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Analysis of Some Chlorinated Pesticides in Adriatic Sea: Case Study: Porto-Romano, Durres, Albania

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Abstract: The aim of this study was to determine organochlorine pesticides levels in water samples from Porto-Romano, one of the main "Hot Spot" in the Albanian coast of Adriatic Sea. Porto Romano is situated only 7 km far from Durres city, and is characterized by a strong pesticide contamination of soil, water and air, due to ex-Chemical Enterprise that produced pesticides for agriculture and other chemicals for leather treatment during communist regime up to 90's in Albania. Water samples were taken in six stations in the Porto-Romano area, in May 2016. Organochlorinated compounds were measured by gas chromatography electron capture detection. These compounds were extracted using liquid-liquid technique using n-hexane as extracting solvent. After extraction the organic phase was dried with 5 g Na_2SO_4 anhidrous, to remove water. A Florisil column was used for the sample clean-up. After the concentration to 1 ml, the samples were injected in GC/ECD HP 6890 Series II. Results showed that even if organochlorine pesticide production stopped by the 90's in Albania, data shows persistent levels of organochlorinated pesticides were still found in all water samples.These data highlight the importance of a continuous environmental monitoring of polluted area subjected to protect human's and wildlife's health.

Keywords: *Porto Romano, organochlorinated pesticides, water samples, gaschromatography*

Introduction

Porto Romano is situated 7 km north of Durrës city, facing the Adriatic Sea. During communism, the area was known for the Chemical Enterprise that produced pesticides for agriculture purposes mainly in agricultural areas such as western cities of the country (Shkodra, Shëngjini, Durrës, Lushnja, Vlora) and sodium dichromate, for leather tanning. The most used organochlorinated pesticides were DDT, Lindane, HCB, Aldrins and Heptachlors. After the 90' the Enterprise was abandoned and hundreds of tons of pesticides seriously contaminated the water, soil and air. The accumulation of organochlorine is connected with their chemical structure and their physical properties such as polarity and solubility. Pesticides present lipophilic chemical characteristics giving them a high stability and, indeed, persistency in the environment. After the communist regime, the population of Porto Romano grew constantly, due to free movement of population, migrants mainly from northern areas Albania. Numerous families settled in this critical contaminated area. Investments in the Porto Romano Hot Spot cleanup started in November 2005 as part of a big World Bank-supported project on the Integrated Coastal Zone Management and Clean-up in Albania. Almost 750 tons of pesticides were repackaged in the storage site and transported to a specialized German disposal site in 2006.

Persistent organochlorine pollutants such as organochlorinated pesticides (OCPs) are a group of compounds of great chemical stability and persistence whose presence in the environment is a clear indication of anthropogenic pollution. The massive and indiscriminate use of these xenobiotics for agricultural purposes caused their widespread diffusion to all environmental compartments including a wide range of organisms such as plankton, fish, marine and land mammals and humans. Several studies have shown that these compounds exert a number of toxic responses including immunotoxicity, reproductive deficits, teratogenicity, endocrine toxicity and carcinogenity/tumor promotion. OCPs are the first class of synthetic pesticides introduced in agricultural and civil uses to counteract noxious insects and insect-born disease (Di Muccio, 1996). Most OCPs have been progressively restricted and then banned in the 1970s in most industrialized countries. In Albania organochlorines were used mostly as insecticides before 90'.

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Materials and Methods

Sampling of water samples in Porto-Romano

The samplings were realized in six different stations in Porto-Romano area. 1.5 L of water were taken from each station. Water samples were tranported to the lab at +4^{o}C.

Figure 1. The satellite map of sampling of sea water samples in Porto-Romano, May 2016

Preparation of samples for organochlorinated pesticides analysis

Liquid-liquid extraction was used for the extraction of organochlorine pesticide residues from sea water samples. 1 L of water, 10 µl PCB-29 as internal standard and 20 mL n-hexane as extracting solvent were added in a separatory funnel. After extraction the organic phase was dried with 5 g Na_2SO_4 anhidrous, for removing water. A Florisil column was used for the sample clean-up. After the concentration to 1 ml, the samples were injected in GC/ECD HP 6890 Series II. Procedural blanks were regularly performed and all results presented are corrected for blank levels. All glassware was rigorously cleaned with detergent followed by pyrolysis at 250°C. 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 (Albanis *et al*, 1994; Rene *et al*, 1999; Fernandez *et al*, 1998; Petric *et al* 1988).

