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Research Paper

Organic Pollutants in Surface Waters of Erseka Region, Albania[#]

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Abstract: In this paper are presented concentrations of organochlorine pesticides, polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH) and BTEX – benzene, toluene, ethylbenzene and xylenes in surface water samples of Erseka region, Albania. Erseka region is situated in South-East of Albania. Water samples were taken in December 2017 in different steams that flowing from Gramozi Mountain. These steams are part of water basin for Devolli and Osumi rivers. Liquid-liquid extraction was used for extracting organochlorine pesticides, PCBs and PAHs from water samples. Clean-up procedure was realized in an "open" florisil column for chlorinated pollutants. Analysis of pesticides and PCBs were realized in HP 6890 Series II, gas chromatograph equipped with μECD detector. For separation of organochlorine pesticides and PCB markers was used Rtx-5 capillary column. Analysis of PAH and BTEX were realized in Varian 450 GC, gas chromatograph equipped with FID detector and VF-1ms capillary column. BTEX were analyzed using HS-SPME method. The highest levels of organochlorine pollutants in surface waters of Erseka region was found for organochlorine pesticides because of their previous uses in agricultural areas near these streams. Volatile PCBs were found in higher concentrations because of their atmospheric origin. PAH and BTEX were found only for 20% of water samples. Their concentration could be because of natural origin or some mechanical business that discharge their wastes directly in these steams. Found levels were lower than previous studies for other water basin areas in Albania.

***Keywords**: Organoclorined pesticides; PCBs; PAH; BTEX; water samples; GC/ECD/FID.*

Introduction

Erseka region is situated in South-East of Albania. It is situated at the foot of the Gramozi Mountain. Erseka is a small alpine town at 1050 meters in altitude, making it one of the highest towns in Albania. Erseka-Kolonja is known for its apple production throughout Albania (Mollas village). The region is also known for honey production. With over 3080 hectares used for farming, the region yields trees, corns, forage crops (which are used for livestock cultivation) and other vegetables. With the region's vast pasture land, the quality of the region's livestock production is high. Erseka-Kolonja farmers currently breed cattles, cows, sheeps and goats. Its livestock produces milk, by-products and meat. Erseka is also renowned for its woodcrafts, stone carving and carpet weaving tradition (Çullaj *et al*, 2005).

Organochlorinated pesticides (OCPs) and polychlorinated pesticides (PCBs) are a group of chlorine compounds of great chemical stability and persistence whose presence in the environment is a clear indication of anthropogenic pollution. Before 90' organochlorine pesticides were used widely in Albania for agricultural purposes. The main agricultural areas were in the western of the country 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. They are chemically highly stable, lipophilic compounds and resist microbial, photochemical, chemical and thermal degradation. 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 (Nuro *et al*, 2014). Polyaromatic hydrocarbons are a large group of compounds with a molecular structure that includes two or more fused aromatic rings. They are widely distributed in the environment as a result of the incomplete combustion of

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organic materials, both of natural (e.g. forest fires) and anthropogenic sources (e.g. motor vehicles, industrial processes,). The spillage of fossil fuel can be a significant source of contamination, as well as the leaching from pipes. The occurrences in the environment and their proved mutagenicity and carcinogenicity, sixteen PAH have been selected by the US EPA as priority pollutants (Gustafson & Dickhurt, 1997). Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) are also major constituents of gasoline. Exhaust emissions from vehicles, as well as evaporative losses from gasoline stations and vehicles, are major sources of BTEX that are released in the atmosphere. There are many different techniques by which organic compounds in water samples can be measured, including gas chromatography with mass spectrometry (EU, 2007; Gustavson and Dickhut, 1997; Mendez *et al*, 2000).

Materials and Method

Water Sampling in Erseka region

Surface water samples were taken in December 2017 in different steams that flowing from Gramozi Mountain. These steams are part of water basin for Devolli and Osumi rivers. The sampling stations are presented in Figure 1. 1 L of water was taken from each sampling station using Teflon bottles. The samples were transported to the laboratory and stored prior to analysis in +4^{o}C.

