ORGANOCHLORINATED PESTICIDE RESIDUES IN SEDIMENTS OF BUNA RIVER

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ABSTRACT

In this paper are shown data for concentrations of organochlorinated pesticides in two sediment samples of River Buna. Sediment sample were taken 600 and 1000 m of river outlet using carrot tube. Depth of sediments sampled were 30 cm. Samples of sediments were divided in fractions of 5 cm. Ultrasonic extraction was used for extracting pesticide residues from fraction sediment river samples. Clean-up procedure was performed using firstly metallic mercury followed a second clean-up procedure in an "open" florisil column. The organochlorine pesticides detected were HCHs (a-, b-, γ- 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. Analyses were done with capillary column HP-5, 30 m long, 0.32 mm internal diameter, 0.25 μm film thicknesses on a gas chromatograph HP 6890 Series Plus, with μECD detector. The found concentrations of the organochlorinated pesticides were in a regression linear curve; higher in depth and lower in surface of sampling sediments. These data suggest the use of these pesticides in adjacent agricultural areas.

Keywords: *Organoclorine pesticides; Sediment analyze; Buna River; Gas Chromatography*

INTRODUCTION

Buna (Bojana) is one of the most important Mediterranean rivers. Also, thanks to the waters from the Drin River, the Buna ranks second place among all tributaries to the Adriatic, measured by the annual discharge, after the Po River in Italy (with 352 m^3/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 SE 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 km^2, because the whole drainage area of Shkodra Lake, the largest lake in southeastern Europe, is also part of it (Pano & Abdyli, 1984).

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. 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). OCP are used extensively as insecticides sterilizes, and herbicides. In particular, those used as insecticides are extremely toxic to living bodies. Most OCPs have been progressively restricted and then banned

in the 1970s in most industrialized countries a widespread environmental pollution has resulted from their use in agriculture and civil uses. Organoclorine pesticides (OCP) in general are lipophilic compounds with noticeable chemical and environmental stability. The accumulation of organochlorine compounds is connected with their chemical structure and their physical properties such as polarity and solubility.

Before 90' organochlorinated pesticides were used widly in Albania for agricultural purposes. The main agricultural areas were in the western of the country (Shkodra, Durresi, Tirana, Fieri, Lushnja, Vlora) but almost every were in the country had been developed different directions of agricultural (fruits, corns, vegetables, etc.). The most used organochlorinated pesticides were DDT, Lindane, HCB, Aldrins and Heptachlors. The scale of pesticides use after 90' in agriculture has decreased, due the change of soil structure. Emigration of many peoples in western country and 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. Unfortunately families have been living in this area of plant after destroying. New houses were building near this territory. 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. Mismanagement of oddments pesticides, for some years after 90' was another source of pesticides contamination not only in area of chemical plant but in a diameter higher; include the waters of Adriatic Sea.

2. MATERIAL AND METHODS

2.1. Sediment sampling

"Carrot" of sediment samples was taken in Buna River, by sediment core sampler, type Beeker. Two stations (600 m and 1000 m distance from Adriatic Sea) were analyzed in this study. Samples were taken in the middle of the river. Depth of sediment was respectively 25 and 30 cm for both stations. Samples were divided into factions with 5 cm. The depth of river in the studied stations was different from 1,5 m to 3 m. Samples were transported to the laboratory and stored in a refrigerator in -4^{o}C. The sediment samples were dried at 30°C and were sieved (size 0.063 mm) at room temperature.

2.2. Extraction and clean-up procedure for sediment samples.

1 g of each dry sediment sample (fraction ≤ 0.063 mm) was weighted into a glass vial of 50 ml. A solvent mixture of 20 ml hexane/dichloromethane (3/1) were added into the sample and extracted for 2 x 30 minutes, in 30^{o}C using an ultrasonic bath. Internal standard (PCB-29) was added previously to each sample (10 µl) prior extraction procedure. Extracts were transferred into glass flasks by careful decantation. The residue was subsequently washed three times with 3 ml of pure dichloromethane and these volumes were combined with the extract. The final extract was concentrated to 5 ml.

The concentrated extracts were then subject of the clean-up procedure. Firstly metallic mercury (for sulphur removal) was added for each extract. The extract was removed from mercury by pipette Pasteur and transfer into a Florisil open glass column. Organochlorinated pesticides were eluted using a 7 ml mixture of hexane/dichloromethane (4/1). The extracts were concentrated to 2 ml for gas chromatographic analysis. IAEA 383 Certified Sample for organochlorinated pollutants was used for method validation (UNEP 1995; Petrick *et al.* 1988; Rene *et al.* 1995).

