STUDY OF ORGANOCHLORINATED POLLUTANTS IN KUNE-VAINI LAGOON

Aurel Nuro, Elda Marku

University of Tirana, Faculty of Natural Sciences, Chemistry Department

E-mail: aurel.nuro@fshn.edu.al

ABSTRACT

In this paper were present data of pollution levels of organochlorinated pesticides and polychlorinated biphenyls (PCB) in water and sediment samples of Kune-Vaini Lagoons. Samples were taken in April 2012. Organochlorinated pesticides are most widely class of organic compounds and most problematic in environments. Organochlorinated pesticides can found far away of applied areas because of atmospheric factors and rain fall of agricultural areas. PCBs are synthetic compounds which are widely used in electrical transformers and generators oils in many countries of Europe and the world. PCB hardly been used in our country, but they have been reported in various environmental analysis due to atmospheric deposition. Analysis of organochlorinated pesticides and PCBs were performed simultaneously by capillary gas chromatography technique with electrons capture dedector (GC/ECD). In the analytical method used ultrasonic extraction for sediment samples. Florisil with 5% water was used for cleaning the sampling procedure. The Rtx-5 capillary column was used for isolation and determination of organochlorinated pollutants. In the studied samples were dedected regularly in large quantities of HCHs, DDT metabolites and volatile PCBs. The presences of organochlorinated pollutants were result of their previous uses for agricultural purposes, by rinsing of agricultural lands and miss-management of stocks of organochlorinated pesticides after 90'.

Keywords: *Organochlorinated pesticides, PCB, sediment analyze, GC/ECD, Kune-Vaini Lagoon*

INTRODUCTION

System of Kune-Vain lagoons is located in the west of Lezha City, in both sides of Drini rivermouth (Lezha). They have an area of more than 4000 ha, covered in the forest vegetation, water area and agriculture area. Kune-Vain system is part of Albania's coastal wetland, is close to the Adriatic Sea, has Mediterranean climate. The water temperature average is 17 degrees C. Salinity of the water is 36.3-39%. Soil types that are found in the lagoon are alluvial, sandy dunes, salty and swampy. Kune-Vain lagoon system appears to be a complex of environmental factors, which have reflected the fauna and flora indicators. The studies carried out in the lagoon to grow about more than 200 species of fishes and 196 species of birds. The main species that participate in the formation of so-called "underwater meadows" lagoons are *naltii Zostera* and *Luppia cirrhaso*. This aquaculture plants together with associated species ecological groups (mostly algae) represent the main source for the production of oxygen, necessary for the existence of fauna. Besides aquatic vegetation, represent important hydro-hygrophilous are forests with species such as *Alnus glutinosa* and *Fraxinus angustifolia*. Especially in Vain lagoon, forest vegetation has suffered many injuries in recent years. Water regime has undergone changes moving towards deterioration, and indiscriminate hunting by prohibited means of fish and birds has led to a reduction of their own. Mass movements of uncontrolled constructions have always been increasing. In these years especially after the '90s, Kune-Vain lagoon has been damaged in geographical and hydrology environment.

The massive use of pesticides for agricultural purposes caused their widespread diffusion to all environmental compartments including a wide range of organisms up to the humans. The term pesticide is used to indicate any substance, preparation or organism used for destroying pests. Synthetic pesticides have been used since in the early to mid twentieth century. 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. (Di Muccio, 1996). Over 800 pesticide active ingredients are formulated in about 21000 different commercial products were used from 60' to 80' all over the world.

Polychlorinated biphenyls (PCBs) are a class of chemical compounds in which 1–10 chlorine atoms are attached to a biphenyl backbone. Commercial PCB mixtures were used in a wide variety of applications and mainly as dielectric fluids in capacitors and transformers, and as heat exchange fluids. They are chemically highly stable, lipophilic compounds and resist microbial, photochemical, chemical and thermal degradation. Unfortunately, the same properties which make PCBs interesting for industrial use cause adverse effects on reproduction, development, and endocrine function including thyroid hormone homeostasis and estrogen-responsive tissues (Erickson, 2001; Rene et al., 1999; Safe, 1994).

