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Unusually Radiogenic Lead (Pb) in Ashtabula River Sediments: An Isotopic Tracing Case Study Using Quadrupole ICP-MS

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Abstract: Unusually radiogenic Pb has been found in sediments of a portion of the Ashtabula River (80°48' W, 41°54' N) near its confluence with Lake Erie. Pb isotopic compositions have been determined by quadrupole ICPMS, revealing that the Pb results from mixing of three sources: crustal Pb, common Pb from industrial pollutant sources, and highly radiogenic Pb associated with U-containing accessory minerals in a Ti ore refining process discharge. Crustal Pb and anthropogenic pollutant common Pb exhibit ^{206}Pb/^{204}Pb ratios of ~ 19, in agreement with findings from published Lake Erie sediment studies. Horizons containing > 10 ppm U exhibit elevated ^{206}Pb/^{204}Pb ratios (23.88 ± 2.57, n = 11) which cannot be accounted for by anthropogenic common Pb sources. Increases in ^{206}Pb/^{204}Pb are not accompanied by corresponding increases in ^{208}Pb/^{204}Pb, with the exception of one horizon that contains 96 ppm Th. The ^{206}Pb/^{204}Pb is correlated with the U concentration ($r^2 = 0.902$). A small tributary of the Ashtabula River, Fields Brook, is the apparent point of origin of the U, Th and radiogenic Pb in the Ashtabula River sediments. These findings demonstrate that the Pb isotopic composition in the environment is subject to local influences from naturally occurring radioactive material sources.

Keywords: Ashtabula River, uranium, NORM wastes, lead isotopes, sediments.

1. INTRODUCTION

Pb isotope ratios have been widely used in environmental studies of sources, transport, and fate of this element [1-8]. This approach relies on the intrinsic variation in Pb isotopic composition arising from inputs of the radiogenic isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb. The isotopic compositions of Pb ores, expressed as ratios with respect to the non-radiogenic ^{204}Pb, are characteristic of the mine source; older Pb ores have accumulated smaller quantities of the radiogenic isotopes, and therefore exhibit lower ratios with respect to ^{204}Pb. Additionally, the ratios ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb tend to be higher for older (less radiogenic) ores due to differences in geologic abundances and rates of decay of the ^{238}U, ^{235}U, and ^{232}Th parents. Pb isotope ratios are not significantly altered by fractionation in chemical transformations [9]; therefore, the source signature is maintained through environmental processes and is only affected by mixing with other contributions from isotopically distinct sources. Pb isotopes, therefore, represent an attractive means of tracing this element's behavior in the environment; isotopic contrasts are frequently very large and readily measured by rapid mass spectrometric techniques such as inductively coupled plasma mass spectrometry (ICPMS).

Most published isotopic studies of Pb in the environment have investigated "common" Pb, namely, Pb evolved from a geologic environment containing ^{238}U, ^{235}U, and ^{232}Th in relative amounts typical of the crust's composition. Pb found in the environment is usually explainable *via* mixing of "background" Pb with one or more sources of pollutant Pb. In many specific situations, such as near smelters, the background signature is overwhelmed by pollutant Pb sources that exclusively describe Pb ratios in the environment [5, 8].

Pb isotopic compositions of U- and Th-rich minerals are significantly different from both naturally occurring and pollutant "common" Pb [10, 11]. The "uranogenic" Pb (i.e. Pb evolving in a U-rich, Th- and Pb-poor chemical environment) signature is characterized by the following: A) higher ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb ratios, with a much larger relative increase in ^{206}Pb/^{204}Pb; and B) little or no relative increase in ^{208}Pb/^{204}Pb. These characteristics are depicted conceptually in Fig. (**1**). Variations in ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb are functions of time and the U/Pb evolution history of the material; older U minerals are characterized by very high ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb. Very young U minerals may, however, exhibit Pb isotope compositions indistinguishable from "common" Pb. The ^{208}Pb/^{204}Pb ratio is frequently unaffected by U mineralization because the ^{208}Pb parent, ^{232}Th, is either absent from the source rocks or is lost during weathering, transport, and formation of secondary U deposits [12]. "Common" Pb, i.e. Pb derived from unmineralized crustal materials or anthropogenic Pb contamination sources, indicates a different pattern on Fig. (**1**). Not only is the ^{206}Pb/^{204}Pb range of these sources more restricted, but incremental increases in ^{206}Pb/^{204}Pb are correlated with increases in ^{208}Pb/^{204}Pb, as illustrated in the gray shaded area, since the Pb therein is derived from source materials reflecting the crustal Th/U of ~ 3.7. Similar distinctions can be made using ratios such as ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb; these ratios are much lower in uranogenic *vs* common Pb. Pb evolving in a Th-rich, U- and Pb-depleted

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environment, i.e. "thorogenic" Pb, is distinguishable from common as well as uranogenic Pb. The addition of thorogenic Pb brings about large perturbations in ^{208}Pb abundances; for example, grossly elevated ^{208}Pb/^{204}Pb ratios are expected in a closed Th-rich system of sufficient age for ^{208}Pb ingrowth.

