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Determination of Organochlorine Pesticides in Soils And Sediments Taken from the Kura-Araks Rivers Systems Using GC/ECD

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Abstract: The organochlorine pesticides (OCPs), due the wide use in agriculture until about 30 years (except the most recent bans by the EU for lindane, methoxychlor and endosulfan) and their chemical stability and slow biodegradation became ubiquitous pollutants. Most OCPs are persistent organic pollutants that have long life cycles in the environment and being transported for long distances. The residues of pesticides in soil can be absorbed by plants, entering the food chain, leading to bioaccumulation. The objective of this study was to determine the presence of 14 OCPs (HCH (α, β, γ,δ), aldrin, α-endosulfan, dieldrin, 4,4'-DDE, endrin, β-endosulfan, 4,4'-DDD, 4,4'-DDT, endosulfan sulfate, endrin aldehyde) in soils and sediments from Kura-Araks rivers systems of the Azerbaijan. The extraction was performed with using methylene chloride/acetone (1:1), after changing solvent to hexane and cleaning-up by SG, samples were analyzed by GC-ECD and confirmation was carried out by GC/MS.

Keywords: Gas chromatography, organochlorine pesticides, Kura-Araks rivers, GCECD, GC/MS

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].

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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].

Recent studies have applied ultrasonic solvent extraction [12], pressurized liquid extraction [13], shake-flask extraction [14] , microwave assisted micellar extraction [15] lowed in some cases by a clean-up step with solid-phase extraction (SPE) [14], or solid-phase micro extraction (SPME) [15-16], Lopez-Aviala et al. [17] evaluated the Soxhlet extraction procedure for extracting OCPs from soils and sediments.

In the determination of OCPs gas chromatography coupled to an electron-capture detector has been considered highly sensitive for the quantification of these compounds [18].

There was obvious deficiency of data for important chemicals, such as organochlorine pesticides contents for Kura-Araks 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 Araks [19].

South Caucasus is one of unique places for environmental chemist and geochemist in world both from geography, geology, natural and artificial affect positions. Situated between Russia in North and Iran and Turkey in South, region is under influence of Black sea and Caspian Sea hydrometeorology processes.

Intensive development in 1950-1990 of mining industry (Armenia), metallurgic (Georgia), chemical, power and processing industries (in all of 3 republics), irrigated agriculture had resulted with dramatically increasing of both water catchment area, sewage realizing into rivers and finally with fully deterioration of water quality. According of official data about 300 million cubic meters of polluted sewage was annually discharged into the river basin within Armenian territory and 265 million cubic meters in Georgia. Although there are not large industrial center on Kura in Azerbaijan territory, rivers and tributaries flow thorough populated agriculture areas and undergo stresses of related activities. It is expected of decreasing concentrations of series of pollutants in Kura and Araks waters because of industrial collapse of Armenia and Georgia. 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) [19]and riverine require the full scale study to understand fates of hazardous pollutants, to control of water quality and adequate planning of water usage.

In this articles investigated soils and sediments 14 pesticides contents from different areas for Kura-Araks rivers systems, applying the Soxhlet extractions and GC-ECD.

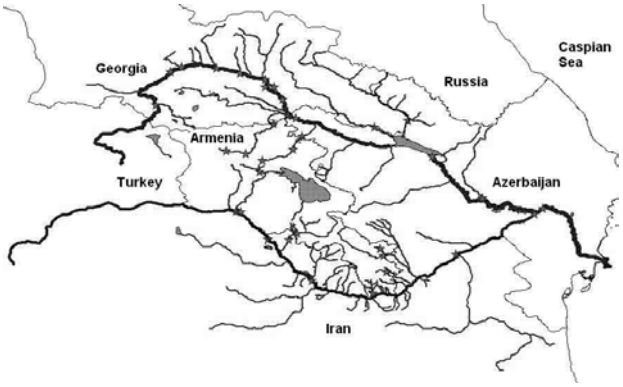

Fig. 1 Kura-Araks watershed

2. Reagents and Materials

For this study 14 OCPs were used: a-, b-, γ- and d-hexachlorocyclohexanes (BHC), 4,4'-DDE ([2,2-bis(p-chlorophenyl)-1,1-dichloroethylene]), 4,4'-DDD(dichlorodiphenyldichloro-ethane), 4,4'-DDT, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin aldehyde. Pesticide standards (purity > 97.0%) and other reagents, were obtained from LGC and Sigma-Aldrich Co. A mixed stock solution, containing all of the OCPs, was prepared in n-hexane. The internal standard (IS) of 2,4,5,6-Tetrachlor-M-Xylene and decachlorobiphenyl was purchased from LGC and Sigma-Aldrich.