Organochlorinated pollutants, particularly the highly chlorinated ones such are organochlorined pesticides, PCBs, Dioxines, etc, have been known to persist in soils, water, sediments and biota of water ecosystems, for long periods of time. Organochlorinated pollutants bind strongly to organic particles in the water column, atmosphere, sediments, and soil. The deposition of particle-bound PCBs from the atmosphere and the sedimentation of them from water are largely responsible for their accumulation in sediments and soils. The absolute and relative concentrations of individual pollutants change over time and from one environmental medium to another because of physical and chemical processes and selective bioaccumulation and metabolism by living organisms. As substantial amounts of PCBs are associated with soils/sediments, the analysis of particulate media generally requires extraction/mobilization with organic solvents, clean up procedure that can include the removal of sulfur and closing treatment of sample with fractionation of different type of compounds. ECD is widely used for the analysis of various environmental pollutants including polychlorinated biphenyls. In the determination of PCBs, gas chromatography (GC) technique is generally utilized to separate the PCB components using electron-capture detector (ECD) for their quantification.

2. MATERIAL AND METHOD

2.1. Sampling of sediments in the Kune-Vain Lagoon

Sediment samples were taken by sediment core sampler, type Beeker, in several stations that representing water system for Kune-Vaini lagoon, in April 2012. Depth of taking sediment was 15 cm for Drin River (three stations) and 30 cm for Kune-Vain lagoon stations (seven stations). Samples were divided into 5 cm layers. Samples were transported to the laboratory and stored in a refrigerator in $+4^{o}C$.

2.2. Standard solutions and chemicals

Stock solutions of organochlorinated pesticides and PCBs with 2 mM concentration were donated by the IAEA/MEL-Monaco. Standard solutions of organochlorinated pesticides and PCBs were prepared separately in n-Hekzan in 50 ng/µl concentrations. They were kept in a refrigerator at a temperature of -4°C. n-Hexane and Dichloromethane were suitable for micro analyze, they were obtained from Merck, Germany. Sulfuric acid, Anhydrous sodium sulfate, Florisil (≥ 400 mesh ASTM) and Silicagel (60-100 mesh ASTM) were obtained also from Merck, Germany (suitable for analysis of pesticide residues with gas chromatographic technique; RPE analytical grade).

2.3. Treatment of sediment sample

Layers of sediment samples were dried at 30^{o}C in thermostat for 24 hours. Were analyzed from each sample the fraction <63 micron with high porosity suitable for higher concentrations of organochlorinated pollutants. To establish the validity of the study method of organochlorinated pesticides in sediment samples was used 383 samples of certified IAEA, sediment sample with known levels of them. 1 gram of sediment sample was extracted using ultrasound bath assisted with n-Hexane/Dichloromethane mixture (3/1 by volume) in 30^{o}C for 30 minutes. Sediment samples were treated with metallic mercury for removal of sulfur compounds. An open florisili column was used for the final purification of the extract. Extracts were concentrated in Kuderna-Danish in 1 ml (Petrick, et al., 1988; Villeneuve, et al., 2004).

2.4. Gas chromatography analyze

Analysis was conducted in HP 6890 Series II, Gas chromatograph equipped with split/splitless injector and µECD detector. For separation of organochlorinated pesticides and PCB markers was used HP-5 capillary column (30 m x 0.32 mm x 0.25 µm). The end of the column is connected to the detector µECD (electron capture detector) suitable for qualitative and quantitative analysis of halogenated compounds. Three parallel injections were made for each sample. 1 µl were injected in splitless mode for all analyzed sample, standards and blank. Helium gas was used as carrier gas (constant flow mode, 1 ml/min) and nitrogen as make-up gas (25 ml/min). Quantitative analysis was based on the internal standard method. PCB 29 was used as internal standard. 10 µl with 5.0 ng/µl concentration was added prior extraction process for each sample.