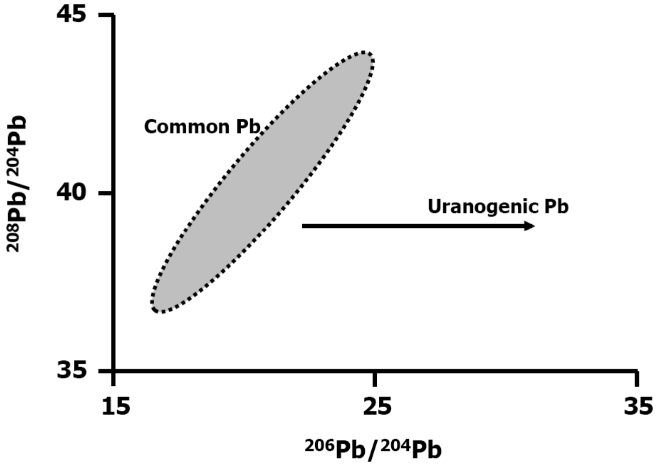

Fig. (1). Plot of ^{208}Pb/^{204}Pb *vs* ^{206}Pb/^{204}Pb showing the expected patterns for common and uranium-associated "uranogenic" lead.

Dickson and co-workers [10, 11] used Pb isotopes as a geochemical exploration tool for locating U deposits concealed by barren overburden. The Pb isotopes approach successfully revealed U mineralization under conditions where other exploration methods were not successful. Few studies, however, have specifically exploited Pb isotopes as a means to investigate contamination sources and transport of daughter-bearing U and/or Th in the environment. One example is the work of Gulson *et al.* [13]; these workers investigated the dissolved-phase and suspended-phase Pb isotopic compositions of waters from the vicinity of a U tailings dam. It was concluded that the surrounding aquifers were unaffected by potential seepage of tailings waters.

There is concern in scientific and regulatory circles over the sources, properties and releases of "naturally occurring radioactive material" (NORM) wastes into the environment. These wastes are comprised of the parents ^{238}U, ^{235}U, and ^{232}Th along with complementary daughters in their respective decay series. For some time, scientific interest has focused upon the radioactivity released by the coal, oil, natural gas, mineral, ore refining, and phosphate fertilizer industries [14]. In order to assess the impact of these waste sources upon the environment, efficient methods of tracking the migration of NORM-associated nuclides in soils, sediments, and natural waters are needed. One objective is to provide quantitatively interpretable contrast between natural background levels and enhanced levels resulting from anthropogenic activities. Environmental studies of NORM problems commonly involve collection and analysis of large numbers of samples, particularly where large areas (e.g. a river drainage basin) are being investigated. It is attractive to use Pb isotopes to study sources, transport and fate of NORM wastes in the environment, as uranogenic and thorogenic Pb signatures would be unusual compared to the restricted range of common Pb ratios. Highly radiogenic Pb is expected to be associated with some NORM wastes of sufficient age, providing no separations have removed Pb from the NORM material.

This paper describes a case study of Pb isotopic compositions of contaminated sediments at Ashtabula, Ohio, USA, where radiogenic Pb associated with anthropogenic NORM contamination significantly influences the observed Pb isotopic compositions. The Ashtabula River drains an area of 350 km^2 and discharges into the central basin of Lake Erie at the city of Ashtabula (80°48' W, 41°54' N, Fig. **2**). There is concentrated industrial development along the river and a tributary, Fields Brook. From the 1940's through the late 1970's, unregulated discharges of hazardous wastes caused contamination of river sediments. The Fields Brook watershed was designated by the US Environmental Protection Agency as a CERCLA ("Superfund") National Priorities List site based upon elevated sediment concentrations of polychlorinated biphenyls and other constituents. The portion of the river channel located south of the 5th St. Bridge has not been dredged since 1962.

Our previous study of sediments in the Ashtabula River indicated that U contamination arising from two distinct anthropogenic sources was present in a 1.5 km portion of the Ashtabula River; U concentrations in dry sediment as high as 188 ppm were identified [15, 16]. U metal of non-natural ^{238}U/^{235}U from a U metal extrusion plant, and NORM wastes derived from a Ti ore refining facility were implicated as the probable sources of this anomalous U contamination. Isotopic measurements of U and Th indicated that the great majority of the U was derived from the Ti ore processing NORM source that contains a full complement of ^{238}U-series nuclides. We demonstrate herein that the NORM source also brings about a highly radiogenic Pb isotopic composition in the contaminated Ashtabula River sediments.