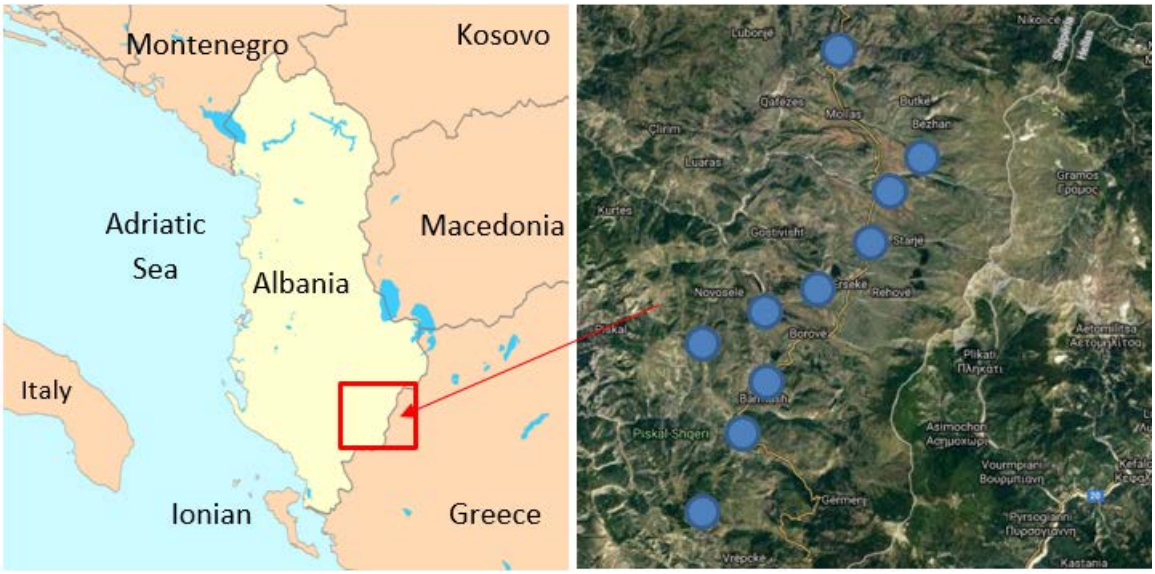

Figure 1. The map of water sampling sites in Erseka Region

GC/ECD analyse of organochlorine pesticides and PCBs in water samples

Liquid-liquid extraction was used for the extraction of organochlorine pesticide residues and polychlorinated biphenyls from water samples of Vjosa River. 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 anhydrous for water removing. 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. Rtx-5 capillary column (30 m x 0.33 mm x 0.25 µm) was used to isolate and determine simultaneously organochlorine pesticides (based on EPA 8081A method) and 7 PCB markers. EPA 8081A Mixture and 7 PCB markers were used for qualitative and quantitative of chlorinated pollutants analyse. Splitless injection was made for 2 ul sample. Injector temperature was held at 280^{o}C. ECD temperature was held at 300°C. Helium was used as carrier gas with 1 ml/min. Nitrogen was used as make-up gas with 25 ml/min. Quantification of chlorinated pollutants was based on external standards. Five points of calibration were selected for chlorinated pollutants to concentrations 10, 20, 50, 100 and 250 ng/l (EU, 2007; Konstantinou *et al*, 2006; Lekkas *et al*, 2004; Wells & Hess, 2000; Vryzas *et al*, 2009).

GC/FID determination of PAHs in water samples

PAHs were extracted using liquid-liquid extraction (LLE) assisted with Dichloromethane solvent. 1 L of water and 20 ml Dichloromethane as extract solvent was added in a separator funnel. After shaking organic phase was collected in a baker when was added 5 g Na_2SO_4 anhidrous for removing water. After concentration in 1 ml Dichloromethane, the samples were injected directly to GC/FID for PAH analyse. Gas chromatographic analyses were realized with a Varian 450 GC instrument equipped with a flame ionization detector and PTV detector. VF-1ms capillary column (30 m x 0.33 mm x 0.25 µm) was used to isolate and determine 13 PAHs compounds. Helium was used as carrier gaz with 1 ml/min. EPA 525 Mixture was used for qualitative and quantitative of PAH analyse. FID temperature was held at 280°C. Nitrogen was used as carrier and make-up gas for both analyses. Hydrogen and air were flame detector gases with 30 ml/min and 300 ml/min, respectively. Quantification of PAH was based on external standards. Three points of calibration were selected for PAH after diluted in dichloromethane to concentrations 20, 50 and 100 µg/L (Nuro *et al*, 2014; Gustafson & Dickhut, 1997).

