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DETERMINATION OF ORGANOCHLORINE PESTICIDES AND RADIONUKLIDES IN SOIL AND SEDIMENT SAMPLES TAKEN FROM THE KURA-ARAS RIVER SYSTEMS

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***Abstract*:** The objective of this study was to determine the presence of 14 OCPs (HCH (α, β, γ, δ), aldrin, α-endosulfan, dieldrin, p,p'-DDE, endrin, β-endosulfan, p-p' -DDD, p-p'-DDT, endosulfan sulfate, endrin aldehyde) and radionuclides (Ra226, Th232, K40, Co60, Cs134, and Cs137) in soil and sediment samples collected from Kura-Aras river systems of the Azerbaijan. The Pearson's r, correlation coefficient was calculated between OCP and Radionuclides. As it turned out, relatively good correlation is observed (0.73 in soils and 0.94 in sediments) between OCP and Cs137 in the investigated samples.

Keywords: Gas chromatography, organochlorine pesticides, GCECD, Kura-Aras Rivers, gamma spectroscopy, radionuclides.

1. Introduction

Organochlorine pesticides (OCP) are one of the most prevalent contaminants [1] and were applied in the second half of the twentieth century worldwide as insecticides and fungicides against pests in fruit growing, horticultural and arable crops [2]. Although the human health effects after exposure to OCPs are not adequately understood it has been considered that these contaminants have an endocrine-disrupting activity and that they have also been implicated in the etiology of various diseases and endocrine-related disorders, such as pancreatic cancer, breast cancer, non-Hodgkin's lymphoma, leukemia, uterine cancer, liver cancer, sexual precocity, cryptorchidism, and low sperm concentration [3].

In Azerbaijan, according with the legislation most of the OCPs were prohibited in 80s, but they can be found in the environment even decades after being banned [1] In the last decades the application of pesticides has become an essential matter for discussion [4]. Soil is considered to be an important agricultural resource which has an ability to retain agro- -chemicals including pesticides [5]. It is known that OCPs still persist in soils [6] because they are not degraded, nor volatilized, nor even leached due to their lipophilicity [7] and strong affinity to soil organic matter (SOM) [8].

Nevertheless sorption of organic pollutants to SOM and other soil particles [9] could not prevent specific plants of taking them up [2]. Consequently is has led to the ingress of OCPs into growing plants and the persistence of their residues [10]. This by its turn affects animals due to the entrance of such pollutants in food chains. Determination of OCPs is therefore of relevant importance and it is fundamental that the methodology for determining residues guarantees true and precise results at appropriately low limits of detection [11].

In the determination of OCPs gas chromatography coupled to an electron-capture detector has been considered highly sensitive for the quantification of these compounds [12].

The main health concern for consumers in the long term due to high radiation exposure is development of cancer. Cancer types and target organs depend on the radionuclides. IAEA estimates that on average, our radiation exposure due to all natural sources amounts to about 2.4

mSv a year - though this figure can vary, depending on the geographical location by several hundred percent. In Canada, the average dose due to naturally occurring background radiation is about 2 mSv per year, of which about one-half comes from the inhalation of naturallyoccurring radon and its short-lived decay products. About 0.7 mSv per year, nationally-averaged, arises from cosmic and terrestrial gamma radiation. The portion of the background dose resulting from ingestion of natural radionuclides in food is about 0.25-0.4 mSv per year. Consuming contaminated food will increase the amount of radioactivity inside a person and therefore increase their exposure to radiation, thereby possibly increasing the health risks associated with radiation exposure. The exact health effects will depend on which radionuclides have been ingested and the amount being ingested [13].

There was obvious deficiency of data for important chemicals, such as organochlorine pesticides contents for Kura-Aras rivers systems. In 2005-2008 years NATO-OSCE 977991 project began to fill of such information gaps and were developing of scientifically based platform for transboundary water quality management issues. Results of few years' monthly studies of pesticides are presented. Pilot projects' data for determination ranges of pesticides and PCBs have also initiated of new approach for processes which control of water quality in Azerbaijan parts of Kura and Aras [14].