2. EXPERIMENTAL

2.1. Sample Collection and Pre-Processing

Sediment cores were collected in summer and fall 1997 using 3 meter lengths of 19 mm i.d. copper tubing. The tubing was inserted and removed manually from the sediment horizon, using rigid steel pipe extention rods as necessary. Following collection, the overlying water column was carefully decanted from the sediment core tube, which was then capped at both ends. Sampling sites were located on a topographic map to within 25 meters, using manmade features (buildings, bridges, etc.) as reference points. The depositional ages of U-rich horizons in one selected core have been previously established using ^{137}Cs chronology [15].

Sediment cores were extruded intact from the 19 mm copper tubes using a fiberglass rod and a compressed paper plunger. The resulting extruded cores produced compressed lengths of 0.75-1.5 meters. Relatively uniform compactions of 40-50% were observed. The intact cores were sectioned into 2 or 4 cm increments using a stainless steel spatula, and wet/dry masses of each layer were recorded. Drying to constant mass was accomplished at 60°C in an air oven. Due to core compression and the resulting uncertainty in the relationship between position in the compressed sediment core and *in situ* depth in the river sediment profile, and to correct for variations in sediment porosity, all sample depths

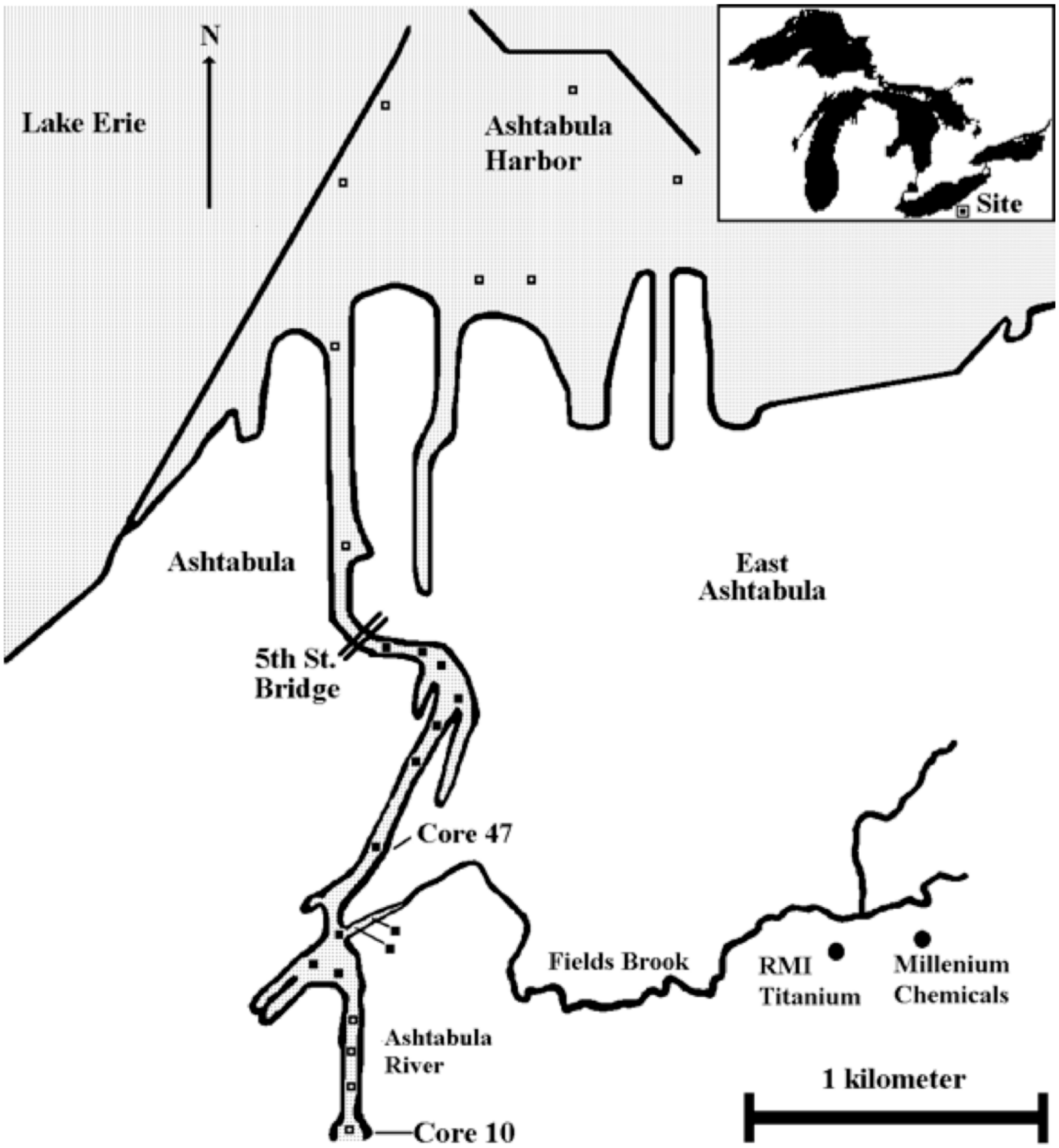

Fig. (2). Site map for the Ashtabula River study area, illustrating core sampling locations and U/Th contamination sources. The small panel in the upper right hand corner depicts the location of the Ashtabula site in the Great Lakes region of North America. U concentration anomalies were detected in cores collected at locations marked as solid squares; no anomalies were detected at hollow square locations.

are referenced on a cumulative overlying dry mass/cross-sectional area basis [17]. The dried sediments were disaggregated using a porcelain mortar and pestle. The Ashtabula River sediments consisted of homogeneous silt-clay materials of < 200 mesh (74 µm) particles.

2.2. Analytical Measurements

Total U, Th, and Pb were determined in sediments by quadrupole ICPMS. 0.25 g sub-samples were dissolved by fusion at 450° C with 2.0 g KOH in a Ni crucible; following fusion, the flux was acidified and diluted to 100 mL with 1.6 M aqueous HNO_3. Prior to analysis, the samples were further diluted 20x or 25x with 1% v/v aqueous HNO_3. Iridium (200 µg/L) was added as an internal standard for ICPMS analysis. The accuracy of U, Th, and Pb concentration measurements was established to be ± 10 % relative through preparation and analysis of NIST 2704 (Buffalo River Sediment) and USGS G-2 granite.