DISCUSSION AND RESULTS

Results obtained from study of organochlorinated pesticides and PCB markers in Kune-Vaini Lagoon were interpreted separately for sediment layers in Drini River and Kune-Vaini Lagoon. All results were in ng/g dry sediment sample. Figure 1 shown total of organochlorinated pesticides in sediments of Drini River (Lezha). The lower layer (0-5 cm) had higher levels of organochlorinated pesticides with 59.2 ng/g dry sediment sample. The lower level was for upper layer (10-15 cm). This is expected because pesticides are not used since the early 90's. This means that the levels of pesticides in the sediments of river Drini are the result of previous use of them for agricultural purposes. Non-use of them makes their levels smaller year after year. Sediment layer represents a period of time. Distribution of organochlorinated pesticides in sediments of Drini River (Lezha) shown higher level were for HCHs, maximum was for 0-5 cm sample with 27 ng/g and the lowest for the 10-15 cm sample with 0.6 ng/g. This is result of previous uses for technical mixture of lindane. There is an equal distribution of HCH's for all samples: b-HCH> Lindane> d-HCH> a-HCH. This distribution is associated not only with use of technical lindane but also with physical-chemical properties of these isomers, mainly their solubility, stability and boiling points. The highest level of DDTs noted in 5-10 cm layer and the minimum for 10-15 cm layer respectively with 18.0 and 7.5ng/g. Rainfall and old resources can be factors that affect in the level and profiling of these pollutants. Distribution of DDT in sediments of Drini River (Lezha) is the same for all sediment layers. This again speaks to the same origin of these compounds. 4,4 '-DDE was the isomer with the highest level. This is one of the main metabolites of DDT.

Figure 2 shown totals for organochlorinated pesticides in sediments of Kune-Vaini Lagoon. The higher level was for 0-5 cm layer with 92,3ng/g. This level was around 2 times higher than level found in sediment samples of Drini River. Note that the levels from layer to layer were lower from deeper to surface. This means that the levels of pesticides in sediments in the lagoon of Vaini are result of previous or use them for agricultural purposes. The same origin of organochlorinated pesticides observed in the distribution of organochlorinated pesticides in sediments of the River Drin (Lezha) is the same for all classes taken in the analysis. Distributions of organochlorinated pesticides in sediments of Kune-Vaini Lagoon were the same for all layers. The high level of HCHs was for 0-5 cm sample with 23ng/g and the lowest for the 10-15 cm sample with 12.6ng/g. This is a result of previous uses of lindane. d-HCH levels were about 20 times higher than levels found in sediments of the Drini rivermouth (Adriatic Sea). The highest level of DDT be noted layer of 0-5 cm and 15-20 cm lower layer respectively 43 and 13.5 ng/g. Distribution of DDT in sediments of Kune-Vaini Lagoon were the same with studied sediments in the river Drin (Lezha). Their profile is the same for all layers of sediment and sediment profiling them on the Drin River. This again speaks to the same origin of these compounds. 4,4 '-DDE was the isomer with the highest level.

Total for PCB markers in sediments of the River Drin (Lezha) were the same for layers 0-5 and 5-10 cm with 13 ng/g. the lower level was for 10-15 cm layer (Figure 3). For the upper layer the level was lower with 2.2ng/g. These concentrations were mainly because of atmospheric deposition (Koci, 1997). The distribution of PCB markers in sediments of the River Drin (Lezha) were the same for all layers obtained in the analysis that is associated with their same origin. PCB 28 and PCB 52 were found at higher levels than others. PCBs in our country are mainly atmospheric origin. Total for PCB markers in sediments of Kune-Vaini Lagoon (Figure 4) were higher for layers 5-10 with 20.3 ng/g. For the layer 10-15 cm their level was about ten times lower. Distribution of PCB markers in sediments Vain Lagoon were the same for all layers obtained in the analysis that is associated with their same origin. PCB 52 was found in higher levels than others. This is due to the physico-chemical properties of PCBs and their sedimentation velocity. PCB 52 concentrations were shown to be the same for all studied sediment layers for lagoon stations. In some layers were found in high amounts PCB-118. This fact cold be connected with direct discherges of waste oils from old transformers or automobile services.