Azerbaijan use Kura water also for drinking which make of river water quality items very sensitive to community. Overall 900 km Kura flows from Georgia boundary till Caspian sea through Azerbaijan (see fig.1) [14] and riverine require the full scale study to understand fates of hazardous pollutants, to control of water quality and adequate planning of water usage.

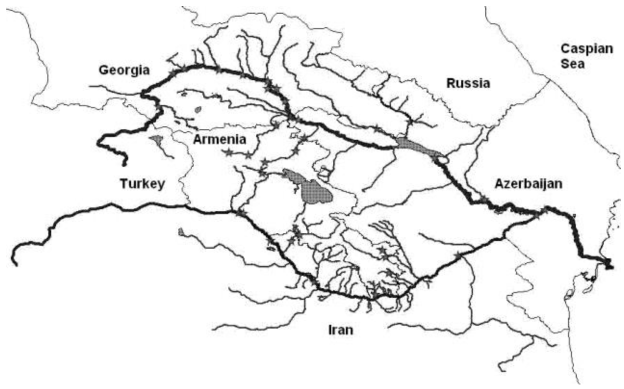

Fig. 1 Kura-Aras watershed

In this articles investigated soils and sediments 14 pesticides contents from different areas for Kura-Aras rivers systems, applying the Soxhlet extractions and GC-ECD, and radionuclides: Ra226, Th232, K40, Co60, Cs134, and Cs137 by Canberra produced Gamma Spectroscopy system with high purity Ge detector.

2. Sampling and preservation

The samples were collected between March and May 2017 year from 18 points of Kura and Aras rivers system from Azerbaijan regions (see table 1). For determination of pesticides, Soil samples were collected from 5-20 cm deep from ground around rivers and placed directly in suitable aluminum containers (0.5 kg). Sediment samples collected from depth of the river in with glass amber bottles (1.0 kg). All samples iced or refrigerated at 4°C from the time of collection until extraction. Before use, soil and sediment samples were air-dried at room temperature and then sifted. Extracts must be stored under refrigeration in the dark and should be analyzed within 40 days of extraction. For measurement radioactivity and determination of radionuclide contents soil and sediment samples were collected from same points and placed in plastic bags. In this article we present results for soils and sediments from 8 points (see table1).

Table 1. Sampling description.

N/N	**River**	**Point description**	**Latitude**	**Longitude**
Az 1	Chrami	Near Georgia boundary	41.3322	45.0686
Az 2	Kura	After combining Chrami with Kura	41.2914	45.1830
Az 3	Kura tributary	AgstafaChay, after dam near Armenia boundary	41.0502	45.2714
Az 11	Araks	Horadiz settlement, between Iran and Azerbaijan	39.4414	47.3521
Az 12	Kura	After combining with Araz	40.0724	48.5313
Az 15	Araks	Before combining with the Kura	40.0146	48.4481
Az 17	Bala Kura	Nefchala district, Banka settlement	39.3821	49.3619
Az 18	Kura	Salyan, Bridge	39.6189	48.9785

3. Method and definitions

3.1 Organochlorine pesticides (OCP). Samples extracted with hexane-acetone (1:1) using EPA Method 3540 (Soxhlet). Then extract cleaned by silica gel using EPA Method 3620) and sulfur clean-up by EPA Method 3660. After cleanup, the extract concentrated to 1 ml and analyzed by injecting a measured aliquot into a gas chromatograph equipped with wide-bore fused-silica capillary column, and using electron capture detector (GC/ECD). The results are calculated for dry weight. OCP were analyzed using a Varian GC-3800 with an ECD apparatus, Auto sampler CP8140, equipped with a capillary column of 30 m, DB-5MS (0.25 mm i.d., 0.25 µm film thickness, (Cat.CP7771)). The oven temperature was programmed starting at 80ºC and held for 0.5 min, followed by increases of 26ºC/min to 175ºC, then 6.5ºC/min to 235ºC, and then 15ºC/min to 300ºC and held 6 min. The injection port was at 250ºC splitless mode, and the detection was carried out at 340ºC. Nitrogen (purity≥99.999%) was used as carrier gas at constant flow rate of 3.0 mL/min, whereas nitrogen (purity≥99.999%) was employed as makeup gas at flow of 27 mL/min. The system was operated by GC Solution Star Workstation software.