Pb isotopic compositions were determined in HNO_3-leached samples by ICPMS. This simplified dissolution procedure was used in lieu of the KOH fusion for the Pb isotopic measurements on account of excessive blank contributions (~ 5-10 % of the sample Pb) encountered with the KOH fusions. 0.25 g of sample were mixed with 5 mL HNO_3 in a capped 30 mL fluorinated ethylene-propylene test tube; the mixtures were heated to 85-90° C for 16-24 hours, then diluted to 50 mL with water. Additional dilution was performed as necessary on the centrifuged leach solutions in order to produce Pb concentrations of 100-200 µg/L. Thallium (150 µg/L) was added as an internal standard for mass discrimination correction as described elsewhere [18, 19]. A Perkin-Elmer Sciex ELAN 500 ICPMS instrument was used for all measurements; this instrument was equipped with an externally mounted 250 mL fluoropolymer spraychamber. Integration parameters were as follows: t_{dwell} = 50 ms; 1 meas/mass spectral peak; 1500 individual peak-hop scans were averaged for each determination. Signals were monitored at m/z 201, 203, 204, 205, 206, 207, and 208; each determination required about 9 minutes collection time. The $^{204}Hg^+$ contribution at m/z was subtracted using the Hg signal measured at m/z 201 as follows: $^{204}Pb_{net}$ = (Total m/z 204 signal) – 0.515 * (^{201}Hg signal) where 0.515 is the $^{204}Hg/^{201}Hg$ atom ratio. Two or three determinations were collected and averaged for most sediment samples. The quality of the Pb isotopic measurements was evaluated through measurements of a NIST 981 (Common Pb) standard; results are shown in Table **1**. Small systematic biases were consistently observed for the Tl-corrected NIST 981 results, and the mean ICPMS biases were used to externally correct all sample measurements. Isotope ratio precisions for sediment samples resemble the NIST 981 precision reported in Table **1**. For sediment samples, internal precisions were as follows: $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$, 0.3%; $^{208}Pb/^{204}Pb$, 0.4%; $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, 0.2%.

Table 1. Summary of Pb Isotope Ratio Results in NIST 981[a]

Ratio	Results
$^{206}Pb/^{204}Pb$	ICPMS: 16.99 ± 0.04 (n = 30)
	Certified: 16.94 ± 0.02
	Bias correction factor: 1.0033 [b]
$^{207}Pb/^{204}Pb$	ICPMS: 15.62 ± 0.05 (n = 30)
	Certified: 15.50 ± 0.01
	Bias correction factor: 1.0080
$^{208}Pb/^{204}Pb$	ICPMS: 36.75 ± 0.16 (n = 30)
	Certified: 36.72 ± 0.02
	Bias correction factor: 1.0007
$^{207}Pb/^{206}Pb$	ICPMS: 0.9192 ± 0.0018 (n = 30)
	Certified: 0.9146 ± 0.0003
	Bias correction factor: 1.0049
$^{208}Pb/^{206}Pb$	ICPMS: 2.163 ± 0.005 (n = 30)
	Certified: 2.168 ± 0.001
	Bias correction factor: 0.9972

[a]Uncertainties are ± one standard deviation; n=number of measurements; measurements were acquired over a three-month time frame. [b]Data were corrected as follows: (raw ratio) / bias correction factor = corrected ratio.

