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A SURVEY OF SOME PRIORITY SUBSTANCES IN DRINKING WATER OF BALLSHI AREA

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This study presented data about concentrations of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and BTEX (benzene, toluene, ethylbenzene and o-, m-, p-xylenes) in drinking water samples of Ballshi area. This area is known for the intense activity in extracting/processing/production of oil since 1940. Also, this area is part of Myzeqeja Field (Southeast Albania), which is the main field in Albania for crops, vegetables and fruits. Seven drinking water samples were taken in the network and three samples from the underground water (wells which is used for drinking water) of Ballshi city and surrounding habitants.



Refinery of oil
processing/production near
Ballshi City



Agricultural activity near
Ballshi area



Organochlorine pesticides, polychlorinated biphenyls, some PAHs and benzene are classified as Persistent Organic Pollutants (POP) as well as priority substances because they are persistent for many years after their application and pose high toxicity.

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ec.europa.eu/environment/water/water-dangersub/pri_substances.htm

Priority substances under the Water Framework Directive

- [Introduction](#)
- [Directive 2013/39/EU amending the WFD and EQSD](#)
- [Directive 2008/105/EC on Environmental Quality Standards](#)
- [Decision 2455/2001/EC on a First list of priority substances](#)
- [Priority Substances supporting information and documentation](#)

Introduction

The first list of priority substances (Annex X to the WFD) was established by way of Decision 2455/2001/EC using the approaches outlined in Article 16 of the WFD.

This first list was replaced by Annex II of the [Directive on Environmental Quality Standards \(Directive 2008/105/EC\)](#) (EQSD), also known as the Priority Substances Directive, which also set environmental quality standards (EQS) for the substances in surface waters. The list was replaced again in 2013 by Annex I to **Directive 2013/39/EU**, which also included EQS and some other provisions on chemical pollutants.

Directive 2013/39/EU amending the WFD and EQSD

Commission [proposal \(COM\(2011\)876\)](#) led to the adoption of **Directive 2013/39/EU** amending the list of priority substances (Annex X to the WFD), and the EQSD. It introduced provisions to improve the functioning of the legislation. It resulted in:

- 12 additional priority substances (45 in total), 6 of them designated as priority hazardous substances;
- stricter EQS for four existing priority substances and slightly revised EQS for three others;
- the designation of two existing priority substances as priority hazardous substances;
- the introduction of biota standards for several substances;
- provisions to improve the efficiency of monitoring and the clarity of reporting with regard to

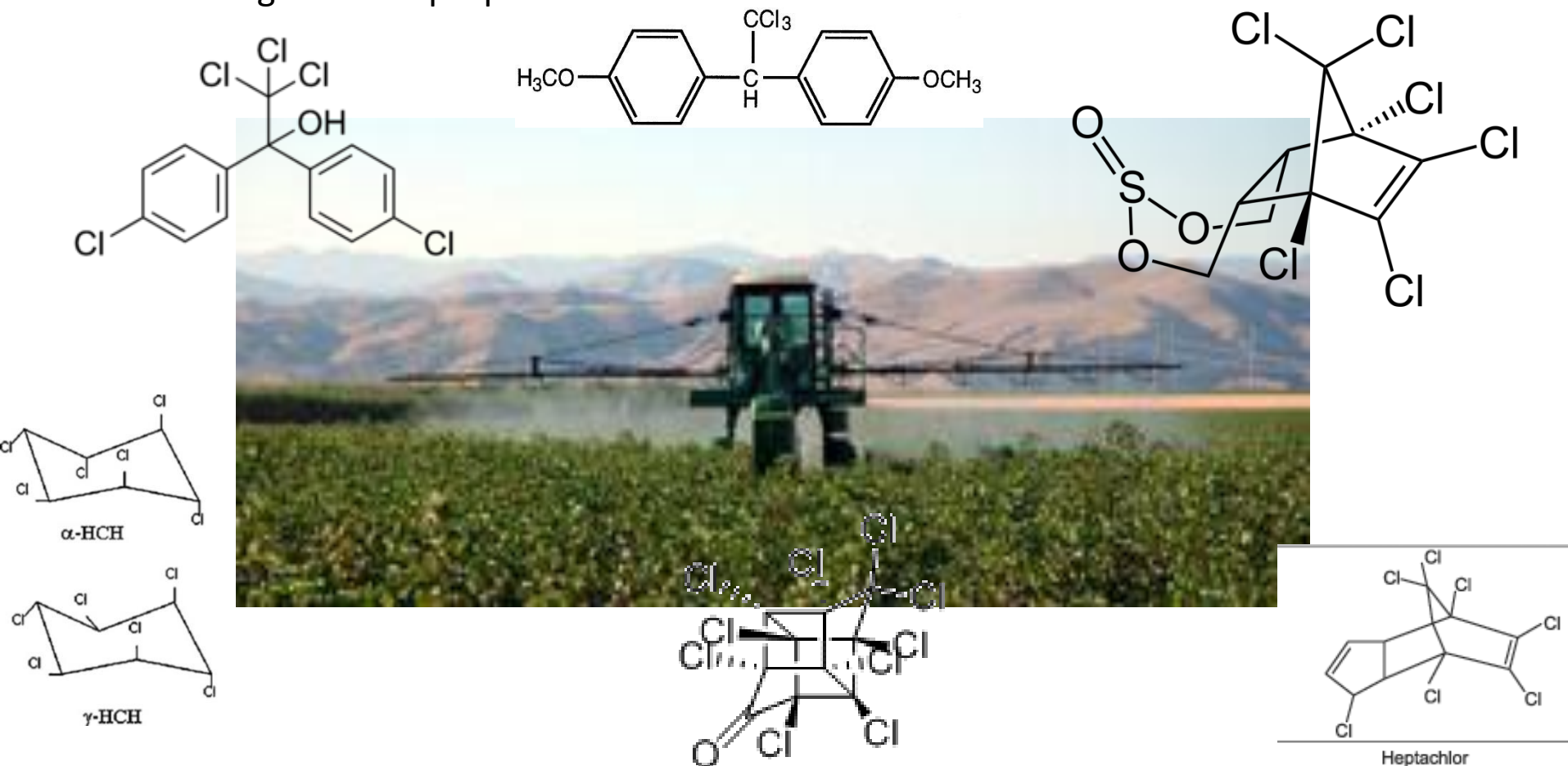
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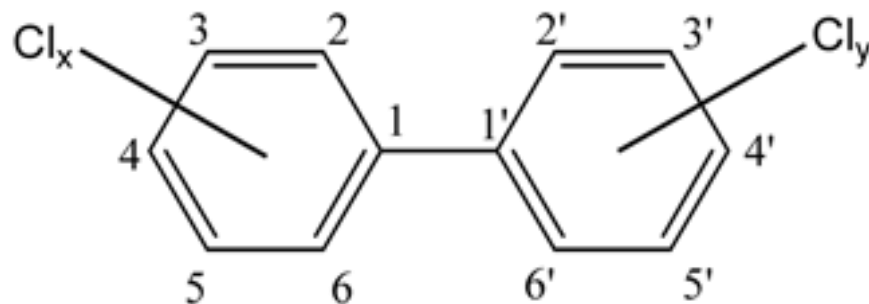
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Organochlorinated pesticides (OCPs) are a group of compounds of great chemical stability and persistence whose presence in the environment is a clear indication of anthropogenic pollution. The massive use of pesticides for agricultural purposes caused their widespread diffusion to all environmental compartments including a wide range of organisms up to the humans. Before 90' organochlorine pesticides were used widely in Albania for agricultural purposes.