3.2 Radionuclides. Before measurement samples were dried, tired, sieved using 2 mm Sieve and homogenized samples placed in measurement containers. Both soil and sediment samples were analyzed for 226Ra, (232Th)228Ra, and other radionuclides via gamma-spectrometry using a Canberra intrinsic germanium detector. All gamma spectrometric analyses were performed in silicone sealed (~100 cm3) plastic containers - beakers after aging for one month to allow for ingrowth of 222Rn and daughters. The photopeaks from the radon daughters 214Pb and 214Bi at 295, 352, and 609 keV were used to quantify 226Ra and the 228Ac peaks at 338 and 911 keV were used for 228Ra [15]. For all samples was calculated geometrical efficiency using special program software "ISOCS LABSOCS". Using 22Na, 155Eu standard source and background specters quality assurance and quality control procedures were performed before measurement of samples.

4. Results and discussion

Results of investigated soil and sediment samples for contents of organochlorine pesticides are given in table 2 and table 3. Positive findings were found in soils for BCH isomers, 4,4'-DDT and its derivate product 4,4'-DDD, and dieldrin. The residues were found in samples produced by organic farming as well as in conventional farming. Also Endosulfan II and Endosulfan-sulphate were registered in low concentrations. The concentration of OCPs in points Az15 (Before combining Araks with the Kura) are reduced to 2 times. In the territory of Az12 (After combining Kura with Araks) and Az18 (Salyan, Bridge, Kura), almost no OCPs (Low concentration) are observed. Results of OCP's and Radionuclide's in soils presents in Tables 2 and Fig 2, and for sediments presents in Tables 3 and Fig 3.

Table 2. Results of chlorinated pesticides in soil samples.

Chlorinated Pesticides (OCP)	Unit	Az1	Az2	Az3	Az11	Az15	Az12	Az 18
		Chrami, Near Georgia boundary)	After joining Qazakh, Shikhli settlement, Khrami Kura	Kura tributary, AgstafaChay, after dam near Armenia boundary	Araks, Horadiz settlement, between Iran and Azerbaijan	(Araks, Before combining with the Kura)	Kura, After combining with Araks	Salyan, Bridge, Kura
		Soil	Soil	Soil	Soil	Soil	Soil	Soil
Aldrin	µg/kgdm	<0.1 ± 0.03	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
a-BHC	µg/kgdm	11.5 ± 0.04	<0.1	9.8	1.2	<0.1	<0.1	<0.1
b-BHC	µg/kgdm	5.2 ± 0.11	4.42	4.3	<0.4	<0.4	<0.4	0.66
d-BHC	µg/kgdm	2.8 ± 0.04	<0.1	2.1	3.9	1.1	<0.1	<0.1
g- BHC (Lindane)	µg/kgdm	<0.1 ± 0.03	<0.1	<0.1	<0.1	<0.1	<0.1	1.36
4,4'-DDD	µg/kgdm	3.2 ± 0.04	<0.1	3	8.5	5.2	<0.1	0.2
4,4'-DDE	µg/kgdm	<0.1 ± 0.04	<0.1	0.8	1.7	3.8	<0.1	0.4
4,4'-DDT	µg/kgdm	4.3 ± 0.29	0.55	<1.0	<1.0	<1.0	<1.0	<1.0
Dieldrin	µg/kgdm	6.5 ± 0.02	<0.1	1.2	4.9	1.6	1.9	<0.1
Endosulfan I	µg/kgdm	<0.1 ± 0.04	<0.1	4.2	2.7	<0.1	<0.1	<0.1
Endosulfan II	µg/kgdm	2.5 ± 0.03	0.73	2.1	3.8	3.5	1.2	<0.1
Endosulfan Sulfate	µg/kgdm	2.3 ± 0.02	0.65	1.8	5.2	1.5	1.5	0.51
Endrin	µg/kgdm	<0.1 ± 0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Endrin Aldehyde	µg/kgdm	<0.1 ± 0.03	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2
SUM OCP	**µg/kgdm**	**38.3**	**6.35**	**29.3**	**31.9**	**16.7**	**4.6**	**3.13**
Ra226	Bk/kg	13.42	13.93	13.93	10.96	19.16	NA	17.72
Th232	Bk/kg	19.82	16.3	16.3	15.68	21.79	NA	19.8
K40	Bk/kg	411.6	392.5	392.5	457.2	496.5	NA	470.2
Co60	Bk/kg	<1.16	<1.1	<1.1	<1.31	<1.36	NA	<0.46
Cs134	Bk/kg	<1.34	<1.26	<1.26	<1.35	<1.51	NA	<0.51
Cs137	Bk/kg	3.347	1.56	1.56	<1.31	7.552	NA	3.097

NA-Not analyzed

Investigation of sediments show that the components observed in soil samples are also observed in sediments.

