^{235}\text{U}/^{238}\text{U}$ ratio; immediately above that are two samples that display EU signatures. The latter samples date to ~1963, consistent with the peak of Fernald’s production of EU materials for the Hanford site. Samples stratigraphically higher in the core have natural $^{235}\text{U}/^{238}\text{U}$ values, but elevated $^{236}\text{U}/^{238}\text{U}$, requiring a component of anthropogenic U and suggesting that some samples may contain a mixture of EU and DU components. These data demonstrate that $^{236}\text{U}$ is more sensitive than the major U isotopes ($^{235}\text{U}/^{238}\text{U}$) as a tracer of environmental contamination from the nuclear industry, and furthermore that the contamination persists in present-day sediment.

Lichen samples collected in the vicinity of Fernald display DU and EU signatures coupled with elevated $^{236}\text{U}/^{238}\text{U}$, suggesting that lichen are viable bio-monitors of airborne U dust that retain the anthropogenic U signature for at least several years and possibly several decades. The positive correlation between ($^{234}\text{U}/^{238}\text{U}$) and $^{235}\text{U}/^{238}\text{U}$ in the lichen samples with an $r^2$ of 1.0 suggest that ($^{234}\text{U}/^{238}\text{U}$) may be a viable isotopic tracer of U contamination in lichen, and largely immune to the significant range of ($^{234}\text{U}/^{238}\text{U}$) in fresh water and bedrock that minimizes its utility as a contaminant tracer in sediment.

Overall, this study shows that the temporal history of U releases to the environment can be effectively recorded in sediment cores, despite potential complications such as bioturbation and prolonged sediment transport times. Additionally, this study demonstrates that combined sediment core and lichen analysis, including both the major and minor isotopes of U, has great potential as both temporal and spatial archives of environmental U contamination, allowing constraints to be placed on the minimum contribution of anthropogenic contaminant U from diverse nuclear sources.
7. References


Hardesty, Timothy L., 1991. Uranium. School of Interdisciplinary Studies (Western College Program), iii-64.


Killough et al., 1999


Makhijani, Arjun, 2000. Radioactivity in the Fernald Neighborhood: Institute for Energy and Environmental Research, SDA, 5,


