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Organochlorine Pesticides Residues for Some Aquatic Systems in Albania

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1. Introduction

The Republic of Albania is situated in Southeastern Europe, in the western part of Balkan Peninsula facing the Adriatic Sea and the Ionian Sea. The coastal area has a surface area of 7000 km² or 25% of the territory. The coast line is 476 km. Marine and coastal environment constitutes resources of high economic and ecological values for the country. Due to the mismanagement of these resources in years, considerable amounts of wastes have been discharged directly or through river flows and atmospheric deposits, into the sea. Adriatic and Ionic Sea as part of the Mediterranean Sea, which does not have an open linkage with the oceanic waters, are inclined to be considerably affected by pollution, due to the absence of its dilution. The highest impacts on marine waters in Albania are related to eutrophication, pollution from heavy metals and POPs, illegal fishing, overexploitation of aquatic fauna and degradation of coastal zones, mostly due to the uncontrolled development.

Shkodra Lake and Ohrid Lake are the most important and multi-dimensional freshwater resources of Albania. These lakes are also considered as the most important transboundary areas in Albania. Shkodra Lake is one of the most important multi-dimensional resources of this region as fishing, hunting, tourism, recreation and aquatic sports resource. Shkodra Lake is considered as one of the most important transboundary lakes in Albania. It is the biggest lake in Balkan region. The lake area varies between 354 km² in low water periods and 506 km² at high water periods. In the maximum, in the Montenegro territory there the lake area is 340 km² and 166 km² in Albania. The most important tributaries, that are sources of water for the lake, are: Moraca, Crnojevica, Orahovstica, Crmnicka, Karatuna, Baragurska rivers (Montenegro side) and Virstica, Proni, Tata, Riola, Vraka, Bunusi and Kiri rivers (from the Albanian side). Occasionally, Shkodra Lake receives water from river Drini too (Albania). This happens when the water level of river is higher than the water level of the lake. During the maximum of water level, the lake depth is over 12 m, and during the minimum is around 8 m. Water level oscillates between 4.7 and 10 m above the sea level. Buna River is the only emissary of Shkodra Lake with medium flow over 300m³/s. The water catchments basin of Shkodra Lake is 5179 km², 1025 km² of which belongs to the Albanian territory. 45 kinds of fish are leaving in the Lake and its effluents. Half of them are permanent and the others migrate through Buna River to the Adriatic Sea. The most characteristic fish is *Cuprinos carpio*, besides *Anguilla anguilla, Mugil cephalus, Mugil ramada,*

Marone labrax, Platichthys flessus italicus, Pachycilon pictum, Alosa fallax nilotica, Acipenser sturio, etc. (Dhora 1995).

Buna River is one of the most important Mediterranean rivers. Also, thanks to the waters from the Drini River, the Buna ranks second place among all tributaries to the Adriatic, measured by the annual discharge, after the Po in Italy (with 352 m³/s). Both rivers together are determinative on Adriatic Sea water balance. Out flowing from Shkodra Lake, Buna immediately joins Drini River water and both rivers discharge into southeast Adriatic Sea. Shkodra Lake – Drini River – Buna River hydrographical complex is very complicated and unique for its hydraulic regime in the world hydrography. Despite being short, the river has quite a large watershed, covering 5,187 km², because the whole drainage area of Shkodra Lake, the largest lake in southeastern Europe, is also part of it (Pano & Abdyli, 1984).

The Ohrid Lake is one of the oldest lakes in the world. The basin of the Ohrid Lake together with the lake belong to the geo-tectonic zone of the South-Eastern holes of Albania. The Ohrid Lake is part of the so-called Desaret Lakes. The flora and fauna of the Ohrid Lake is unique in the Balkans and wider. The lake's biota is constrained by several abiotic factors, among which the geographic location, the water basin play an important role. The low temperature lake's water makes the biologic processes be developed slowly, while the plankton (the phytoplankton and zooplankton) are characteristic and interesting (Topi et al. 2006). The number of the endemic kinds is high and makes up about 60% of the organisms that live in the lake. About 60% of the fishes in the lake are endemic, particularly the various kinds of fishes such as *Salmo letnica, Salmo truta, Salmothynus ohridanus, Cyprinuscarpio, Leuciscus cephalus albus, Alburnus alburnus alborella, Rutilus rubillioohridanus, Cobitis taenia ohridana, Anguilla anguilla,* etc,. Water basin of Ohrid Lake is huge. Prespa Lake is therefore considered to be a part of the Lake Ohrid watershed.

Complex Lagoonary of Butrint is located 4 km south of Saranda, it is 140,000 m², opposite to the island of Corfu and near the Greek-Albanian border. The area is mainly composed of wetland and lakes and crossed by two rivers: Pavllo Bistrica in the north and south. In the east, the Mountain Mile Complex (824 m) separates the interior of the complex Lagoonary Albania. Less than ten kilometers from the island of Corfu, Butrinti was linked to the Mediterranean by the Vivari canal, which ran from the Butrinti Lake to the Ionian Sea.The area has a great value for its scenery and contains a variety of natural habitats, semi-natural and artificial. These include areas covered with oak, typical Mediterranean scrub, the salt lake Bufi (ray), salt water lagoon of Butrint, the salty marshland Alinures, spills and Pavllos Bistrica River, halophytic lands with plants (which live in the salty earth) and agricultural land. Beside it is the Butrinti (Bouthroton) site which is full of ancient history and is one of Albania's most popular tourist attractions. Mussels *Mytulus Galloprovinciulis* from the lake are famous all over the world, as fresh and wholesome, and include a variety of sizes and natural flavored.

Aquatic areas showed above are some of most important aquatic areas in Albania. For these areas are studied different type of samples for evaluating levels and distribution of organochlorinated pesticides.

What are organochlorinated pesticides in short terms?

The modern history of pesticides dates back to World War II when for the first time the insecticidal properties of DDT were recognized. DDT was first introduced on a large scale to fight fleas, lice, flies and mosquitoes and reduce the spread of insect borne diseases such as malaria and yellow fever. Many public health benefits have been realized by the use of

pesticides, but their potential impact on the environment is substantial too (Di Muccio, 1996). Over 800 pesticide active ingredients are formulated in about 21000 different commercial products. Most of organochlorinated pesticides have been progressively restricted and then banned in the 1970s in most industrialized countries, a widespread environmental pollution has resulted from their before use. Organochlorinated pesticides are usually big molecules with a big number of chlorine atoms attached their molecules; they can persist without changes for many years in application areas. Water irrigations can take away pesticides from these application areas mainly to the surface waters. Organochlorinated pesticides solubility in water it's limited (depend on their Kow), they are mostly lipophilic compounds so they attend to connect in the suspend matter, to precipitate in sediments, to accumulated and concentrated in biota of aquatic systems.

Albania is a country rich with lakes, rivers, and many effluents. Shkodra Lake, Ohrid Lake and Prespa Lakes are the large lakes in Albania and Balkan Peninsula. Water basin of these lakes is huge with many effluents and close with them has many fields used for agricultural purposes. Shkodra Lake and Adriatic Sea are connected between each other with Buna River. The most important rivers are Drini, Buna, Mati, Ishmi, Erzeni, Shkumbini, Semani, Vjosa and Bistrica. All rivers start in the east of Albania, in mountain areas, and finish to the Adriatic Sea. They are very fast (except Buna River) so the pesticide residues or other materials deposited in the sea. For many industries in Albania (also Lindane Plant), the waste of them were discharged for many years directly to the sea. These areas are located especially close to Durres and Vlora bay. Before 90' organochlorinated pesticides were used widely in Albania for agricultural purposes. The main agricultural areas were in the western of the country, but almost every were had been developed different directions of agricultural (fruits, corns, vegetables, etc.). The districts where the larger quantities have been used are Fieri, Lushnja, Tirana, Vlora. The most used chlorinated pesticides were DDT, Lindane, HCB, Aldrins and Heptachlors. Lindane was produced in the country at Lindane Plant, in Porto-Romano, near Durresi City. Other chlorinated pesticides were imported mostly from eastern countries. The scale of their use after 90' in agriculture has decreased, due the change of soil structure. Emigration of many peoples in western country and also free movement inside the country were two main factors that impact directly in agriculture areas and it's developing. Use of pesticides generally has decreased, because of large areas were not using for agricultural purposes and other areas were used for building new houses and industries. Except this, many chemical industries, include Lindane Plant, were stopped or destroyed. The former has generated the expired pesticides, which due to the inappropriate conditions of conservation and storage have been damaged. The other part of expired or out of use pesticides, to be disposed of, has been distributed in various districts of the country. In the country after 90' had a large amount of stocks of pesticides (1000 ton). About 45% of all pesticides in the country have been evaluated as "hazardous class". Different projects were done last years for isolate and eliminate pesticides and other pollutants. These wastes are not pretreated; it is very difficult to find precise data on the amount of industrial solid wastes stores in various parts of the country. Mismanagement of oddments pesticides, for some years after 90' was another source of pesticides contamination. Before use of pesticides, their persistence, water irrigation, their ability to concentrate in sediments and biota adding other factors suggest us to study levels of organochlorinated pesticides in above aquatic systems.

For studding organochlorinated pesticides in environmental samples are developed many methods and techniques. Pesticide residues in environmental samples are found in very

lower levels. Qualitative and quantitative analyze of organochlorinated compounds performed usually by modern chromatographic techniques. Gas chromatography (GC) technique equipped with electron-capture detector (ECD) or mas-spectrometry detection (MS) are most favorable technique for pesticide residue analyze. Many columns and other part of GC are suggested for pesticide analyze. For gas chromatographic technique in mostly of samples needed different steps before injecting in GC. Sample preparation prior to the determination of many environmental pollutants including organic pesticides in water, sediment, and biota samples usually consists of many steps because of the complexity of the matrix. Extraction of the target compounds and clean-up for the extract are the most critical steps in the analytical procedure when it comes to complete recovery of the target substances. For extraction of organochlorinated pollutants different methods are used: from classical Soxhlet extraction to automated extractions method as Accelerated Solvent Extraction (ASE) and Supercritical Fluid Extraction (SFE). For solid samples ultrasonic extraction is widely used, as well. The main goal of the clean-up step(s) is to remove substances that could interfere with the final determination and quantization of target compounds. Removal of interfering substances can be accomplished in many different ways. For example, copper is often used as sorbent for retaining elementary sulphur from sediment samples. Solid-phase extraction (SPE) is still the dominant method for extracts purification. A large number of sorbents are used for the isolation of organic compounds from the extract solutions include alumina, Florisil, ion-exchange resins, silica gel and many silica-based sorbents.

2. Material and methods

2.1 Chemicals

Organic solvents and reagents. n-Hexane, dichlorometane of special grade for pesticide residue analysis were purchased from Merck, Germany. Organic solvents particularly dichlorometane which is toxic, were handled with care observing safety precautions, using efficient fume hoods and wearing protective gloves. Anhydrous sodium sulphate (Na_2SO_4) from Merck, Germany. Florisil ($\geq$ 400 mesh ASTM) and silicagel (60-100 mesh ASTM) were purchased from Merck, Germany. H_2SO_4 with 95-97% purity for GC analyses was purchased by Merck. The sodium sulfate, florisil and silica gel were pre-extracted with hexane/dichloromethane (4/1) in a Soxhlet extractor, dried and were rinsed with hexane/dichloromethane (4/1) just before utilization. All glassware was rigorously cleaned with detergent followed by pyrolysis at 300°C.

Pesticides solution and standarts. Organochlorinated pesticides stock solutions from 5 mM concentration were donated by IAEA/MEL-Monaco. Standard solutions of pesticides and PCB-s were prepared by dissolving their stock solutions in n-hexane in concentartion 50 ng/μl and storing them in refrigerator in glass bottles with PTFE-faced screw caps. The organchlorine pesticides detected were HCHs (a-, b-, g- and d-isomers) and the DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), Hexachlorobenzene (HCB), Heptachlor, Heptachlor epoxide, Methoxychlor and Mirex.

IAEA-383 homogenized sediment sample donated by IAEA/MEL-Monaco, France (International Atomic Energy Agency/ Marine Environmental Laboratory) was used as CRM for sediment samples. IAEA-435 tuna fish was used as biota CRM (provided by IAEA/MEL-Monaco, France International Atomic Energy Agency/Marine Environmental Laboratory).

2.2 Study areas

Study areas were: Adriatic Sea (three sampling stations; Vlora Bay, Porto-Romano and Velipoja), Ohrid Lake, Shkodra Lake, Butrinti Lake and Buna River. These areas were selected in different locations of Albania as representative of huge hydrological systems found in the country. Samples were collected for a period of five years (2005-2010). Data presented here shown levels and distribution of organochlorinated pesticides in water, sediments and biota for selected stations. Sampling was done based in Reference Method No 6, UNEP, 1993. Fig. 1. Geographic position of studied aquatic locations in Albania.

2.3 Water

Water sampling. Water samples were sampling at Vlora Bay (Adriatic Sea), Butrinti Lake, Shkodra Lake and Buna River. Water samples were taken on surface of water in PTFE bottle. For organochlorinated pesticide analyze were taken 1 L of water from each station. Water samples were transported to the laboratory and stored in a refrigerator in +4 °C.

Fig. 1. Geographic position of studied aquatic locations in Albania.

Preparation of water samples for GC analysis. Liquid-liquid extraction was used for the extraction of organochlorine pesticide residues from water samples. 1 L of water, 10 µl PCB-

29 as internal standard and 20 mL n-hexane (extracting solvent) were added in a separatory funnel. After separation the organic phase was dried with 5 g Na_2SO_4 anhidrous, for water removing. A Florisil column was used for the sample clean-up. The extract was concentrated at 1 ml for analyzing by GC-ECD.

