Determination of Uranium in Environmental Samples from the Nile Delta and the Adjacent Regions of Egypt Using Laser Fluorimetry

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خلاصة

تم تقدير التركيز الكلي لليورانيوم في عينات تربة ونبات أخذت من أماكن مختلفة من دلتا النيل شرق وغرب الدلتا ومدن قناة السويس والاسكندرية بجمهورية مصر العربية.
تم استخلاص اليورانيوم من العينات المذابة باستخدام المذيب العضوي ميثيل ايزوبيوثيل كيتون لتعيين التركيز الكلي لليورانيوم باستخدام فلورومتري أشعة الليزر وقد تم تقدير تركيز اليورانيوم ـ راديوم لنفس العينات باستخدام مطياف الجرمانيوم عالي النقاوة وقد وجد أن تركيز اليورانيوم يتراوح بين 0.6 ـ 4.4 بيكروجرام/ جرام للتربة ويتراوح بين 0.032 ـ 0.17 بيكروجرام للنبات.

Abstract

Total uranium content was determined in soil and plant samples taken from various areas in the Nile Delta. Samples from east and west of the Delta, the Suez canal's cities and from Alexandria region were analyzed using laser fluorimentry (LF). Uranium was extracted from digested ashed samples with methyl-isobutyl ketone (MIBK) and measured using laser fluorimeter. The radium content of the same soil samples was determined using gamma spectrometry (GS). The uranium content of plant samples was determined using (LF), since it has a detection limit lower than that of (GS). The uranium content varied between 0.6-4.4 μg/g and 0.032-0.17 μg/g for soil and plant samples respectively.

Introduction

Radiation exposure resulting from natural radiation has received a wide attention. Current estimates show that 48% of the annual effective dose to the world population is due to natural radiation; 57% of that exposure is attributed to Ra-226, a member of the U-238 decay series (UNSCER 1989, Cla 1989).

An environmental study was initiated by the CLERMIT* (Central Laboratory for Environmental Radiation Measurements Inter-comparison and Training) of the Atomic Energy Authority of Egypt for the distribution of natural radionuclides in soil and plant samples using gamma spectrometry (Shawky 1991). In this work, the uranium concentration in the same samples was determined using laser fluorimetry technique (Ghods et al 1990). This was undertaken to check the secular equilibrium between uranium and its gamma emitting decay daughters within the soil samples. Laser fluorimetry is simple accurate and the detection limit is low enough to measure biological samples with low uranium content (Veselsky 1985). The limit of detection in water is around 0,05 ng/g and the precision is about 15% at the 1 ng/g level (Veselsky 1988).

The differences between uranium concentration and Ra-226 in most of the soil samples indicate the absence of a secular equilibrium among the uranium decay series.

Experimental

Sample collection:

The region of interest was divided into nine squares each about 50 km wide as shown in Fig.1. Six to ten samples were collected from each square. The distance between neighboring samples ranged from 10 -20 km. Some squares contained bodies of water and prairie from which no samples could be obtained.

Sampling was carried out using the corer method (EPA 1977), where a corer of 10.5 cm diameter and depth of 25 cm was used (ASTM 1983). As the sampling sites were randomly selected in the cultivated lands of the Nile Delta, the sites were fertilized with phosphate, potassium and other fertilizers which contain trace concentration of uranium.

These sites experience regular flood irrigation with the Nile river water, and seasonal plowing.

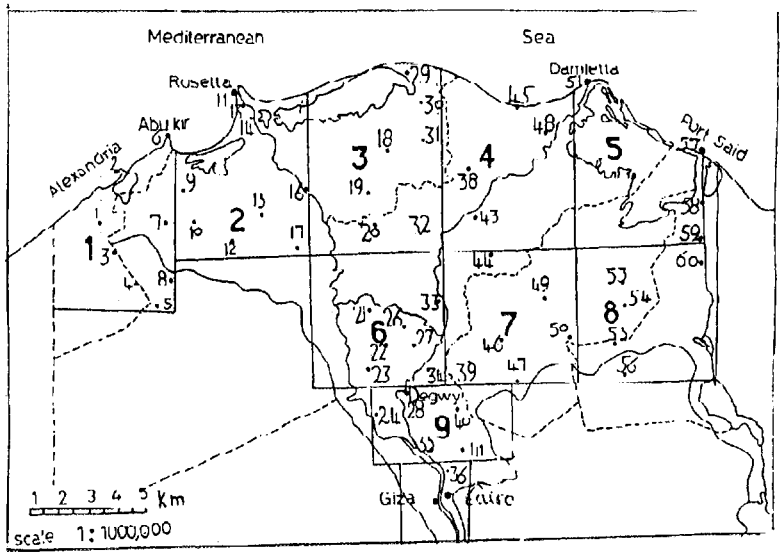

Fig. (1) : Location of soil and plant samples all over the Nile Delta and the north coast.