Solvents used in the extraction and cleanup procedures include methylene chloride, acetone must be exchanged to *n*-hexane prior to analysis. All solvents should be pesticide grade in quality equivalent, and each lot of solvent should be determined to be free of phthalates.

- Sodium sulfate anhydrous, coarse granular for analysis, 0.63-2.0 mm emsure#ACS (VWR, 1.06637.9025)- treat at 350-400°C for 4 h and store in a desiccator.
- Silica gel, Davidson 923, 100/200 mesh(VWR, 15173LX), (- treat at 350-400°C for 4 h and store in a desiccator
- Sand (for Blank, white quartz -50+70 mesh, Sigma, 274739)- treat at 350-400°C for 4 h and store in a desiccator.
- Glass wool Superfi 11µm Cardboard (VWR, 519-3102) - treat at 350-400°C for 4 h and store in a desiccator.

3. Sampling and Preservation

The samples were collected between March and May 2017 years from 18 points of Kura and Araks rivers system from Azerbaijan regions (see table 1). Soils collected from 5-20 cm deep from ground around rivers and placed directly in a 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. In this article we present results for soils and sediments from 5 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 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

4. Standards and Calibrations

The standard solutions (stock, calibration, internal) were stored at 4±4°C in the dark condition. All stock standard solutions must be replaced if routine QC indicates a problem. Other standard solutions must be replaced after six months or sooner if routine QC indicates a problem. Stock standard solutions (1000 mg/L) - may be prepared from pure standard materials or can be purchased as certified solutions. Preparation of stock standard solutions should be carried out by accurately weighing 0.0100 g of pure compound. After dissolving of the compound in hexane it should be diluted to volume in a 10-mL volumetric flask. Calibration standards were prepared at five different concentrations by dilution of the composite stock standard with hexane. In this method internal standard calibration was used. A constant amount of the internal standard was added to all samples before extraction. That same amount of the internal standard was also included in each of the calibration standards. In the extract, the peak response ratio of the target compound to the internal standard was compared with a similar ratio derived for each calibration standard. This ratio was termed the response factor (RF) or relative response factor (RRF), indicating that the target compound response was calculated relative to that of the internal standard. During preparation of calibration standards, the same amount of the internal standard solution was added to each calibration standard. Therefore, the internal standard concentration was the same in each calibration standard, whereas concentrations of the target analytes will vary. In this method the internal standard solution contains two internal standards: Decachlorobiphenyl and 2,4,5,6-Tetrachloro-m-xylene. For each of the initial calibration standards, the RF values were calculated for each target analyte relative to one of the internal standards as follows:

$$\mathbf{RF=(As \times Cis)/(Ais \times Cs)}$$

Where:
As -peak response of the analyte,
Ais - peak response of the internal standard,

Cs - concentration of the analyte, ng/ml;
Cis - concentration of the internal standard, ng/ml.

4.1 Data Analysis and Calculations

The concentration of components in the original wet solid sample C was calculated from the following equation:

$$\mathbf{Cw = [As \times Amount(IS)] / [Ais \times RF \times M\ samp],}$$

Where:
Cw - concentration of compound of interest in the original wet solid sample, ng/g;
As – peak area of the compound of interest;
Ais – peak area of the corresponding internal standard;
Amount(IS) – the amount of internal standard added to the sample, blank, calibration standard solution and QC samples in 1 ml of extract;
RF-the corresponding response factor; and Msamp – mass of wet sample taken for extraction, g.
For converting the result to a dry matter basis, the following equation is used:

$$\mathbf{Cd = (Cw \times 100) / DM}$$

Where:
Cd – concentration of compound of interest in the dry sample, ng/g;
Cw - concentration of compound of interest in the wet sample, ng/g; and
DM – the percent dried weight of the sample.