2.4 Sediments

Sediment sampling. Sediment samples collected at different aquatic locations of Albania; Adriatic Sea (Vlora Bay, Velipoja), Shkodra Lake and Buna River. Standard sediment Van Veen grab with 440 cm^3 of volume was used for sediment sampling. Twenty two stations among Vlora Bay were choosing for this study and three stations in different depth of Velipoja sea shore (Adriatic Sea stations). Six stations were chosen to represent different conditions of the Shkodra Lake and seven stations in Buna River. For all sediment stations are analysed surface corer with a layer of 5 cm. Samples were transported to the laboratory and stored in a refrigerator in +4°C. The samples were air-dried, grinded and sieved. Particles of 0.063 mm were taken for analysis.

Sediment treatment. The sediment samples (1 gram dry weight) were transferred into glass ampoules for extracting with dichloromethane-hexane (1/3), after a standard solution of PCB-29 was added as internal standard. Extraction was carried in ultrasonic bath in 30⁰C for 30 minutes. The preliminary clean-up of sample extract was carried out with elemental Hg to remove sulphur compounds from the sediment samples. Further clean up was performed using a column made of two layers. The upper layer was silica gel activated in 300⁰C and impregnated with 45% sulphuric acid. The down layer of the column was made of florisil activated in 250 ⁰ C and deactivated with 5% distilled water. The elution was carried on with 12 ml dichloromethane-hexane (1/4). The final volume of samples was 1ml using Kuderna-Danish for evaporate. IAEA 383 certified sediment sample for chlorinated pollutants was used for method validation.

2.5 Biota

Biota samples. Fish specimens were taken in random mode from the catch of local fishermen in Vlora Bay, Velipoja, Shkodra Lake and Ohrid Lake. A total of 32 fish species and 102 specimens has been analyzed, respectively 9 species with 26 specimens from Vlora Bay, 10 species with 33 specimens from Velipoja, 9 species with 24 specimens from Shkodra Lake and 7 species with 19 specimens from Ohrid Lake. Fish species for all stations were: Vlora Bay (*Engraulis encrasicholus*, *Lithognathus mormyrus, Solea vulgaris, Mullus barbatus, Mugil cephalus, Trachurus trachurus, Belone belone gracilis, Dicentrarchus labrax, Lichia amia, Mytulus galloprovincialius*); Porto-Romano (*Mytulus galloprovincialius*); Velipoja *(Mullus barbatus, Sphyraena sphyraena, Pargus coeruleosticus, Uranoscopus scaber, Merluccius merluccius, Scomber scombrus, Dicentrarchus labrax, Boops boops, Trigla lyra)*; Shkodra Lake (*Cyprinus carpio, Anguilla Anguilla, Carassius gibelio, Pseudorasbora parva, Scardinius knezevici, Mugil cephalus, Alburnus scoranza, Allosa agone)*; Ohrid Lake *(Salmo letnica, Salmo ohridanus, Squalius cephalus, Salmo truta, Cyprinus carpio, Alburnus scoranza, Rutilus ohridanus) and* Butrinti Lake *(Mytulus galloprovincialius).* The mussels, *Mytilus Galloprovincialus* were collected in Vlora Bay, Porto-Romano, and Butrinti Lake with a number of 75 species for each station. Before treatment mussels were divided in five groups with 15 members' based in their length. The biota (fish and mussels) samples were transferred to an aluminum container and stored at -10°C.

Preparation of biota samples for GC analysis. For all biota samples were analyzed tissues. The method was based on EN 1528/1/2/3/4 (2000) for determination of organochlorinated pesticides and PCBs in biota samples. Prior analyzing biota samples were homogenized with anhydrous sodium sulphate. 1 g fresh weight of organism tissue was extracted by ultrasonic bath assisted extraction with 20 ml mixture of hexane/dichloromethane (3/1). The extract was purified firstly by shaking with 15g silica gel treated with 45% sulfuric acid for lipid hydrolysis. After filtration, the extract was concentrated in Kuderna Danish to 5 ml volume and a second purification on a column of Florisil with 5% water was performed. (Petrick et al, 1988; Koci, 1997) Organochlorinated pesticides were eluted with 10 ml of a mixture of hexane/dichloromethane (5/1). The extract was concentrated at 1 ml for analyzing by GC-ECD. Homogenized tuna sample IAEA 435 was used for method validation.

2.6 Apparatus and chromatography

Gas chromatographic analyses were performed with an HP 6890 Series II gas chromatograph equipped with a ^{63}Ni electron-capture detector and a split/splitless injector. The column used was a HP-5 capillary column [low/mid polarity, 5% (phenyl methyl siloxane)] (25 m x 33 mm I.D.x 25 mm film thick). The split/splitless injector and detector temperatures were set at 280^{0}C and 320^{0}C, respectively. Carrier gas was He at 1.8 ml/min and make-up gas was nitrogen 28,2 ml/min. The initial oven temperature was kept at 60^{0}C for 4 min, which was increased, to 200^{0}C at 20^{0}C/min, held for 7 min, and then increased to 280^{0}C at 4^{0}C/min for 20 min. The temperature was finally increased to 300^{0}C, at 10 ^{0}C/min, held for 7 min. The total run time was 38 min. Injection volume was 2 μl, when splitless injections were made. Organochlorine pesticide quantification was performed by internal standard method. The relative response factors of the different compounds were determined by injecting the standard solutions of organochlorinated pesticides spiked with the same solution of internal standards PCB 29 as that used for spiking the samples. Procedural of blanks were regularly performed and all results presented are corrected for blank levels. Quality assurance procedures included the analyses of marine sediment reference materials IAEA 385 and tuna fish homogenized certified sample IAEA 435 to determine the precision and the accuracy of the method (Schantz et al, 1993; Marku and Nuro, 2005).

3. Results and discussion

Data presented below are interpreted in order of aquatic locations selected. These locations have own characteristics, but except this, are way to see status of Albania aquatic body in order of organochlorinated pesticides. All data represent mean value for a group of experimental for a selected station or species.

Vlora Bay. In Vlora Bay were analyzed water, sediment, fish and mussel samples. Organochlorinated pesticides level in water samples of Vlora Bay (Figure 2) were with a minimum value of 17,1 ng/L to the maximum value of 53,4 ng/L. Mean value for analyzed water samples was 28,9 ng/L. Higher values of pesticide residues were found in water samples in the center of bay compared with water samples near seashore. Distribution for these found levels in different stations it's connected from water current inside and outside bay. Total of organochlorinated pesticides was higher also for sediment station number 43, 44 and 45 (Figure 3) sampling in the center of bay. Minimum value for organochlorine pesticides residues in sediment sampling in Vlora Bay were 6,7 ng/g to 138,7 ng/g, mean

value was 34,42 ng/g dry sediment. Two are the most favorable factors for this distribution of pesticides in sediments of bay: Before uses of pesticides for agricultural issues in Vlora region (mostly as insecticides). Applied pesticides in these areas after irrigation go throughout the sea. The current of water into the bay is the second factor. Pesticide stability, their chemistry and sediment conditions are factors affect levels of pesticide residues in water and sediment samples. Figure 4 shown data about the total of organochlorine pesticides in fish samples of Vlora Bay. The sample of *Mugil cephalus* with 107.4 ng/g f.w. (fresh weight) was the most polluted one among the fish species analyzed for organochlorined pesticides in Vlora Bay. The sample of *Solea vulgaris* from the same area was the "cleanest" one with 37,5 ng/g f.w. Mean value for pesticide residues in fish samples was 67,1 ng/g f.w. Found levels in fish samples were almost 2 - 5 time higher than levels found in water and sediments of Vlora Bay. About levels of pesticide residues found in fish samples it's evident higher levels than water and sediments but we must evaluate also fish species, their position in food chain and their age, sex, ect,. Very interests were found levels of pesticide residues in mussels *Mytulus galloprovincialius* sampling in Vlora Bay. Minimum value was 152,8 ng/g f.w; maximum value was 379,1 ng/g f.w. and mean value 259,7 ng/g f.w. Mussels which are water altering bivalves have been shown to concentrate many organic contaminants, providing a direct representation of pollutant bioavailability are used mostly as bio-indicators of marine areas. Levels of orgnochlorinated pesticides found in these organisms are related with levels of these pollutants in water by a factor of 10 times. This connection is shown also for the fact that higher polluted were mussels of group five that are higher in age and weight, and minimum of pollution for mussels of group two that were smaller one.

Profile of organochlorine pesticides is the same for all type of samples analysed in Vlora Bay (Figure 6). *p,p'*-DDE was found in greatest concentration among pesticides for all samples. The second pollutants were DDT metabolites, *o,p'*-DDE and *p,p'*-DDD. DDT levels were comparable with DDE for sediment samples. This is not linked with uses of DDT at last for agricultural purpose because after 90' in our country it is banded. Degradation of DDT in sediment is slow. Lindane was not the first isomer in total HCH contribution. *d*-HCH and *b*-HCH concentrations were higher than the other isomers, because of their tendencies to accumulate in fatty tissue. It's evident the level of *b*-HCH in mussel samples. HCB concentration was higher mostly in fish and mussel samples, because of its Kow and bioavability for concentration in upper steps of food chain.

Porto-Romano, Durres, Adriatic Sea. *Mytulus galloprovincialius* mussel samples were analyzed in Porto-Romano, Adriatic Sea. Mean level of organochlorinated pesticides in mussel samples was 220,6 ng/g f.w.; minimum was for second group with 107,4 ng/g f.w. and maximum for fifth group with 397,5 ng/g f.w. (Figure 7). Levels of organochlorinated pesticides in Porto-Romano, Durres were comparable with levels found for mussels analyzed in Vlora Bay. For this station the old industries located in this area such as Lindane Chemical Plant of Porto-Romano, Durres represent the major polluting factor, followed by agricultural contribution and other possible sources of contamination such as the water-based contribution, atmospheric factor, etc. There is comparability between pesticide residues data in Vlora and Porto-Romano obtain for other areas of Adriatic Sea.

The most frequently detected pesticides for Porto-Romano were *p,p*-DDE (Figure 8). *p,p*-DDT was in higher levels than o,p-DDE and p,p-DDD, also in higher levels than p,p-DDT levels found in mussel samples in Vlora Bay. This would have principally agricultural component although there are also other possible sources of contamination such as
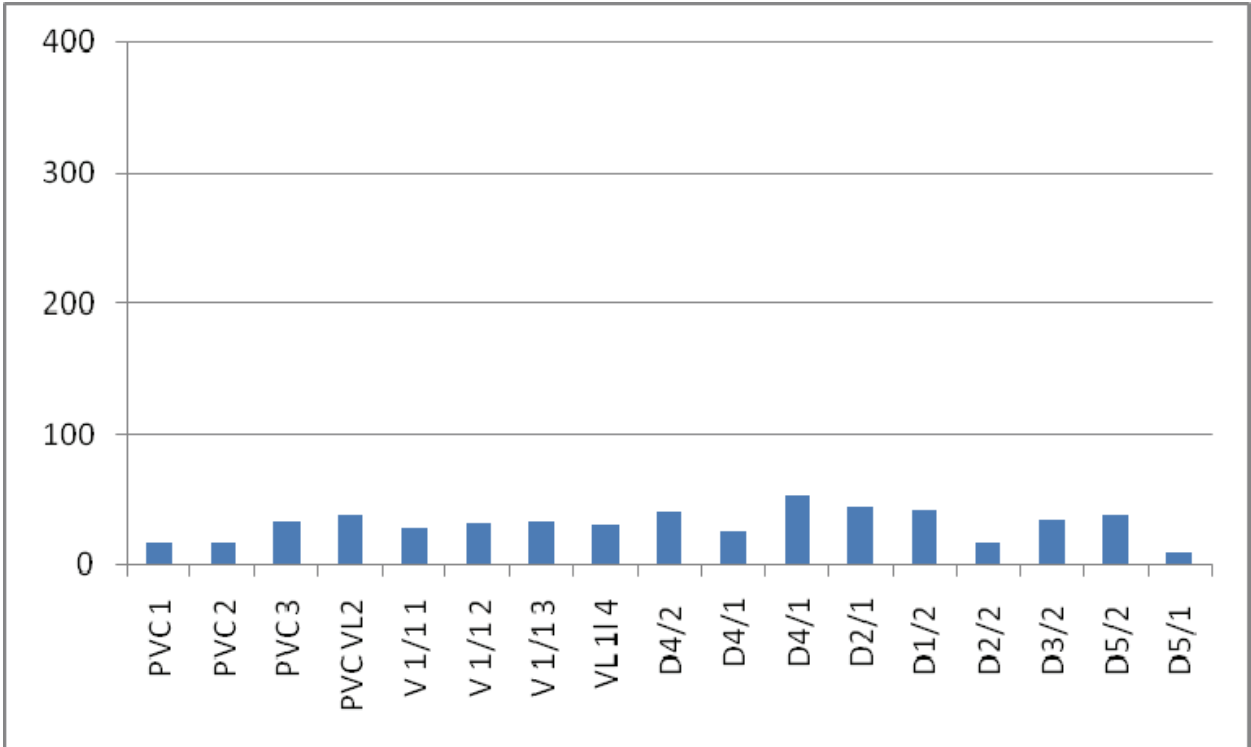
Fig. 2. Total of organochlorinated pesticides in water samples of Vlora Bay
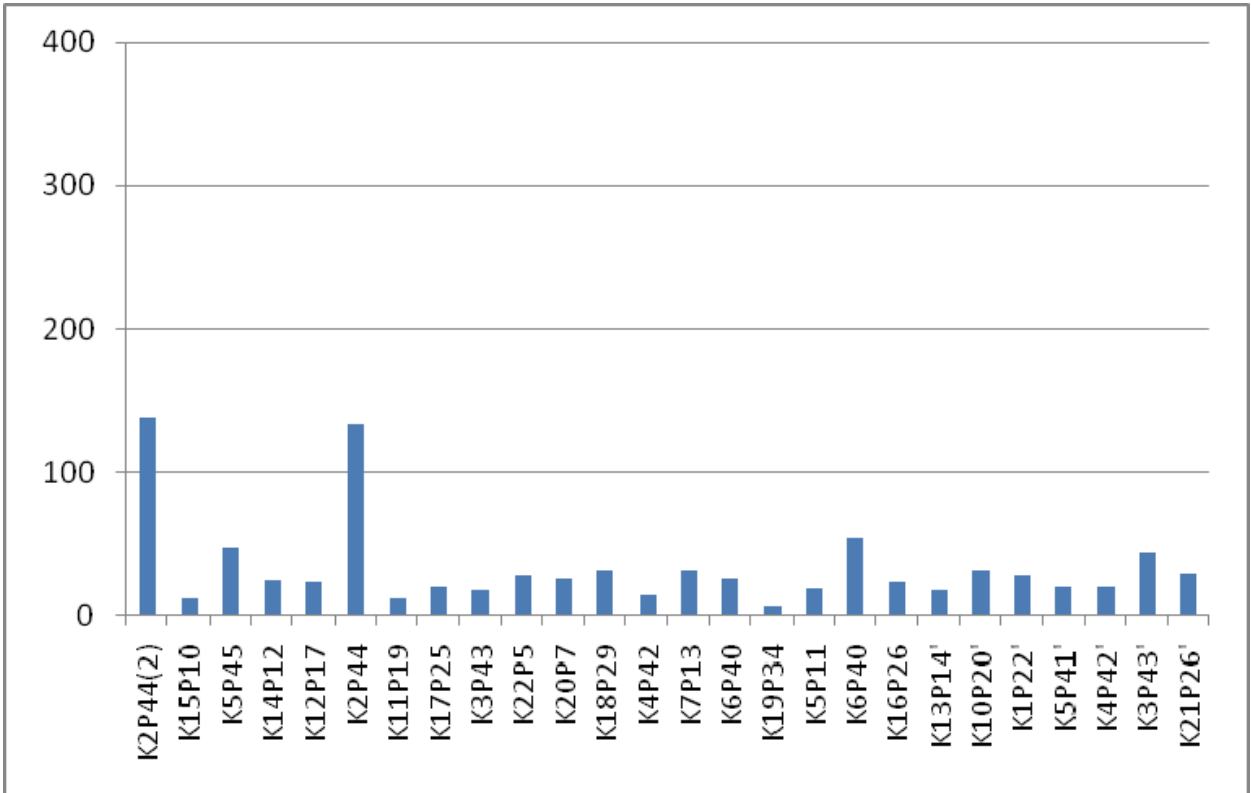