HS/SME-GC/FID analyse of BTEX in water samples

Headspace solid phase micro extraction (HS-SPME) technique was used to trace BTEX in water samples. 5 mL of water sample was placed in a 10 mL headspace vial (5 replicate vials for each sample) to adsorb BTEX. The vials were placed in a heating block for 60 min at 50°C. Extraction of volatile compounds was done using a 100 µm Polydimethylsiloxane fibre in a SPME manual holder. Direct injection in HS mode was performed in 280ºC (20 sec) in a PTV injector. Helium was used as carrier gas in constant flow mode with 0.8 ml/min. FID temperature was held at 280°C. Quantification of BTEX was based on external standards. Three calibration points were selected with 10, 25 and 50 µg/L for BTEX. The method used for determination of VOCs in water samples by capillary GS was optimized for the duration and temperature of extraction, and GC parameters (Mendez *et al*, 2000; Nuro *et al*, 2014).

Results

Determination of organochlorine pesticides, their residues, polychlorinated biphenyls, PAH and BTEX was realized for 14 different steams that flowing from Gramozi Mountain. These steams are part of water basin for Devolli and Osumi rivers. Organochlorine compounds, their metabolites and PCB markers were extracted using liquid-liquid technique using n-hexane as extracting solvent. GC/ECD technique was used for determination of organochlorine pollutants. PAHs were extracted also using liquid-liquid technique using dichloromethane as extracting solvent followed by GC/FID technique. For BTEX analyse in water samples was used HS/SME technique with PDMS fibre followed by gas chromatography flame ionization detector. Found data were presented in graphical mode for the total of each class of pollutants, their individual distribution of each pollutant for each sample and pollutants profile.

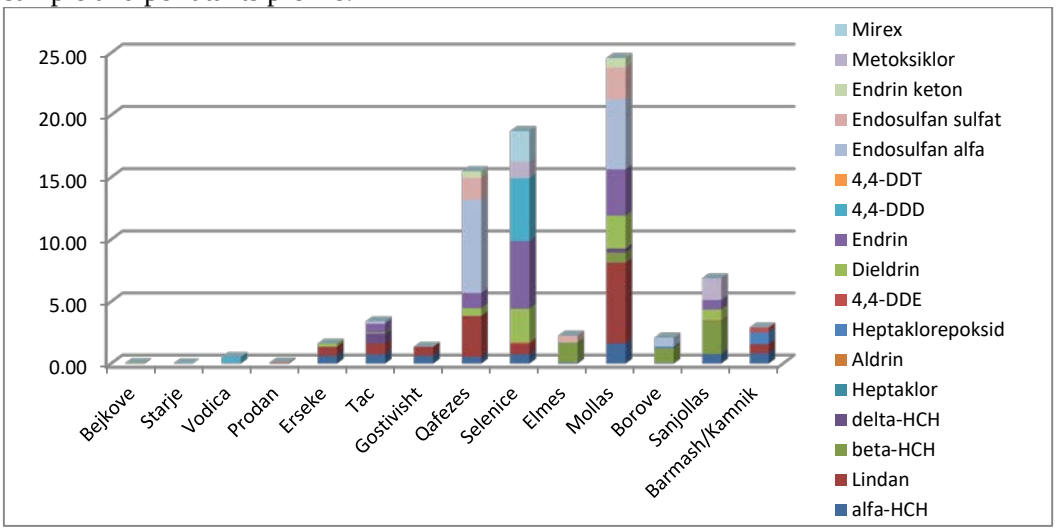

Figure 2. Total of organochlorine pesticides (ng/l) in water samples from Erseka Region