5. Extraction Procedure

The soil samples were extracted according to a previously described method Bring the analytical batch of samples to room temperature. Decant and discard any water layer on a sediment sample. Discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly, especially composited samples.

5.1 Weigh 40 g of sample into a 500 mL flask. Record the weight to the nearest 0.1 g.

5.2 The sample must be properly prepared by thoroughly mixing it with sodium sulfate, so that it forms a free-flowing powder prior to the addition of the solvent. Then two internal standards are adding.

5.3 Solid samples should beextracted with methylene chloride-acetone (1:1) using Soxhlet extraction. Place 250 mL of methylene chloride-acetone (1:1) into a 500-mL round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 24 hrs.

5.4 Allow the extract to cool after the extraction is completed.

5.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

5.6 Add one or two clean boiling chips to the K-D flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column.Place the K-D

apparatus on a hot water bath (80-90°C) so that the concentrator tube is partiallyimmersed in the hot water and the entire lower rounded surface of the flask is bathed with hotvapor. Adjust the vertical position of the apparatus and the water temperature as required tocomplete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of thecolumn will actively chatter, but the chambers will not flood. When the apparent volume of liquidreaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for atleast 10 minutes.

5.7 Exchange the methylene chloride-acetone with hexane by adding 50 mL of hexane to the 500 ml round-bottom flask. Concentrate on water bath (at 85°C) until ~1 ml extract.

5.8 Hexane extract is transferring into 10 ml vials used for concentration by N2 blowing. Do concentration of extract by N2 blowing till 1 ml. Now extract is ready for cleanup.

5.9 Immediately after weighing the sample aliquot to be extracted, weigh an additional 5- to10-g aliquot of the sample into a tared crucible. Dry this aliquot overnight at 105 °C. Allow to cool in a desiccator before weighing. Calculate the percent dry weight as follows:

DM (%) = (g of dry sample/ g wet of sample) x 100

6. Sample Cleanup

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis.

6.1 Sulfur cleanup.

Elemental sulfur is encountered in many sediment samples, marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine pesticides. Therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques.

a) In this method copper powder was used for sulfur cleanup.
b) Activated copper preparation for sulfur cleanup. Added approximately 50 g of copper powder to 50 ml of concentrated hydrochloric acid. Swirl the contents to remove any oxidised surface layer from the copper. Decant the supernatant acid from the copper and discard the acid. Repeatedly rinse the copper with distilled water and discard the water until all the acid has been removed (pH=7). The copper was then rinsed thoroughly sequentially with acetone, dichloromethane then finally hexane and the solvent discarded. The activated copper was then stored under hexane until required for use.
c) Before sulfur cleanup, added about 0.5 g of activated copper into extract and mix for 30 min. using shaker. After this procedure extract was ready for silica gel cleanup.

6.2 Silica gel cleanup. Silica gel was used to separate single component organochlorine pesticides from some interferants.

a) Before using, the silica gel was activated for at least 1 hr. at 200°C. Deactivated this to 3.3% with reagent water in a flask. Mixed the contents thoroughly and allowed to equilibrate for 30 min.
b) Silica gel column prepare:

- Wash the silica gel column (ID=10 mm) with DCM
- Place glass wool into column
- Wash of prepared layer by hexane
- 1/4 column is filling by hexane
- Add 3 g deactivate silica gel
- Add 0.5-1 cm treated sodium sulphate
- Remove of hexane with stop in a few mm above sodium sulphate

Transfer the sample extract (1 mL in hexane) onto the column. Rinse the extract vial twice with 1 to 2 mL of hexane and add each rinse to the column. Elute the column with 80 mL of hexane (Fraction I) at a rate of about 5 mL/min. Remove the collection flask and set it aside for later concentration. Elute the column with 50 mL of hexane (Fraction II) and collect the eluate. Perform a third elution with 15 mL of methylene chloride (Fraction III). The elution patterns for the organochlorine are shown in below table.