3. RESULTS AND DISCUSSION

3.1. Pb, Th, and U Concentrations

U and Th contamination was found along a 1.5 km course of the Ashtabula River, as indicated in Fig. (**2**). Elevated U concentrations have been found in all coring locations identified by solid symbols, while no anomalies were found in sediments north and south of this zone. Previous work [15, 16] established that the U contamination post-dates the 1963/1964 ^{137}Cs fallout maximum horizon. Based upon preliminary Pb isotopic studies, as well as findings in previous work, one dated core from the U-contaminated sector (Core 47) was selected for detailed study herein.

Core 10, obtained from the Ashtabula River approximately 0.5 km upstream of the Fields Brook confluence, is considered to represent uncontaminated sediment deposited during the 1993-1997 time frame. This location is upstream of the industrialized portion of the Ashtabula River basin and is unaffected by pollutant discharges originating from Fields Brook. Previous analytical work has demonstrated U and Th concentrations in Core 10 resembling crustal concentrations; analysis of 18 individual 2 cm horizons revealed 3.0 ± 0.3 ppm U (average ± SD) and 10 ± 1 ppm Th. By comparison, Mason [20] has reported crustal averages of 1.8 and 7.2 ppm, respectively, for U and Th. The present study found Pb concentrations of 24 ± 7 ppm for the same group of eighteen Core 10 sediment horizons.

Comparisons between Pb concentrations in Core 10, Core 47, and pre-industrial Lake Erie sediments are presented in Table **2**. The Pb concentrations suggest that Core 10 and the uppermost horizons of Core 47 consist of sediment which is largely unaffected by anthropogenic Pb contamination. The Lake Erie sediment data are reported in previous studies [4, 21]; both of these groups found consistent Pb concentrations of ~ 20 ppm in pre-1860 horizons from Lake Erie's western, central and eastern basins. The bottom horizons of Core 47, however, appear to indicate anthropogenic Pb contributions. Nine horizons of Core 47 located at depths > 57 g/cm^2 exhibited 47 ± 12 ppm Pb which is significantly higher ($p < 0.0001$, two-sample t-test) than the Core 10 average, the average concentration in uppermost horizons of Core 47, and averages of all groups of pre-industrial sediment. The > 57 g/cm^2 horizons were deposited in the 1960-1965 timeframe (note the 1963 marker from ^{137}Cs chronology which occurs at 64 g/cm^2). The higher concentrations in the bottom portion of Core 47 are concordant with substantial inputs of anthropogenic Pb in Lake Erie basin sediments [4, 21] deposited during the same time period.

Elevated Pb concentrations were also found in sediment horizons containing anthropogenic Th and U contamination. This trend was clearly evident in sediments of Core 47 (refer to Fig. **3**) as well as other cores collected from the impacted portion of the Ashtabula River and the Fields Brook confluence. Pb concentrations of 77 ± 25 ppm (average ± SD) are present in Core 47 horizons from the 48-57 g/cm^2 interval; these levels are significantly greater ($p < 0.001$) than any of the groups of sediments representing material unaffected by anthropogenic influences.

3.2. Common Pb in Ashtabula River Sediments

An examination of the Pb isotopic compositions of Core 10 sediments, the non-U contaminated horizons of Core 47 and pre-industrial Lake Erie sediments reveals similar isotopic compositions comprised of common Pb. Small but significant ($p < 0.05$) differences are evident when comparing our Core 47 and Core 10 results *vs* those previously reported for Lake Erie sediments [4, 21], the latter reflecting material eroded from a much larger area than

Table 2. Pb, Th, and U Concentrations; Pb Isotopic Composition In Core 10, 47, and Pre-Industrial Lake Erie Sediments