2.3. Equipment and chromatography

The organchlorine pesticides detected were HCB, HCHs (a-, b-, γ- and d-isomers) and the DDT-related chemicals (o,p'-DDE, p,p'-DDE, p,p'-DDD, p,p'-DDT). 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 30 m x 0,32 mm i.d. x 25 μm film thickness). The split/splitless injector and detector temperatures were set at 280^0C and 320^0C, respectively. Helium was used as carrier gas at 1ml/min and nitrogen was used as make-up gas 25 ml/min. The relative response factors of the organochlorinated pesticides were determined by injecting the standard solutions of 25 ng/μl.

DISCUSION OF RESULTS

Results obtained from study of organochlorinated pesticides in sediment layers of Buna River were interpreted by meaning of data. All results were in ng/g dry sediment sample. In Figure 1 was shown total of organochlorinated pesticides in sediment layers of Buna River. Organochlorinated pesticides were found in all layers of analyzed sediment samples. The maximum concentration was for 5-10 cm layer with 119.2 ng/g. Note that this maximum was primarily concerned with the influence of 4,4-DDE, and HCB found in greater amounts than other fractions. Total of organochlorinated pesticides from deeper layer on the surface was a linear curve downward. It is associated with previous use of pesticides and their deposition in sediments of Buna River. Rate of sedimentation, rate of pesticide degradation in different layers, new incoming from rainfall or mismanagement of old pesticides could be primary factors. Different layers respond to different years. Distribution of organochlorinated pesticides in sediments of Buna River was shown in Figure 2. The distributions of pesticides in different layers were the same because of the same origin. The different concentrations are connected with the factors that noted above. Deeper layers respond previous years when uses of pesticides were more intense. In Figure 3 was shown the profile of organochlorinated pesticides in sediment layers of Buna River. It was clear that higher levels belong 4,4-DDE because of previous uses of DDT and its metabolic processes in sediments river. The higher levels were shown also for HCHs and HCB. DDT, Lindane and HCB were used mainly before 90' in our country and also in agricultural areas around of Buna River, Shkodra Lake and Drini River. All these water systems have their contribution in found pesticide levels in layers of sediments for Buna River because it is outlet for all waters in Adriatic Sea (Nuro et al. 2008; Marku & Nuro 2005). In Figure 4 was shown DDT and its metabolites concentrations in sediment layers of

Buna River. DDTs were pesticides that had higher contribution. It is notable that contribution of DDTs in sediment layers corresponds to a linear descending curve. The maximum was for 25-20 cm layer with 67.8 ng/g and the minimum was for upper layer (25-30 cm) with 12.4 ng/g. These levels are associated with massive uses of DDT before '90, interruption of this process and new arrivals from rainfall of the agricultural areas. Interesting was the profile of DDTs in sediment samples where clearly was shown the highest levels in any fraction for 4,4-DDE. This fact is associated with degradation of DDT. DDT was not detected in the upper layer of the analyzed sediment samples. DDE is the main metabolite of DDT, it is also very stable. In Figure 5 was shown total and distribution of HCHs in sediment layers of Buna River. Presences of HCHs in layers of sediment sample were different compared to data found on the DDT. They respond to a linear curve upward. For deeper faction noticed their minimum of total with 9.4 ng/g and the maximum was for the surface layer with 56.7 ng/g. This profile is not associated with use of Lindane last years. It was shown increasing of b-HCH concentration form deeper to surface layers. Lindane reduced year after year because of degradation process in sediment. Levels of b-HCH could be increased because its ability to be accumulated in the organic layer of sediment layer and also with lindane degradation processes. HCB in sediment layers of Buna River was shown in Figure 6. The presence of HCB in the "carrot" of sediment in the river Buna is similar to DDT which corresponds to linear descending. Its previous uses and degradation are factors that suggest these levels.