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 Rtx-5 (30mx x 0.33mm x 0.25 um) capillary column. The split/splitless injector and detector temperatures were set at 280^{o}C and 320^{o}C, respectively. Carrier gas was He at 1 ml/min and make-up gas was nitrogen 25 ml/min. The initial oven temperature was kept at 60^{o}C for 4min, which was increased, to 200^{o}C at 20^{o}C/min, held for 7 min, and then increased to 280^{o}C at 4^{0}C/min for 20min. The temperature was finally increased to 300^{o}C, at 10^{o}C/min, held for 7 min. Injection volume was 2µl, when split less injections were made. OCP quantification was performed by internal standard method. PCB 29 was used as internal standard (Nuro & Marku 2012; Andral et al, 2004.)

Results and Discussion

The study of organochlorine pesticides and PCBs levels in the Porto-Romano waters was conducted on six water samples, taken in different areas of this ecosystem, in May 2016. Their analysis was based on the capillary gas chromatography technique with ECD detector. Organochlorine pollutants data were reported in µg/L water. The average level of organochlorine pesticides in the water samples of Porto-Romano was 34.3 µg/L (Figure 2). The highest concentration, equal to 150.2 µg/L, was found at station 6, located in north-west of Porto-Romano. Station 2, 3 and 4 presented lower levels of organochlorine pesticides and their residues. Detected levels ranging from 9.2µg/L to 16.8 µg/L. Station 3 was choose as reference station for this study. OCP levels mostly correlated to the persistency of old pollution of these areas produced by Chemical Enterprises, probably maintained high by water currents. By analyzing the concentration of major pesticides found in the sampled areas, the OPCs profile revealed the following levels: Endrine> Dieldrine> DDT> DDE> EndrinAldehyd> Aldrine> b-HCH > Endosulfane (Fig.3). Endrine and other cyclopentadienyl pesticides were indeed the main pollutants found in all water stations. DDTs were found also in high concentrations. For all samples the levels of individual organochlorinated pesticides were lower than the allowed levels (100 µg/L) for surface waters according the National norms.

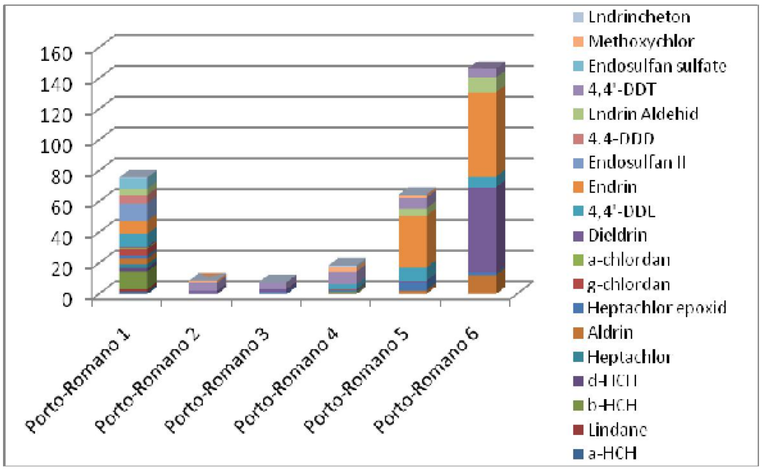

Figure 2. Total concentrations of organochlorinated pesticides (µg/L) in sea water samples. Porto Romano May 2016

Among the hexachlorocyclohexane (HCH), station 1 in the south-west of Porto-Romano was the most polluted with 16.2 µg/L. In stations 2, 3, 5 and 6 the HCHs were not detected or were lower than limit of detection (Fig.4). Beta-HCH > delta-HCH > alpha-HCH > gamma HCH (Lindane) was the profile of hexachlorocyclohexane concentrations in sea waters (Fig.5). These levels were comparable to those reported from previous studies for other stations of Adriatic Sea. Note that for Porto-Romano station the reported values for the previous years were only in biota samples (Mytulus Galloprovincialius) in the range from 5 to 55ug/g fresh sample (Nuro & Marku, 2012). This means that after years, HCH contamination of the area did not change, due to the chemical stability of HCH and by the continuous flushing of these compounds from ex-Chemical Enterprise areas. Cyclopentadienyl pesticide concentrations were the most abundant pollutants of the sea water samples of Porto-Romano. This can be accounted for a high persistency but also for the degradation of HCHs into chlorinated compounds at higher mass (Figure 6). Profile of cyclopentadienyl pesticides in sea water samples of Porto-Romano showed that the main pesticides were Endrin, Dieldrin and Aldrin (Figure 7). This profile is different from another study where it was mainly found degradable products as heptachlor epoxide (Nuro and Marku, 2012). However it could be possible that these pesticides are still used in agriculture near Porto-Romano with other commercial names. Note that cyclopentadienyl pesticides are not allowed from 90' in Albania. DDTs were found almost in all stations in the same level. Average level of DDTs was 9.8 µg/L (Figure 8). These levels were comparable with reported levels for these areas in previous studies (Nuro & Marku, 2012). It was observed that DDT levels were higher than its metabolites (Fig.9). This could be because of its slow degradation into the water and sediments, perhaps associated to water washout and momentum concentration.

