Query Details

---

1. Author names: Please confirm if the author names are presented accurately and in the correct sequence (given name, middle name/initial, family name). Author 1 Given name: [María Isabel] Last name [Sánchez-Báscones], Author 6 Given name: [Ana Isabel] Last name [Barrado-Olmedo]. Also, kindly confirm the details in the metadata are correct.

> All names and corresponding affiliations are corrects.

In any case, we include the ORCID of the authors below.
The last co-author was not available to provide his ORCID

https://orcid.org/0000-0002-7330-8554 Edmundo Escareño-Juarez
https://orcid.org/0000-0003-4658-7575 Rafael Pardo
https://orcid.org/0000-0003-2409-6716 Catalina Gasco-Leonarte
https://orcid.org/0000-0002-3635-7920 Marisol Vega
https://orcid.org/0000-0003-4175-9067 María Isabel Sánchez-Báscones

2. Please provide a definition for the significance of bold in the Tables 1 and 3.

> Bold typography from Tables 1 and 3 has been removed

Determination of natural uranium by various analytical techniques in soils of Zacatecas State (Mexico)

Edmundo   Escareño-Juárez,   [1]✉

Email edmundo.escareno@uaz.edu.mx

Rafael   Pardo,   [1]

Catalina   Gascó-Leonarte,   [2]

Marisol   Vega,   [1]

María Isabel   Sánchez-Báscones,   [1]

Ana Isabel   Barrado-Olmedo,   [2]

[1] Department of Analytical Chemistry, Faculty of Sciences, University of Valladolid, Campus Miguel Delibes, Paseo de Belén 7, 47011 Valladolid, Spain

[2] Unit of Environmental Radioactivity and Radiological Surveillance, Center for Energy, Environment and Technology Research (CIEMAT), Av. Complutense 40, 28040 Madrid, Spain

Abstract

^{238}U is a radionuclide present in the earth's crust that provides 65.9% of annual average radiation dose and represents 99.27% of total uranium. ^{238}U has been determined in samples from undisturbed topsoil in the Zacatecas State, Mexico, using several analytical techniques. ICP-MS and α-spectrometry produced the most reliable results. Uranium concentrations found in topsoil samples (0.4–3.7 mg kg^{-1}) were similar to its average crustal abundance (2.8 mg kg^{-1}) and indicate high homogeneity without evidence of enrichment. The average concentration of 2.1 mg kg^{-1} can be established as uranium background level in the topsoil of Zacatecas (Mexico).

AQ1

Keywords

^{238}U
Topsoil
Background concentration
ICP-MS
α-Spectrometry
Enrichment factor

Introduction

Radionuclides with a long half-life such as uranium represent nowadays, along with other toxic trace elements, an important category of inorganic pollutants to be monitored. Human activities affect the distribution of natural radioactivity on Earth. The transformation of natural resources containing Naturally Occurring Radioactive Materials (NORM) generates by-products that have found their way into the environment. Additionally, the Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) are also produced by human activities and are constantly modifying the distribution of radionuclides on Earth. Lastly, natural incidents, including geologic and seismic events and forest fires, have also impacted the distribution of natural radioactivity [1].

Uranium is an element of the actinide series. Naturally occurring uranium (^{nat}U) is a mixture of three radionuclides (^{234}U, ^{235}U and ^{238}U), all of which decay by both alpha and gamma emissions. Typical concentration range of uranium from 0.3 to 11.7 mg kg^{-1} is found and an average concentration in the Earth crust of 2.8 mg kg^{-1} has been estimated [2, 3, 4]. The most abundant isotope, ^{238}U, makes up about 99.27% of naturally occurring uranium and is ubiquitous in nature. The half-lives of uranium isotopes are very long. With a half-life of 4.5 billion years, ^{238}U possesses the slowest decay rate and the lower specific activity of all uranium isotopes, it is hardly fissible and is the father of the 4n + 2 decay series. Uranium has both chemical and radiological toxicity but, given its long half-life, is more chemotoxic than radiotoxic [1, 5, 6, 7, 8].

AQ2

Atoms of ^{238}U and ^{235}U decay through a chain of many other radioisotopes to stable lead isotopes [1]. The UNSCEAR 2016 Report informed an average activity concentration of around 30 Bq kg^{-1} (1.2 mg kg^{-1}) for uranium in rock and soil. Both ^{238}U and ^{234}U, when they are in secular equilibrium, contribute 48.9% of the total alpha particle activity of natural uranium, while ^{235}U contributes 2.2% [1, 9, 10].

The knowledge of the amount of radioactivity in the different environmental matrices has been a concern in many countries and has led to its determination in order to evaluate the activity of natural and anthropogenic radionuclides in different areas [11]. Nuclear forensic investigations use a number of analytical methods, both non-destructive and destructive, to evaluate material purity, isotopic composition, trace element content, and morphology [12]. They must be

sensitive and reliable to detect the habitually low-level concentrations of uranium in environmental samples. Several spectrometric methods have been developed for the determination of trace uranium.

The determination of uranium isotopes in soil and sediments is generally complicated because chemical recoveries are variable due to interference from matrix effects mainly caused by major salt ions. These effects are especially troublesome because there is a strong sample-dependency involving the composition and mineralogy of soil samples [13].

All analytical techniques used in this work, α-spectrometry (α-spec), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma double focusing sector field mass spectrometry (ICP-SF-MS), X-ray fluorescence (XRF) and X-ray diffraction (XRD) are frequently used for uranium determination and for soil characterization. ICP-OES and XRF are photon-counting techniques, while α-spectrometry, ICP-MS and ICP-SF-MS are ion-counting techniques [14].

The α-spectrometry technique is a well-established methodology and is the most widely used method to determine the contents of uranium isotopes emitting alpha particles in different types of environmental samples. Usually it involves a set of sequential steps according to the type of analytical matrix, which enlarges the duration and cost of the analysis since more laboratory resources (materials and personal) are consumed. However, the results are highly reliable when using a certified tracer that allows obtaining the chemical recovery of the whole process.

ICP-OES is widely used as a suitable technique for the determination of metals because of its high sensitivity and multi-element determination capability. The determination of uranium by ICP-OES is not affected by interferences caused by the formation of carbides and uranium oxides, however, other spectral interference problems and some matrix effects may occur in the determination of trace amounts of uranium in complex matrices, such as soil samples.

ICP-MS is currently considered one of the most powerful analytical techniques for the determination of the total concentration and isotopic composition of the actinide elements and is a multi-element technique thus allowing fast and sensitive determination of trace levels of these elements. ICP-SF-MS is also a

multi-element technique with improved sensitivity, allowing the determination of actinide elements in liquid samples at concentrations below 1 pg mL^{-1} [15].

