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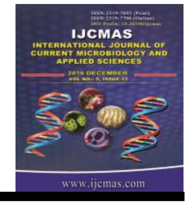

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Analysis of Some Organic Pollutants in Drinking Water using Capillary Gas Chromatography Technique

Oljana Pine* and Aurel Nuro

Tirana University, Faculty of Natural Sciences, Chemistry Department, Albania
**Corresponding author*

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In this paper are presented concentrations of organochlorinated pesticides and polychlorinated biphenyls in drinking water samples of Tirana water network stations, groundwater and commercial water from markets. The samplings were realized for eight different stations in network stations, five groundwater stations and ten commercial waters in January 2014. Water samples were analyzed with capillary gas chromatography technique with ECD. The water samples were extracted with hexane, dried with anhydrous sodium sulphate and cleaned up in an open Florisil micro-column. Rtx-5 (30mx x 0.33mm x 0.25 um) capillary column used for separation of organochlorinated pollutants. The most frequently detected pesticide where DDT metabolites, Aldrines and volatile PCBs. All the concentration levels of these chlorinated pollutants were below the EU Directive 98/83/EC.

Introduction

Persistent organochlorines such as organochlorinated pesticides (OCPs), polychlorinated pesticides (PCBs) and Dioxins 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 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. The modern history of pesticides dates back to World War II when for the first time the insecticidal properties of DDT were recognized. 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. Before 90' organochlorinated pesticides were used widely 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. 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 them to accumulate in biota. In Albania PCBs are used mainly in transformer oils after 90', but the source of pollution is mostly airborne origin with predominance of most volatile PCB congeners like Aroclor 1240, 1254 (Koci, 1997).

Albania is a country rich in water. Its overall renewable resources amount is 41.7 x 10^9 m^3 or 13.3 x 10^3 m^3 per capita, out of which about 65% are generated within Albania and the rest originates from the neighboring countries. The major water resource is surface water.

According to data reported by UNICEF (2001), about 97% of the Albanian population has access to clean drinking water; about 80% of the water originates from groundwater, the remaining 20% from surface water. About 85% of the water is produced by public systems, in urban areas available directly at home, but in rural areas often only at public taps and standpipes.

The region of Tirana possesses wide natural geological features that offer abundant water resources of good quality.

Drinking water supply for the capital area is estimated to be about 83.7 x 10^6 m^3 $year^{-1}$, with an average daily flow of around 2.8 m^3 sec^{-1} obtained from three different water sources: surface water (Bovilla Reservoir), natural underground springs, and artesian pumped wells. About 57 x 10^6 m^3 are obtained from Bovilla Reservoir.

Materials and Methods

Sampling of drinking water

Water samples were taken in January 2014in different stations of Tirana City from different origin and source. The samplings were realized for eight different stations in network stations, five groundwater stations and ten commercial waters in markets of Tirana. The sampling sites from network or underground water are presented in Figure 1. 1.5 L of water were taken from each station. Water samples were tranported in $+4^oC$.

Preparation of samples for organochlorinated pesticides and PCB analysis

Liquid-liquid extraction was used for the extraction of organochlorine pesticide residues and polychlorinated biphenyls from drinking 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.

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^{0}C and 320^{0}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^{0}C for 4min, 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 20min. The temperature was finally increased to 300^{0}C, at 10^{0}C/min, held for 7min. Injection volume was 2µl, when splitless injections were made. OCP quantification was performed by internal standard method. PCB 29 was used as internal standard. The following organchlorinated pesticides: Hexachlorobenzene (HCB), Dieldrin, Endrin, alfa-, beta-, delta- and gama-isomer (Lindane) of Hexachlorocyclohexane, Heptachlor, Heptachlor epoxide, DDT-related chemicals (*o*,*p*-DDE, *p*,*p*-DDE, *p*,*p*-DDD, *p*,*p*-DDT), Methoxychlor and Mirex were detected.