Wu, YanHong, Liu, Enfeng, Bing, HaiJian, Yang, XiangDong, Xue, Bin, and Xia, WeiLan., 2010. Geochronology of Recent Lake Sediments from Longgan Lake, Middle Reach of the Yangtze River, Influenced by Disturbance of Human Activities. Science China, Earth Sciences 53, 1188-1194.
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Table 1: Elemental and isotopic data for sediment and lichen samples. Measured averages (n=10) and certified values for U isotope ratios in NBS005a are also listed. Replicate analyses of sediment samples are indicated in italics and were measured on separate aliquots of powder and their respective leachates. $^{236}$U and $^{137}$Cs values below detection limit denoted by b.d.l..
Figure 1: Map depicting the locations of sample collection in relation to the FFMPC in southwest Ohio.
Figure 2: United States Department of Energy (DOE) record of yearly uranium releases to the atmosphere from the FFMPC (Environment, 1990).
Figure 3: Variation in $^{137}$Cs activity versus depth in core. $^{137}$Cs activities below detection limits can be assigned to pre-1953, before significant global fallout due to atmospheric nuclear testing. Peak $^{137}$Cs activities reflect the year 1963, due to peak atmospheric nuclear testing prior to the Limited Test Ban Treaty of 1963 (Perkins and Thomas, 1980). The top of the core reflects present-day sediment at the time of sample collection in June of 2011.
Figure 4: Uranium versus thorium concentration for sediment samples (replicated samples plotted as average of replicates in this and following figures). A well-defined linear trend is observed for most samples (shown in blue). However, seven consecutive samples (demarcated in green) deviate from this trend, suggesting that these samples have an additional source of U.
Figure 5: Sediment U concentrations versus depth in the core. The samples demarcated in green correspond to samples in figure 4 that have anomalously elevated U relative to Th concentrations, and define peak U concentrations in the core.
Figure 6: $^{235}\text{U}/^{238}\text{U}$ versus depth in the sediment core. Samples at the very base of the core have natural $^{235}\text{U}/^{238}\text{U}$ ratios (0.00725±0.00001 as indicated in orange), whereas those immediately above the base (samples 03 to 11 at depths of 76 to 60 cm, respectively) have DU or EU signatures. Samples from the upper half of the core (sample 20 at a depth of 60 cm and higher) have natural $^{235}\text{U}/^{238}\text{U}$ signatures.
Figure 7: $^{236}\text{U}/^{238}\text{U}$ versus depth in the sediment core. $^{236}\text{U}/^{238}\text{U}$ is essentially non-naturally occurring (natural $^{236}\text{U}/^{238}\text{U} = 10^{-13}$ indicated in orange) and thus, any measurable $^{236}\text{U}/^{238}\text{U}$ can be attributed to an anthropogenic source. The lowermost sample (sample 01) contains no measurable $^{236}\text{U}$, suggesting that it pre-dates anthropogenic activity from the FFMPC. Samples immediately above the base (sample 02 at depth of 38 cm and higher samples) all contain measurable $^{236}\text{U}$. 
Figure 8: $^{234}$U/$^{238}$U activity ratios (designated as ($^{234}$U/$^{238}$U)) versus $^{235}$U/$^{238}$U in the sediment core. Samples with natural $^{235}$U/$^{238}$U ($0.00725 \pm 0.00001$ demarcated in orange) indicate a local background range for ($^{234}$U/$^{238}$U) of 1.09 to 1.22, represented by the darker orange field. Samples with DU signatures (low $^{235}$U/$^{238}$U) deviate from the background ($^{234}$U/$^{238}$U) values and may be reflecting input of DU with correlated low $^{235}$U/$^{238}$U and $^{234}$U/$^{238}$U signatures ($r^2 = 0.87$).
Figure 9: a) $^{235}\text{U}/^{238}\text{U}$, b) $^{236}\text{U}/^{238}\text{U}$ and c) $^{234}\text{U}/^{238}\text{U}$ of the lichen samples versus distance from the FFMCPC. d) $^{234}\text{U}/^{238}\text{U}$ versus $^{235}\text{U}/^{238}\text{U}$ in lichen samples. All of the lichen samples display non-natural $^{235}\text{U}/^{238}\text{U}$ signatures and elevated $^{236}\text{U}/^{238}\text{U}$, which suggests that lichens are viable bio-monitors of airborne U dust. The sample closest to the FFMCPC has an EU signature, while the remaining two lichen samples have DU signatures. Samples also display $^{234}\text{U}/^{238}\text{U}$ outside of the proposed local background range (1.09 to 1.22). The positive correlation of $^{234}\text{U}/^{238}\text{U}$ with $^{235}\text{U}/^{238}\text{U}$ ($r^2 = 1.0$) suggests that $^{234}\text{U}/^{238}\text{U}$ is an effective tracer of nuclear contamination in lichen.
Figure 10: The apparent correspondence between a) known releases of uranium dust from the FFMPC; b) U concentration in the sediment core; c) $^{235}\text{U}/^{238}\text{U}$ ratios in the sediment core and d) $^{236}\text{U}/^{238}\text{U}$ ratios in the sediment core, using an inferred depth-time relationship based on the $^{137}\text{Cs}$ data (see text for further discussion). The largest increase in U concentration corresponds temporally to the largest estimated release of U dust from the FFMPC (early-mid 1950s). Elevated U concentrations in the core persist during the time of the second largest estimated release of U dust (mid-1960s). The sediment core $^{235}\text{U}/^{238}\text{U}$ profile shows a contribution of DU contamination corresponding with the earliest release that is followed by the second release of predominantly EU. The $^{236}\text{U}/^{238}\text{U}$ profile in the sediment core shows two distinct peaks that correspond to the timing of the estimated releases, and indicate that the transition from DU to EU $^{235}\text{U}/^{238}\text{U}$ signatures occurred as two distinct releases.