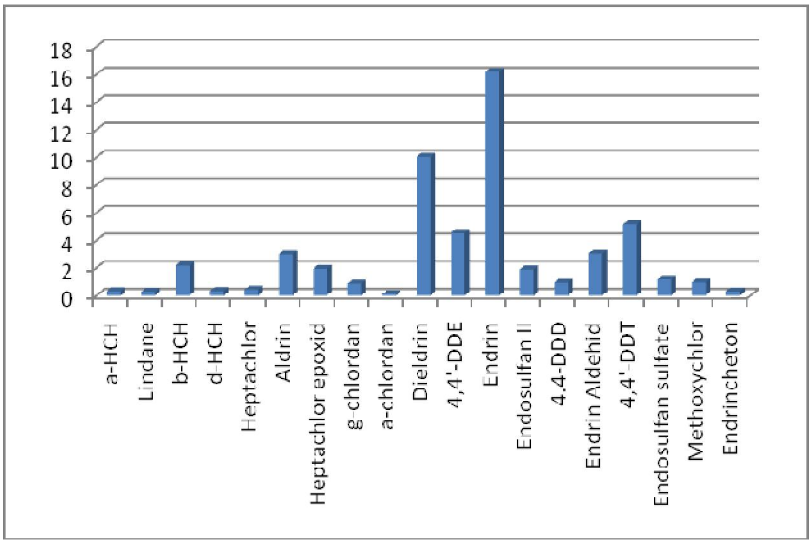

Figure 3. Profile of organochlorinated pesticides (µg/L) in sea water samples. Porto Romano May 2016

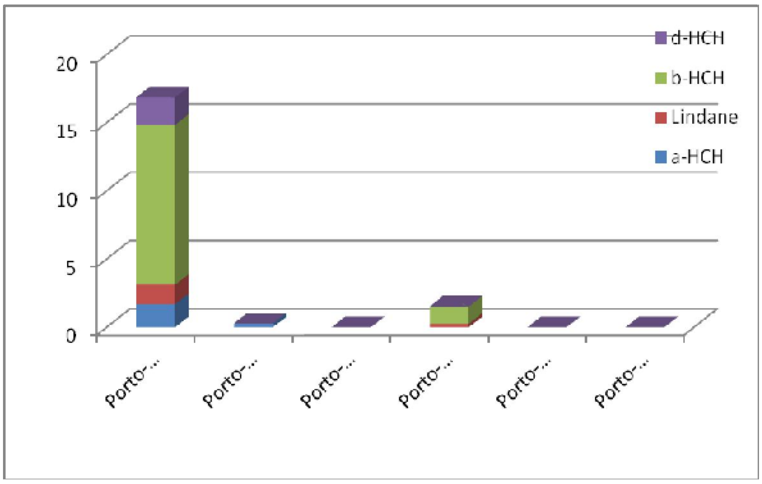

Figure 4. Total concentration hexachlorocyclohexanes (HCHs) (µg/L) in sea water samples. Porto Romano May 2016