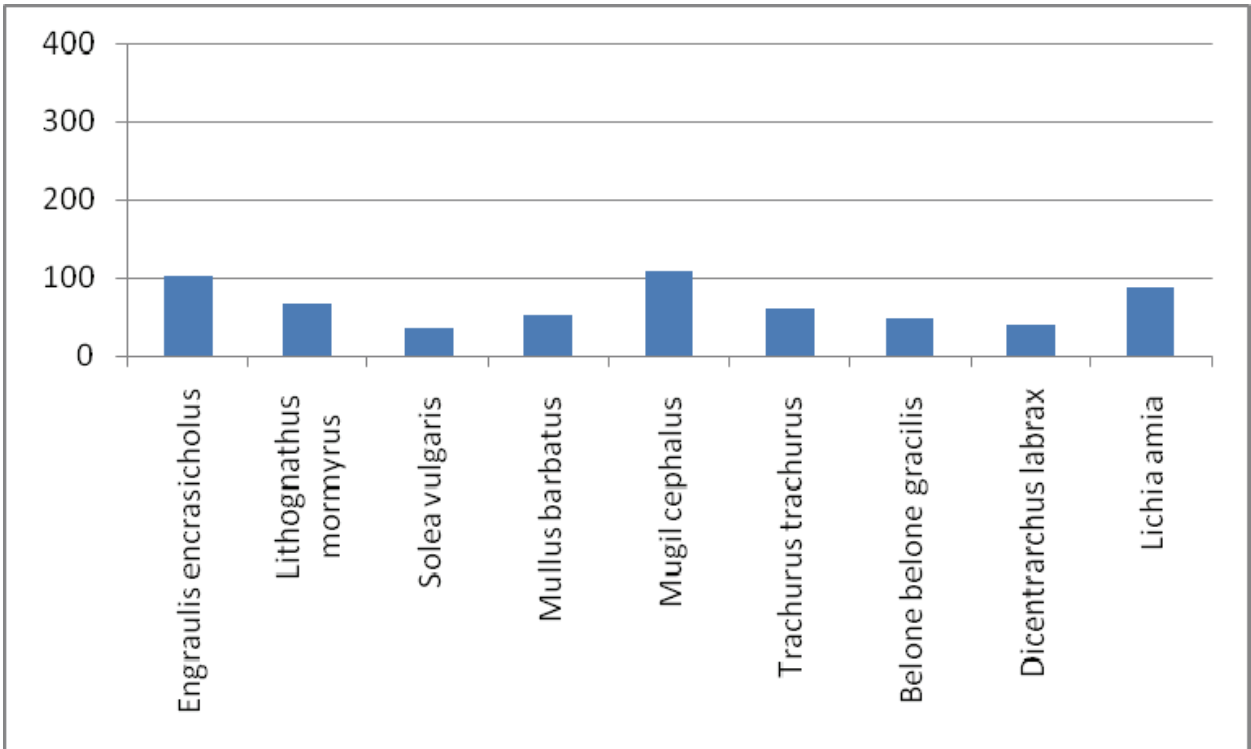Fig. 3. Total of organochlorinated pesticides in sediment samples of Vlora Bay

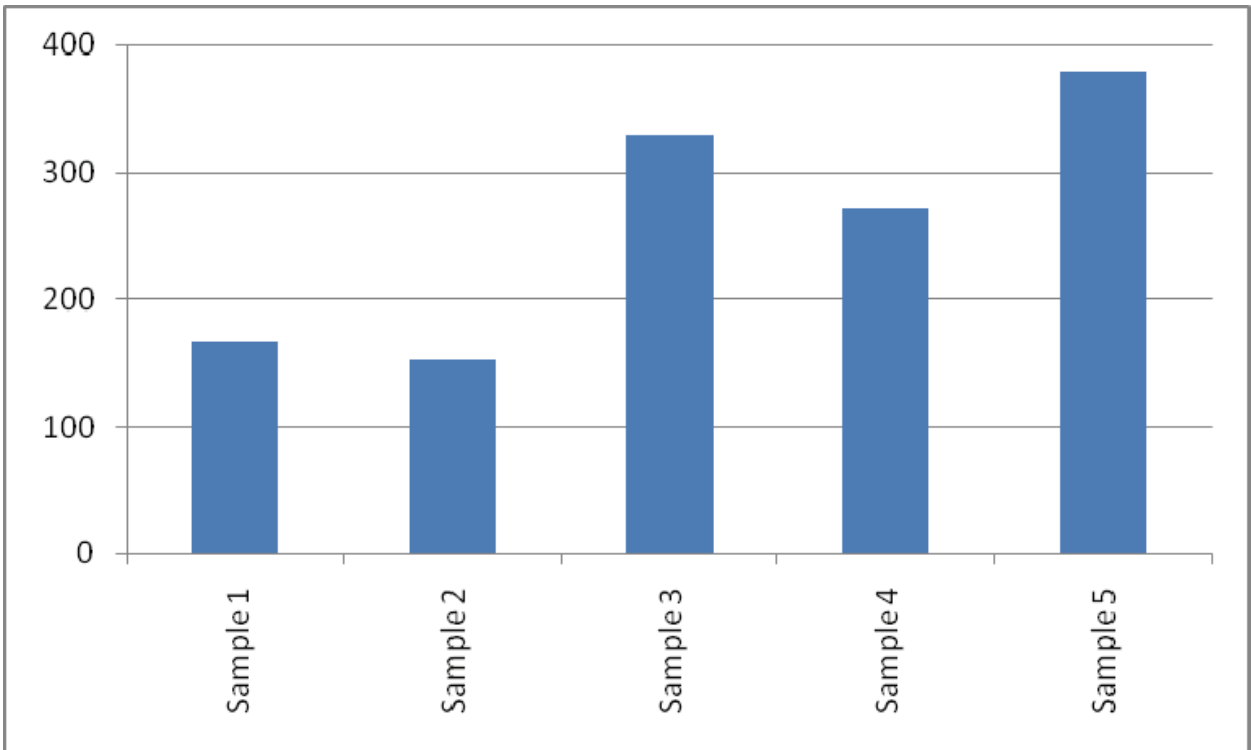Fig. 4. Total of organochlorinated pesticides in fish samples of Vlora Bay

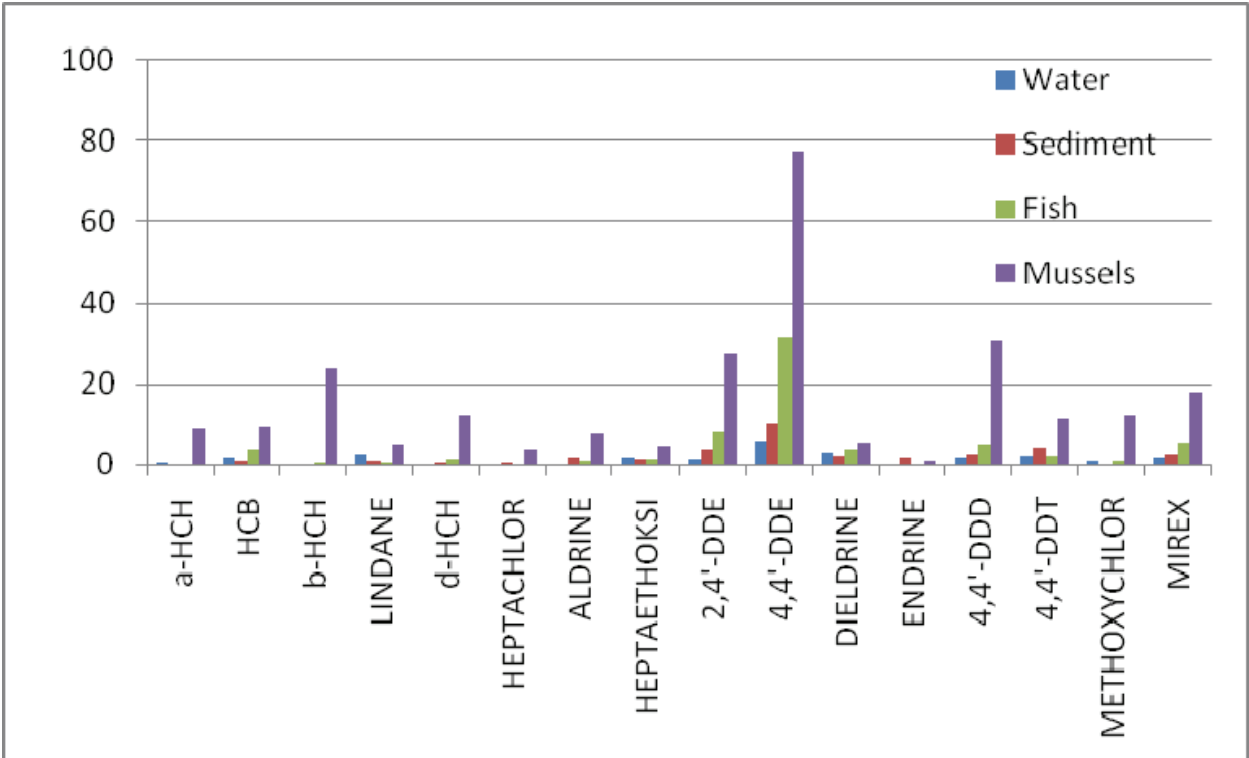Fig. 5. Total of organochlorinated pesticides in mussels *Mytulus galloprovincialius* of Vlora Bay

Fig. 6. Average of organochlorinated pesticides in water, sediment, fish and mussel samples of Vlora Bay

mismanagement of oddments pesticides, irrigation of surfaces where these pesticides were used by rainwater, drift, water-based contribution and atmospheric component. HCHs were expected to be found for analyzed samples because this station it's near old Lindane Chemical Plant in Porto-Romano. Was interest the fact that Lindane was in lower levels than *b*-HCH and *d*-HCH isomer. *b*-HCH concentration was higher than the other isomers' concentrations because of its higher tendencies to accumulate in fatty tissue. The a/g HCH ratio, an indicator of current technical HCH application, was lower. Again this likely reflects recent use of HCH formulations, or possibly ongoing releases of HCH isomers from waste repositories.

Velipoja, Adriatic Sea. Sediment and fish samples were sampling in Velipoja, third location of Adriatic Sea, in North Albania. In Figure 9 are shown data about organochlorinated pesticides in sediment samples of Velipoja. Sediment samples were choosing in different depth of Adriatic Sea in front of Buna river mouth. It was evident that Buna rivermouth (in Adriatic Sea) was the most polluted station with 173,8 ng/g dry sediment. Lower concentration of pesticide residues were found going to the higher depth of Adriatic Sea (far away from Buna river mouth). Sediment sampled in 100 m depth was lower level for total of organochlorinated pesticides with 25,2 ng/g dry sediment. Influence of Buna River is main factor for this distribution of pesticide residues in sediments of Adriatic Sea for this station.