Some components, such as: BHC and DDT isomers, Endosulfan I, are relatively higher in sediment samples. This can be explained by the fact that rain water is dumped from the soil of OCPs and poured into rivers. OCPs fall into the bottom of the river because they are not soluble in water, and these sediments can accumulate anywhere by moving along the river flow direction. Therefore, the number of components can vary in different places in different ways.

Table 3. Results of chlorinated pesticides in sediment samples.

Chlorinated Pesticides (OCP)	Unit	Az1	Az3	Az11	Az15	Az12	Az 17
		Chrami, Near Georgia boundary	Kura tributary, AgstafaChay, after dam near Armenia boundary	Araks, Horadiz settlement, between Iran and Azerbaijan	Araks, Before combining with the Kura	Kura, After combining with Araks	Neftchala, Banka settlement, Bala Kur, 1st Mayak
		Sediment	Sediment	Sediment	Sediment	Sediment	Sediment
Aldrin	µg/kgdm	1.2 ± 0.03	1.8	<0.1	<0.1	<0.1	2.78
a-BHC	µg/kgdm	23.2 ± 0.04	<0.1	10.2	<0.1	1.2	<0.1
b-BHC	µg/kgdm	1.2 ± 0.11	5.2	4.5	1.2	2.3	<0.1
d-BHC	µg/kgdm	3.2 ± 0.04	<0.1	1.2	5.4	<0.1	0.2
g- BHC (Lindane)	µg/kgdm	0.6 ± 0.03	1.2	<0.1	<0.1	0.6	1.39
4,4'-DDD	µg/kgdm	<0.1 ± 0.04	<0.1	5.2	<0.1	3.2	0.53
4,4'-DDE	µg/kgdm	<0.1 ± 0.04	<0.1	<0.1	<0.1	2.5	0.82
4,4'-DDT	µg/kgdm	8.2 ± 0.29	5.6	<1.0	<1.0	<1.0	4.43
Dieldrin	µg/kgdm	1.2 ± 0.02	3.5	12.5	3.2	3.8	0.45
Endosulfan I	µg/kgdm	<0.1 ± 0.04	<0.1	3.7	<0.1	<0.1	<0.1
Endosulfan II	µg/kgdm	4.2 ± 0.03	2	4.6	<0.1	5.2	4.22
Endosulfan Sulfate	µg/kgdm	1.8 ± 0.02	<0.1	2.1	<0.1	3.1	1.5
Endrin	µg/kgdm	<0.1 ± 0.01	<0.1	<0.1	<0.1	1.2	2.15
Endrin Aldehyde	µg/kgdm	<0.1 ± 0.03	<0.1	<0.1	<0.1	<0.1	1.17
SUM OCP	**µg/kgdm**	**44.8**	**19.3**	**44**	**9.8**	**23.1**	**19.64**
Ra226	Bk/kg	11.91	12.14	NA	20.92	NA	21.74
Th232	Bk/kg	16.84	16.07	NA	24.07	NA	26.02
K40	Bk/kg	422.9	425	NA	502.9	NA	498.2
Co90	Bk/kg	<1.22	<1.21	NA	<1.14	NA	<1.14
Cs134	Bk/kg	<1.31	<1.35	NA	<1.28	NA	<1.32
Cs137	Bk/kg	1.645	0.9437	NA	1.014	NA	<1.24