Results and Discussion

Figure 2 presents the experimental data for the organochlorine pesticide residues found by gas chromatographic technique in analyzed drinking water samples of Tirana City. The average concentration of organochlorine pesticides for drinking network water samples was 3.6 ng/L, for water samples taken from the underground water stations was 1.6 ng/Land for packed water samples was 1.8 ng/L. The highest value was found in the U8 sample taken in Kombinat with 13.2 ng/L. For all network water samples in Tirana city were found organochorinated pesticides and their residues concentrations. Note that total concentrations for all samples were lower than accepted maximum level (50 ng/L). These founds could be because of the main water resource for Tirana city, Bovilla Lake. It is an open artificial lake that could be influenced from agricultural areas near the lake, rainfall, atmospheric factors, etc. For U8The highest value was found in the untreated water sample taken from– U8 (13.2 ng/L). The most polluted underground water sample was U11 (Sauk). This station is supplied from Shen Meria and Mullet spring that are affected because of previous use of chlorinated pesticides in fruit trees and other agricultural activities. The lower levels for spring water samples were found for other sampling stations. Geology and hydrogeology are the main factors that affect the low level for organochlorine pesticides in these sites. U18, U21, U14 and U15 were found to have the highest level with organochlorinated pesticides. The different origin of packed water could be the main factor. Average concentrations for individual organochlorine pesticides for network, underground and packed water samples are shown in figure 3. Distribution profile of organochlorine pesticides is the almost the same for all drinking water samples because the same origin of pollution. The most frequently detected pesticide were HCHs, DDE (DDT metabolites) followed by heptachlors and Aldrines.All the concentration levels of these chlorinated pollutants were below the EU Directive 98/83/EC.

Total concentration of HCHs found in drinking water samples are shown in figure 4. Average level of HCHs for water samples of drinking water network was 0.75 ng/L; for the underground water samples almost in the beground level and for the packed water 0.4 ng/L. The highest levels of HCHs were found in the U8 sample with 11.05 ng/L because of fact that network water is coming from Bovilla Lake that collects water from surface and underground sources from a region where lindane was the pesticide of major use. Concentration levels of lindane and the other HCH-isomers were lower for underground water samples, because hydrogeology factor. The same distributions for all samples suggest the same origin of pollution for all HCHs (Figure 7). The concentration of lindane was lower compared with other isomers because their physical properties.

In conclusion, the higher concentration levels were found in water samples taken from Tirana drinking water network. The highest value was found for the untreated water sample from Bovilla Lake. Bovilla Lake collects water from surface and underground sources from a region where the pesticides were used for agricultural reasons. The highest concentration for the underground drinking water was found in Mullet sampling site. Shen Maria source and some other sources (Mullet spring) were very affected from chlorinated pesticides, because of their previous use in this area. Geology and hydrogeology can be the main factors that affect the low concentrations of organochlorine pesticides in underground water samples. Distribution profile of organochlorine pesticides was the same for drinking water network and underground water stations, because of the same origin of pollution. The most frequently detected pesticide was p,p'-DDE followed by γ-HCH (Lindane) and HCB. p,p'-DDE was in higher level than other pesticide residues, because of p,p'-DDT degradation processes. HCB was the second pollutant, found in high concentrations. It was used mainly as insecticide in fruit trees. Lindane concentrations were found higher HCH-isomers. All the concentration levels of these chlorinated pollutants were below the EU Directive 98/83/EC.