The XRF technique is very versatile, has the capability for fast sample throughput, in situ analysis with portable instruments, multi-element capacity, non-destructive. With modern instruments, the sensitivity is close to that of radiometric methods.

Each technique has advantages and shortcomings relative to non-spectral or spectral interferences, precision, accuracy, cost (acquisition, operation and maintenance), sample type (solid or liquid), lab-ware and apparatus employed in the analysis. The applicability of the method must also take into consideration whether each detection technique is overly complex or requires extensive and laborious separation or preconcentration steps [11]. On the other hand, the simultaneous use of analytical techniques based on different physical principles for the detection and measurement of a given analyte can help to identify matrix effects and to obtain accurate results.

The State of Zacatecas (Mexico) is known for its large deposits of silver and other minerals and there is scarce and very old information about the amount of actinides present in this area [16]. The objective of this study is to determine the concentration of uranium in the topsoil of some undisturbed areas of the state of Zacatecas using different analytical techniques, radiometric and non-radiometric, to optimize the procedures and to select the most appropriate methodologies taking into account the analytical parameters, such as accuracy and time of analysis. Finally, after excluding the occurrence of soil enrichment by uranium, the results will be used to estimate the background concentration of uranium in pristine topsoil of Zacatecas state.

Experimental

Study area

For this work, samples of undisturbed topsoil from the State of Zacatecas (Mexico) and surrounding areas (Fig. 1) have been investigated. Three quarters of Zacatecan territory correspond to arid and semi-arid zones. Of these, 14% offer favorable conditions for agriculture, 79% for livestock and 7% are covered with timber and non-timber forests. In the central part of the state there are

chestnut soils, abundant in semi-arid zones and characterized by having a layer of *caliche* or loose lime. This type of soil is favorable for the development of agriculture and livestock. Towards the northeast of Zacatecas soils characteristic of the arid and semi-arid zones of central and northern Mexico can be found [16]. In the State of Zacatecas there are several mining industries that extract mainly silver, zinc and gold.

Fig. 1

Situation of the State of Zacatecas in the Mexican Republic and location of the sampling points (M1–M32) in the State and its surroundings

All 32 sampling points selected were located in areas never used for agriculture, industry or housing. Four of them belong to Aguascalientes State, one to Nuevo León State, and the rest (27 samples) were taken in Zacatecas State. Most of the samples were collected near populated areas and have been labelled M1 to M32. Sampling was carried out under similar conditions from undisturbed areas close to secondary roads, thus facilitating the access. Previous studies about the homogeneity of the distribution of uranium in these sites demonstrated that there are not significant variations between samples taken at 0–10 cm or 40–50 cm depth. Therefore, all samples in this work were taken at topsoil.

Materials and instrumentation

All reagents used were of analytical reagent grade. The UTEVA® resin was supplied by Eichrom Technologies (USA). The ^{232}U tracer was supplied by CIEMAT (Madrid, Spain). A certified reference material CRM (GBW07402) was purchased from the Institute of Geophysical and Geochemical Exploration (Langfang, China).
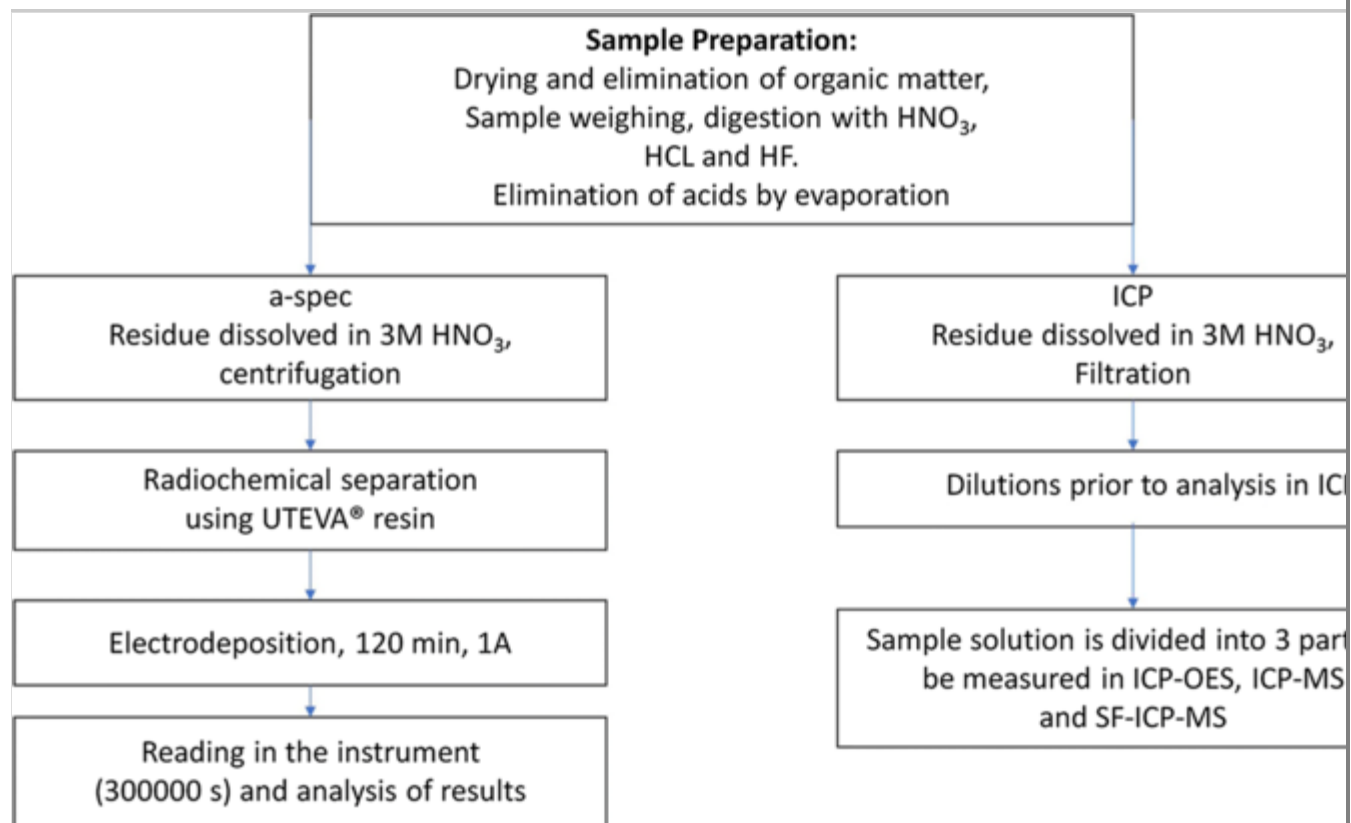
X-ray fluorescence and X-ray diffraction measurements were carried out using Bruker XRF S8 Tiger and XRD G8 Discover instruments (Bruker Corporation, USA), ICP-OES 725-ES and ICP-MS 7500c from Agilent Technologies (California, USA) were employed for uranium determination in dissolved samples. The ICP-SF-MS instrument used was the Element® XR manufactured by Thermo Scientific (Bremen, Germany). The "S" type electrodeposition cell was supplied by Tracerlab GmbH (Koeln, Germany). Alpha emissions of electrodeposited uranium were measured with AAN-01-00 Alpha-Analyst spectrometers (Canberra Industries Inc., USA). The data were managed with Microsoft Excel® and Statgraphics® Centurion XVII.