Components	**RT, min**	**Fraction I**	**Fraction II**	**Fraction III**
IS-2,4,5,6-Tetrachloro-M-Xylene	5.65	+	-	-
Alpha-BHC	6.27	+	+	
Beta-BHC	6.68			+
Gamma-BHC	6.81			+
Delta-BHC	7.32			+
Heptachlor	8.12	+		
Aldrin	8.85	+		
Heptachlor Epoxide Isomer B	9.71			+
Endosulfan I (Alpha)	10.54			+
4 , 4 ' - DDE	11.08	+		
Dieldrin	11.19			+
Endrin	11.68			+
Endosulfan II (Beta)	11.98			+
4 , 4 ' - DDD	12.11			+
Endrin Aldehyde	12.35			+
Endosulfan Sulfate	12.94			+
4 , 4 ' - DDT	13.05	+		+
IS-Decachlorobiphenyl	17.13	+		

Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. Fractions may be combined, as desired, depending upon the specific pesticides of interest or level of interferences and concentrated, to 1 ml and analyzed by GC/ ECD. For the reliability of component

identification, qualitative analysis was performed on a GC/MS Trace DSQ (Thermo-Electron, Finnigan, USA).

7. Gas Chromatography – Electron Capture Detector

OCP were analyzed using a Varian GC-3800 with an ECD apparatus, Auto sampler CP8140, equipped with a capillary column of 30 m, DB-35MS (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.

8. Gas Chromatography - Mass Spectrometry (GC/MS)

In addition, the real samples with positive results by GC-ECD were analyzed using a Thermo Trace-Ultra gas chromatograph coupled to an quadrupole mass detector Thermo DSQ, operated in the electron impact ionization (EI) at 70 eV. The ion source temperature was 250 C and the MS transfer temperature, 250 C. The system was operated by Xcalibur v 1.3 software. Confirmation of residues was carried out by GC-MS/SIM using a Agilent column fitted with an DB-5MS (30 m 0.25 mm, 0.25 μm film thickness) column operating in the splitless mode; helium was used as carrier gas at a constant flow rate of 1.3 mL/min. The injector was maintained at 240 C. The oven temperature was programmed starting at 40 C and held for 2 min, followed by increases of 30 C/min to 220 C, held for 5 min, then 10 C/ min to 270 C, and held for 1 min. For the identification of pesticides, the retention time, and three ions, the NIST and Wiley pesticide libraries were used. The SIM conditions were fixed for each compound, trying to select as precursor ion the one with the highest m/z ratio and abundance.

9. 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 (Fig.1) 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), almost no OCPs are observed.

Table 2. Results of chlorinated pesticides in soil samples.

Chlorinated Pesticides	Unit	Az1 (Chrami, Near Georgia boundary)	Az3 (Kura tributary, AgstafaChay, after dam near Armenia boundary)	Az11 (Araks, Horadiz settlement, between Iran and Azerbaijan)	Az15 (Araks, Before combining with the Kura)	Az12 (Kura, After combining with Araks)
		Soil	Soil	Soil	Soil	Soil
Aldrin	µg/kgdm	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03
a-BHC	µg/kgdm	11.5 ± 0.04	9.8 ± 0.04	1.2 ± 0.04	<0.1 ± 0.04	<0.1 ± 0.04
b-BHC	µg/kgdm	5.2 ± 0.11	4.3 ± 0.11	<0.4 ± 0.11	<0.4 ± 0.11	<0.4 ± 0.11
d-BHC	µg/kgdm	2.8 ± 0.04	2.1 ± 0.04	3.9 ± 0.04	1.1 ± 0.04	<0.1 ± 0.04
g- BHC (Lindane)	µg/kgdm	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.04
4,4'-DDD	µg/kgdm	3.2 ± 0.04	3.0 ± 0.04	8.5 ± 0.04	5.2 ± 0.04	<0.1 ± 0.04
4,4'-DDE	µg/kgdm	<0.1 ± 0.04	0.8 ± 0.04	1.7 ± 0.04	3.8 ± 0.04	<0.1 ± 0.04
4,4'-DDT	µg/kgdm	4.3 ± 0.29	<1.0 ± 0.29	<1.0 ± 0.29	<1.0 ± 0.29	<1.0 ± 0.29
Dieldrin	µg/kgdm	6.5 ± 0.02	1.2 ± 0.02	4.9 ± 0.02	1.6 ± 0.02	1.9 ± 0.02
Endosulfan I	µg/kgdm	<0.1 ± 0.04	4.2 ± 0.04	2.7 ± 0.04	<0.1 ± 0.04	<0.1 ± 0.04
Endosulfan II	µg/kgdm	2.5 ± 0.03	2.1 ± 0.03	3.8 ± 0.03	3.5 ± 0.03	1.2 ± 0.03
Endosulfan Sulfate	µg/kgdm	2.3 ± 0.02	1.8 ± 0.02	5.2 ± 0.02	1.5 ± 0.02	1.5 ± 0.02
Endrin	µg/kgdm	<0.1 ± 0.01	<0.1 ± 0.01	<0.1 ± 0.01	<0.1 ± 0.01	<0.1 ± 0.01
Endrin Aldehyde	µg/kgdm	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03
Total	µg/kgdm	38.3	29.3	31.9	16.7	4.6