Sediment Group	Pb, ppm	Th, ppm	U, ppm	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
Core 10[a] (n = 5)[b]	11 ± 1[c]	10 ± 1	3.0 ± 0.3	18.72 ± 0.30	15.71 ± 0.07	38.79 ± 0.52	0.838 ± 0.011	2.072 ± 0.008
Core 47, top (n = 6)	26 ± 3	11 ± 2	3.7 ± 0.7	19.17 ± 0.10	15.83 ± 0.04	39.49 ± 0.14	0.826 ± 0.004	2.059 ± 0.013
Core 47, bottom (n = 9)	47 ± 12	11 ± 2	3.7 ± 0.7	18.88 ± 0.09	15.69 ± 0.04	38.69 ± 0.19	0.830 ± 0.003	2.058 ± 0.008
Core 47, U-contaminated (n = 11)	77 ± 25	45 ± 21	96 ± 55	23.88 ± 2.57	16.06 ± 0.18	39.95 ± 1.20	0.679 ± 0.065	1.690 ± 0.188
Graney, Eastern Basin[d] (n = 6)	17 ± 1	NR	NR	19.17 ± 0.01	15.67 ± 0.01	39.00 ± 0.03	0.8174 ± 0.0002	2.035 ± 0.001
Ritson, Western Basin[e] (n = 7)	17.3 ± 0.4	NR	NR	19.45 ± 0.06	15.66 ± 0.06	38.94 ± 0.12	0.805 ± 0.001	2.002 ± 0.002
Ritson, Central Basin (n = 8)	20 ± 2	NR	NR	19.21 ± 0.05	15.67 ± 0.02	38.89 ± 0.07	0.815 ± 0.002	2.024 ± 0.004
Ritson, Eastern Basin (n = 8)	18.4 ± 0.5	NR	NR	19.21 ± 0.09	15.64 ± 0.04	38.95 ± 0.19	0.814 ± 0.002	2.027 ± 0.004

[a] Core 10 consisted of eighteen 2 cm horizons. Pb concentrations were also determined in 2 cm horizons (24 ± 7 ppm).
These eighteen horizons were composited to produce five 6-8 cm horizons which were used to obtain the results reported in Table 2.
[b] Number of sediment horizons. [c] All uncertainties are ± one standard deviation.
[d] Data are from Graney *et al.* [4]. [e] Data from Ritson *et al.* [21]. NR = Th and U concentrations are not given in [4] and [21].

the Ashtabula River watershed. It is also possible that our ICPMS results exhibit small uncorrected biases when compared to the Lake Erie results [4, 21]; both of these groups utilized thermal ionization mass spectrometry in their work.

Comparisons between the top and bottom portions of Core 47 indicate that the earlier horizons (containing higher Pb concentrations) contain Pb that is significantly less radiogenic than Pb in the more recent top horizons. This result is additional evidence that the bottom horizons contain significant anthropogenic Pb input. Similarly, Pb deposited in Lake Erie sediments [4, 21] during the time interval of greatest anthropogenic flux (i.e. ~ 1930-1980) was significantly less radiogenic than Pb contained in pre-1860 sediments.

3.3. Radiogenic Pb in Ashtabula River Sediments

Fig. (**3**) demonstrates that the U- and Th-contaminated Core 47 horizons contain Pb of unusual, highly radiogenic isotopic composition. Input of radiogenic Pb, derived from Ti ore refining, is evidently responsible for the observed isotopic compositions. This contention is supported by several observations.

First, all horizons containing > 10 ppm U exhibit ^{206}Pb/^{204}Pb > 20, while relatively unaffected horizons containing < 7 ppm U, exhibit ^{206}Pb/^{204}Pb < 20. Sample 47m, located at a depth of 54.1 g/cm^2, exhibited the following extreme ratios: (^{206}Pb/^{204}Pb, 29.00 ± 0.09; ^{207}Pb/^{204}Pb, 16.39 ± 0.05; ^{208}Pb/^{204}Pb, 39.92 ± 0.13; ^{207}Pb/^{206}Pb, 0.5649 ± 0.0006; and ^{208}Pb/^{206}Pb, 1.3763 ± 0.0010). For horizons containing > 10 ppm U, the ratios ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb are all significantly related to sediment U concentrations. An example of this pattern is shown for ^{206}Pb/^{204}Pb in Fig. (**4**). Varying inputs of pollutant (i.e. "common") Pb probably account for the deviations from the Fig. (**4**) trendline.