Experimental procedures

After milling, the samples were homogenized, sieved to 0.2 mm and calcined (600 °C/4 h) to remove moisture and organic matter. Total digestion with a mixture of HNO_3:HCl:HF was carried out for a complete dissolution of the samples and determination of total uranium. The following steps in sample preparation depended strongly on the analytical technique used and are schematized in Fig. 2.

Fig. 2

Flow-chart for α-spectrometry and ICP-MS

```
┌─────────────────────────────────────────────────┐
│                Sample Preparation:              │
│         Drying and elimination of organic matter,│
│         Sample weighing, digestion with HNO₃,   │
│                   HCL and HF.                    │
│         Elimination of acids by evaporation      │
└─────────────────────────────────────────────────┘
        │                                │
        ▼                                ▼
┌──────────────────────┐      ┌──────────────────────┐
│       a-spec         │      │        ICP           │
│ Residue dissolved in │      │ Residue dissolved in │
│   3M HNO₃,           │      │   3M HNO₃,           │
│   centrifugation     │      │   Filtration         │
└──────────────────────┘      └──────────────────────┘
        │                                │
        ▼                                ▼
┌──────────────────────┐      ┌──────────────────────┐
│ Radiochemical        │      │ Dilutions prior to   │
│ separation           │      │ analysis in IC       │
│ using UTEVA® resin   │      │                      │
└──────────────────────┘      └──────────────────────┘
        │                                │
        ▼                                ▼
┌──────────────────────┐      ┌──────────────────────┐
│ Electrodeposition,   │      │ Sample solution is   │
│ 120 min, 1A          │      │ divided into 3 par   │
│                      │      │ be measured in       │
│                      │      │ ICP-OES, ICP-MS      │
│                      │      │ and SF-ICP-MS        │
└──────────────────────┘      └──────────────────────┘
        │
        ▼
┌──────────────────────┐
│ Reading in the       │
│ instrument           │
│ (300000 s) and       │
│ analysis of results  │
└──────────────────────┘
```

For α-spectrometry radiometric technique, 2 g of topsoil were weighed with ± 0.1 mg precision into PTFE vessels and 0.1 Bq of ^{232}U added as tracer. Subsequently, 8 mL of 65% nitric acid, 6 mL of 36% hydrochloric acid and 3 mL of 49% hydrofluoric acid were added to the vessels. The samples were then subjected to total digestion in a Milestone Ethos Plus microwave oven using a heating program consisting of 10 min of heating from room temperature to 180 °C at a constant rate, followed by 10 min at constant temperature of 180 °C. After digestion, the excess acids were removed by evaporation and the residues were diluted with 15 mL of 3 M HNO_3. Then the solutions were centrifuged (5000 rpm/15 min) and the supernatant transferred to the uranium-selective UTEVA$^{®}$ ion exchange resin using the analytical procedure ACS07 from Eichrom Technologies [17]. After separation and elution, the solution is submitted to electrodeposition stage as described in analytical procedure SPA02 from Eichrom Technologies [18], leaving an 8 mm distance between the anode and the stainless-steel disc where uranium is deposited.

Samples, CRMs and radiation background were measured for 300,000 s in two different 'Alpha Analyst' α-spectrometers (Canberra Industries Inc., USA), located at the University of Valladolid (UVa) and the Center for Energy,

Environment and Technology Research, CIEMAT (Spain) using similar instrumentation and under the same conditions. The data collected in α-spectrometry were processed in MS-Excel to estimate the specific activity and uncertainty. Activity values of ^{238}U were converted to mass using the factor 12.35 Bq kg^{-1} = 1 mg kg^{-1}.

The ^{238}U activity was calculated using the following equation:

$$A_U = \frac{TC_U - BC_U}{\varepsilon \cdot m \cdot CR \cdot t \cdot i}$$

1

where A_U symbolizes the activity in Bq g^{-1}, TC_U is the total accounts for the peak of ^{238}U (4198 + 4151 keV), BC_U is the background accounts in the energy of ^{238}U, ε is the efficiency of the detector (0.15), m is the sample mass, in g, CR is chemical recovery estimated from the activity of the ^{232}U tracer (0.80), t is measurement time (300,000 s) and i is the isotopic abundance for ^{238}U (0.99275 according to IUPAC [19]).

For ICP-OES and ICP-MS analysis, 0.5 g of topsoil were weighed and subjected to digestion, following the same procedure as for α-spectrometry, the excess acids removed by evaporation, and residue dissolved in 25 ml of 4% Please, substitute 4% by 3M nitric acid. This sample solution was divided into 3 aliquots to be measured by ICP-OES, ICP-MS and ICP-SF-MS without further pretreatment. In the case of ICP-OES, the emission energy registered at 409.013 nm was used for uranium quantification as it was more selective. For ICP-MS only the mass/charge ratio of ^{238}U was selected for quantification in combination with the internal standard method of calibration to verify the stability of the instrument during the measurement; ^{103}Rh in ICP-MS and ^{115}In in ICP-SF-MS were used as the internal standards. No isotopic tracers were used in this technique. The uranium concentration in the liquid samples were calculated by interpolation in the calibration curves elaborated with certified standard solutions.

Limits of detection (LOD) for uranium determination by these techniques were estimated. For α-spectrometry, LOD value was 0.032 mg kg^{-1} (0.40 Bq kg^{-1}), calculated according to the ISO 11929:2010 standard [20]. For ICP-OES, ICP-MS and ICP-SF-MS the LOD values were calculated from the slope and square

root of the residuals of the calibration plots, resulting in 3.5 mg kg^{-1} for ICP-OES, 0.1 mg kg^{-1} for ICP-MS and 6.4 µg kg^{-1} for ICP-SF-MS.