Fig.1 Map of (▲) network and (○) underground water samples in Tirana City

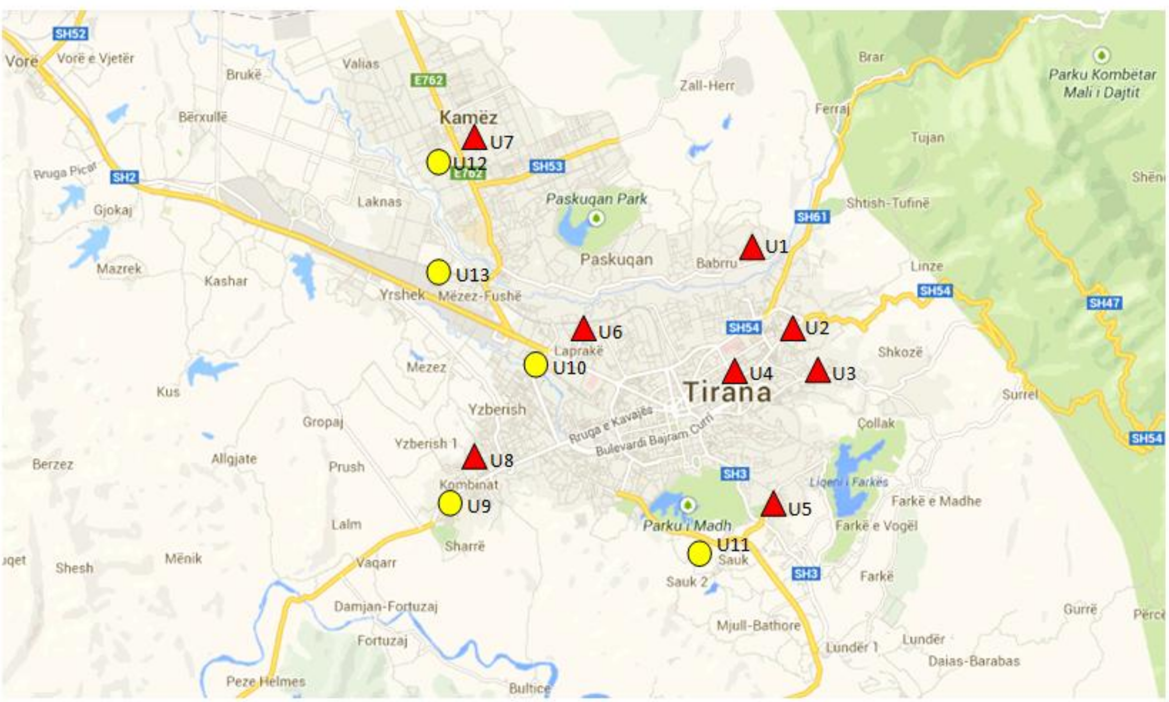


Fig.2 Total concentration for organochlorine pesticides in analyzed drinking water samples

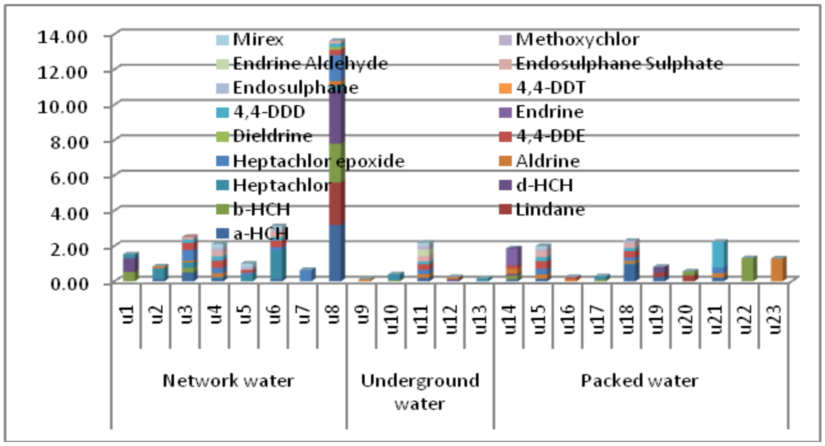


Fig.3 Profile of organochlorine pesticides in network, underground and packed drinking water samples of Tirana