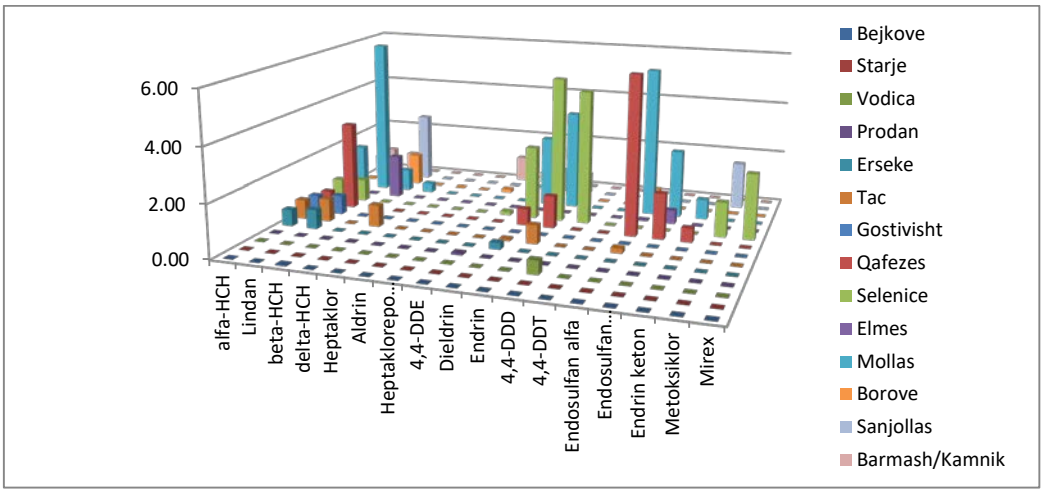

Figure 3. Distribution of organochlorine pesticides (ng/l) in water samples, Erseka Region

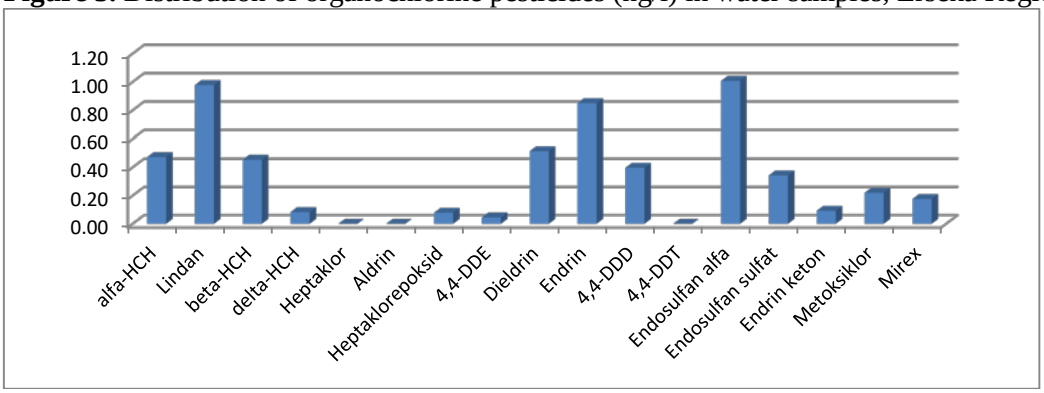

Figure 4. Profile of organochlorine pesticides (ng/l) in water samples from Erseka Region