In this work XRF was used as a semiquantitative technique obtaining values very close to the other techniques and to the CRM value used for this study, see Table 1. Contents of major soil constituents (Si, Al, Fe) were also determined by this technique.

Table 1

Measured uranium concentrations, measurement uncertainties (u) and certified value for CRM GBW07402 obtained by the methods tested

Analytical technique	U concentration in mg kg^{-1} (u)
Certified value	1.4 (0.3)
α-spec	1.8 (0.5)
ICP-OES	8.9 (1.1)
ICP-MS	1.3 (0.14)
ICP-SF-MS	1.7 (0.1)
XRF	2

Results and discussion

The CRM GBW07402 was used to validate the results of the techniques used in this work. The results are shown in Table 1. From these results and taking into account the high detection limit of ICP-OES for uranium (3.5 mg kg^{-1}), it was concluded that the procedure employed with ICP-OES detection is not adequate for the low levels of uranium in soil samples. The ICP-OES instrument used in this work for the measurement of uranium in topsoil has a radial reading configuration. In this procedure, the sample was not separated or purified and that resulted in matrix and spectral interferences in almost all wavelengths, giving values above the other techniques used, being iron and in less extent calcium the main interfering elements. Uranium and thorium can interfere in some nearby wavelengths (λ), as an example U at λ = 401.899 and Th at λ =

401.913 nm. Therefore, the results obtained for total uranium in soil samples by this technique were disregarded.

The major components and crystalline structures present in the samples were identified using XRF and XRD, respectively. The main crystalline phases found by XRD were quartz, plagioclases and potassium feldspar, whereas the major components were silicon (48–77% SiO_2), aluminum (11–25% Al_2O_3) and iron (2–8% Fe_2O_3).

Table 2 shows the results obtained for uranium in the samples by the different analytical techniques used in this study, and the uncertainties associated with each value estimated using the GUM procedure (Guide for the Expression of Measurement Uncertainty) [21]. The values obtained by XRF, although semi-quantitative, have been included in Table 2.

Table 2

Summary of results of U concentration, in mg kg^{-1}, measured in the 32 topsoil samples by the analytical techniques used in this work

Sample code	XRF	α-Spec	ICP-MS	ICP-SF-MS
M1	4	1.8 (0.4)	1.5 (0.14)	2.1 (0.1)
M2	3	2.2 (0.6)	1.6 (0.14)	2.2 (0.1)
M3	4	1.1 (0.3)	2.1 (0.14)	2.5 (0.1)
M4	6	1.1 (0.3)	2.0 (0.14)	2.4 (0.1)
M5	3	1.3 (0.6)	1.1 (0.14)	1.3 (0.1)
M6	3	2.9 (0.7)	2.4 (0.14)	2.8 (0.1)
M7	3	2.6 (0.6)	2.2 (0.14)	2.6 (0.1)
M8	2	2.0 (0.4)	1.0 (0.14)	1.3 (0.1)
M9	3	2.0 (0.4)	1.9 (0.14)	2.3 (0.1)
M10	6	2.3 (0.5)	1.9 (0.14)	2.3 (0.1)
M11	4	2.7 (0.6)	2.5 (0.14)	3.0 (0.1)
M12	4	2.7 (0.6)	2.6 (0.14)	3.0 (0.1)
M13	5	2.5 (0.6)	2.6 (0.14)	3.2 (0.1)

Measurement uncertainties are given in brackets as expanded uncertainties (k = 2)

Sample code	XRF	α-Spec	ICP-MS	ICP-SF-MS
M14	4	3.2 (0.7)	2.9 (0.14)	3.1 (0.1)
M15	3	2.3 (0.5)	2.0 (0.14)	2.5 (0.1)
M16	4	2.1 (0.5)	2.1 (0.14)	2.6 (0.1)
M17	3	1.4 (0.3)	1.4 (0.14)	1.9 (0.1)
M18	6	3.5 (0.8)	2.4 (0.14)	2.9 (0.1)
M19	3	1.5 (0.3)	1.3 (0.14)	1.8 (0.1)
M20	4	2.7 (0.6)	2.7 (0.14)	3.2 (0.1)
M21	3	1.0 (0.2)	1.0 (0.14)	1.4 (0.1)
M22	3	1.4 (0.4)	1.6 (0.14)	2.0 (0.1)
M23	3	2.4 (0.5)	3.1 (0.14)	3.8 (0.1)
M24	2	1.7 (0.4)	1.7 (0.14)	1.4 (0.1)
M25	4	2.2 (0.5)	2.5 (0.14)	2.9 (0.1)
M26	3	0.4 (0.1)	0.5 (0.14)	0.9 (0.1)
M27	4	1.9 (0.4)	2.0 (0.14)	2.0 (0.1)
M28	3	1.5 (0.3)	1.5 (0.14)	1.9 (0.1)
M29	4	2.9 (0.6)	2.5 (0.14)	3.0 (0.1)
M30	7	3.7 (0.8)	3.5 (0.14)	4.1 (0.1)
M31	6	2.4 (0.5)	2.2 (0.14)	2.7 (0.1)
M32	4	1.7 (0.4)	1.9 (0.14)	2.2 (0.1)
Measurement uncertainties are given in brackets as expanded uncertainties ($k = 2$)				

In order to assess if there are statistically significant differences among the results provided by the different techniques used for U determination, significance tests for matched pairs were applied. The parametric t test for paired samples was used, along with the nonparametric sign test and the Wilcoxon signed-rank test, which were also applied to avoid misinterpretations derived from lack of normality. Table 3 shows a posteriori p values of the comparisons performed.

Table 3

Summary of p-values obtained in hypothesis testing for comparison of analytical techniques for uranium determination

Comparative	t Test	Sign test	Wilcoxon signed rank test
XRF and α-spec	1.5×10^{-9}	7.1×10^{-8}	1.2×10^{-6}
XRF and ICP-MS	3.2×10^{-11}	3.0×10^{-7}	9.1×10^{-7}
XRF and ICP-SF-MS	5.7×10^{-9}	3.0×10^{-7}	1.8×10^{-6}
α-Spec and ICP-MS	0.4779	0.3268	0.2517
α-Spec and ICP-SF-MS	4.6×10^{-4}	1.3×10^{-3}	9.0×10^{-4}
ICP-MS and ICP-SF-MS	1.6×10^{-13}	4.9×10^{-7}	1.4×10^{-6}

There are no significant differences between α-spectrometry and ICP-MS (p value > 0.05). However, significant differences were found, at the 95% confidence level (p value < 0.05), between the results of α-spectrometry and ICP-SF-MS and between ICP-MS and ICP-SF-MS. The semi-quantitative XRF results were significantly higher with respect to the quantitative techniques. Statistical parameters shown in Table 4 such as kurtosis coefficient, skewness and p-value of the normality test demonstrate that the results of α-spectrometry, ICP-MS and ICP-SF-MS belong to normal (Gaussian) distributions, whereas XFR (and ICP-OES, not shown) provided non-normal distributions of results.