Sample preparation and measurements for laser fluorimetry:

One gram samples were dried and ashed at 600 C for 3 hr. Sub-samples from the ash were analyzed according to the procedure developed by Ghods et al, (1990). It should be mentioned that the quenching effect in (LF) caused by interfering elements such as Fe, Mn Cu, Ni, and "organic matter" was eliminated by either dilution or by using an internal uranium standard spike and detecting the reduction in extraction recovery. The uranium concentration in (ng/n) was calculated from the following formula [Nguyen and Veselsky 1988 and Veselsky 1981]

$$U(ng/g) = \left(\frac{D_1}{D_2 - D_1}\right)\left(\frac{V_1}{V_2}\right)C$$

Where:

D_1 is the instrument reading due to the sample only,

D_2 is the instrument reading due to sample plus uranium standard (Spike),

V_1 The volume of the added standard in (ml),

V_2 The volume of sample in (ml), and

C The concentration of uranium standard solution in (ng/g).

For plant samples, two parallel samples each of 1 g were prepared, one of them was spiked with 1 mg uranium standard (1 mg/ml) which was used to determine a concentration factor for quenching (Veselsky 1981) as follows:

$$U(ng/g) = \frac{C}{B}.A$$

Where:

C the concentration of uranium in the standard solution used for spiking ng/g

B the concentration of uranium standard found in the sample,

A the uranium content of the sample (ng/g),

U the uranium concentration in (ng/g).

Laser fluorimetry for uranium analysis:

The measurements are performed by a laser fluorimeter (Sintrex UA-3) and are based on the fluorescence of an uranyl complex formed by the addition of a buffered inorganic complexing reagent FLURAN (Sodium pyrophosphate, sodium dihyrogen phosphate) to the sample during analysis. Analysis with a sensitivity of about 0,05 ng/g of uranium can be made without preconcentration or treatment of the sample even in the presence of many potentially interfering species.

Not like conventional fluorimetry the source of excitation here is UV light provided by a nitrogen laser tube.

Quality Control

Several certified reference material were analyzed using the procedure outlined above. The results are listed in Table 1.

Table (1): Uranium content in some reference materials

Material	Certified value µg/g	This study µg/g	Other labs µg/g
Urban particulate NIST 1648	5.5 ± 0.1	5.4 ± 0.2	-----
Pine needles NIST 1575	0.020 ± 0.004	0.022 ± 0.001	0.014 ± 0.006
Spruce-Needles, CLV2	3.6	3.66 ± 0.04	---------

They are in good agreement with those reported by other laboratories and the certified uranium content of the corresponding materials.

Sample preparation and measurement for gamma spectroscopy:

The collected samples were weighed individually, air dried for 4 d, pulverized, homogenized and sieved to pass through 2 mm mesh.

The meshed soil samples were transferred to marinelli beakers (250, 500, 750, or 1000 ml capacity) for gamma analysis. Each soil sample was weighed and carefully sealed for 4 weeks to reach secular equilibrium between Ra-226 and its respective progeny. The activity of Bi-214 and Pb-214 in equilibrium with their parents was assumed to represent the U238 activity.

Experimental set-up:

Spectra for different soil samples were measured using a high resolution gamma-ray spectrometer.

The spectrometer was based on an IGC 3019 coaxial hyper-pure germanium detector with 133 cc effective volume.The detector has a photopeak relative efficiency of about 30 % and an energy resolution of 1.95 KeV FWHM for the 1332 KeV gamma transition of Co-60. To reduce the gamma ray background, the detector was shielded by a cylindrical lead shield with a fixed bottom and a moving cover. The

lead shield contained two inner cocentric cylinders of copper and cadmium.

The gamma transitions of energies 351.9 keV (Pb-214), 609.3 keV, 1120.3 keV, 1238.1 keV and 1764.4 keV (Bi-214) were used to determine the concentrations of the Ra eu.