Buna River and its water basin are located in a huge agricultural region. Before use of pesticides, rain fall of these areas, sedimentation process and sedimentation transport, pesticides stability and lower velocity of pesticides degradability are factors that affect in the profile and in the total of pesticide residue in Vleipoja station. Total concentrations of pesticides for fish samples in Velipoja were in range from 43.9 ng/g f.w. to 91.2 ng/g f.w. respectively for *Raja clavata* and *Uranoscopus scaber* (Figure 10). Mean value were 58,1 ng/g
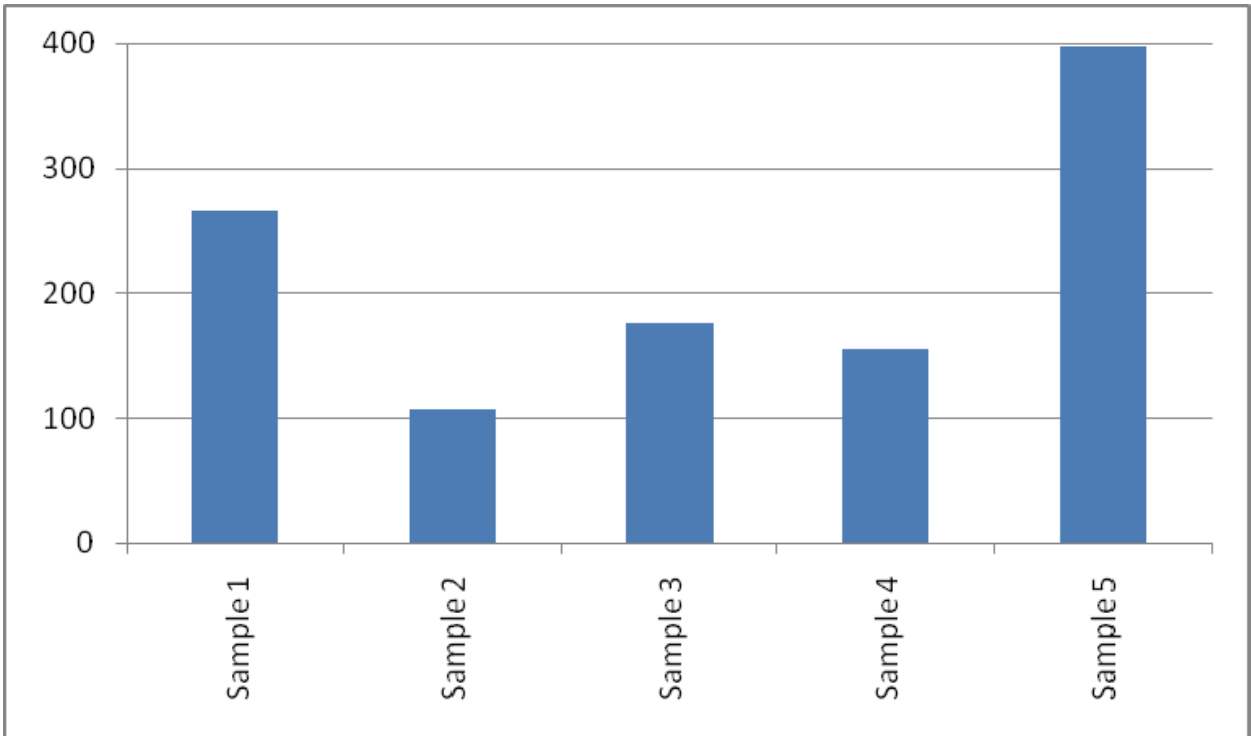
Fig. 7. Total of organochlorinated pesticides in mussels *Mytulus galloprovincialius* of Porto-Romano, Durres, Adriatic Sea
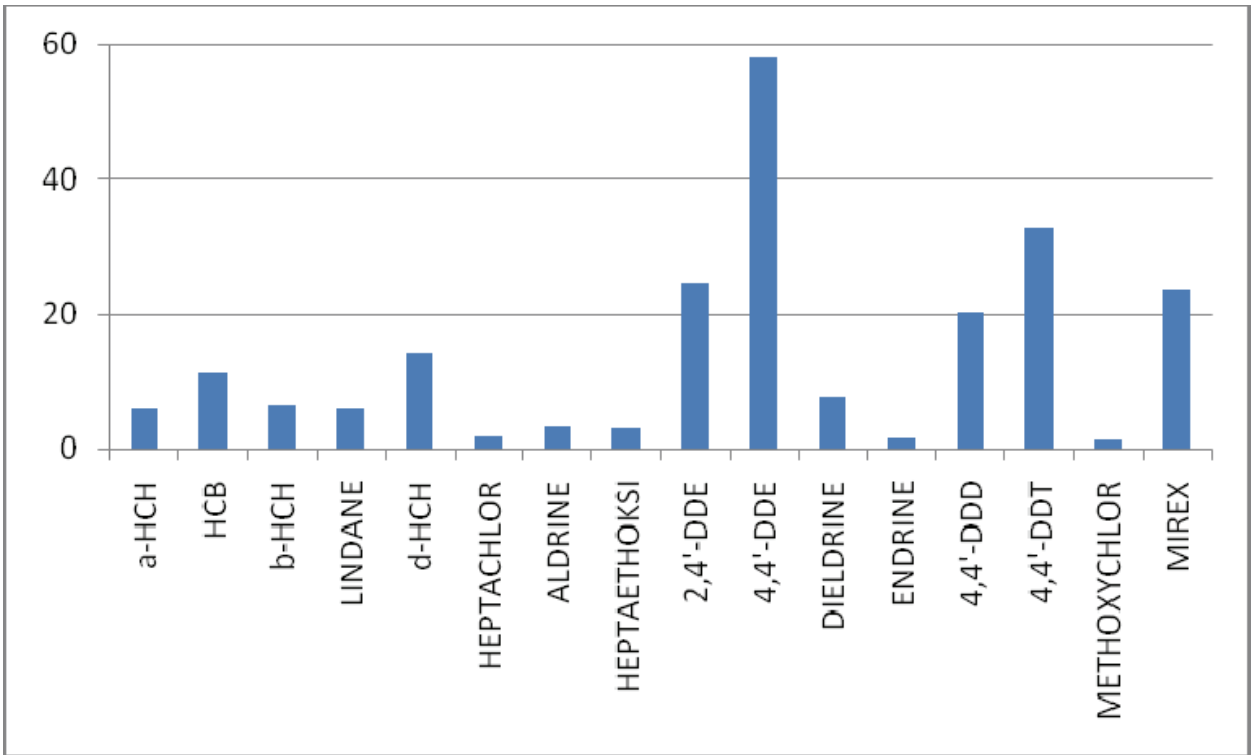

Fig. 8. Profile of organochlorinated pesticides in mussels *Mytulus galloprovincialius* of Porto-Romano, Durres, Adriatic Sea

 f.w. Found value were comparable with levels of pesticide residue in fish samples of Vlora Bay. Profile of organochlorine pesticide dedected for sediment and fish samples of Velipoja are shown in Figure 11. For fish sampes could saw that is the same profile found in samples of Vlora Bay or Porto-Romano. The higher pesticide concentrations were for DDT and its metabolite and HCH isomers. p,p-DDE concentration was higher than other pesticides in fish samples of Velipoja followed from b-HCH concentration. Pesticide profile for sediments of Velipoja it's quite different from profile of fish samples and also different from profile found for sediments of Vlora Bay. Were evident higher concentration of HCHs and Heptachlors followed from DDTs and Aldrine. Apart from above factors this station could be affected from other factors. Another important factor could be water current in this part of Adriatic Sea.

Shkodra Lake. In Shkodra Lake were sampling water, sediment and fish samples. In Figure 12 are shown total of organochlorinated pesticides in water samples of Shkodra Lake. Pesticide residues in water samples ranged from 17,6 to 83,4 ng/L. Shkodra Lake has a huge water basin. The concentrations of the organochlorinated pesticides (except DDTs and Lindane) suggest little use of these pesticides in adjacent agricultural areas. Some residues detected in the lake sediments may be also the result of agriculture runoff. Water cycle and water current in Shkodra Lake could be affect in levels of pesticide residues and profile of them in different stations of water samples in Shkodra Lake. The total concentrations of organochlorinated pesticides for sediment stations are shown in the Figure 13. The highest values correspond to Station 5 with 98.6 ng/g dry sediment. Station 5 is situated close to the main bridge of the lake, where Buna River begins to flow. The lower concentration was for Station 6 with 29,6 ng/g dry sediment. Station 6 was close to Vraka village (500 m far away). Note that sediments are rockier in this side of lake. The total concentrations of chlorinated pesticides in the different fish samples of Shkodra Lake are shown in Figure 14. The samples
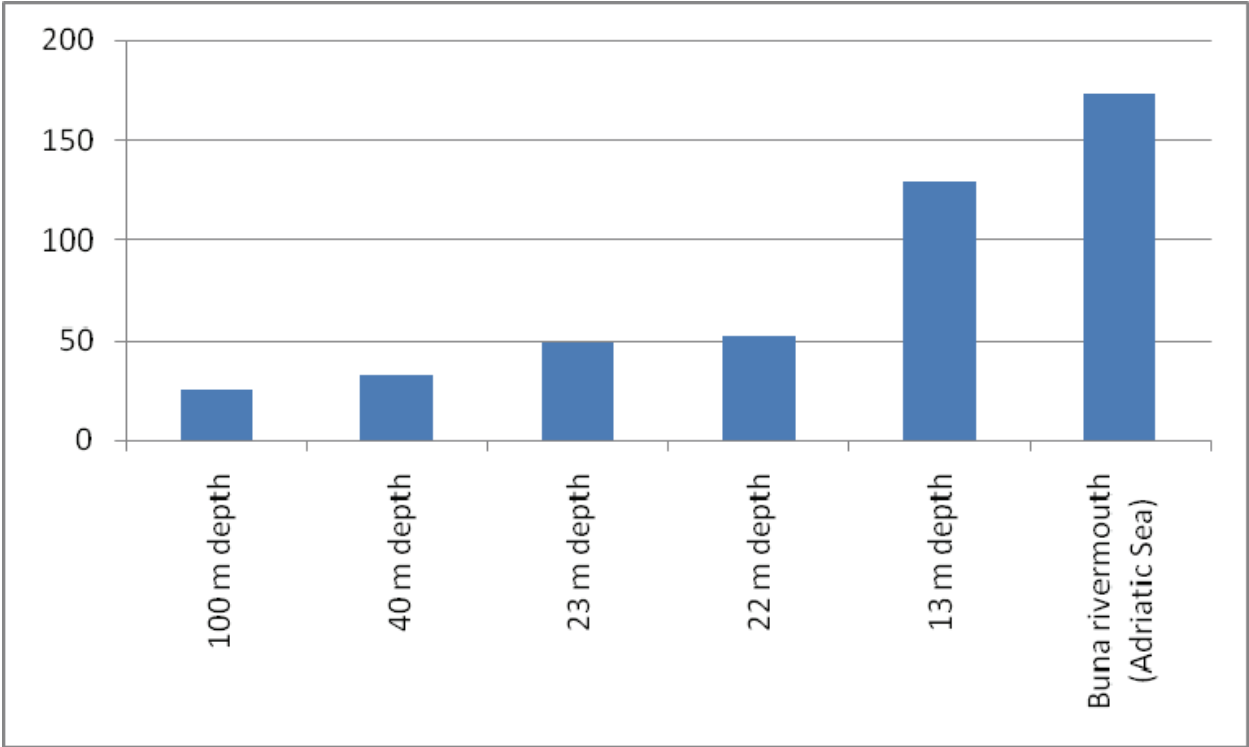

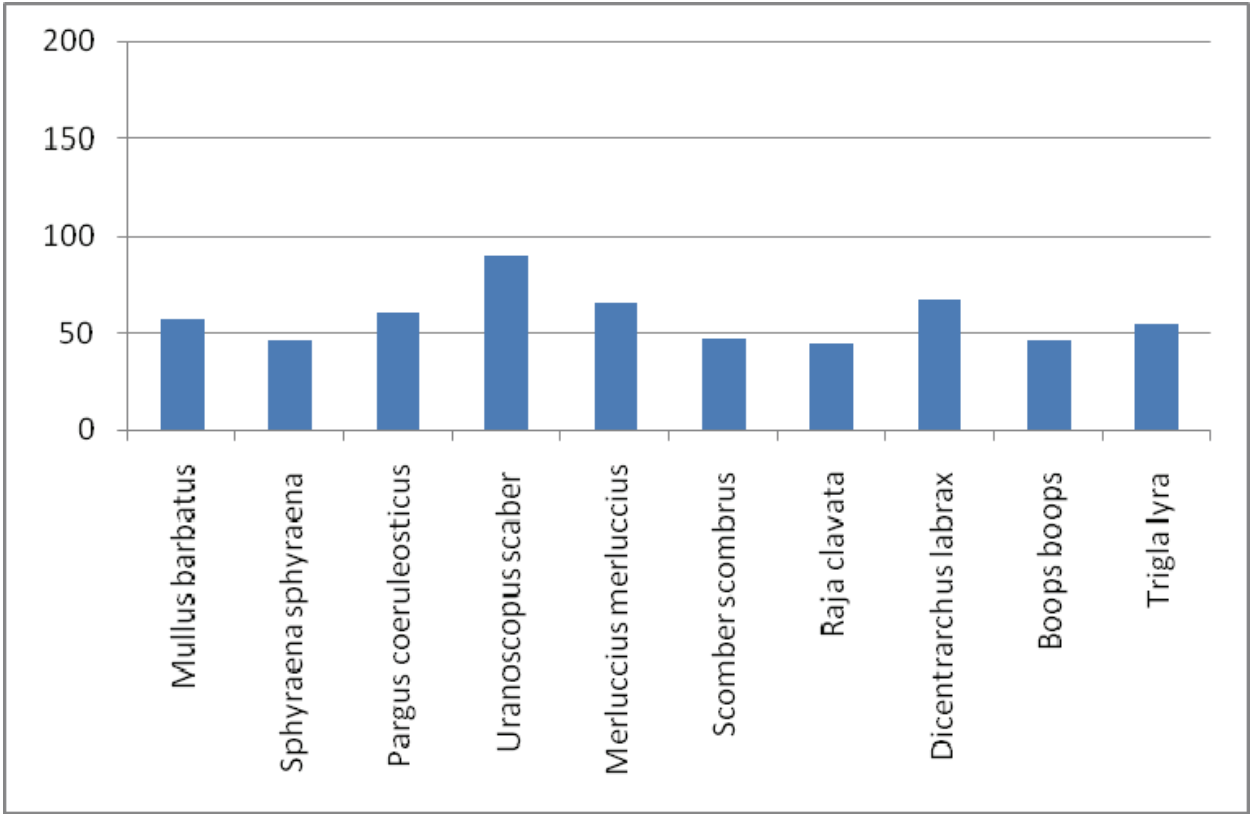Fig. 9. Total of organochlorinated pesticides in sediments of Velipoja, Adriatic Sea