Table 4

Descriptive statistics of the U results

Statistical parameter	XRF	α-Spec	ICP-MS	ICP-SF-MS
Mean	3.84	2.07	2.01	2.42
Median	4.0	2.05	2.0	2.45
Standard deviation	1.22	0.76	0.66	0.73
Kurtosis	0.51	− 0.25	0.03	− 0.02
Skewness	1.00	0.12	− 0.07	0.05

Statistical parameter	XRF	α-Spec	ICP-MS	ICP-SF-MS
Normality test, p value	0.0003	0.9794	0.9964	0.8989
RSD (%)	31.8	36.9	32.9	30.3

The isobaric interferences that occur in ICP-MS, ^{238}Pu and ^{238}U or ^{241}Am and ^{241}Pu, cannot be resolved spectroscopically when these radioisotopes are found in the analyzed sample, even using the ICP-SF-MS. Again, these analytical problems could be overcome by using appropriate ICP-OES emission wavelengths for the analytes of interest because the isotopes mentioned emit light at different wavelengths. The high resolution (HR-) ICP-OES can provide isotopic information, improving the detection system of the instrument. However, as we have pointed out before, it is necessary to make a previous separation of the uranium to eliminate spectral and matrix interferences.

The dilution used (1:50) does not give good results when using ICP-OES for uranium quantification likely due to strong spectral and matrix interferences. For α-spectrometry measurements, radiochemical separation was performed using UTEVA$^{®}$ resins without vacuum chamber, all the stages were by gravity in order to allow a better retention and the washing of the resin, obtaining average chemical yield of 68% ($u = 5.9$, $k = 1$) for the ^{232}U tracer. Figure 3 shows a typical spectrum obtained in α-spectrometry of the natural isotopes of uranium (^{nat}U) in secular equilibrium and ^{232}U used as a tracer, with good resolution, indicating good radiochemical separation and low auto-absorption of alpha particles.

Fig. 3

Alpha spectrum for ^{nat}U of the one typical sample, showing the ^{232}U used as tracer
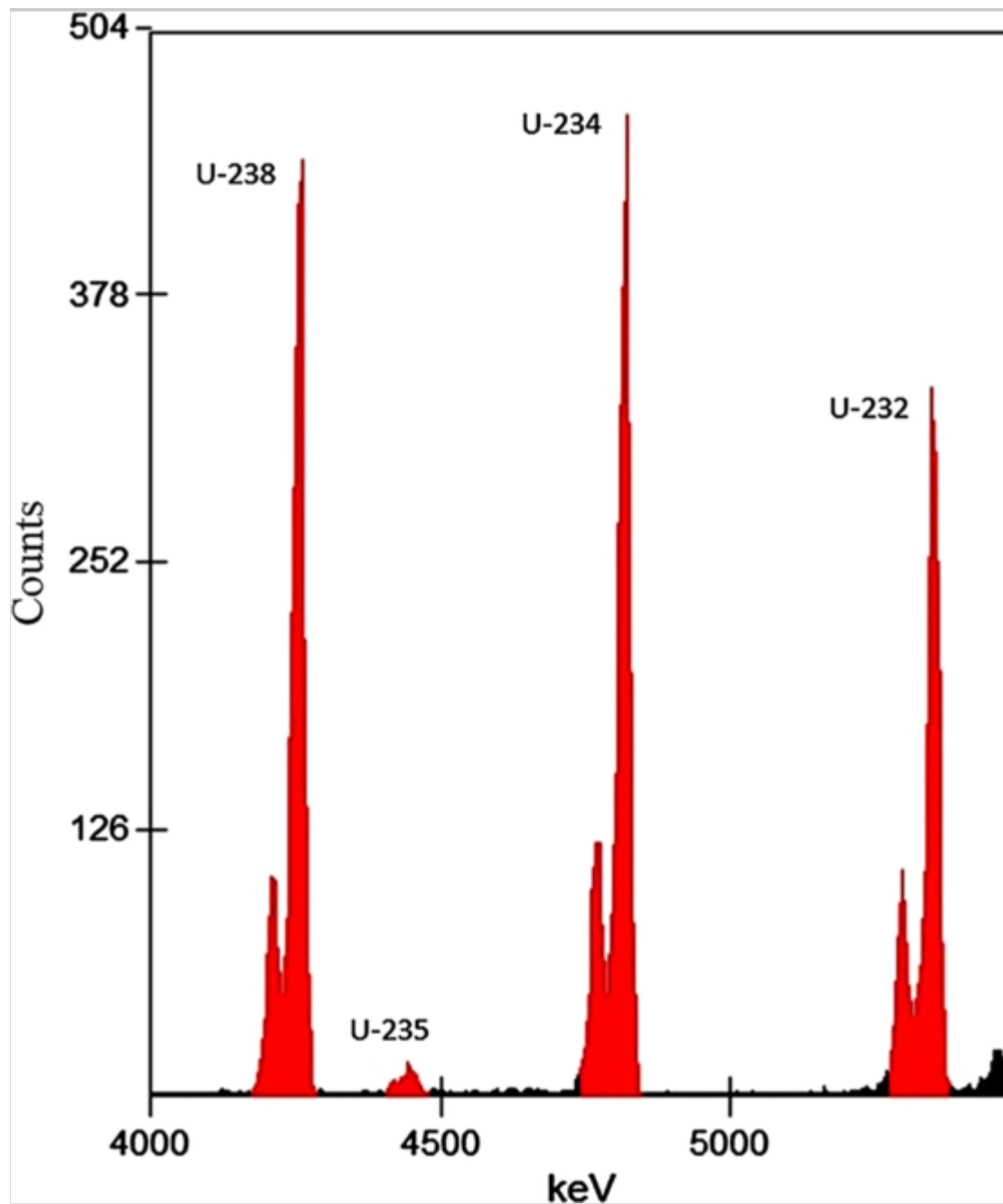
The α-spectrometry resolves the problem of precise isotope determination, but with the disadvantage of hard chemical preparation and long measurement times. α-spectrometry is a reliable, specific and accurate technique for determination of isotopic composition of natural uranium in samples with low and very low contents of this element.