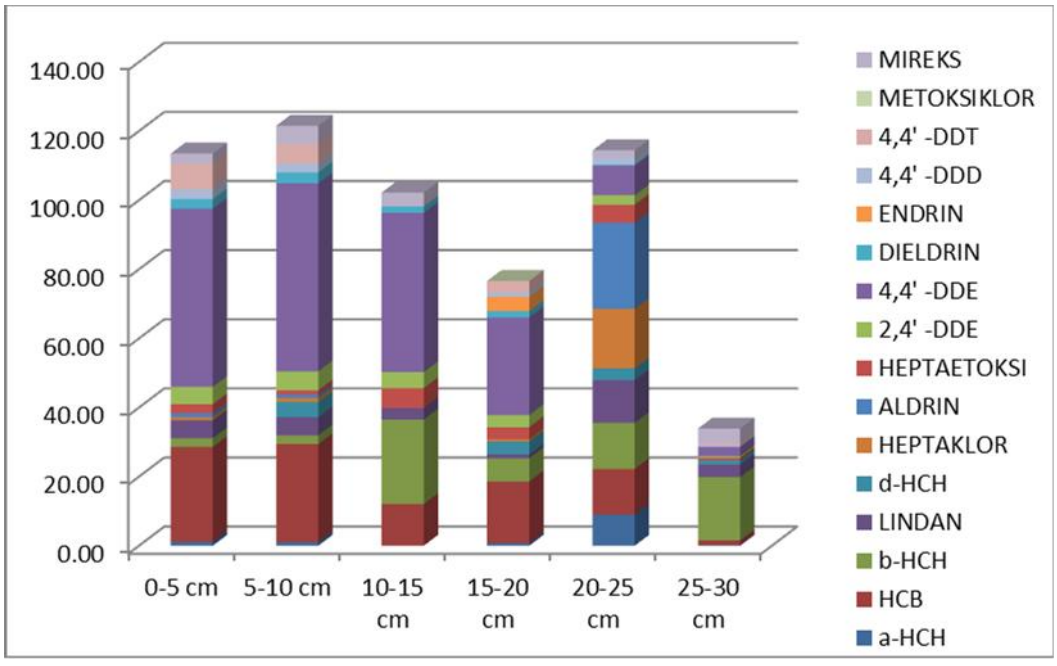

Figure 1. Total of organochlorinated pesticides in sediment layers of Buna River

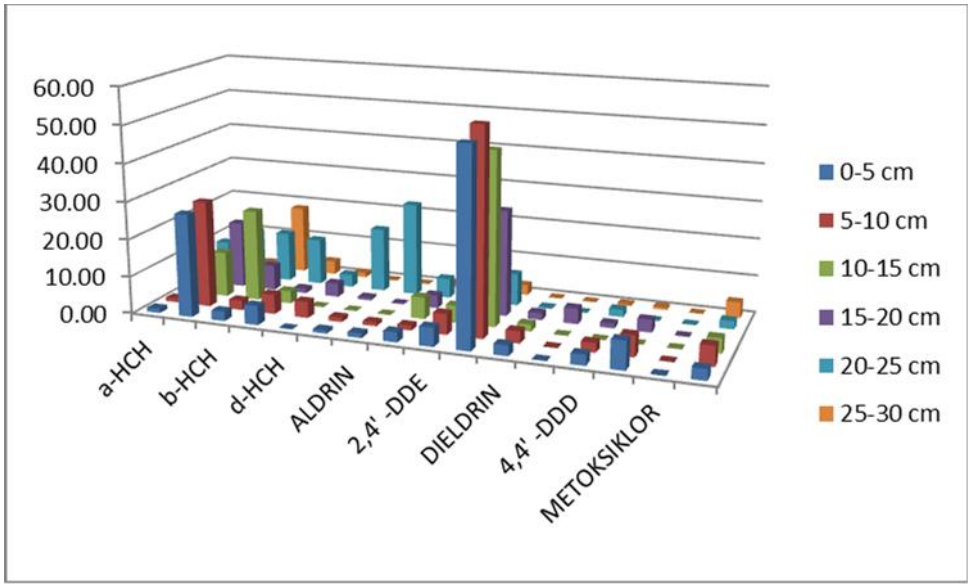

Figure 2. Distribution of organochlorinated pesticides in sediment layers of Buna River