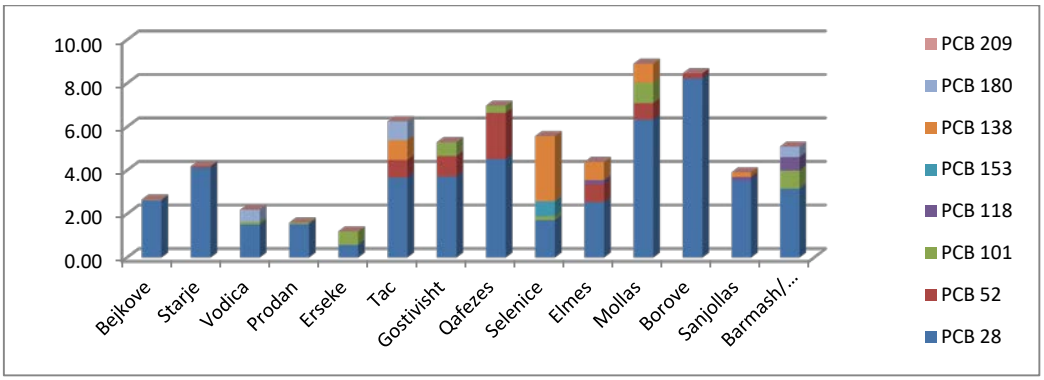

Figure 5. Total of PCB (ng/l) in water samples from Erseka Region

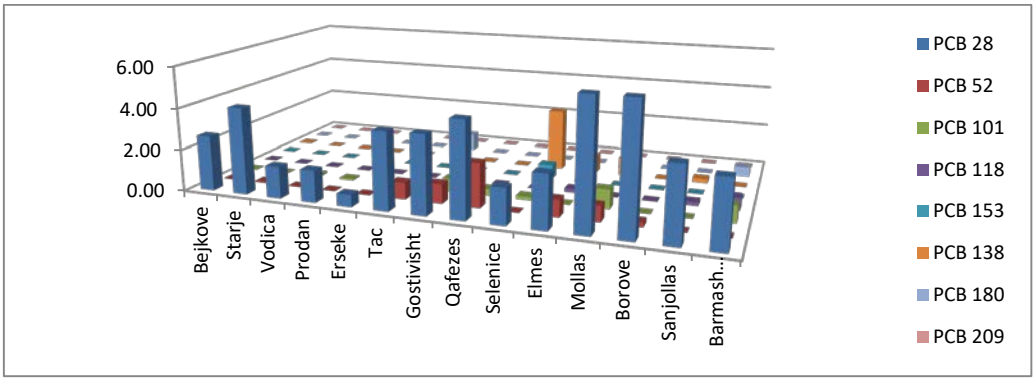

Figure 6. Distribution of PCB (ng/l) in water samples from Erseka Region

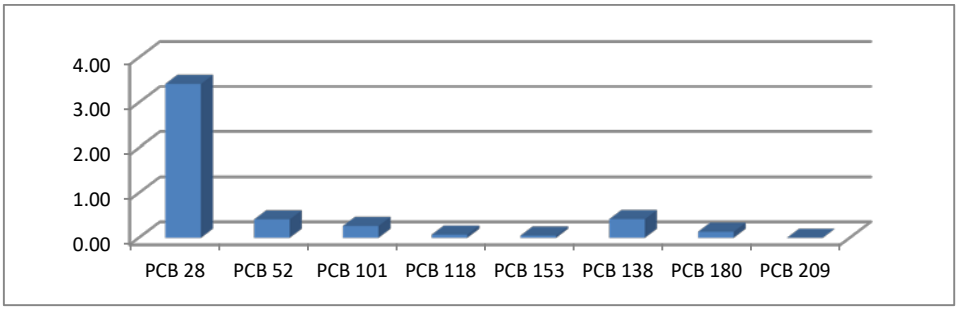

Figure 7. Profile of PCB (ng/l) in water samples from Erseka Region

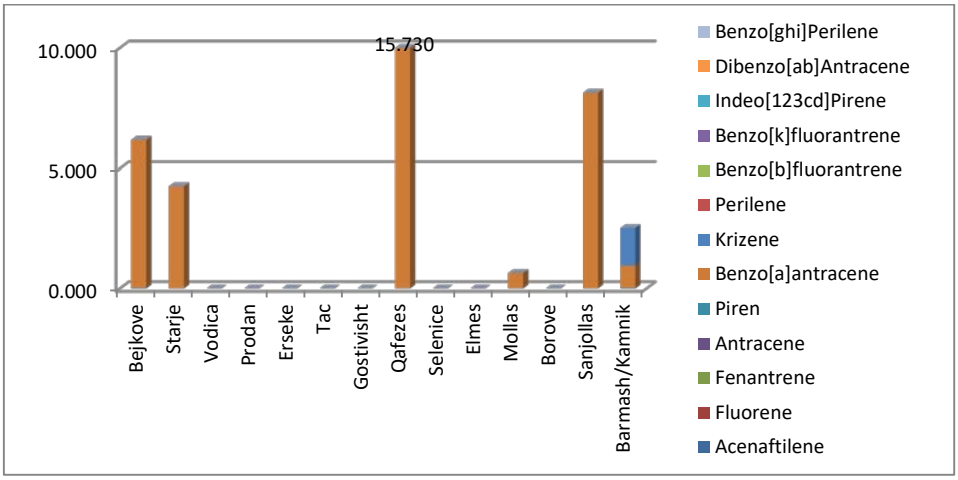

Figure 8. Total of PAH (ug/l) in water samples from Erseka Region

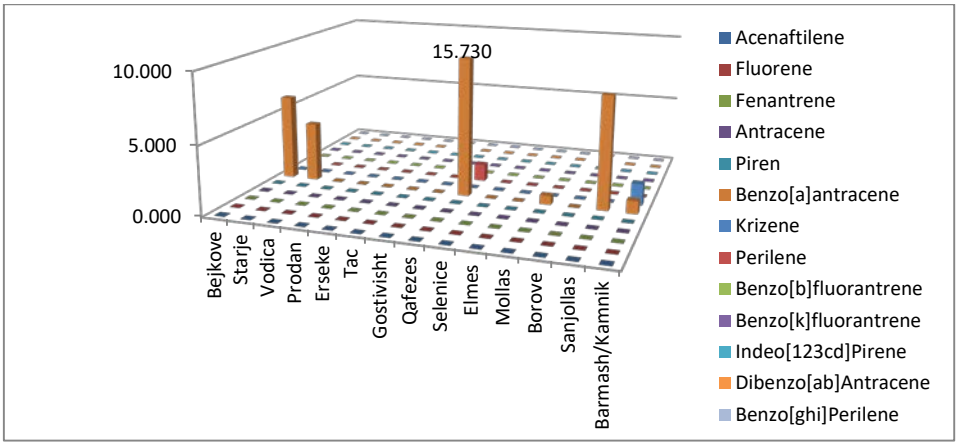

Figure 9. Distribution of PAH (ug/l) in water samples from Erseka Region

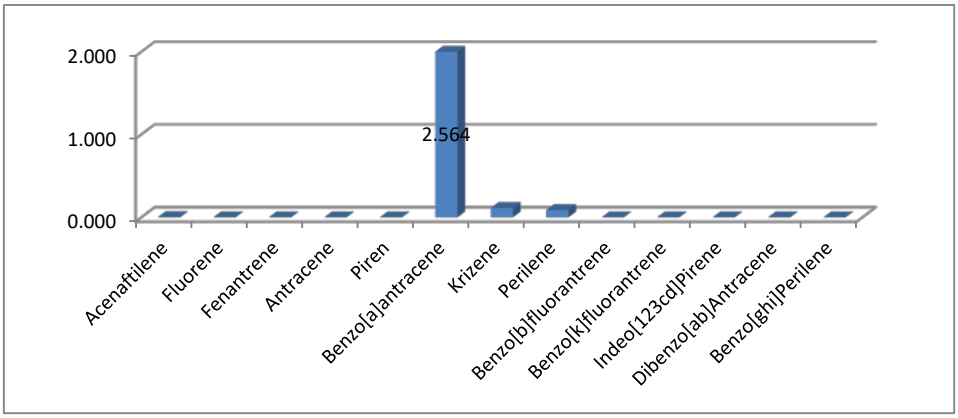

Figure 10. Profile of PAH (ug/l) in water samples from Erseka Region

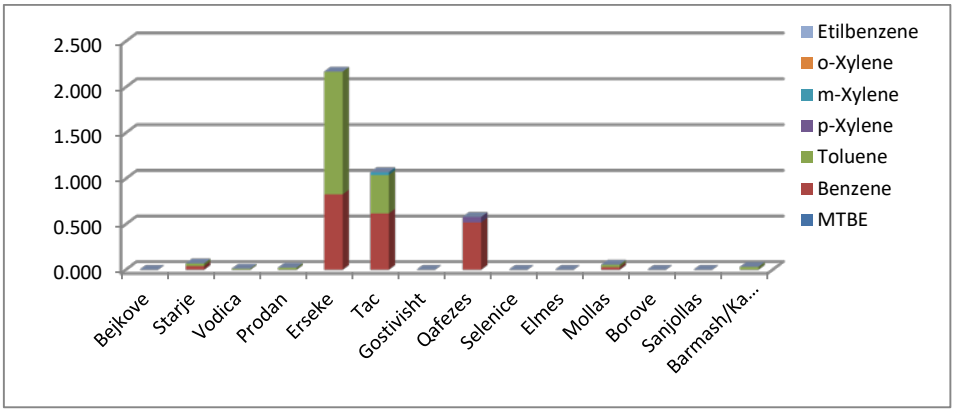

Figure 11. Total of BTEX (ug/l) in water samples from Erseka Region

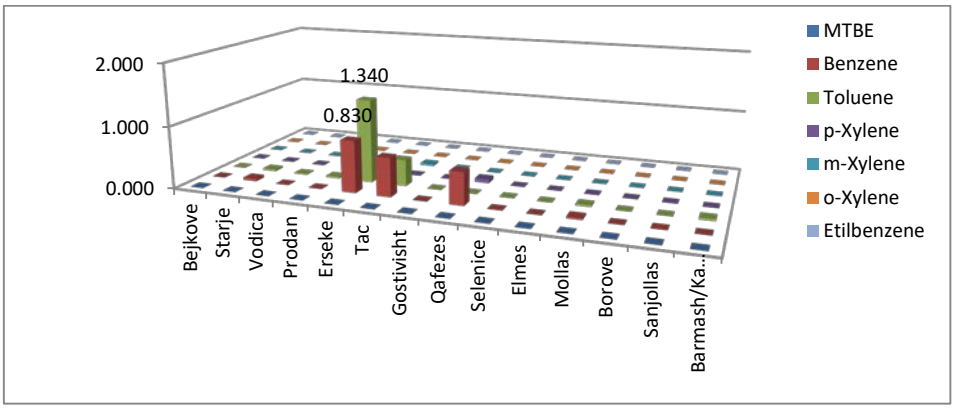

Figure 12. Distribution of BTEX (ug/l) in water samples from Erseka Region

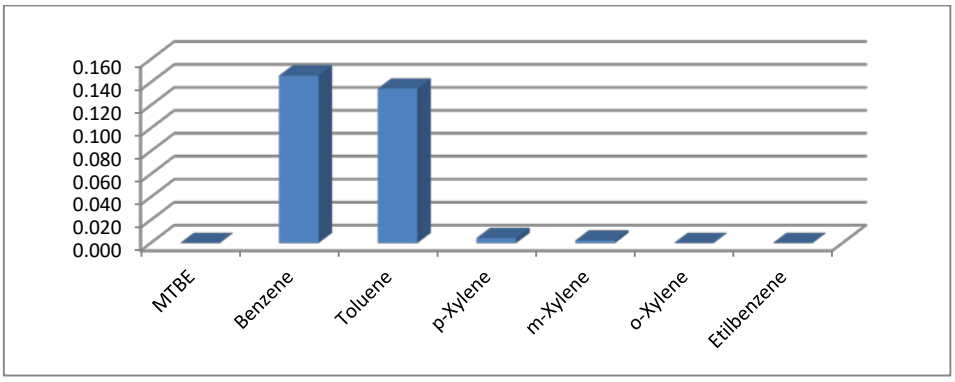

Figure 13. Profile of BTEX (ug/l) in water samples from Erseka Region

Discussion