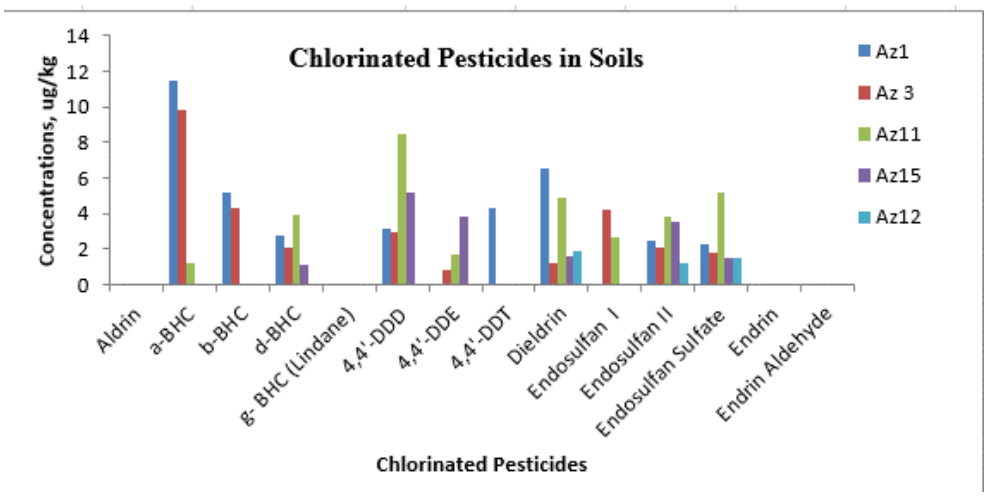

Fig. 1. Chlorinated pesticides in soil samples.

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

Some components, such as: BHC and DDT isomers, Dieldrin and Endosulfans, are relatively higher in sediment samples (Fig. 2). 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	Unit	Az1 (Chrami, Near Georgia boundary)	Az3 (Kura tributary, AgstafaChay, after dam near Armenia boundary)	Az11 (Araks, Horadiz settlement, between Iran and Azerbaijan)	Az15 (Araks, Before combining with the Kura)	Az12 (Kura, After combining with Araks)
		Sediment	Sediment	Sediment	Sediment	Sediment
Aldrin	µg/kgdm	1.2 ± 0.03	1.8 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03
a-BHC	µg/kgdm	23.2 ± 0.04	<0.1 ± 0.04	10.2 ± 0.04	<0.1 ± 0.04	1.2 ± 0.04
b-BHC	µg/kgdm	1.2 ± 0.11	5.2 ± 0.11	4.5 ± 0.11	1.2 ± 0.11	2.3 ± 0.11
d-BHC	µg/kgdm	3.2 ± 0.04	<0.1 ± 0.04	1.2 ± 0.04	5.4 ± 0.04	<0.1 ± 0.04
g- BHC (Lindane)	µg/kgdm	0.6 ± 0.03	1.2 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	0.6 ± 0.03
4,4'-DDD	µg/kgdm	<0.1 ± 0.04	<0.1 ± 0.04	5.2 ± 0.04	<0.1 ± 0.04	3.2 ± 0.04
4,4'-DDE	µg/kgdm	<0.1 ± 0.04	<0.1 ± 0.04	<0.1 ± 0.04	<0.1 ± 0.04	2.5 ± 0.04
4,4'-DDT	µg/kgdm	8.2 ± 0.29	5.6 ± 0.29	<1.0 ± 0.29	<1.0 ± 0.29	<1.0 ± 0.29
Dieldrin	µg/kgdm	1.2 ± 0.02	3.5 ± 0.02	12.5 ± 0.02	3.2 ± 0.02	3.8 ± 0.02
Endosulfan I	µg/kgdm	<0.1 ± 0.04	<0.1 ± 0.04	3.7 ± 0.04	<0.1 ± 0.04	<0.1 ± 0.04
Endosulfan II	µg/kgdm	4.2 ± 0.03	2.0 ± 0.03	4.6 ± 0.03	<0.1 ± 0.03	5.2 ± 0.03
Endosulfan Sulfate	µg/kgdm	1.8 ± 0.02	<0.1 ± 0.02	2.1 ± 0.02	<0.1 ± 0.02	3.1 ± 0.02
Endrin	µg/kgdm	<0.1 ± 0.01	<0.1 ± 0.01	<0.1 ± 0.01	<0.1 ± 0.01	1.2 ± 0.01
Endrin Aldehyde	µg/kgdm	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03	<0.1 ± 0.03
Total	µg/kgdm	44.8	19.3	44	9.8	23.1