Fig. 10. Total of organochlorinated pesticides in fish samples of Velipoja, Adriatic Sea
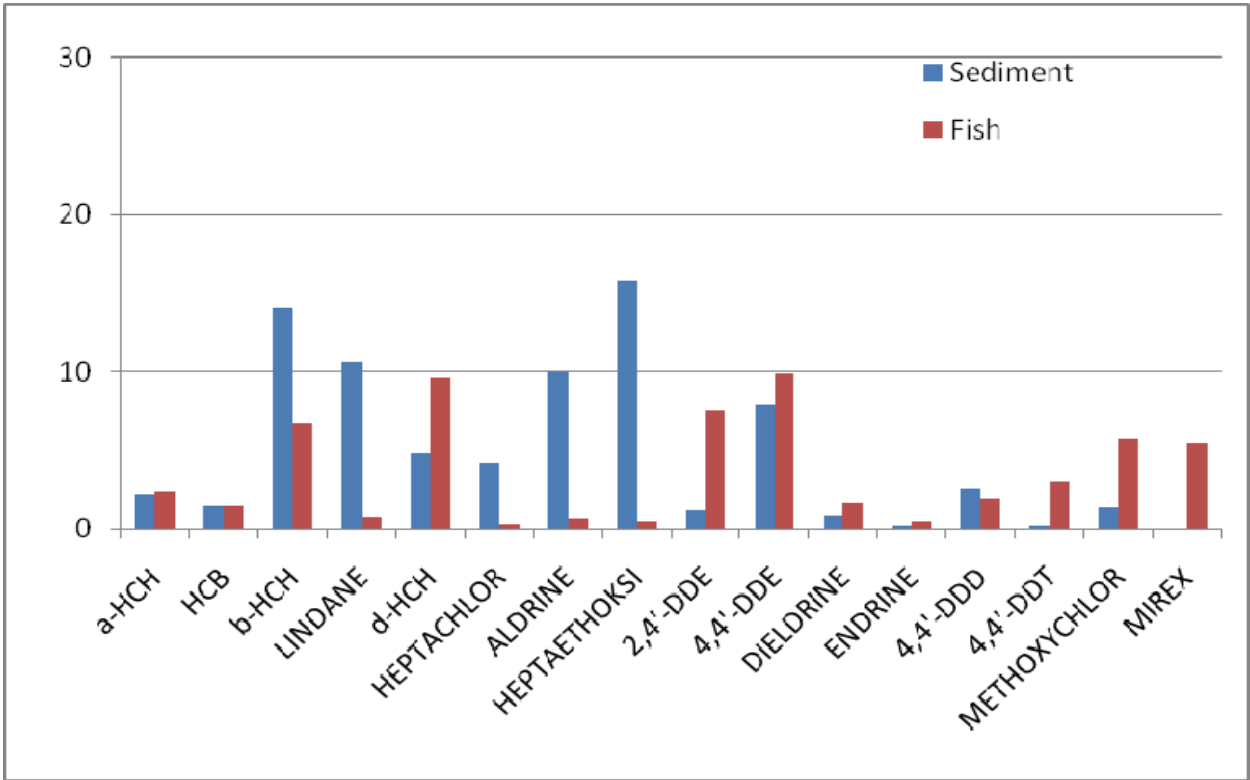

Fig. 11. Average of organochlorinated pesticides in sediment and fish samples of Velipoja, Adriatic Sea

of *Allosa agone* fom Shkodra Lake had the maximum concentration with 80,5 ng/g f.w. and *Rutilus ohridanus* the minimum with 31,2 ng/g f.w. These levels suggest correlations with water and sediment levels found for Shkodra Lake. Found pesticide residue levels for fish samples of Shkodra Lake were comparable with levels of fish samples of Adriatic Sea. Most of fish species are migratory and stay in the lake not all over the year. They migrate to Adriatic Sea, through Buna River, which is a natural communicating channel to the sea. Before use of pesticide for agricultural reasons, individual pesticide properties and pesticide residues from rain water flow and Shkodra Lake effluents are factors for levels ofound in samples of lake.

The mean concentrations of analyzed individual organochlorinated pesticides in water, sediment and fish samples of Shkodra Lake are shown in Figure 15. The concentrations of DDT & metabolites and HCH isomers were higher than other pesticides for both sediment sampling. The highest concentrations found in sediments were for 4, 4'-DDT at with 21.7 ng/g dry weight because of lower degradation process in sediments. Aldrine, Heptachlor, Mirex and Heptachlorepoxide were present in very low concentrations, sometimes even non detectable. DDT and metabolites concentrations in fish species show a different profile from the sediments. The concentrations of p,p'-DDT are lower than the concentrations of its metabolites. The higher value of $\sum$DDTs' is found for both sampling in Carp (*Cyprinos carpio*), which is the famous characteristic fish (non migratory) of Shkodra Lake. Lindane concentrations in fish are in the same range with concentrations reported for Adriatic fish (Albanian coast). Differently to the sediments, the profile of HCH isomers in some migratory fish shows relatively high values of Lindane, compared with other HCH isomers.

Buna River. In Buna River were analyzed water and sediment samples. Organochlorinated pesticide levels in water samples are shown in Figure 16. Maximum level was for Middle of
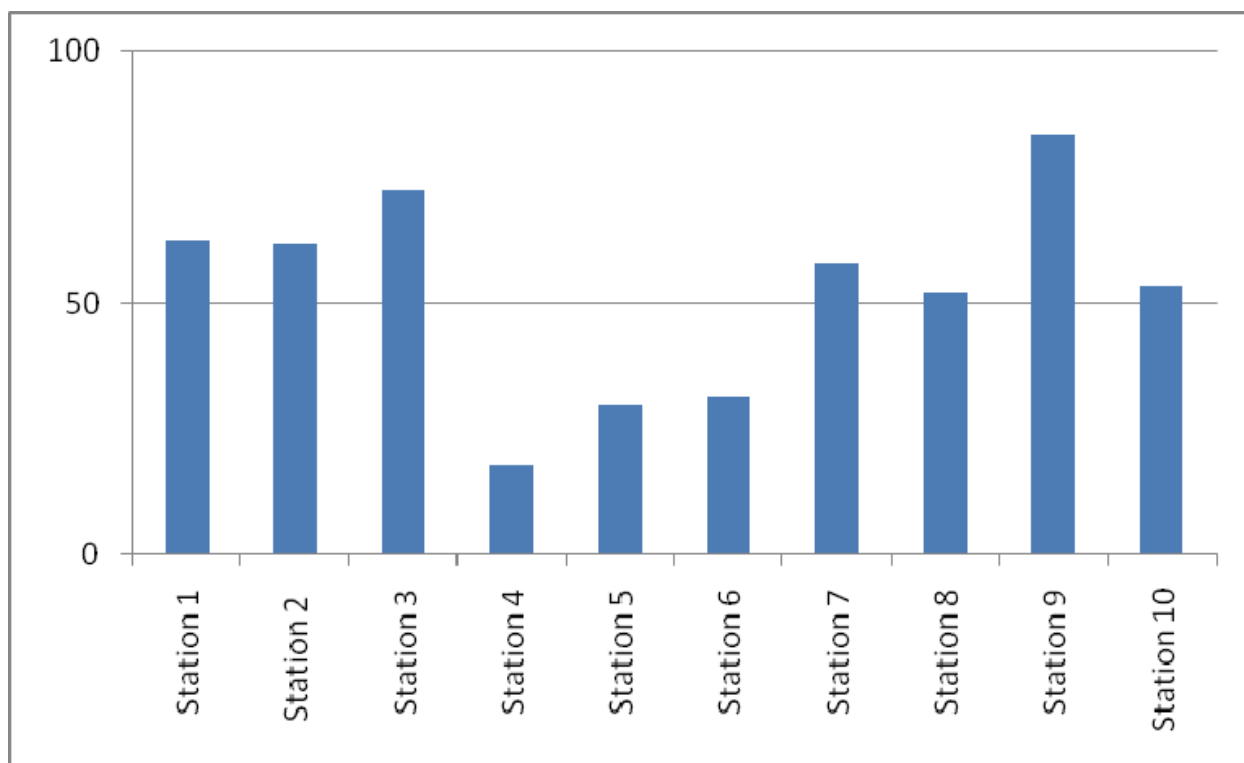

Fig. 12. Total of organochlorinated pesticides in water samples of Shkodra Lake
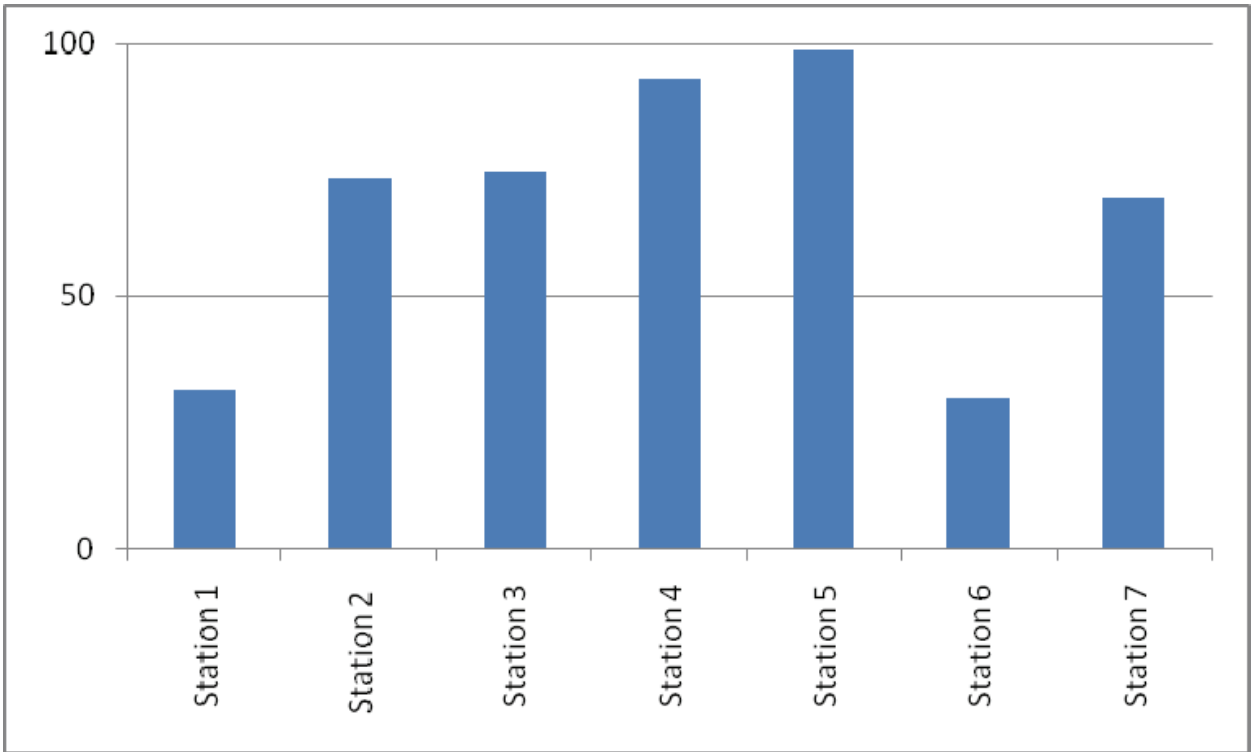
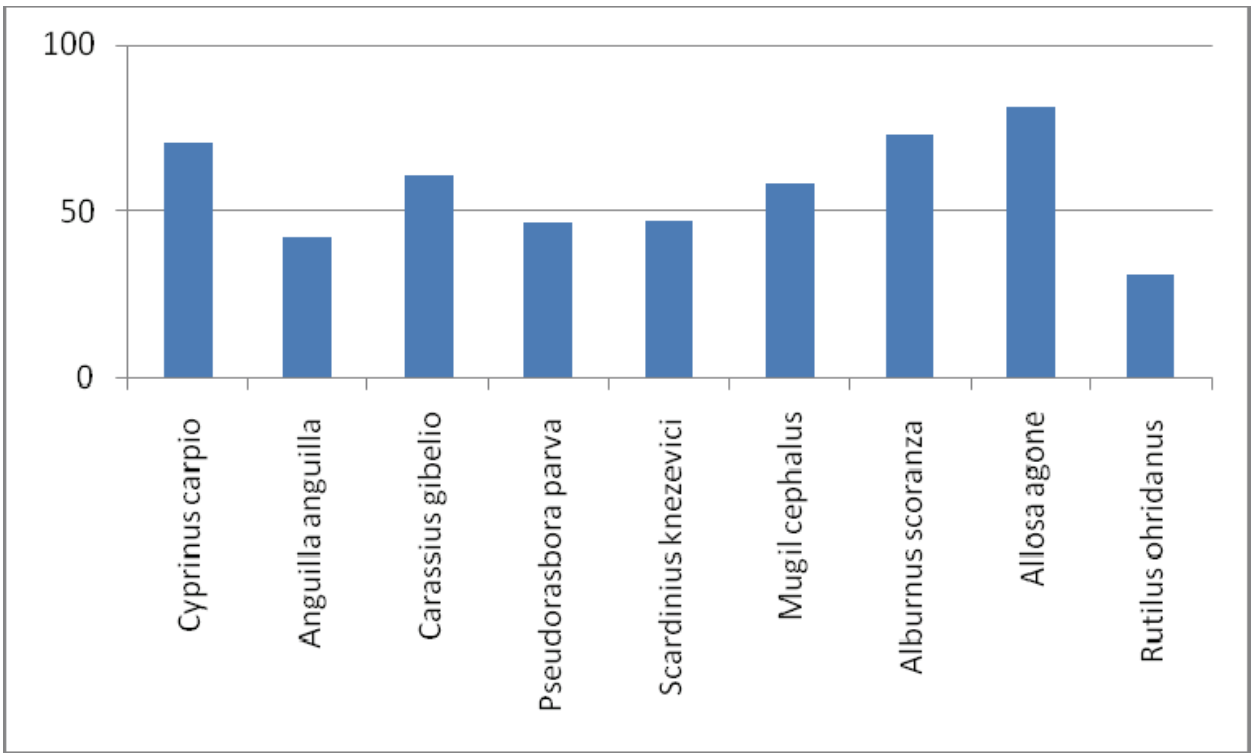Fig. 13. Total of organochlorinated pesticides in sediments of Shkodra Lake