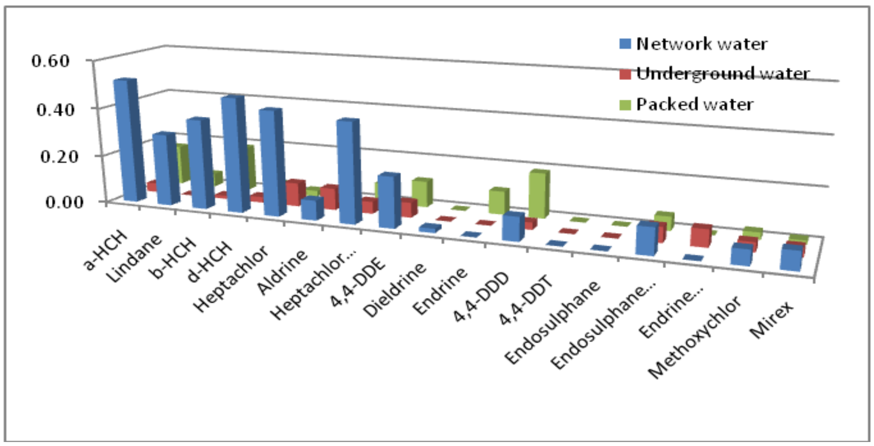


Fig.4 Total concentration for HCH in drinking water samples of Tirana

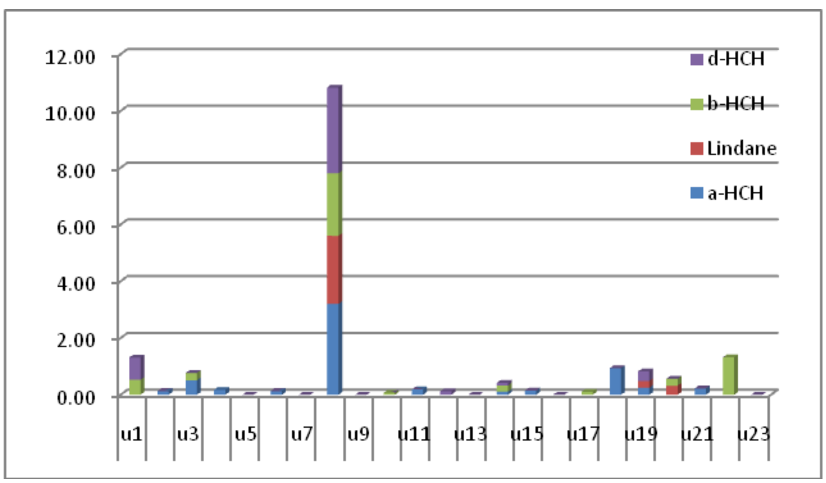


Fig.5 Profile of HCH in analyzed drinking water samples of Tirana

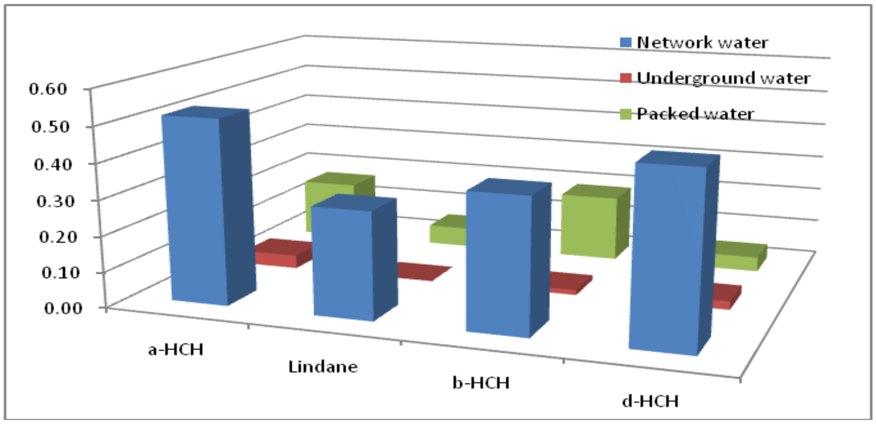


Fig.6 Total concentration for DDTs in analyzed drinking water samples

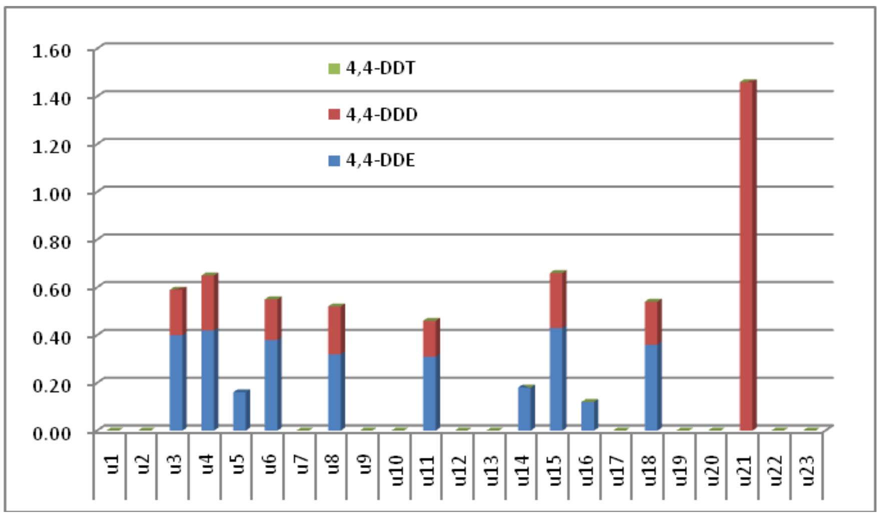


Fig.7 Profile of DDTs in analyzed drinking water samples of Tirana

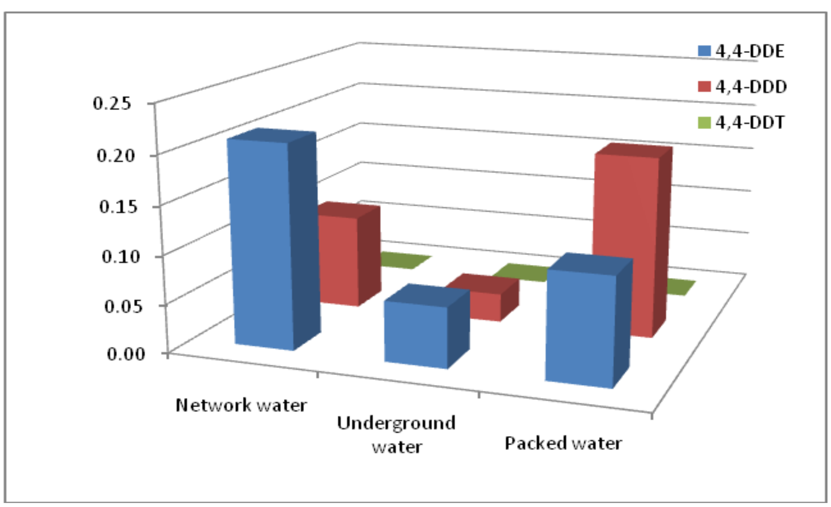


Fig.8 Total concentrations of PCB markers in analyzed drinking water samples in Tirana

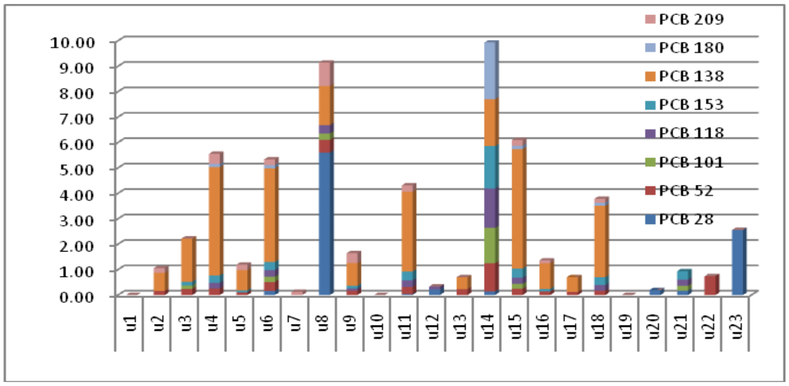
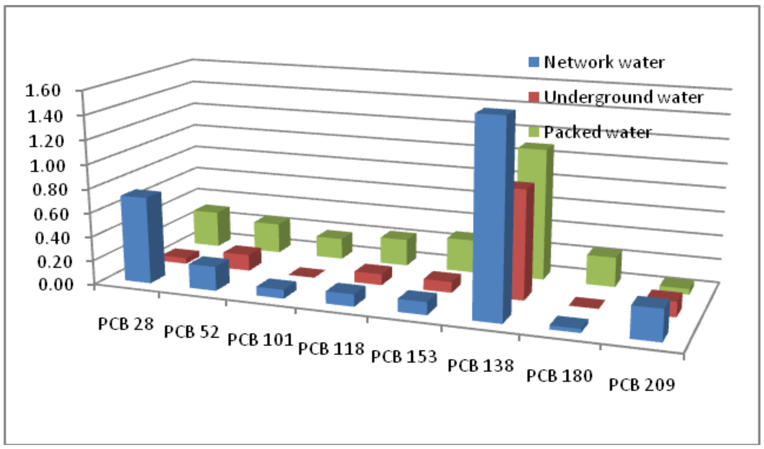


Fig.9 Profile of PCB markers in analyzed drinking water samples in Tirana



The concentrations of PCB markers for water samples of drinking water network were similar to the underground water samples. The highest levels of PCB markers were found for the untreated water samples taken from Bovilla Lake, because it collects water from surface and underground sources, from a huge region. In general, the concentrations of PCB markers were lower for underground water samples, except Sauk sampling site. In this one, elevated concentrations were found, probably because of some industries growing in this area or because of submersible water pumps whose oil may be contaminated with PCBs.. The same distribution profile was found for both types of water samples, suggesting the same origin of pollution. Elevated concentrations of volatile PCB congeners reflect the fact that PCBs in our country have mainly atmospheric origin. The enforceable maximum contaminant level for PCBs in public water systems in USA is 0.5μg/L (EPA, 2001). All drinking water samples in Tirana City were far below this limit. There are no maximum levels for PCBs in EU Directive 98/83/EC for drinking water.

Up to now, no substantial measures have been taken for the proper management of the catchments area and for the protection of the drinking water quality in Tirana. As a consequence, a continuous monitoring of the Bovilla Reservoir and its surrounding catchments area, in addition to a new watershed management strategy, is urgently needed.

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