Figure 2 show the total of organochlorine pesticides in water samples of Erseka Region, December 2017. The higher concentration was for Mollas station steam with 24.6 ng/l. Selenica, Qafezes and Sanjollas were other most polluted stations. Previous use of pesticides for agricultural purpose in these areas could be the main factor. Fourth areas are most known for fruits, corns and vegetable cultivation. For the 70% of the stations the levels of organochlorine pesticides were lower than 5 ng/l. The average level of organochlorine pesticides and their residues was 5.7 ng/l. This value is very low compare with other areas in Albania water ecosystems (Nuro *et al* 2010, Como *et al* 2012). This is expected because few areas of Gramozi Mountain are used in agriculture. It is used mostly as a pasture for the sheep, goat and cow. The use of pesticides in this area has been limited. Another reason is higher flow of steams from the Gramozi Mountain due to their slope. The flow and the volume of water in these steams is higher in December because of the higher amounts of rainfall in this season. The distribution of organochlorine pesticides (Figure 3) in water samples from Erseka Region was almost the same for fourth polluted stations because the origin of pollution

is the same. It was noted that some pesticides were in higher levels for some stations. This could be because of punctual sources or new arrivals from different effluents and drainage canals of agricultural areas. Profile of organochlorine pesticides (Figure 4) were: HCHs > Aldrines > Endosulfanes > DDTs. Degradation products of pesticides were in higher concentrations because of their previous use. The higher levels were also for Endosulfan alfa and Lindane that could be in use in this area. All concentrations of pesticides were lower than permitted levels for surface waters conform Directive 2008/105/EC. The found levels for organochlorinated pesticides in waters of Erseka Region were lower than reported levels for other water ecosystems in Albania.