The relative effeciency calibration was carried out using Ra-226 source for energy from 186 keV to 2500 keV. These relative efficiencies were normalized using water. Three different concentrations for amarinelli beaker size were used in the measurements (11). The accumulation time for each sample ranged from 6-10 h.

Results

Table 2 shows a comparison between uranium and Ra-226 content of soil samples obtained by (LF) and (GS) and the difference percentage on the average between them expressed as Diff. (%).

These differences were expected since (LF) based on the detection of Ra-226 and its progeny and referred these values to U-238 (Ra eU).

The results were classified into 4 groups as follows:

Group 1: The coastal areas at the north of the Delta shows an average uranium content of 1.5 + 0.5 mg/g (18.6 + 6.2 Bq/kg).

Some exceptions were found at locations number 11,12 (Rosetta) and 45 (Ras El-barr) showing average uranium content of 7.5 + 2.2 mg/g (93 + 27 Bq/kg).

Group 2: The area between the north coast and the core of the Delta shows an average uranium content of 3.4 + 0.7 mg/g (42+9Bq/kg).

Group 3: The core of the Delta shows average uranium content of 2.1 + 0.5 mg/g (26 + 6 Bq/kg).

Group 4: The adjacent areas east and west the Delta show the lowest uranium content with an average of 1.2 + 0.2 mg/g (15 + 2.5 Bq/kg).

Some areas identified by locations number 1, 47 and 53 were found to have elevated levels of uranium.

Table 3 shows the uranium content of plant samples using (LF),which ranged between 32 up to 167 ng/g (0.4 up to 2 Bq/kg) of dry weight.

1) Beans **2) Wheat** **3) Garlic**

The rest of plant samples are grass.

Table (2): Uranium content of soil samples from different locations in the Nile Delta using laser fluorimetry (L.F) and gamma spectroscopy (G.S)

Table (2): Uranium content of soil samples from different locations in the Nile Delta using laser fluorimetry (L.F) and gamma spectroscopy (G.S)

Sample No.	U (μg/g) LF	U (μg/g) GS	Diff. (%)	Sample No.	U (μg/g) LF	U (μg/g) GS	Diff. (%)
1	3.0	2.2	30	31	2.9	1.6	58
2	4.8	0.8	143	32	2.7	1.4	63
3	1.0	1.1	10	33	2.0	1.0	67
4	1.6	1.0	46	34	1.8	1.6	12
5	2.4	0.8	100	35	4.9	1.1	127
6	1.6	0.9	56	36	2.1	1.4	40
7	2.2	1.2	59	37	3.0	1.6	61
8	2.4	0.9	96	38	2.9	1.7	52
9	1.2	1.4	15	39	3.3	1.4	81
10	2.8	1.3	73	40	1.0	1.5	40
11	9.6	5.1	61	41	3.0	1.0	100
12	2.2	1.3	51	42	1.7	0.5	109
13	0.9	1.2	29	43	1.9	1.7	11
14	4.4	1.3	109	44	2.0	1.3	42
15	2.6	2.1	21	45	0.6	0.4	40
16	2.4	1.4	53	46	2.1	0.8	90
17	2.7	1.7	45	47	2.0	1.6	22
18	2.3	1.4	49	48	1.1	0.7	44
19	2.0	1.5	29	49	3.3	1.2	93
20	2.2	1.5	38	50	1.6	1.2	29
21	3.2	1.4	78	51	2.3	2.5	8
22	2.6	0.8	105	52	1.2	0.7	53
23	1.3	1.3	0	53	2.3	0.5	128
24	2.0	1.6	22	54	1.5	1.1	31
25	2.3	1.4	49	55	1.3	0.4	106
26	2.3	1.6	36	56	1.8	1.1	48
27	1.8	1.4	25	57	0.5	0.4	22
28	1.3	2.3	56	58	2.0	1.1	58
29	2.9	0.8	114	59	1.0	0.8	22
30	2.1	1.0	71	60	1.4	0.7	67

Table (3): Uranium content of plant samples and soil samples from the same sampling site

Sample No.	U. in plant (ng/g)	U. in soil (ng/g)
9	97	1200
151	32	2600
17	60	2700
19	48	2000
23	102	1300
24	47	2000
26	92	2300
272	30	1800
32	132	2700
36	84	2100
40	80	1000
432	43	1900
47	47	2000
48	85	1100
49	167	3300
60	109	1400

Discussion

The Delta province was a site of marine sedimentation throughout its geological age. Carbonate rocks are the most abundant in north Sinai and the northern part of the western desert. The surface layer of most of the Delta is cultivated land and can be classified as deposits formed through sedimentation processes by the Nile river [Soliman and Faris 1963].