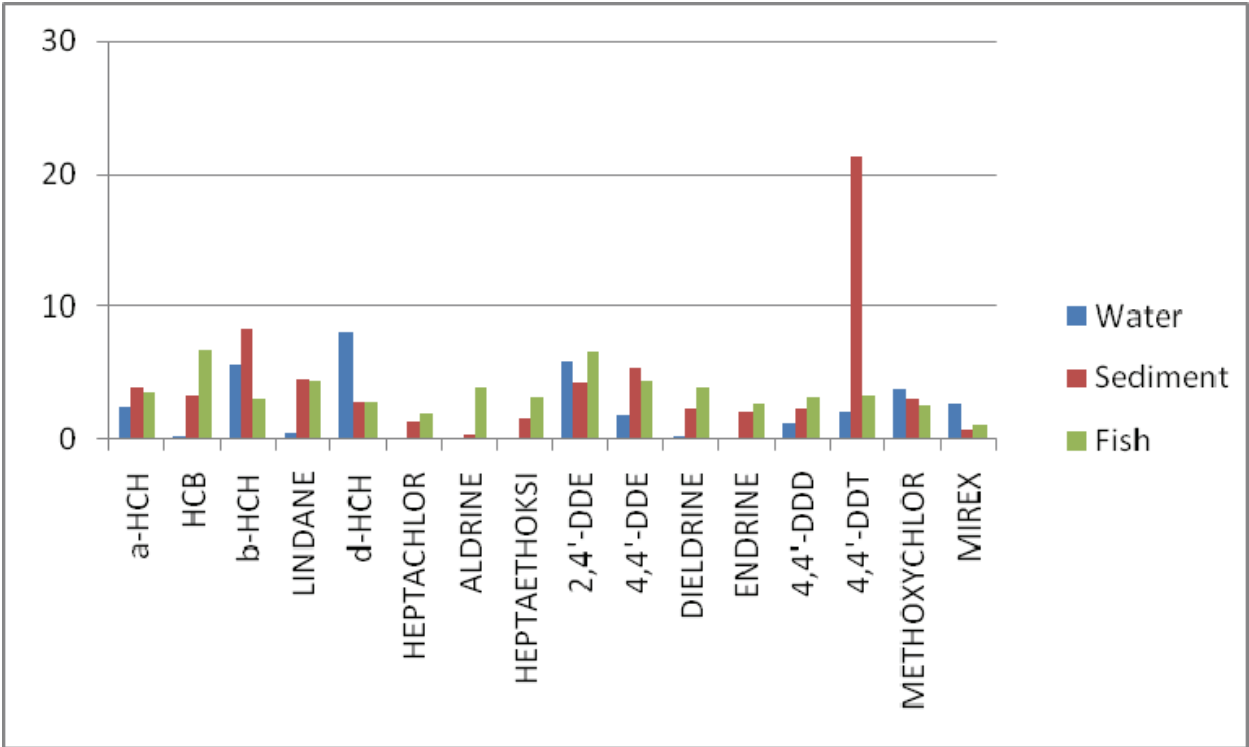Fig. 14. Total of organochlorinated pesticidesin fish samples of Shkodra Lake

Fig. 15. Average of organochlorinated pesticides in water, sediments and fish samples of Shkodra Lake

Buna sample with 101,2 ng/L, minimum value was for Buna Start station with 38,8 ng/L and mean value was 57,9 ng/L. It's evident the fact that levels of water samples are in almost in the same levels with sediment sample in Buna River. Buna River had high sedimentation because its hydrogeology, water volume and water rate, adding anthropogenic factor. Sediment samples were taken in the surface of river bed. Their depths were no more than 5 cm, (data found are evidence for pollution in last year's). Organochlorinated pesticides were found in all sediment samples studied. Run off of agricultural land near the river it's not the only factor. Other sources could be water and water matter of Drini River and Shkodra Lake. Total concentration of organochlorinated pesticides was shown in Figure 17. Mean value for pesticide residue levels in sediment of Buna River was 65,0 ng/g dry sediment. The highest level was found for the sample 800 m from the river mouth with 116,6 ng/g dry weight. The lowest levels was found for station 200 m from river mouth with 16,7 ng/g dry weight. "Buna start" station (point of connection between Buna River and Shkodra Lake) was 75.5 ng/g dry sediment. Levels of pesticide residues in Buna rivermouth was 70,0 ng/g dry sediment, lower than concentration found in Buna rivermouth in Adriatic Sea. Water current and different sedimentation rate are the main factors for this fact. Concentration levels were the same with levels of organochlorinated pesticides found in sediment samples of Shkodra Lake (Marku & Nuro, 2005). Organchlorinated pesticides profile was shown in Figure 18. It's evident the fact that DDE has the higher concentration than other pesticides in water and sediment samples DDT use was banded in our country after 90'. Degradation of DDT, DDE stability and their chemical and physical properties can affect the distribution of DDT and their metabolites. DDT was the second of this group not because of recent use but because of the lower degradation rate for DDT in sediments. Levels of DDTs in sediment sample in Buna River were lower than DDT levels found in sediment samples of

Shkodra Lake. HCB is the second contributor because of their before use of this insecticide in fruit trees. HCHs are found in all sediment samples. In addition the higher concentrations were for b-HCH in sediment samples. This is connected with other factors such as chemistry of HCHs, and atmospheric depositions, rather than agriculture runoff. HCHs data correlate with levels and distribution of these pollutants in sediment samples of Shkodra Lake. Lindane was used as insecticide in adjacent agricultural but their level was lower.

Ohrid Lake. In Ohrid Lake were analyzed fish samples. Sum of organochlorinated pesticides in fish samples was shown in Figure 19. Mean value was 69,2 ng/g f.w. *Rutilus ohridanus* had the higher value with 87.8 ng/g f.w. Minimum concentration for Ohrid Lake fishes was found for the sample of *Cyprinus carpio* with 40.3 ng/g f.w. Pesticide residue levels for fish samples of Ohrid Lake were in the comparable levels with fish samples of Shkodra Lake. Distribution of pesticides in fish samples of Ohrid Lake were also the same with profiles of pesticide residues in Shkodra Lake. The same origins of organochlorinated pesticides suggest this fact. Run off of agricultural land near the lakes and in its water basin is main factor for levels and distribution found in Ohrid Lake. Water cycle in Ohrid Lake and analyzed fish species are also important factors for data collected.

Butrinti Lake. In Butrinti Lake were analyzed sample of water and *Mytulus Galloprovincialius* mussels. In water samples of Butrinti Lake mean value of organochlorinate pesticides total was 14,0 ng/L, with a minimum of 7,3 ng/L and maximum of 30,7 ng/L (Figure 21). Levels found for water samples in Butrinti Lake were lower from levels found in Vlora Bay, Adriatic Sea or Shkodra Lake. Levels of total for organochlorinated pesticides for mussel *Mytulus Galloprovincialius* of Butrinti Lake were also lower than levels found in mussel samples in Vlora and Porto-Romano (Figure 22). Except this was interest the high difference in profile of pesticide residues for water and mussel samples of
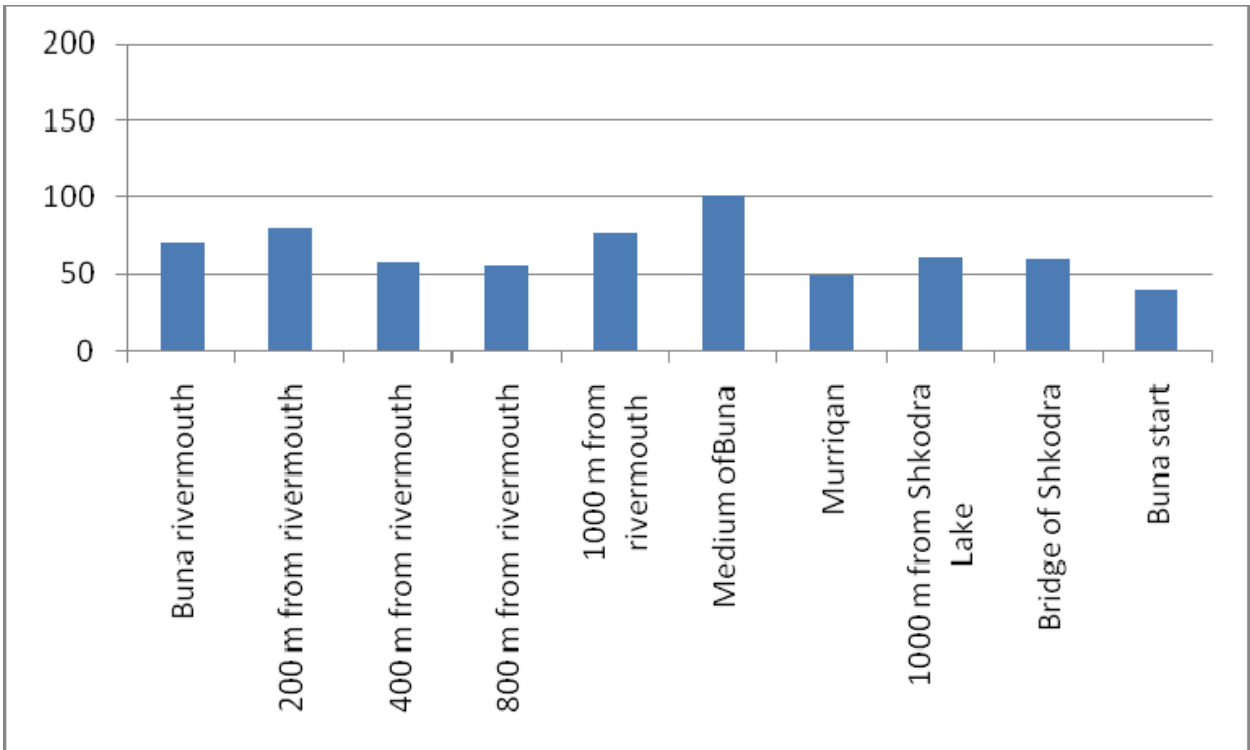

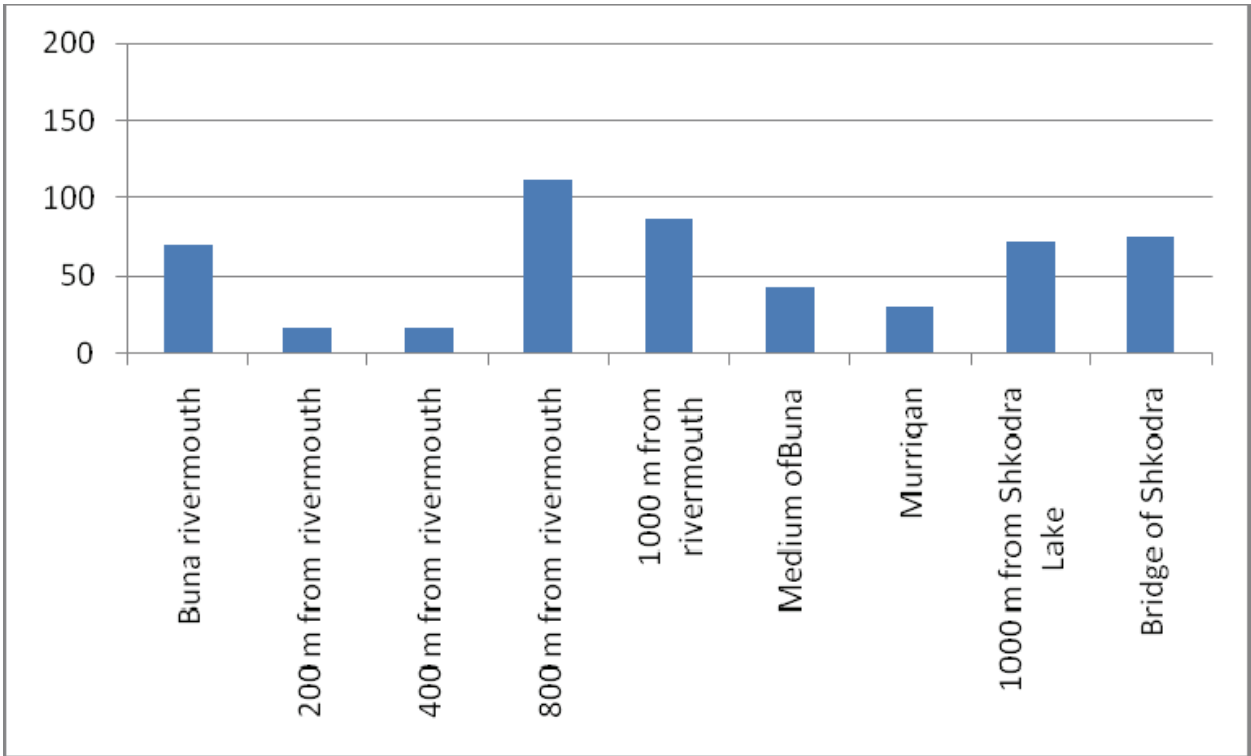Fig. 16. Total of organochlorinated pesticides in water samples of Buna River