Figure 5 show the total of PCB markers in water samples of Erseka Region. The higher level was also for Mollas station with 8.9 ng/l. Average of PCB markers was 4.8 ng/l. Distribution of PCBs (Figure 6) were almost the same for all samples because of the same pollution origin. PCB 28 was found in higher level for all stations. PCB 28 is a volatile congenier. This fact confirm that PCBs in this area could be because of atmospherical factors. Discharging of wastes from industries and mechanical businesses could affect levels and profile of PCB. Profiles of PCBs (Figure 7) were: PCB 28 > PCB 52 > PCB 138 > PCB 101. PCB 118, PCB 153, PCB 180 and PCB 209 were not detected in analyzed water samples. The levels of PCBs in waters of Erseka Region were lower than reported levels for other water ecosystems in Albania

PAHs in water samples for each station of Erseka Region were shown in Figure 8. PAHs weren't detected for 10 water samples. PAHs were observed in higher concentration in Qafezes station with 15.7 μg/l. It was noted the presence of Benzo[a]antracene for Qafezes, Sanjollas, Bejkove and Starje samples (Figure 9). Profile of PAH was almost because of Benzo[a]anthracene (Figure 10). This could be connected with a natyral beground or punctual sources for these stations. Some mechanical buisneses discharging their wastes directly in these steams. For all studied stations PAH levels were lower than reported levels in other ecosystem in Albania (Nuro *et al*, 2014). Total of PAHs were lower than permitted level (50 ng/L) for surface waters conform Directive 2008/105/EC.

Total of BTEX in water samples for each of studied stations of Erseka Region steams was given in Figure 11. Erseka (2.2 ug/l), Tac (1.0 ug/l) and Qafezes (0.5 ug/l) stations were observed to have the maximum level. BTEX weren't detected for other water samples. For all studied water samples the average level of BTEX were 2.8 μg/l. BTEX presence in the water river could be the main factors: natural inputs, automotive transport, natural begrounf, direct discharges of some mechanical industries in these steams. Distribution of BTEX in water samples was shown in Figure 12. BTEX were shown to have the same distribution because of the same pollution origin. Profile of BTEX (μg/l) in water samples taken in Erseka region (Figure 13) were: Benzene > Toluene > Xylenes. BTEX levels in water samples were lower than reported levels in other ecosystem in Albania (Nuro *et al,* 2014). Benzene concentration was lower than permitted level (10 ng/L) for surface waters conform Directive 2008/105/EC.

Conclusions

This is a first study on organic pollutants on surface waters of Erseka Region. Study f these surface waters is important because a good part of these waters (on their first part) that emanate from the Gramozi Mountain are in use for drinking water in population of this area. Note that, this area after the 1990s has a large number of tumor cases for the population. Water pollution could be one of the main reasons. Along with this work, it was realized analyzes of drinking water for Erseka city and for the villages around it. The levels of analyzed organic pollutants were foudn below the levels of LOD for GC/ECD and GC/FID techniques. These streams are part of the river basins of Devolli and Osumi, which are two important rivers for our country. The highest levels of organochlorine pollutants in surface waters of Erseka region was found for organochlorine pesticides because of their previous uses in agricultural areas near these streams. The higher concentration was for Mollas station. It is most known for fruit tree cultivation. Volatile PCBs were found in higher concentrations because of their atmospheric origin. PAH and BTEX were found only for 20% of water samples. Their concentration could be because of natural origin or some mechanical business that discharge their wastes directly in these steams. Found levels were lower than reported studies for other water basin areas in Albania. Gramozi Mountain isn't in use for agricultural purposes and isn't affected mostly from industrial businesses. Another reasons were higher flow of waters in December

(diliuition factor) and the higher slope of steams in these areas. All analyzed pesticides, PCB, PAH and BTEX were lower than permitted level for surface waters conform Directive 2008/105/EC. Study of organic pollutants in this area should continue for a longer time combined with other data (microbiological, radiological, epidemiological, etc) to be more complete.

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