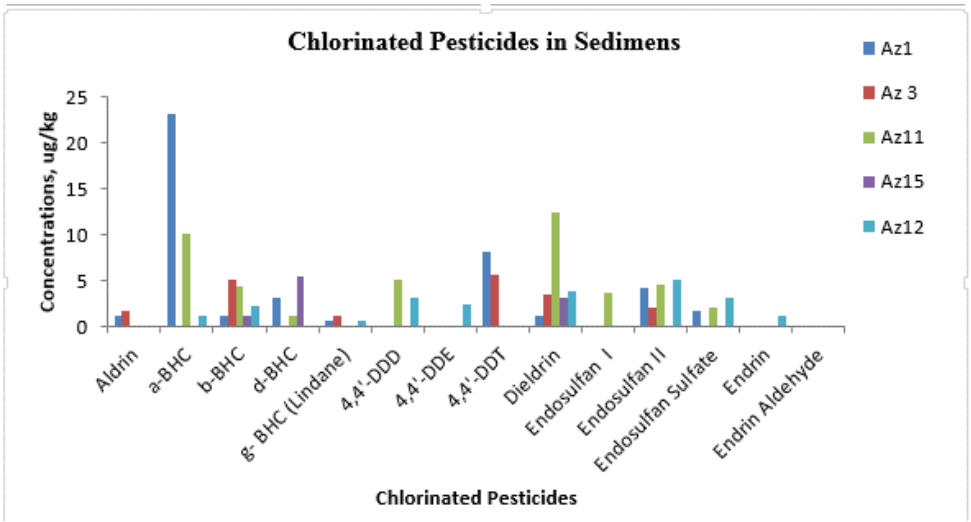

Fig. 2. Chlorinated pesticides in sediment samples.

10. 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 dichloro dipheny lethane (DDE), dichloro diphenyl dichloromethylmethane (DDD), dichloro diphenyl trichloromethylmethane (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.

References

[1]. Negoita, T. G.; Covaci, A.; Gheorghe, A. and Schepens, P. (2003) - Distribution of polychlorinated biphenyls (PCBs) and organochlorine pesticides in soils from the East Antarctic coast. Journal of Environmental Monitoring, 5,2: 281- 286.

[2]. Hilber, I.; Mader, P.; Schulin, R and Wyss, G. S. (2008). Survey of organochlorine pesticides in horticultural soils and there grown Cucurbitaceae. Chemosphere, 73,6: 954-961.

[3]. Botella, B.; Crespo J.; Rivas, A.; Cerrillo, I.; Olea-Serrano, M.F. and Olea, N. (2004) - Exposure of women to organochlorine pesticides in Southern Spain. Environmental Research, 96,1: 34-40.