NA-Not analyzed

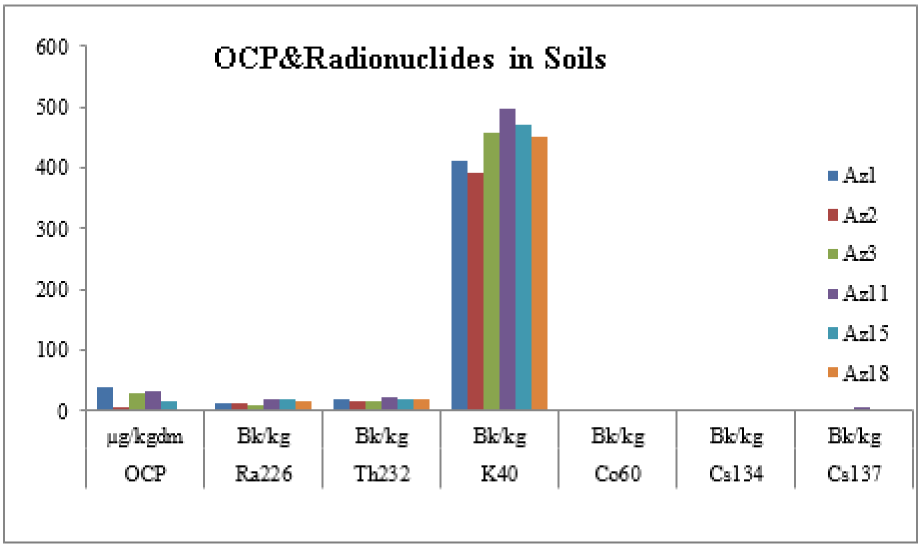

Fig 2. OCP&Radionuclides in Soil samples.

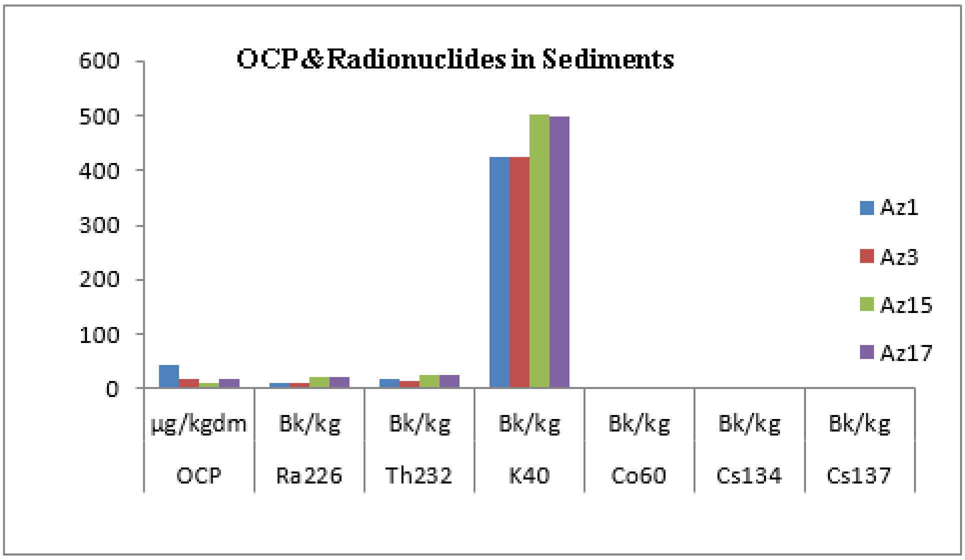

Fig 3. OCP&Radionuclides in Sediment samples.

There are a few different types of correlations, but the one we will use is the Pearson correlation. A correlation, r, is a single number that represents the degree of relationship between two measures. The correlation coefficient is a value such that between from -1 to 1. A positive correlation indicates a relationship between x and y measures such that as the values of x increases, the values of y will also increase. A negative correlation indicates the opposite as the values of x increase, the values of y will decrease. The closer the correlation, r, is to -1 or 1, the stronger x and y are related. The negative sign does not indicate anything about strength - it just signifies that correlation is negative. If r is close or equal to 0, it means there is a weak or no relationship between the measures. The relationship between OCP and Radionuclides concentrations was tested by a Pearson's r correlation analysis of replicate values. Pearson correlation coefficient, also known as Pearson's r, a measure of the strength and direction of the linear relationship between two variables that is defined as the (sample) covariance of the variables divided by the product of their (sample) standard deviations.