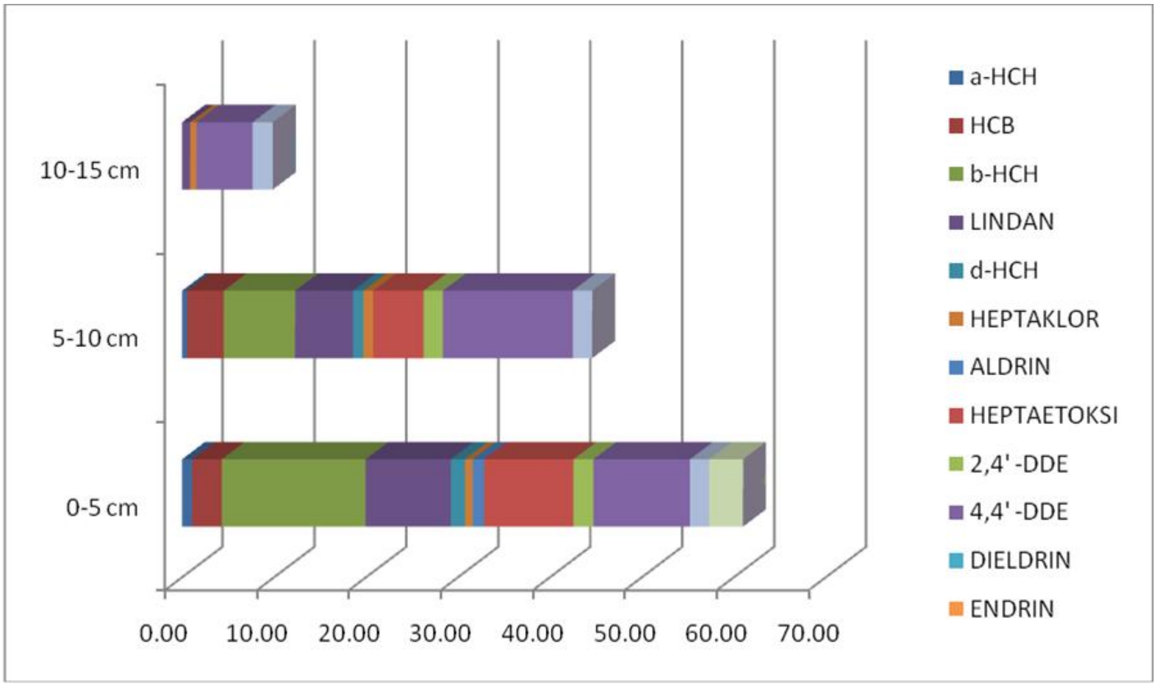

Figure 1. Organochlorinated pesticides in sediments of Drini River (Lezha)