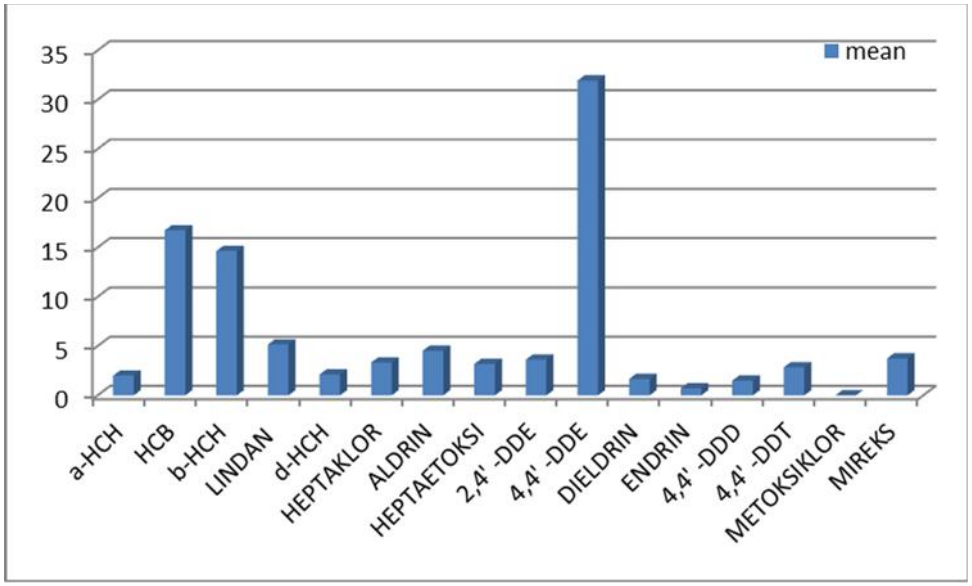

Figure 3. Profie of organochlorinated pesticides in sediment layers of Buna River