[4]. Asensio-Ramos; Hernandez-Borges, M.J.;Ravelo-Perez, L.M. and Rodriguez-Delgado, M.A. (2010) - Evaluation of a modified QuEChERS method for the extraction of pesticides from agricultural, ornamental and forestal soils. Analytical and Bioanalytical Chemistry, 396,6: 2307-2319.

[5]. Rashid, A.; Nawaz, S.; Barker, H.; Ahmad, I. and Ashraf, M. (2010). Development of a simple extraction and clean-up procedure for determination of organochlorine pesticides in soil using gas chromatography-tandem mass spectrometry. Journal of Chromatography A, 1217,17: 2933-2939.

[6]. Zhang, H.B.; Luo Y.M.; Zhao, Q.G. ;Wong, M.H. and Zhang, G.L. (2006) - Residues of organochlorine pesticides in Hong Kong soils. Chemosphere, 63,4: 633-641.

[7]. Connell, D.W.; Miller, G.J.; Mortimer, M.R.; Shaw, G.R. and Anderson, S.M. (1999) - Persistent lipophilic contaminants and other chemical residues in the Southern Hemisphere. Critical Reviews in Environmental Science and Technology, 29,1: 47-82.

[8]. Ahmad, R.; Nelson, P.N.and R.S. Kookana (2006) - The molecular composition of soil organic matter as determined by 13C NMR and elemental analyses and correlation with pesticide sorption. European Journal of Soil Science, 57,6: 883-893.

[9]. Prosen, H.; Fingler, S.; Zupancic Kralj L. and Drevenkar, V. (2007) - Partitioning of selected environmental pollutants into organic matter as determined by solid-phase microextraction. Chemosphere, 66,8: 1580-1589.

[10]. Waliszewski, S.M.; Carvajal O.; Gomez-Arroyo, S. ; Amador-Munoz, O.;Villalobos-Pietrini, R.; Hayward- -Jones, P.M. and Valencia-Quintana, R. (2008) - DDT and HCH isomer levels in soils, carrot root and carrot leaf samples. Bulletin of Environmental Contamination and Toxicology, 81,4: 343- 347.

[11]. Wiilkowska, A. and Biziuk, M. (2011) - Determination of pesticide residues in food matrices using the QuEChERS methodology. Food Chemistry,125,3: 803-812.

[12]. Tor, A.; Aydin, M.E. and Ozcan, S. (2006) - Ultrasonic solvent extraction of organochlorine pesticides from soil. Analytica Chimica Acta, 559,2: 173-180.+

[13]. Vega Moreno, D.; Sosa Ferrera, Z.; Santana Rodriguez, J.J.; Pocurull Aixala, E. and Borrull Ballarin, F. (2008) - Determination of organochlorine pesticides from agricultural soils using pressurized liquid extraction. Soil & Sediment Contamination, 17,1: 1-11.+

[14]. Dabrowska, H.; Dabrowski, L.; Biziuk, M.; Gaca, J. and Namiesnik, J. (2003) - Solid-phase extraction clean-up of soil and sediment extracts for the determination of various types of pollutants in a single run. Journal of Chromatography A, 1003,1-2: 29-42.

[15]. Vega Moreno, D.; Sosa Ferrera Z. and Santana Rodiguez J.J. (2006) - Microwave assisted micellar extraction coupled with solid phase microextraction for the determination of organochlorine pesticides in soil samples. Analytica Chimica Acta, 571,1: 51-57.

[16]. Mohammad A. Mottaleb, Mohammad Z. Abedin, Determination of Chlorinated Pesticides in Soil by Solid Phase Extraction-Gas Chromatography, Analytical Sciences Vol. 15 (1999) No. 3 P 283-288.

[17]. V. Lopez-Avialia, K. Bauer and J. Milanes, J. AOAC Int., 76, 864 (1993).

[18]. Fenik J. T. M. A. B. M. (2011). Properties and determination of pesticides in fruits and vegetables. Trac-Trends in Analytical Chemistry.

[19]. Suleymanov B.A., Ahmedov M.M., Ibadov N.A., Humbatov F.Y., Hazardouz pollutant database for kura-araks water quality management, NATO Science for peace and Security-C: NATO Journal Information © Springer. Netherlands 2008, pp.171-182.