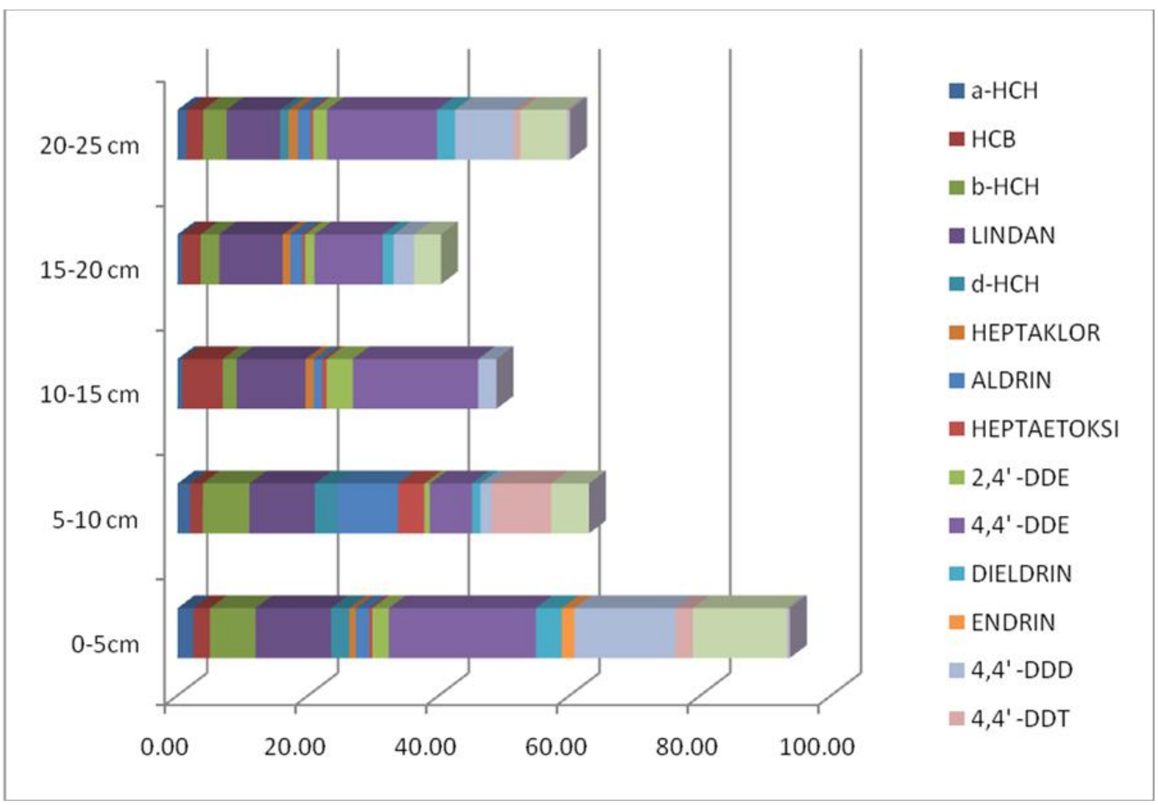

Figure 2. Organochlorinated pesticides in sediments of Kune-Vaini Lagoon

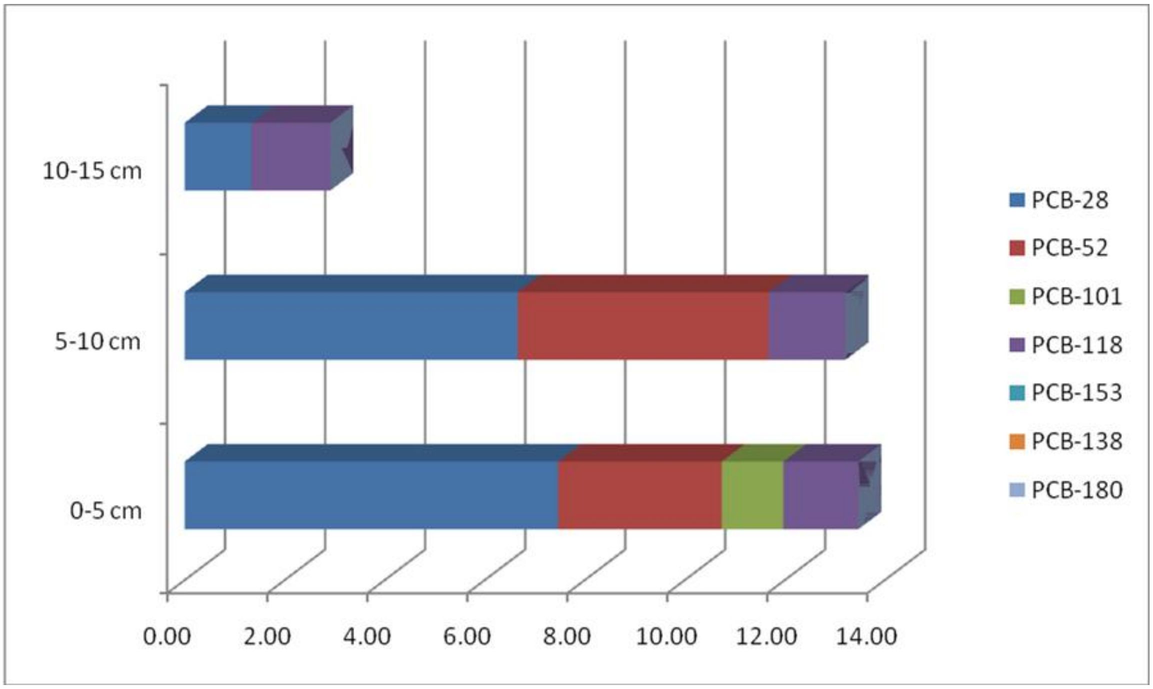

Figure 3. PCB markers in sediments of Drini River (Lezha)