Table 4 shows some statistical parameters of the distributions of uranium concentration in the soils measured by the different techniques. The variability of uranium in the sampled area was close to 30% (expressed as relative standard

deviation, % RSD), which can be considered low considering the low average concentration and the narrow concentration range. Therefore, the occurrence of ^{238}U in pristine topsoil of Zacatecas state can be interpreted as highly homogeneous.

Contamination of topsoil by a given toxic element can be assessed using different factors or indexes such as geo-accumulation index, I_{geo}, and enrichment factor, EF.

The geo-accumulation index of uranium in topsoil of Zacatecas state has been calculated as [22, 23, 24]:

$$I_{geo} = log_2 \left(\frac{C_U}{1.5 \times B_U} \right) \qquad 2$$

where C_U is the concentration of uranium in the sample measured by α-spectrometry, B_U is the background concentration of uranium and the factor 1.5 is introduced to minimize the effect of lithological variations in the soils that affect locally the background concentration. In this study, the average uranium concentration in the upper earth crust, 2.8 mg kg^{-1}, was used as background value [2, 3, 4] since the background level of uranium for undisturbed topsoil of Zacatecas state is not available yet.

According to the geo-accumulation index calculated the soil can be classified as [22]: < 0 practically unpolluted; 0–1 unpolluted to moderately polluted; 1–2 moderately polluted; 2–3 moderately to strongly polluted; 3–4 strongly polluted; 4–5 strong to very strongly polluted; and > 5 very strongly polluted. The values of the geo-accumulation index obtained for the 32 soil samples ranged from − 3.4 (sample M26) to − 0.2 (sample M30), thus demonstrating that topsoil in the studied area is not polluted by uranium, being the levels of this element similar to the average concentration in the earth crust.

An alternative index to evaluate soil contamination by a metal is the use of the enrichment factor, which reduces the bias caused by grain size and mineralogy by using normalized data [23, 25, 26]. Enrichment factor was calculated as:

$$EF = \frac{\left(\frac{C_U}{C_R}\right)_{sample}}{\left(\frac{C_U}{C_R}\right)_{background}}$$

3

The concentration ratio of uranium and a reference (normalizing) element was calculated in the soil sample and compared with the ratio calculated from background concentrations. Background levels of elements used were average estimations in the upper continental crust [2, 3, 4]. Conservative elements such as Al or Fe have been frequently used as reference element for geochemical normalization as their variability in the upper crust is low [27]. In this work Al variability (23% RSD) was lower than that of Fe (39%) and therefore Al concentration, determined by XRF, was used as normalizing element. The scale described by Sutherland [23] was used to evaluate soil pollution by uranium: EF < 2, depletion to minimal enrichment (no or minimal pollution); EF 2–5, moderate enrichment; EF 5–20, significant enrichment; EF 20–40, very highly enriched; EF > 40, extremely high enrichment.

EF values ranging from 0.1 (sample M26) to 3.8 (sample M18) were obtained, this last sample being the only one showing EF value > 2. It can thus be concluded that uranium concentration in undisturbed topsoil from the investigated area of Zacatecas state does not exceed the average crustal abundance. The mean uranium concentration found in this study by α-spectrometry, 2.1 (1.6, k = 2) mg kg^{-1}, can be then proposed as the background value for this element for the investigated area.

Table 5 displays values of uranium found in soil from other regions and countries obtained from the UNSCEAR 2000 report [28], using spectrometric techniques. Values from other referenced published works are also included in this list.

Table 5

Natural uranium contents in soil. Data not referenced are from UNSCEAR 2000

Region/country	^{238}U (mg kg^{-1})		Region/country	^{238}U (mg kg^{-1})	
	Mean	Range		Mean	Range
[a]Range and mean value found in this work by α-spectrometry					

Region/country	^{238}U (mg kg^{-1})		Region/country	^{238}U (mg kg^{-1})	
	Mean	Range		Mean	Range
Algeria	2.4	0.2–8.9	Germany		0.9–26.6
Egypt	3.0	0.5–9.7	Ireland	3.0	0.6–9.7
Port Hope Harbor, Canada [29]		0.24–93.6	Netherlands		0.4–4.3
Costa Rica	3.7	0.9–10.5	Switzerland	3.2	0.8–12.1
Aldama, Chihuahua, Mexico [30]	2.0	1.7–18.1	Switzerland [31]	2.3	
Zacatecas-Guadalupe urban area, México [32	1.8	0.8–3.0	United Kingdom		0.2–26.6
United States	2.8	0.3–11.3	Bulgaria	3.2	0.6–15.3
Chao Phraya, Thailand [33]		1.1–6.1	Hungary	2.3	1.0–5.3
Recife, Brazil [10]	150.0	30–500	Poland	2.1	0.4–9.7
Tongliao, China [34]	2.2		Romania	2.6	0.6–4.8
China	2.7	0.2–55.6	Russian Federation	1.5	0.0–5.4
Hong Kong SAR	6.8	2.0–10.5	Slovakia	2.6	1.2–10.5
Mongolia [35]		0.8–2.5	Albania	1.9	0.5–7.7
India	2.3	0.6–6.5	Croatia	8.9	6.7–14.5
Japan	2.3	0.2–4.8	East Anatolian, Turkey [36]		1–20.2
Kazakhstan	3.0	1.0–9.7	Salamanca, Spain (baseline) [37]	62.0	
Malaysia	5.3	4.0–6.9	Greece	2.0	0.1–19.4
Thailand	9.2	0.2–29.8	Portugal	4.0	2.1–6.6
Armenia	3.7	1.6–6.3	Urgeiriça, Portugal [38]	6.7	3.52–31.24
Syrian Arab Republic	1.9	0.8–5.2	Cunha Baixa, Portugal [38]	1.2	

[a]Range and mean value found in this work by α-spectrometry

| Region/country | ^{238}U (mg kg^{-1}) | | Region/country | ^{238}U (mg kg^{-1}) | |
	Mean	Range		Mean	Range
Lithuania	1.3	0.2–2.4	Bure, France (Forest) [39]	2.5	
Norway	4.0		Zacatecas, Mexico[a]	2.1	0.4–3.7
[a]Range and mean value found in this work by α-spectrometry					

This table shows the high values reported so far for soil in Recife, Brazil [10] in sedimentary rock and in Salamanca, Spain [37] in the vicinity of an uranium mining site. It is interesting to highlight the uranium concentrations reported by Mireles et al. [32] in the "urban zone" of Zacatecas-Guadalupe (Mexico) using instrumental neutron activation analysis (INAA). The results of Mireles et al. are very similar to the concentrations found in undisturbed topsoil of Zacatecas in our study using α-spectrometry. However, the mean U concentration and range of values in our study are slightly larger. Bigalke et al. [31], Slobodan et al. [29] and Santos-Francés et al. [37] performed their measurements with the ICP-MS analytical technique, while Haribala et al. [34], Hirose et al. [35], Baykara et al. [36], Santawamaitre et al. [33] and Colmenero-Sujo et al. [30] used gamma-spectroscopy to make their measurements. On the other hand, Pourcelot et al. [39] used Thermal Ionization Mass Spectrometry (TIMS).