A second finding is that the U-contaminated horizons' isotopic compositions cannot be accounted for by regional sources of anthropogenic (common) Pb pollution. The Lake Erie sediment studies [4, 21] provide estimates of isotopic compositions of post-1930 Pb deposition from sources such as gasoline, coal combustion, and industrial processes. For example, Graney *et al.*'s [4] dated Eastern Basin cores exhibit ^{206}Pb/^{204}Pb ratios in the 18.7-19.1 range for the 1930-1990 time frame; Ritson *et al.* [21] found similar ratios in pollutant-affected recent horizons of three cores from the Western, Central and Eastern Basins of Lake Erie. It is well-established that significant changes in Pb isotopic compositions for US anthropogenic Pb pollution have occurred since the mid-1960's; this trend is primarily the result of increasing utilization of Missouri ores in the US Pb supply. For example, the average ^{207}Pb/^{206}Pb in US gasoline Pb was estimated to be ~ 0.870 prior to 1967, then decreased to ~ 0.833 by 1974 and ~ 0.813 by 1977 [1]. However, these compositions cannot account for the unusually low ^{207}Pb/^{206}Pb ratios of 0.565 – 0.782 which are found in the U-contaminated horizons of Core 47. Moreover, it is not plausible to account for the highest ^{206}Pb/^{204}Pb and lowest ^{207}Pb/^{206}Pb ratios of Core 47 based upon direct input of Pb pollution specifically originating from Missouri Pb ores. Studies by Doe and Delevaux [22] and Heyl *et al.* [23] suggest ^{206}Pb/^{204}Pb ratios of ~ 20-23 would be expected from ores from the economically important southeast Missouri mining district.

A third finding is that the U-contaminated sediments display Pb isotopic compositions in accordance with the expected "uranogenic" pattern of Fig. (**1**). This result is depicted in the Fig. (**5**) plot of ^{208}Pb/^{204}Pb *vs* ^{206}Pb/^{204}Pb. It is observed that increases in ^{206}Pb/^{204}Pb are not associated with corresponding increases in ^{208}Pb/^{204}Pb, as one expects for "common" and Missouri Pb; instead, increases in ^{206}Pb/^{204}Pb occur with relatively small or no increase in ^{208}Pb/^{204}Pb. One horizon, however, located at 50.6 g/cm^2 depth, clearly exhibits an elevated ^{208}Pb/^{204}Pb of 43.20 ± 0.15. This horizon also contains the highest observed Th concentration (96 ppm), so it seems plausible that ^{232}Th-rich minerals containing significant quantities of ingrown ^{208}Pb have produced this effect.

The specific mineral phase(s) hosting the U, Th and Pb have not been identified, and identification of these phases is the subject of ongoing work. Our previous study [15]