Fig. 17. Total of organochlorinated pesticides in sediments of Buna River
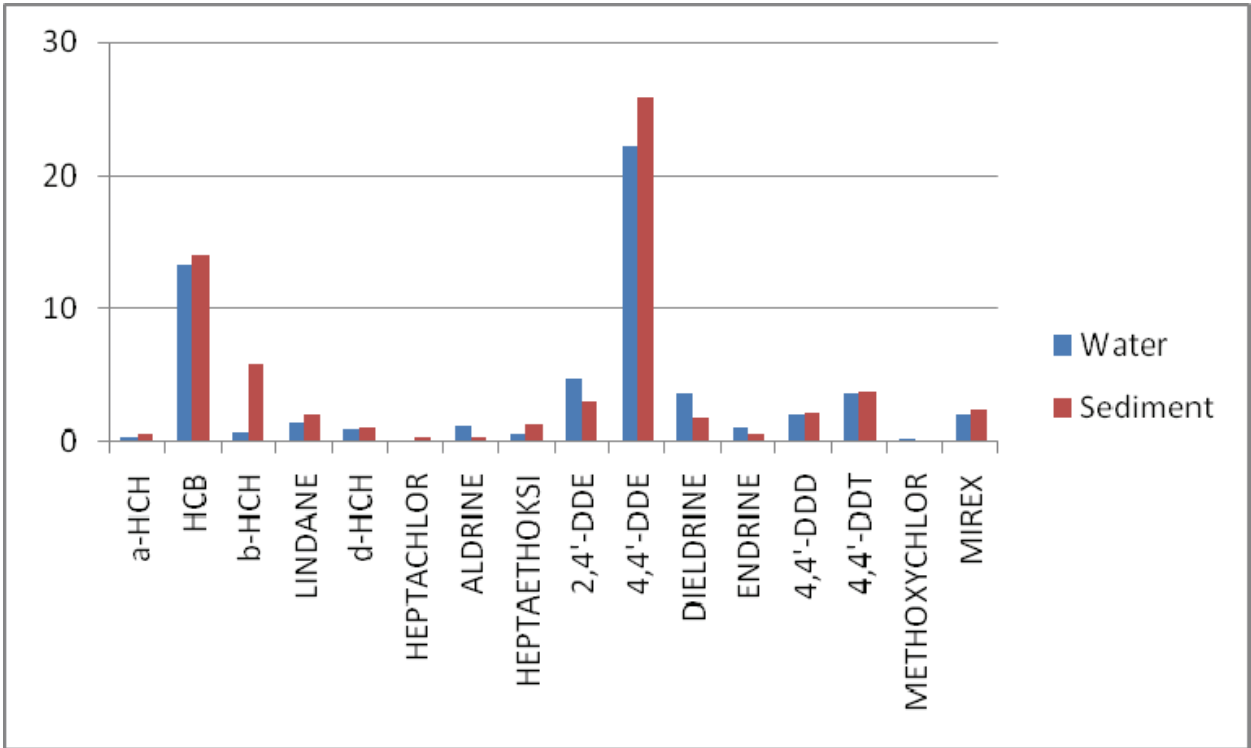

Fig. 18. Average of organochlorinated pesticides in water and sediment samples of Buna River
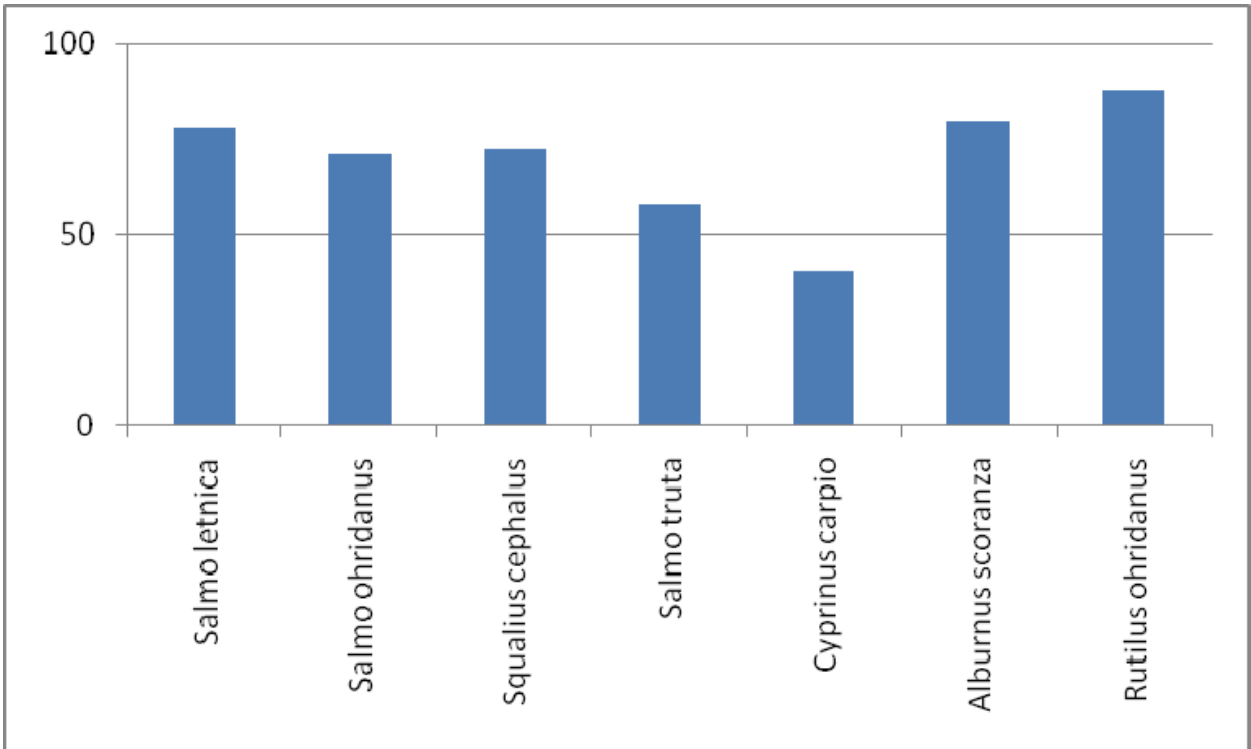
Fig. 19. Total of organochlorinated pesticides in fish samples of Ohrid Lake
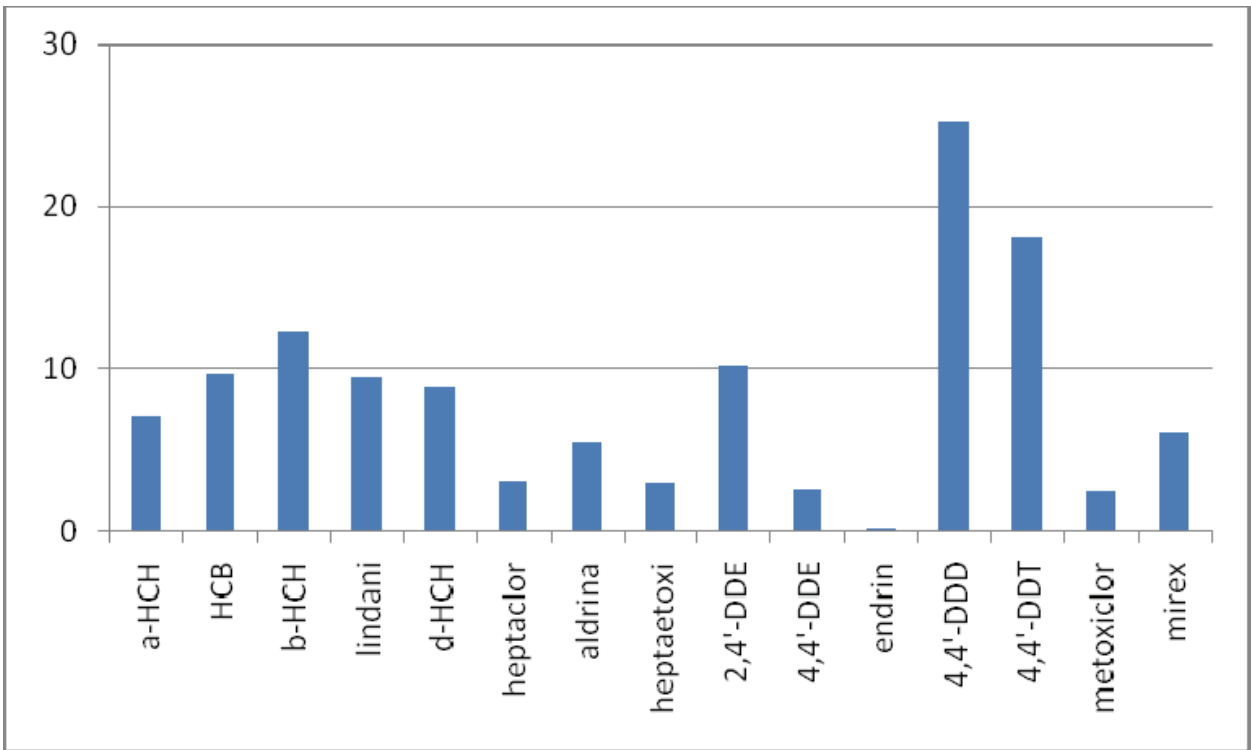

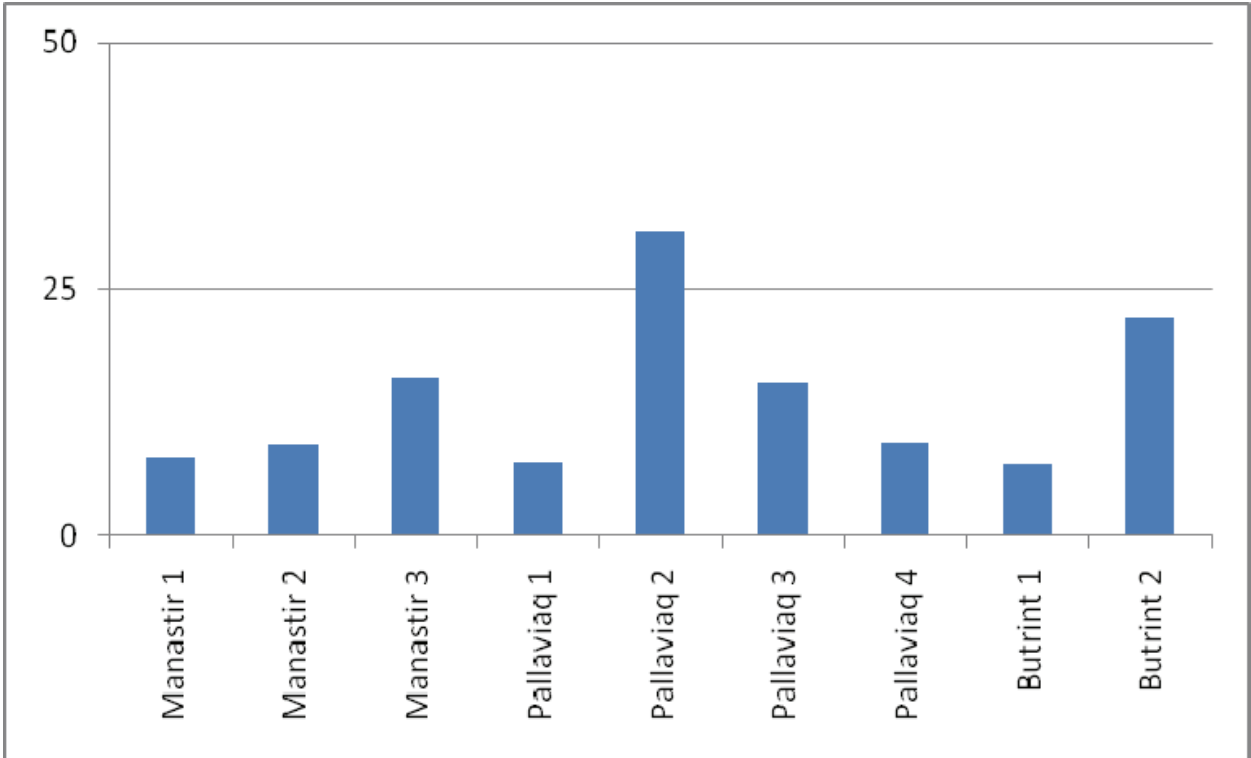Fig. 20. Average of organochlorinated pesticides in fish samples of Ohrid Lake