The Pearson's r, correlation coefficient was calculated between OCP and Radionuclides. As it turned out, relatively good correlation is observed between OCP and Cs137 in the investigated samples (Table 4).

Table4. Pearson's r, correlation coefficient

Pearson's r, correlation coefficient in Soils		Pearson's r, correlation coefficient in Sediments	
	OCP		**OCP**
Ra226	-0.23	Ra226	-0.66
Th232	0.22	Th232	-0.57
K40	0.22	K40	-0.69
Co60	-	Co60	-
Cs134	-	Cs134	-
Cs137	**0.73**	**Cs137**	**0.94**

5. Conclusions

The obtained results showed that some of investigated 14 compounds OCP tend to be very persistent, as they are still found although they were banned decades ago.

The data obtained by us in the course of works on objects, give some graphic representation of the dynamics of geochemical processes and the degree of contamination of the Kura-Aras water area by the example of the main geochemical properties of bottom sediments.

The most toxic substances entering the water area are dichlorodiphenylethane (DDE), dichlorodiphenyl dichloromethylmethane (DDD), dichlorodiphenyltrichloromethylmethane (DDT), a-BHC, b-BHC, d-BHC, Dieldrin, Endosulfan II and Endosulfan sulfate.

The results obtained with this study reveal the importance of monitoring on a regular basis the levels of OCPs. The Pearson's r, correlation coefficient was calculated between OCP and Radionuclides. As it turned out, relatively good correlation is observed between OCP and Cs137 in the investigated samples

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ОПРЕДЕЛЕНИЕ ХЛОРОРГАНИЧЕСКИХ ПЕСТИЦИДОВ И РАДИОНУКЛИДЫ В ОБРАЗЦАХ ПОЧВЫ И ДОННОГО ОТЛОЖЕНИЯ ИЗ РЕК КУРА-АРАКС

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Резюме: Целью этого исследования было определить наличие 14 ОХП (HCH (α, β, γ, δ), альдрина, α-эндосульфана, дильдрина, p, p'-DDE, эндрина, β-эндосульфана, p-p ' -DDD, p-p'-DDT, сульфат эндосульфана, эндриновый альдегид) и радионуклиды (Ra226, Th232, K40, Co60, Cs134 и Cs137) в образцах почвы и осадков из систем рек Кура-Аракс в Азербайджане. Коэффициент корреляции r' Пирсона рассчитывался между ОХП и радионуклидами. Как оказалось, наблюдается относительно хорошее корреляция (0,73 в почвах и 0,94 в осадках) между ОХП и Cs137 в исследуемых образцах.

Ключевые слова: Газовая хроматография, хлорорганические пестициды, GC ECD, река Кура-Аракс, гамма-спектроскопия, радионуклиды.

XLORÜZVİ PESTİSİDLƏRİN VƏ RADİONUKLİDLƏRİN KÜR – ARAZ ÇAY SİSTEMİNDƏN GÖTÜRÜLMÜŞ TORPAQ VƏ DİB ÇÖKÜNTÜSÜ NÜMUNƏLƏRİNDƏ TƏYİNİ

N.Ə. İbadov, F.Y. Hümbətov, M.Ə. Səmədov, S.Ş. Məmmədzadə, N.Ş. Kərimova

Xülasə: Bu tədqiqat işinin məqsədi 14 XÜP (HCH (α, β, γ, δ), aldrin, α-endosulfan, dieldrin, p, p'-DDE, endrin, β-endosulfan, pp-DDD, p- p-DDT, endosulfan sulfat, endrin aldehid) və radionuklidlərin (Ra226, Th232, K40, Co60, Cs134 və Cs137) Azərbaycanın Kür-Araz çay sistemlərindən götürülmüş torpaq və dib çöküntüsü nümunələrində təyinindən ibarət idi. XÜP və radionuklidlər arasında Pirson korrelyasiya əmsalı r ' hesablanmışdır. XÜP və Cs137 arasında, araşdırılan nümunələrdə nisbətən yaxşı korrelyasiya müşahidə edilir (torpaqlarda 0.73, dib çöküntülərində isə 0.94).

Açar sözlər: Qaz kromatoqrafiyası, organoklor çöküntüsü, GC ECD, Kür-Araz çayları, gamma spektroskopiyası, radionuklidlər.