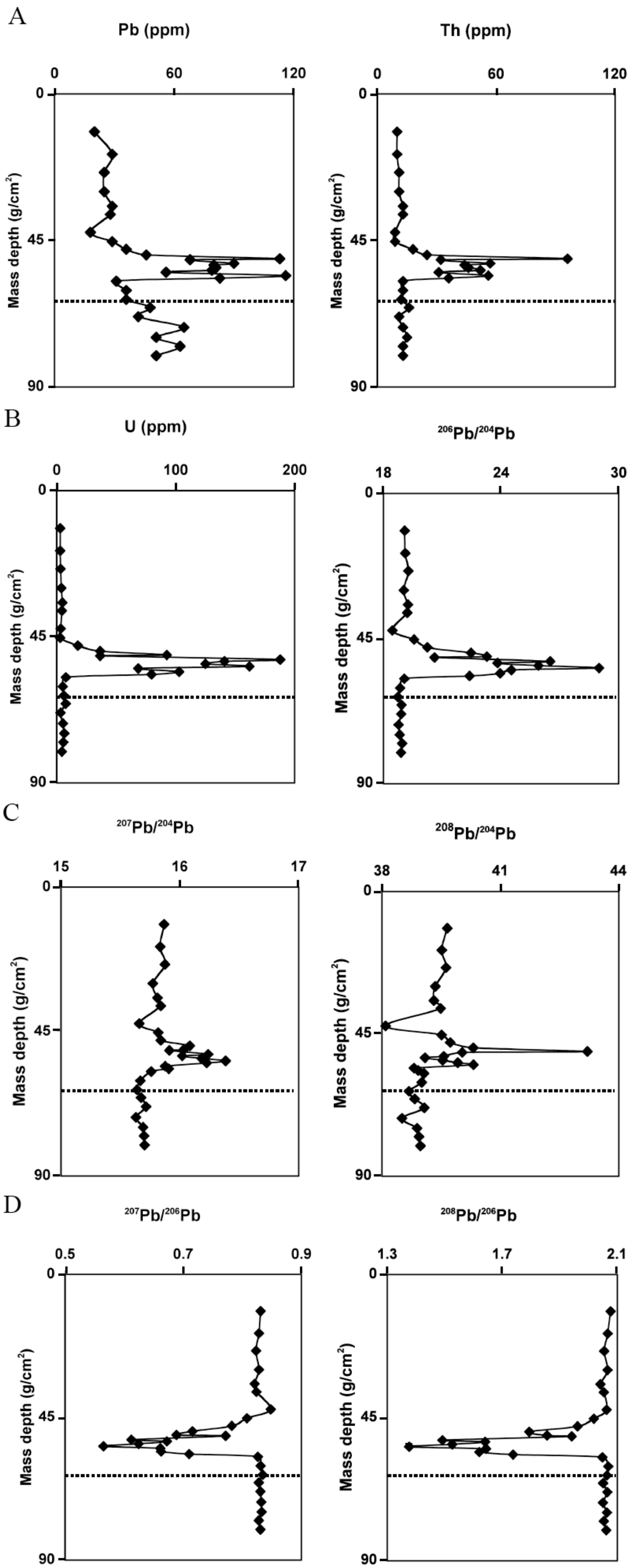

Fig. (3). A-D. Concentrations of Pb, Th, U, and Pb-isotopic results for Core 47, Ashtabula River. The dotted line in each panel indicates the position of the 1963 ^{137}Cs date [15].

indicated that elevated concentrations of U and Th were also associated with increases in Zr, Nb, Hf, Ta, and W concentrations. It is most likely that U, Th, and radiogenic Pb reside in mineral phases present in the ilmenite concentrates processed at the Ti ore facility.

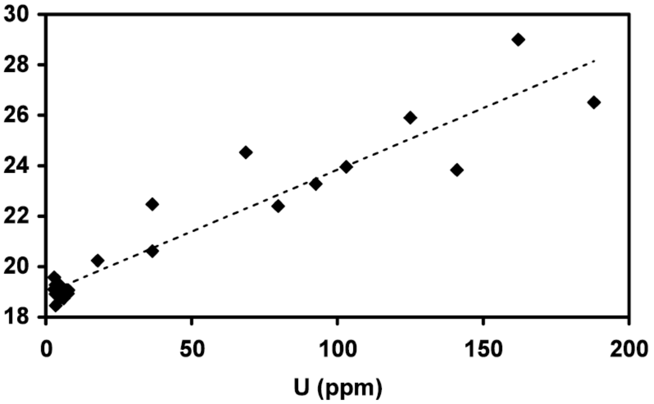

Fig. (4). Plot of ^{206}Pb/^{204}Pb *vs* U concentration (ppm) for Core 47, Ashtabula River. Trendline: ^{206}Pb/^{204}Pb = (18.95 ± 0.22) + (0.049 ± 0.003)*[U]; $r^2 = 0.902$.

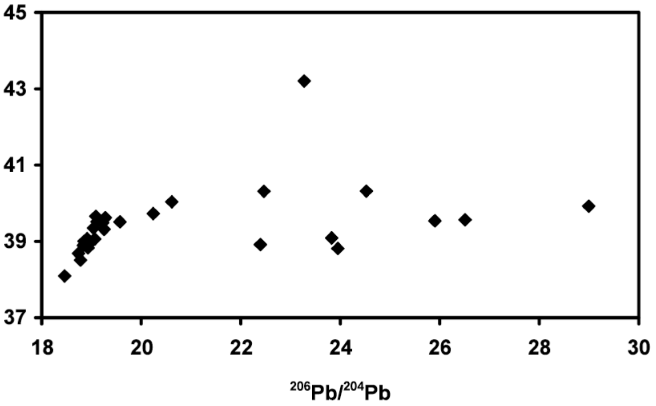

Fig. (5). Plot of ^{208}Pb/^{204}Pb *vs* ^{206}Pb/^{204}Pb for Core 47, Ashtabula River.

4. CONCLUSIONS

This study has demonstrated that highly radiogenic Pb from a NORM waste source strongly influences the observed isotopic composition in sediments of the Ashtabula River. The Pb isotopic compositions are correlated with sediment U concentrations and are in accordance with the expected pattern for "uranogenic" Pb. Pb pollution sources consisting of "common" Pb cannot account for the observed ^{206}Pb/^{204}Pb ratios of 20-29 in U-contaminated sediments. In contrast, Ashtabula River sediments not containing elevated U exhibit common Pb isotopic compositions.

The stable Pb isotope method may be useful for investigating sources, fate and transport of NORM wastes in other environmental settings. One clear advantage is that Pb isotope ratios would be unaffected by chemically separated U derived from U chemicals, alloys, or the nuclear fuel cycle; the "uranogenic" signature is specifically produced by daughter-containing U-rich minerals. For sites having probable contamination from anthropogenic U sources, Pb isotope measurements should be conducted in concert with other measurements such as U isotopes. The applicability of Pb isotopes will depend upon factors such as magnitude of releases, U concentration of the source material, age of U/Th-bearing wastes, and the concentrations and isotopic composition of background and pollutant Pb in the local environment.

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