Fig. 21. Total of organochlorinated pesticides in water samples of Butrinti Lake
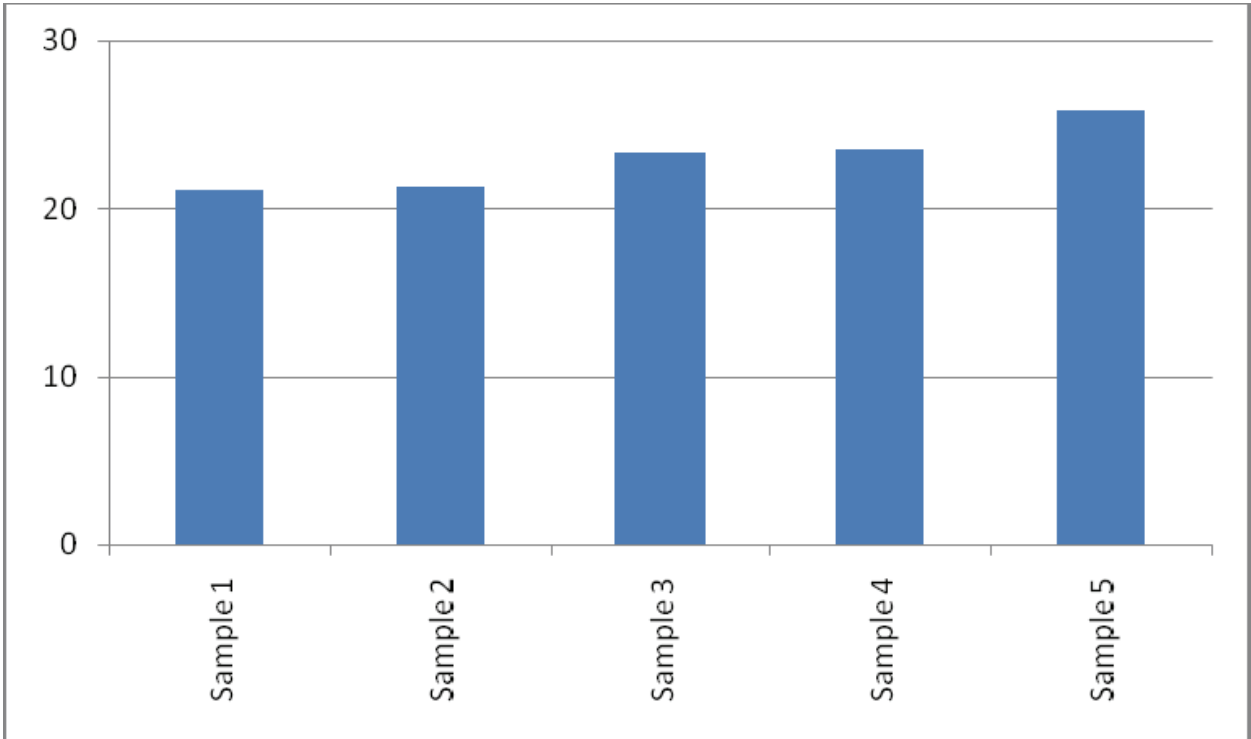

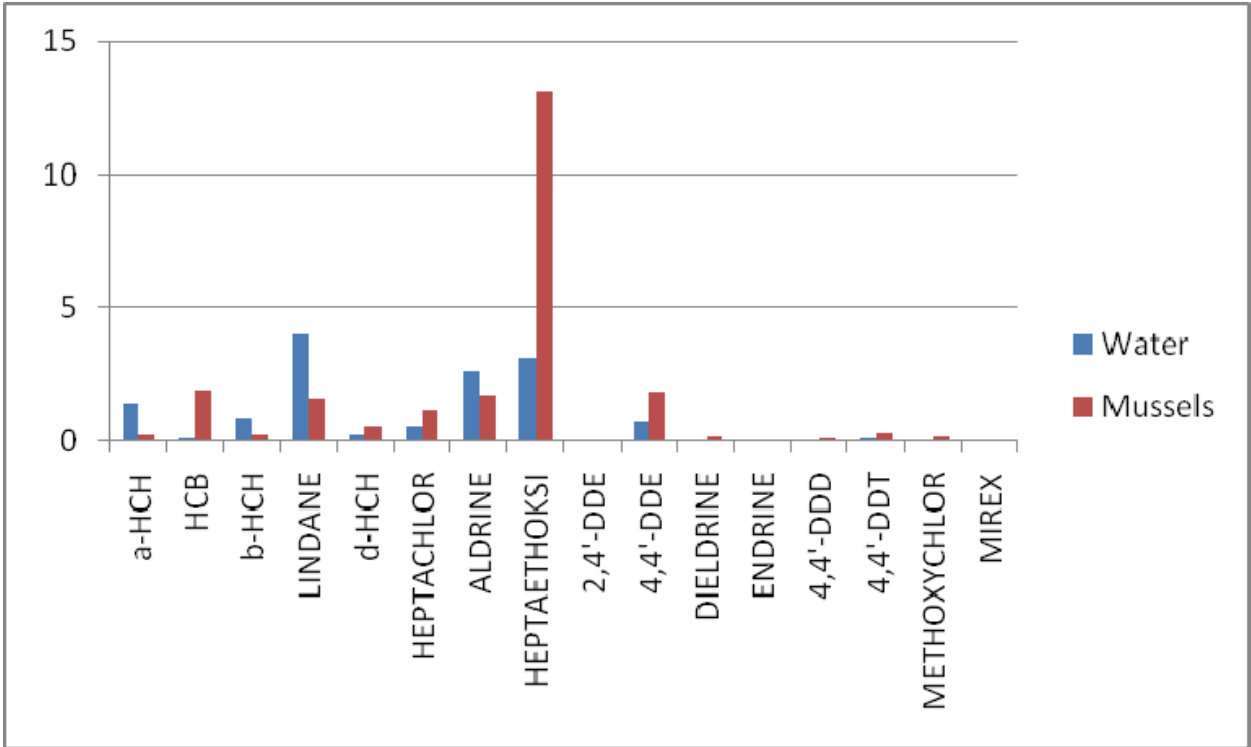Fig. 22. Total of organochlorinated pesticides in mussel *Mytulus galloprovincialius* of Butrinti Lake

Fig. 23. Profile of organochlorinated pesticides in water and mussel samples of Butrinti Lake

Butrinti Lake compared with other same samples. Profile of pesticide residues in water and mussel samples of Butrinti Lake were almost the same (Figure 23). HCHs were major pollutants in water samples followed from Heptachlors and Aldrine. Heptachlors were the first pollutants in fish samples followed from HCHs. Lindane for both samples type was in higher concentration than other HCH isomers. HCB was found in higher levels in mussel samples than in water samples. DDE was found in lower levels. Pesticides were used for agricultural purposes also in agricultural areas in fields near Butrinti Lake before 90′. Butrinti Lake has a communication channel with Ionian Sea that can affect in found levels for pesticide residues in water samples of lake.

4. Conclusions

In this study were included different aquatic locations of Albania with their own characteristics. Difference in their position and the other characteristics followed from selected samples for each aquatic location can shown a correct thought about levels and distribution of organochlorined pesticides in Albania. In all studied aquatic locations were shown presence of organochlorinated pesticides. These compounds were used insensitive mostly as insecticide for agricultural purposes before 90′. Note the organochlorinated pesticides are not in use after 90′ in Albania, but their before use and their stability are main factors for founding them in all systems. Aquatic systems are affected from pesticide residues mainly as result of agriculture runoff. Discharging of many industrial and agricultural wastes directly in to the sea, rivers and lakes is another factor that affect in found levels of pesticide residues. Organochlorinated pesticides are not hydrophilic compounds for this reason levels of pesticides found in water samples were always lower the sediments of biota samples for the same locations. Levels of pesticides in water samples

for Adriatic Sea, Buna River and Shkodra Lake were in the same levels. Butrinti Lake were in low concentration. Their geographic position include specifics for studied locations (water current, nearest from agricultural field, ect,.)

Sediment of aquatic systems considered as archive for organic pollutants, so interpreted of data found for pesticide residue were very interest. Concentration of pesticides in sediments of Buna river mouth (Adriatic Sea), station was higher than in other sediment samples because of Buna River influence. Going to the depth of Adriatic Sea concentrations were lower. Sediment of Shkodra Lake and Buna River were almost in the same range and distribution between them because of their geographic connection. It's shown a difference in profile of pesticides between Velipoja (Adriatic Sea) and Buna River because of water currents of Adriatic Sea influence. Water current influence was also shown for sediment samples of Vlora Bay.

Concentrations of organochlorine pesticides due to their use in Albania before 90' and also for their stability and affinity for their accumulation in fish tissue were main factors for found levels in fish samples. The highest values of total pesticides were found in some fish species, to concentrate many organic contaminants, because of pollutant bioavailability, but also species characteristics (specimen, age, sex, ect,.). Levels of pesticide residues found in fish samples of Vlora Bay was comparable to fish samples of Velipoja. Fish samples of Adriatic Sea were in the same levels of pesticide residues with levels of fish samples of Shkodra and Ohrid Lake, because it's known a migratory communications between both aquatic systems. Concentrations of organochlorine pesticides found in Shkodra Lake and Ohrid Lake are due to their use in Albania before 90', their stability and affinity for accumulation in animal tissue, as well as relatively limited rate of water circulation in these basins. Pesticides profile shows differences between the two lakes. DDT and their metabolite, as well as HCHs levels were in higher levels in samples of Ohrid Lake compare to the samples of Shkodra Lake. Levels of each chlorinated compound are connected mostly to the geographic position, water basin and water currents in these basins. Levels of organochlorinated pesticides were in the same range with other studies in Adriatic Sea, Shkodra Lake and Ohrid Lake. Mussels *Mytulus Galloprovincialius* were studied in two stations in Adriatic Sea (Vlora Bay and Porto-Romano) and Butrinti Lake. Mussel samples were most polluted compared with other type of samples because of they are water filtering and tend to concentrate in their tissue especially liophilic pollutants such are organochlorinated pesticides. Levels of pesticide residues found in mussels of Butrinti Lake were lower than levels found for mussel samples in Adriatic Sea.

For all samples DDTs were in higher concentrations compared with the other organochlorinated pesticide residues analyzed. DDE, metabolite of DDT was found in the higher level for all samples. Before use of DDT, degradation of DDT, DDE stability and their chemical and physical properties can affect in this fact. The concentrations HCH isomers were second compared with other pesticides for analyzed samples. Profiles of HCHs were not the same for all samples. In sediment samples the higher concentration was found for Lindane. Lindane was used as insecticide in adjacent agricultural but for a great number of biota samples and water samples was found in higher concentration beta isomer of HCH. This is connected with other factors such as chemistry of HCHs, and atmospheric depositions, rather than agriculture runoff. Beta isomer of HCH has a great potential of concentrations in lipids than other isomers. Hexachlorbenzene (HCB) was the third pollutant found almost for all samples. Before often use of this insecticide in fruit trees was

the main factor. Aldrine, Heptachlor, and Methoxychlors were present in very low concentrations, sometimes even no detectable. Different concentrations and profile found for pesticides between different sampling stations and between different types of samples are connected with before use of pesticides and with their chemical-physical properties.

5. References

Di Muccio, (1996). Organoclorine, Pyrethrin and Pyrethroid Insecticides: Single Class, Multiresidue Analysis of. Pesticides. *Pesticides*. 6384-6411

Dhimitër Dhora (1995). *Shkodra Lake*

Dritan Topi, Pandeli Troja, Koste Koci, Elda Marku, Aurel Nuro (2006) "Same experimental dates about the levels of chlorinated pesticides and PCBs in the biota of Ohrid Lake". www.BALWOIS.net/Conference/Balwois 2006/articles

E.Marku, A. Nuro, (2005) Chlorinated pesticides in the sediments and fish species of Shkodra Lake. *Journal of Environmental Protection and Ecology*; Vol.6, No.3:539-549

EN 1528-1. (2000) Part 1: Fatty Food-Determination of Pesticides and polychlorinated biphenyls [PCBs]

EN 1528-2. (2000) Part 2: Extraction of fat, Pesticides and polychlorinated biphenyls [PCBs and -Determination of Fat Content

EN 1528-3. (2000). Part 3: Clean-up methods

EN 1528-4. (2000) Part 4: Determination, Confirmatory tests, miscellaneous

G.Rene van der Hoff, P. van Zoonen, (1999). Trace analysis of pesticides by gas chromatogaphy. *Journal of Chromatogaphy A*, 843 301–322

Koci, K. (1997) The trend of POP pollution in the Albanian Adriatical coast: Case study: PCBs (1992-1996) Proceedings of subregional awareness raising workshop on POPs. Slovenia

Pano N. Abdyli B. (1984) – Hydrology of Albania. Monography. Institute of Hydrometeorology. Academy of Science, Tirana, pp 94-146, 360-397.

Petrick, G., Schulz, D.E. and Duinker, J.C. (1988). Clean-up of environmental samles for analysis of Organochlorine compounds by gas chromatography with electron-capture detection. *Journal of Chromatography*, 435, 241-248.

Reference Method No 6, UNEP/FAO/IAEA/IOC: UNEP, (1993) Sampling of selected marine organisms and sample preparation for the analysis of chlorinated hydrocarbons.

Schantz, M. M., Parris, R. M., Kurz, J., Ballschmiter, K. and Wise, S.A., (1993). Comparison of methods for the gas-chromatographic determination of PCB congeners and chlorinated pesticides in marine reference materials. Fresenius *Journal of Analytical Chemistry*, 346. 766-778.
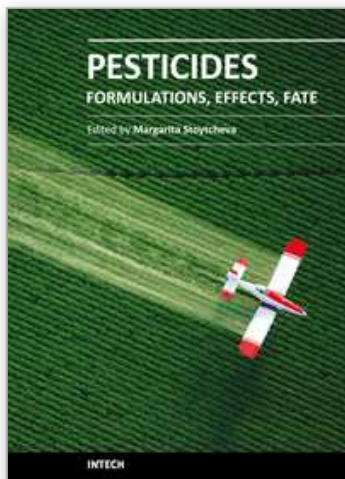
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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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