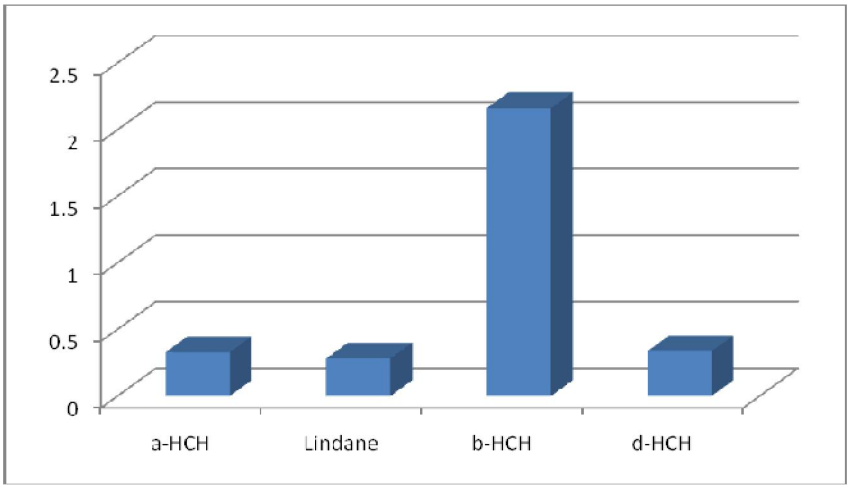

Figure 5. Profile of HCHs (µg/L) in sea water samples. Porto Romano May 2016

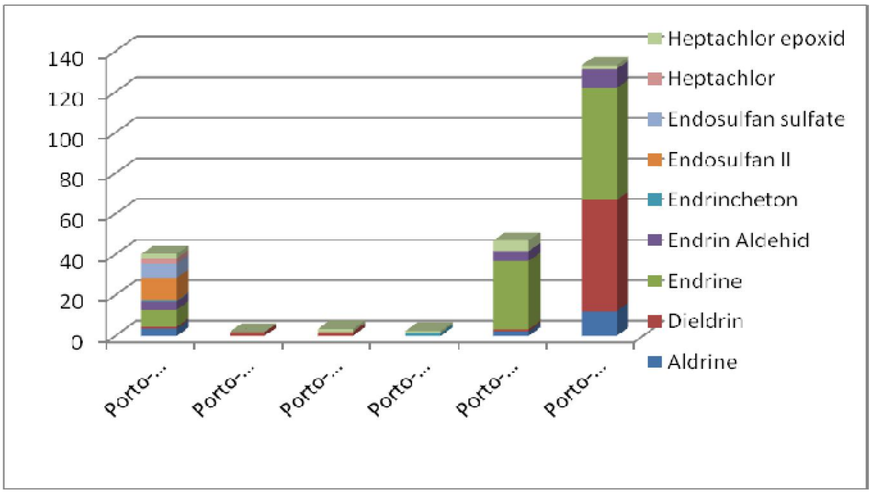

Figure 6. Total concentrations of cyclopentadienyl pesticides (µg/L) in sea water samples. Porto Romano May 2016

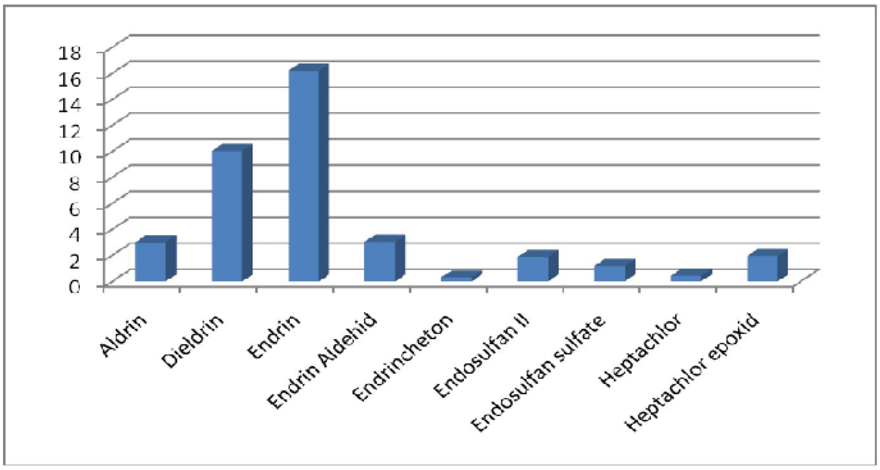

Figure 7. Profile of cyclopentadienyl pesticides (µg/L) in sea water samples. Porto Romano May 2016