According to the morphological features of soil sections, the Delta area could be roughly divided into four main areas:

i) The area at the north coast considered as coastal marine sand deposits and composed of medium-sized grains with very little radioactivity [NCRP 1975].

The exceptional areas with enhanced uranium content can be identified by dark coarse sand. Usually dark sand contains accessory minerals as monazite, zirconium, thorite, granite,rutile and other heavy minerals. Grains of monazite contain high concentrations of thorium [Frondel 1956] and those of zirconium contain high concentrations of uranium and thorium [Larsen et al 1956].

ii) The area in between the core of the Delta and the north coast considered as alluvio - marine deposits.

It is formed mainly of heavy dark brown clay to muddy clay rich in clay minerals and the radionuclides of natural decay series (which decay to a stable isotope of lead through a sequence of radionuclides e.g U-232 decay series) [NCRP 1975].

iii) The area at the core of the Delta is mainly composed of alluvial deposits recently constituted and composed of fine grains of clay, silt or mud which usually contain at least 35% clay minerals and is capable of adsorbing the series radionuclides [Koster 1988].

iv) The areas east and west of the Delta considered as desert plain deposits. This soil could be yellowish sand, calcareous sand or muddy sand and contains high concentration of calcium carbonate up to 16% and low level of radioactivity. Uranium is adsorbed by clay, carbon, aluminum, manganese and silica. This precipitation or adsorption of uranium is inhibited in the presence of the carbonate ion, which account for this low uranium concentration [Bell 1954]. The areas with elevated uranium content are newly developed for cultivation where different types of fertilizers are added extensively to the soil. The phosphate fertilizers contain natural radionuclides in specific activities appreciable exceeding the average specific activity found in common soils, thus possibly contributing to the total content of soil radioactivity [Pfister and Pauly 1979] . As the uranium content of plant samples is very low, so it could not be measured using (GS) and the reported values are due to (LF).

Conclusion

The uranium content given by (LF) is not always matching the radium content given by (GS). The (GS) study based on the measurement of radon, daughters and referred these values to the uranium content of the samples assuming the presence of secular equilibrium within the uranium series.

Muktahr et al, (1991), found a good correlation between uranium and radium-226 content in rock samples with a difference on average of about 11 %. However, it is known that all decay products of U-238 are in radioactive equilibrium with their precursors if not subjected to chemical or physical separation [Schuttelkof 1981]. This is valid only in case of source rock because uranium can be leached from its material,

the intermediate decay products have different chemical properties and half lives long enough to permit significant separation from their precursors and the gaseous members can be lost. The milling process may have influences on the emanation of the gaseous decay products and the equilibrium is distorted. It was also found that the concentration of the uranium daughter Pb-210 deviates towards higher and lower values as compared with Ra-226 concentration [UNSCEAR 1986]. The same applies when Pb-210 and Po-210 are compared with each other.

Parts of these finding can be explained by different exhalations of Rn-222 from different types of soil. These deviations may indicate that radium has its own geochemical pathways which are both function of its ground parents and which are independent of them. on the other hand the investigated area is cultivated land which experience regular flood irrigation, plowing and fertilization which could disturb the soil radioactivity. This may explain the differences between uranium and its decay daughters which ranged from 9.5% up to unity as shown in table 2.

Plants uptake of radionuclides from soils is affected by numerous processes and factors. Because of the multiplicity of factors, plant-to-soil concentration ratios exhibit considerable variation. Among these factors are; the physicochemical form of the radionuclide, plant species, soil characteristics, fertilizers and agriculture chemicals [Till et al 1983].

The soil acidity (expressed as pH)can affect the availability of elements from soil. In high pH soil, insoluble precipitates may be formed with carbonate, hydroxyl, phosphate or sulfide ions which will significantly reduce the availability to plants. In acidic soils the hydrogen ions can displace other cations thereby making radionuclides more available to plant. The decomposition of organic matter tends to change the soil from oxidizing to reducing environment, reducing uranium from its mobile hexavalent state to its immobile tetravalent state [Till et al 1983]. This may explain the low uranium content of plant samples which needed a technique with low detection limit such as the laser fluorimetry.

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