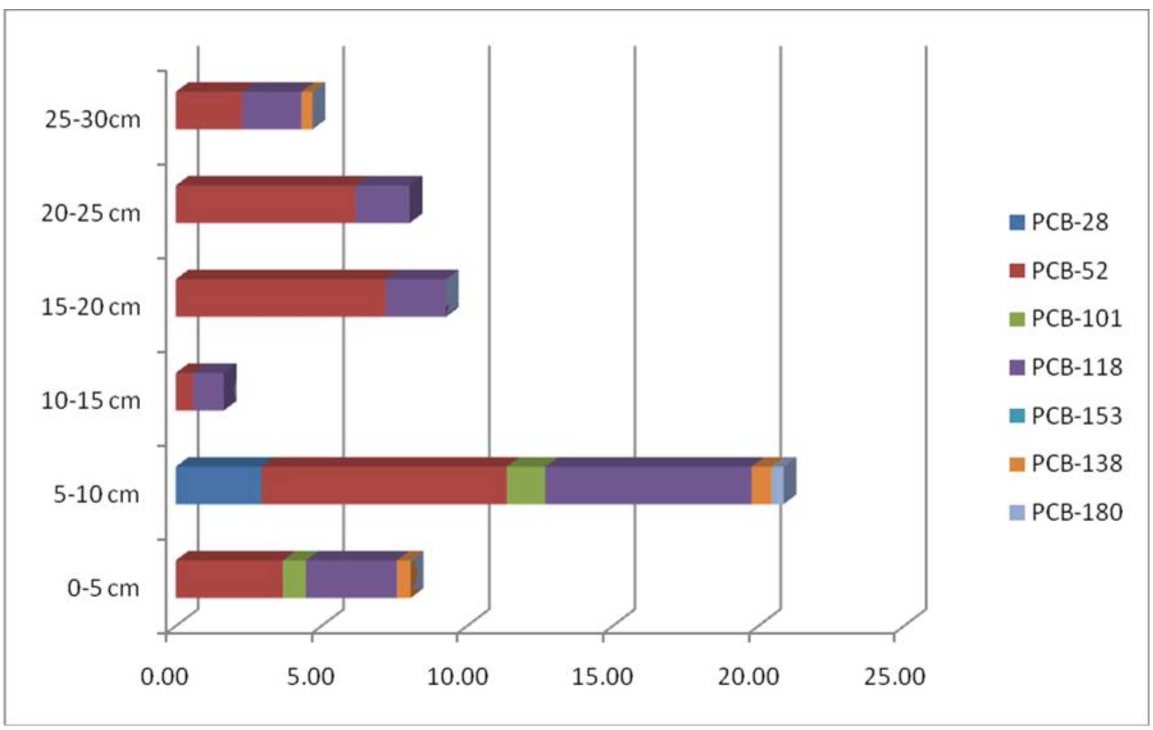

Figure 4. PCB markers in sediments of Kune-Vaini Lagoon

CONCLUSIONS

Three sediment samples of Drini River (Lezha) and seven sediment samples of Kune-Vaini Lagoon were analyzed in this study. Results of organochlorinated pesticides and PCB markers in Kune-Vaini Lagoon were interpreted separately for sediment layers in Drini River and Kune-Vaini Lagoon. The lower sediment layer (0-5 cm) had higher levels of organochlorinated pesticides for all studied stations. This is expected because pesticides are not used since the early 90's. This means that the levels of pesticides in the sediments of river Drini are the result of previous use of them for agricultural purposes. Non-use of them makes their levels smaller year after year. Sediment layer represents a period of time. Distribution of organochlorinated pesticides in sediments of Drini River (Lezha) and Kune-Vaini Lagoon shown higher level were for HCHs, DDT metabolites and volatile PCBs. Rainfall and old resources can be factors that affect in the level and profiling of these pollutants. This again speaks to the same origin of these compounds. 4,4 '-DDE was the isomer with the highest level. This is one of the main metabolites of DDT. d-HCH levels in Kune-Vaini Lagoon were about 20 times higher than levels found in sediments of the Drini rivermouth (Adriatic Sea).

Total for PCB markers in sediments of the River Drin (Lezha) and Kune-Vaini Lagoon were the higher for layers 0-5 and 5-10 cm. For the upper layer the level was lower. These concentrations were mainly because of atmospheric deposition. The distribution of PCB markers in sediments of Drini River (Lezha) and Kune-Vaini Lagoon were the same for all layers obtained in the analysis that is associated with their same origin. PCB 28 and PCB 52 were found at higher levels than others. PCBs in our country are mainly atmospheric origin. In some layers were found in high amounts PCB-118. This is due to the physico-chemical properties of PCBs and their sedimentation velocity. PCB 52 concentrations were shown to be the same for all studied sediment layers for lagoon stations.

REFERENCES

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

Erickson M.D. (2001) Introduction: PCB properties, uses, occurrence, and regulatory history. In: Robertson, L.W., Hansen, L.G. (Eds.), PCBs: Recent Advances in Environmental Toxicology and Health Effects. The University Press of Kentucky, Lexington, Kentucky, pp. 131–152.

Rene G., 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

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. J. of Chromatography, 435, 241-248.

Safe, S., (1994) Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment. Rev. Toxicol. 24(2):87–149.

Villeneuve, J-P., Carvalho, F.P., Horvat, M., Cattini, C. (2004) Worldwide intercomparison on the determination of organochlorinated pesticides, PCBs and petroleum hydrocarbons in a mussel tissue homogenate, IAEA-142. Intern. J. Environ. Studies. Vol. 64/1, pp. 437-452