The comparison of the results in this study with the average crustal abundance of total uranium estimated by different authors and with uranium concentrations found experimentally in different locations worldwide, indicates that the undisturbed (pristine) topsoil of Zacatecas State area is not enriched with this chemotoxic and radiotoxic element, and the uranium concentration found in this study can be used as baseline or background value for the region.

Conclusions

The average ^{238}U concentration found in the topsoil of the State of Zacatecas by ICP-MS and α-spectrometry is consistent with the reported concentrations at the surface of the Earth's crust (Table 5) and does not exceed the average crustal abundance, resulting in no evidence of alterations in surface concentrations in these areas for this isotope, as shown by the values found for the geo-

accumulation index, I_{geo}, and the enrichment factor, EF. The results indicate that ^{238}U has a great degree of homogeneity between *Please, change between by within* these sampled areas, allowing the assignment of 2.1 (1.6 *Please, insert ± symbol before the value 1.6* , k = 2) mg kg^{-1}, as the background uranium concentration of the area.

The most adequate analytical techniques to quantify ^{238}U in topsoil with the analytical procedures used in this work are the *Please, remove the article* α-spectrometry and ICP-MS, which also provide information on the isotope ratios present in the sample.

It can be concluded that to accurately measure uranium in topsoil extracts by ICP-OES it is advisable to carry out prior sample separation, purification and preconcentration. It is important to eliminate elements such as iron and calcium from the solution and to eliminate the main spectral and matrix interferences of uranium to achieve reliable results.

The results obtained with ICP-MS are more reliable than those of ICP-SF-MS when using a dilution ratio 1:50. By not using isotopic tracers in these techniques the cost of the analysis is lower. It is demonstrated that using an ICP-MS with an octupole reaction cell, ^{238}U can be measured reliably enough without any prior purification and/or preconcentration procedure, in a much lower time and cost than α-spectrometry.

Finally, it has been demonstrated that cross-validation of two or more independent analytical procedures helps identifying the potential limitations of a specific analytical method intended to analyze a selected element/isotope. An agreement of results obtained by at least two independent analytical methods, in turn, essentially improves the credibility of the analytical data acquired.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Acknowledgements

(Spain), the Environmental Radioactivity and Radiological Surveillance Unit of the Center for Energy, Environment and Technology Research (CIEMAT, Spain), the Carolina Foundation (Spain), the Ministry of Foreign Affairs of Mexico and the Autonomous University of Zacatecas (Mexico), for their collaboration in carrying out this work.

 Complaince Switch for "Compliance"   **with ethical statement**

Conflict of interest   The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

References

1. Vandenhove H, Hurtgen C, Payne TE (2010) In: Atwood DA (ed) Radionuclides in the environment. Wiley, New York

2. Taylor SR, McLennan SM (1995) The geochemical evolution of the continental crust. Rev Geophys 33:241–265. https://doi.org/10.1029/95RG00262

3. McLennan SM (2001) Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochem Geophys Geosyst 2:2000GC000109. https://doi.org/10.1029/2000GC000109

4. Rudnick RL, Gao S (2014) Composition of the continental crust. In: Turekian K, Holland H (eds) Treatise on geochemistry, vol 4, 2nd edn. Elsevier, Amsterdam. https://doi.org/10.1016/B978-0-08-095975-7.00301-6

5. Santos JS, Teixeira LSG, Araújo RGO, Fernandes AP, Korn MGA, Ferreira SLC (2011) Optimization of the operating conditions using factorial designs for determination of uranium by inductively coupled plasma optical emission spectrometry. Microchem J 97:113–117. https://doi.org/10.1016/j.microc.2010.08.002

6. WHO (2011) Guidelines for drinking-water quality. Guidelines for drinking-water quality, 4th edn. World Health Organization: Geneva, Switzerland. http://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151_eng.pdf;jsessionid=708454E890F22E255EA3D95BA676BC72?s Accessed 09 Jan 2019

7. USDOHAHS (2013) Toxicological profile for uranium. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, USA. https://www.atsdr.cdc.gov/ToxProfiles/tp150.pdf. Accessed 09 Jan 2019

8. Betti M, Aldave de las Heras L (2004) Glow discharge spectrometry for the characterization of nuclear and radioactively contaminated environmental samples. Spectrochim Acta B 59:1359–1376. https://doi.org/10.1016/j.sab.2004.07.006

9. Maher K, Bargar JR, Brown GE (2013) Environmental speciation of actinides. Inorg Chem 52:3510–3532. https://doi.org/10.1021/ic301686d

10. UNSCEAR (2017) Sources, effects and risks of ionizing radiation, UNSCEAR 2016 report to the General Assembly, with scientific annexes. United Nations Scientific Committee on the Effects of Atomic Radiation, New York. http://www.unscear.org/docs/publications/2016/UNSCEAR_2016_Report-CORR.pdf. Accessed 09 Jan 2019

11. Santos JS, Teixeira LSG, dos Santos WNL, Lemos VA, Godoy JM, Ferreira SLC (2010) Uranium determination using atomic spectrometric techniques: an overview. Anal Chim Acta 674:143–156. https://doi.org/10.1016/j.aca.2010.06.010

12. Doyle JL, Kuhn K, Byerly B, Colletti L, Fulwyler J, Garduno K, Keller R, Lujan E, Martinez A, Myers S, Porterfield D, Spencer K, Stanley F, Townsend L, Thomas M, Walker L, Xu N, Tandon L (2016) Nuclear forensic analysis of a non-traditional actinide sample. Talanta 159:200–207. https://doi.org/10.1016/j.talanta.2016.06.028

13. Boryło A (2013) Determination of uranium isotopes in environmental

samples. J Radioanal Nucl Chem 295:621–631. https://doi.org/10.1007/s10967-012-1900-1

14. Karpas Z (2015) Analytical chemistry of uranium: environmental, forensic, nuclear and toxicological applications, 1st edn. CRC Press, Boca Raton

15. Becker JS (2005) Inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation ICP-MS for isotope analysis of long-lived radionuclides. Int J Mass Spectrom 242:183–195. https://doi.org/10.1016/j.ijms.2004.11.009