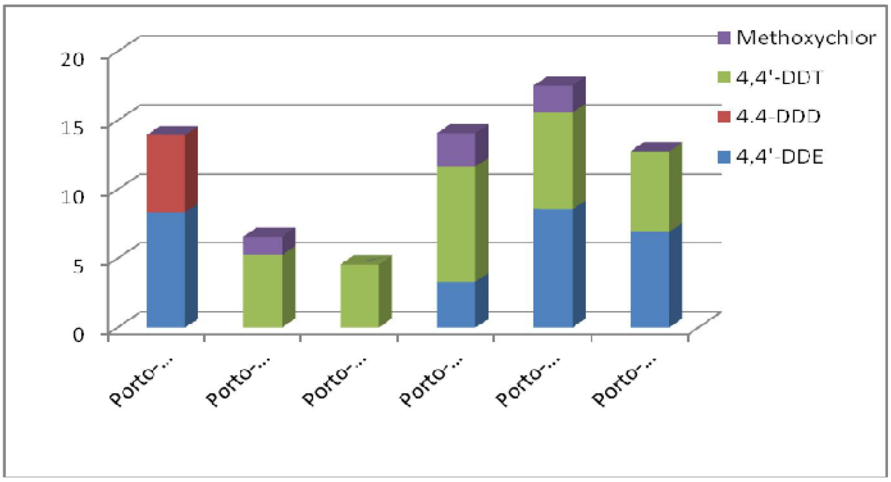

Figure 8. Total concentrations of DDTs (µg/L) in sea water samples. Porto Romano May 2016

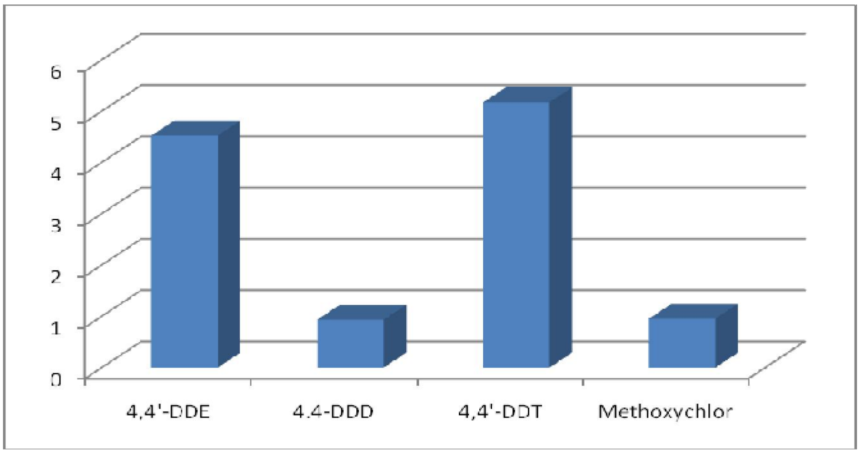

Figure 9. Profile of DDTs (µg/L) in sea water samples. Porto Romano May 2016

Conclusions

Presence of different kinds and concentrations of OCPs were determined in Adriatic Sea close to Porto Romano area in Albania. The presences of OCPs were evident in sea water samples of Porto-Romano stations. The OCPs level in the water samples of Porto-Romano was 34.3µg/L. The highest concentrations of pesticides were found in north-west of Porto-Romano station. Levels of organochlorine pesticides were found to be associated mainly with old pollution of these areas also favored by water currents. Organochlorine pesticides origin could be mainly from their previous discharges from ex-Chemical Enterprise. Endrine and other cyclopentadienyl pesticides were the main pollutants for all water stations. DDTs were found also in higher concentration. Hexachlorocyclohexane and its isomers were found in two stations. Their profile was: beta-HCH > delta-HCH > alpha-HCH > gamma HCH (Lindane). Cyclopentadienyl pesticides were the higher pollutants in these areas. Profile of cyclopentadienyl pesticides in sea water samples of Porto-Romano showed that the main pesticides were Endrin, Dieldrin and Aldrin. Their stability could be an important factor. It's also possible that degradation of Lindane and other isomers, bring other chlorinated compounds with higher mass, increasing in higher concentrations these kinds of pesticides. Also DDTs were found almost in all stations in the same level. DDT and HCHs levels were comparable with reported levels for these areas in previous studies. It was noted that DDT levels were higher than its metabolites; this could be because the slow degradation in water and sediment for this pollutant. Cyclopentadienyl pesticides profile was different from other reported studies, where were found mainly the degradable products as heptachlor epoxide (Nuro & Marku, 2012).

We suggest, this study should continue for years and should increase the number of samples and the sampling frequencies. We suggest also analyzes in biota and sediment samples for a better understanding about the levels and physical-chemical changes that occur in this ecosystem. Addition of an epidemiological study may clarify the impact of these pollutants in the population of this area.

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