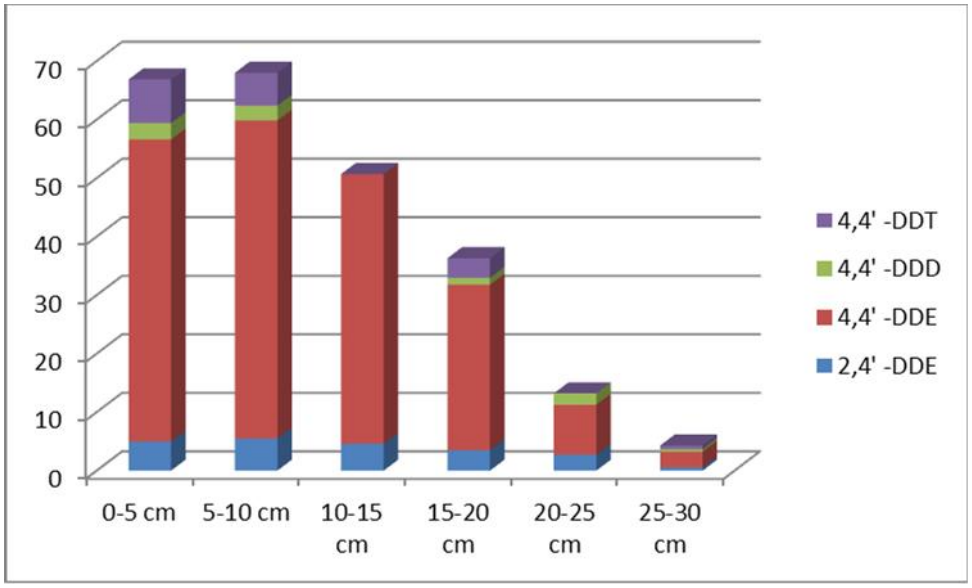

Figure 4. DDTs in sediment layers of Buna River

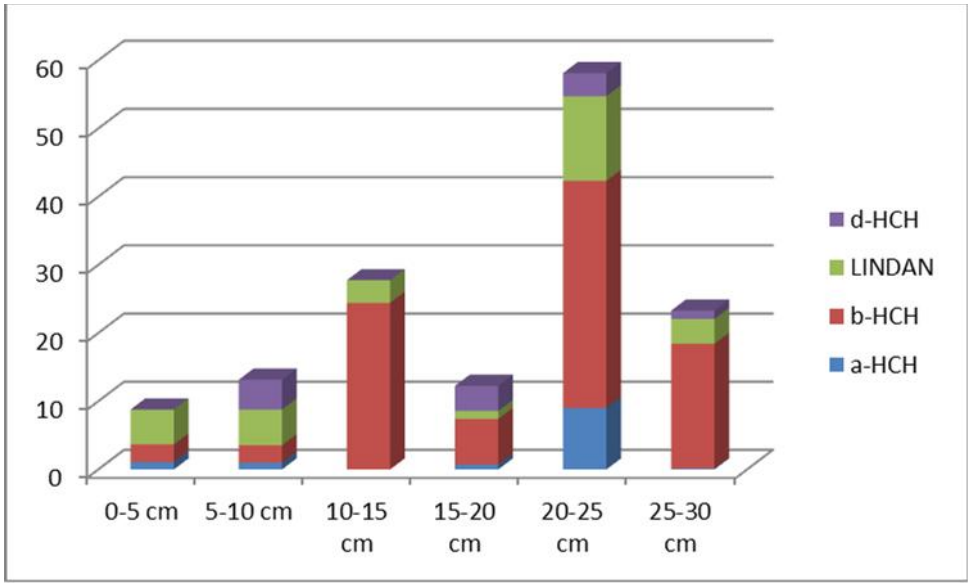

Figure 5. HCHs in sediment layers of Buna River

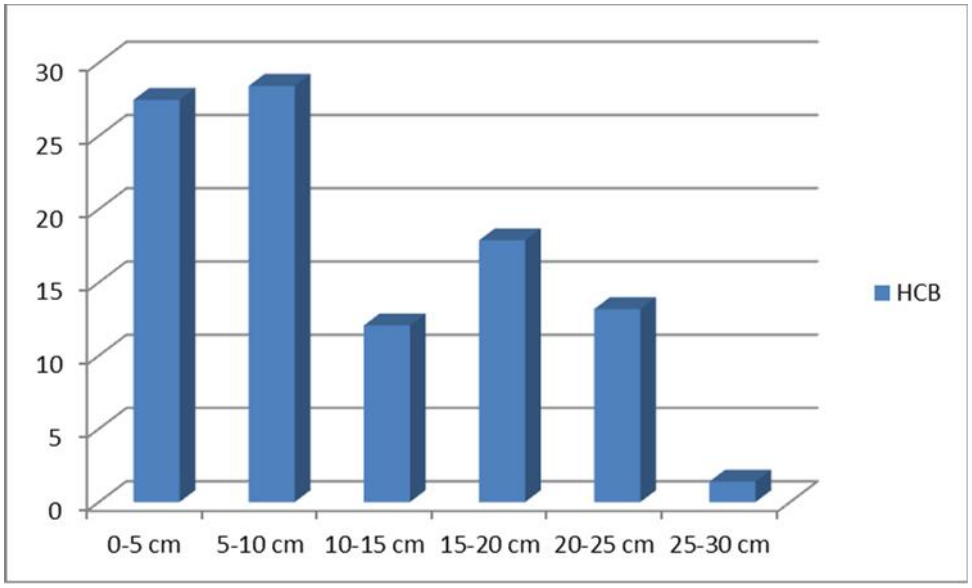

Figure 6. HCB in sediment layers of Buna River

CONCLUSIONS

Buna River due to the nature geological and anthropogenic impacts of Drin River has a high sedimentation process. Sediment samples were taken at a depth of 25 cm and 30 cm to study the time profile of organochlorinated pollutants in two stations. Organochlorinated pesticides are present in the sediment samples and this is expected because of their previous uses for agricultural purposes. Watershed scale makes these sediments "supplied" constantly with new levels of these pollutants. Regarding the profile of organochlorinated pesticides found in sediments clearly have higher levels of DDE. HCB is a second tributary due of its previous uses. b-HCH isomer has higher level than Lindane in studied sediment samples. This is related to the chemistry of these isomers. Total of organochlorinated pesticides from deeper layers on the surface was a downward linear curve. It is associated with deposits of organochlorinated pesticides in previous years. Different layers respond to different years. Fractions deeper respond to previous years when and uses of pesticides were more intense.

REFERENCES

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

Nuro A., Marku E., Beqiraj S., Kambellari E., (2008) Determinations of bioaccumulation and bioconcentration factors of organochlorine pesticide residues in fish samples of Shkodra Lake. The International Conference of the Biological and Environmental Sciences of Albania. Proceedings book of Conference, ISBN 978-99956-772-06; 471-478

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

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 samples for analysis of Organochlorine compounds by gas chromatography with electron-capture detection. J. of Chromatography, 435, 241-248.

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

UNEP (1995) Reference Methods for marine pollution studies. Nr 71.