16. INAFED (2018) Instituto Nacional para el Federalismo y el Desarrollo Municipal. http://siglo.inafed.gob.mx/enciclopedia/EMM32zacatecas/mediofisico.html. Accessed 23 Jul 2018 (**in Spanish**)

17. Eichrom Technologies LLC (2014) Uranium in soil. Analytical procedure ACS07, rev. 1.6. https://www.eichrom.com/wp-content/uploads/2018/02/acs07-16_uranium-in-soil.pdf. Accessed 10 Jan 2019

18. Eichrom Technologies LLC (2014) Analytical procedure SPA02, rev. 1.0. Electrodeposition of actinides (Source preparation). https://www.eichrom.com/wp-content/uploads/2018/02/spa02-10_electrodeposition.pdf. Accessed 10 Jan 2019

19. Meija J, Coplen TB, Berglund M, Brand WA, De Bièvre P, Gröning M, Holden NE, Irrgeher J, Loss RD, Walczyk T, Prohaska T (2016) Isotopic compositions of the elements 2013 (IUPAC technical report). Pure Appl Chem 88:293–306. https://doi.org/10.1515/pac-2015-0503

20. ISO 11929:2010 Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation—fundamentals and application. International Organization for Standardization, Technical Committee ISO/TC 85/SC 2 Radiological protection

21. JCGM 100:2008 GUM 1995 with minor corrections (2008) Evaluation of

measurement data—guide to the expression of uncertainty in measurement. Joint Committee for Guides in Metrology (JCGM/WG 1)

22. Muller G (1969) Index of geoaccumulation in sediments of the Rhine River. J Geol 2:108–118

23. Sutherland RA (2000) Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ Geol 39:611–627. https://doi.org/10.1007/s002540050473

24. Abrahim GMS, Parker RJ (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ Monit Assess 136:227–238. https://doi.org/10.1007/s10661-007-9678-2

25. Buat-Menard P, Chesselet R (1979) Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. Earth Planet Sci Lett 42:399–411. https://doi.org/10.1016/0012-821X(79)90049-9

26. Lee PK, Touray JC, Baillif P, Ildefonse JP (1997) Heavy metal contamination of settling particles in a retention pond along the A-71 motorway in Sologne, France. Sci Total Environ 201:1–15. https://doi.org/10.1016/S0048-9697(97)84048-X

27. Wang J, Liu G, Lu L, Zhang J, Liu H (2015) Geochemical normalization and assessment of heavy metals (Cu, Pb, Zn, and Ni) in sediments from the Huaihe River, Anhui, China. CATENA 129:30–38. https://doi.org/10.1016/j.catena.2015.02.008

28. UNSCEAR (2000) Sources and effects of ionizing radiation, UNSCEAR 2000 Report to the General Assembly, vol. I. United Nations Scientific Committee on the Effects of Atomic Radiation, New York. http://www.unscear.org/unscear/en/publications/2000_1.html. Accessed 09 Jan 2019

29. Jovanovic SV, Pan P, Wong L (2012) Bioaccessibility of uranium in soil samples from Port Hope, Ontario, Canada. Environ Sci Technol

46:9012–9018. https://doi.org/10.1021/es3021217

30. Colmenero Sujo L, Montero Cabrera ME, Villalba L, Rentería Villalobos M, Torres Moye E, García León M, García-Tenorio R, Mireles García F, Herrera Peraza EF, Sánchez Aroche D (2004) Uranium-238 and thorium-232 series concentrations in soil, radon-222 indoor and drinking water concentrations and dose assessment in the city of Aldama, Chihuahua, Mexico. J Environ Radioact 77:205–219. https://doi.org/10.1016/j.jenvrad.2004.03.008

31. Bigalke M, Ulrich A, Rehmus A, Keller A (2017) Accumulation of cadmium and uranium in arable soils in Switzerland. Environ Pollut 221:85–93. https://doi.org/10.1016/j.envpol.2016.11.035

32. Mireles F, Davila JI, Pinedo JL, Reyes E, Speakman RJ, Glascock MD (2012) Assessing urban soil pollution in the cities of Zacatecas and Guadalupe, Mexico by instrumental neutron activation analysis. Microchem J 103:158–164. https://doi.org/10.1016/j.microc.2012.02.009

33. Santawamaitre T, Malain D, Al-Sulaiti HA, Bradley DA, Matthews MC, Regan PH (2014) Determination of ^{238}U, ^{232}Th and ^{40}K activity concentrations in riverbank soil along the Chao Phraya river basin in Thailand. J Environ Radioact 138:80–86. https://doi.org/10.1016/j.jenvrad.2014.07.017

34. Haribala B, Hu C, Wang G, Xu X, Zhang S (2016) Assessment of radioactive materials and heavy metals in the surface soil around uranium mining area of Tongliao, China. Ecotoxicol Environ Safe 130:185–192. https://doi.org/10.1016/j.ecoenv.2016.04.002

35. Hirose K, Kikawada Y, Igarashi Y, Fujiwara H, Jugder D, Matsumoto Y, Oi T, Nomura M (2017) Plutonium, ^{137}Cs and uranium isotopes in Mongolian surface soils. J Environ Radioact 166:97–103. https://doi.org/10.1016/j.jenvrad.2016.01.007

36. Baykara O, Doğru M (2009) Determination of terrestrial gamma, ^{238}U, ^{232}Th and ^{40}K in soil along fracture zones. Radiat Meas 44:116–121.

https://doi.org/10.1016/j.radmeas.2008.10.001

37. Santos-Francés F, Gil Pacheco E, Martínez-Graña A, Alonso Rojo P, Avila Zarza C, García Sánchez A (2018) Concentration of uranium in the soils of the west of Spain. Environ Pollut 236:1–11. https://doi.org/10.1016/j.envpol.2018.01.038

38. Abreu MM, Magalhães MCF (2017) Assessment and reclamation of soils from uranium mining areas: case studies from Portugal. In: Bech J, Bini C, Pashkevich M (eds) Assessment, restoration and reclamation of mining influenced soils, 1st edn. Elsevier, Amsterdam

39. Pourcelot L, Calmon P, Chabaux F, Conil S, Galy C, Granet M, Lascar E, Leclerc E, Perrone T, Redon PO, Rihs S (2017) Comparative repartition of ^{226}Ra, ^{238}U, ^{234}U, ^{230}Th and ^{232}Th in a variety of soils sampled from geological formations in the NE of the Basin of Paris. Appl Geochem 84:314–324. https://doi.org/10.1016/j.apgeochem.2017.07.017