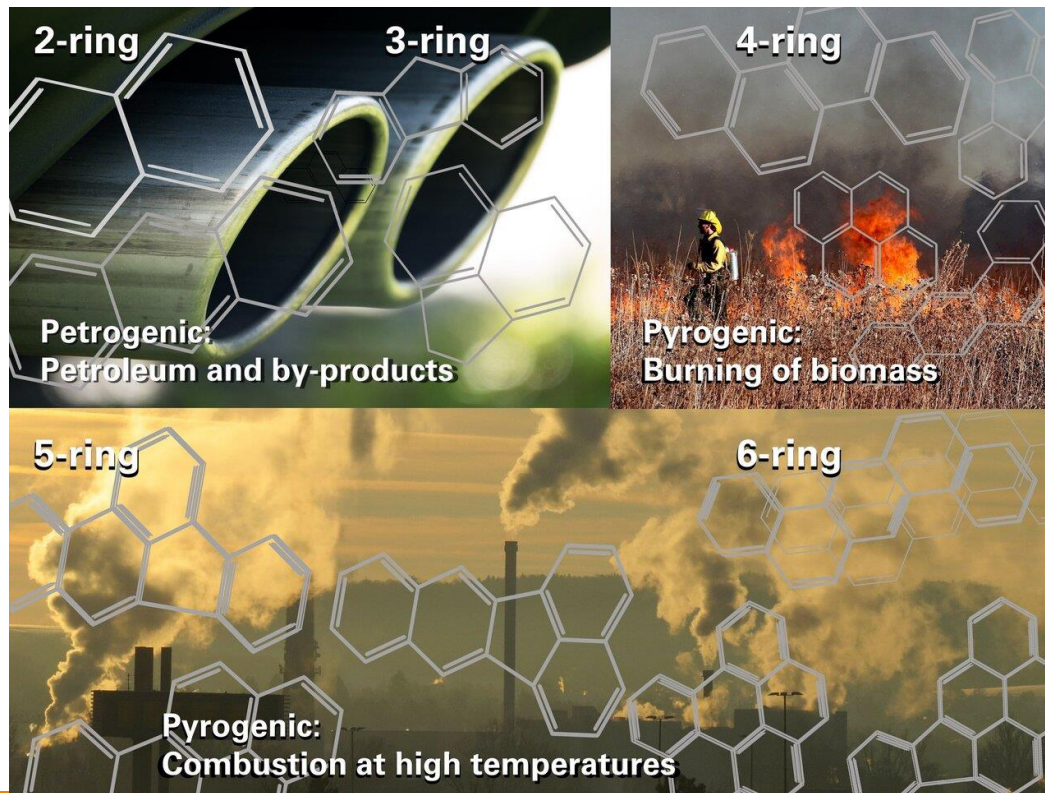


Commercial PCB mixtures were used in a wide variety of applications. They are chemically highly stable, lipophilic compounds and resist microbial, photochemical, chemical and thermal degradation (Lang, 1992). In Albania PCBs are used mainly in transformer oils after 90', but the source of pollution is mostly airborne origin with predominance of most volatile PCB congeners



Polycyclic aromatic hydrocarbons (PAHs)

PAH are priority organic pollutants, which are ubiquitously found in the atmospheric, aquatic, and terrestrial systems and therefore are closely monitored in the environment. Some of them such as Benzo[a]anthracene are genotoxic, mutagenic, carcinogenic, and/or teratogenic. Low molecular weight PAHs and BTEX move easily in nature with long range distances because of their volatility. Higher molecular members of this class of pollutants are relatively immobile due to their large molecular volumes and are less volatile, relatively insoluble in water, and more lipophilic than the lower molecular members. They also are known to stay longer in the environment.



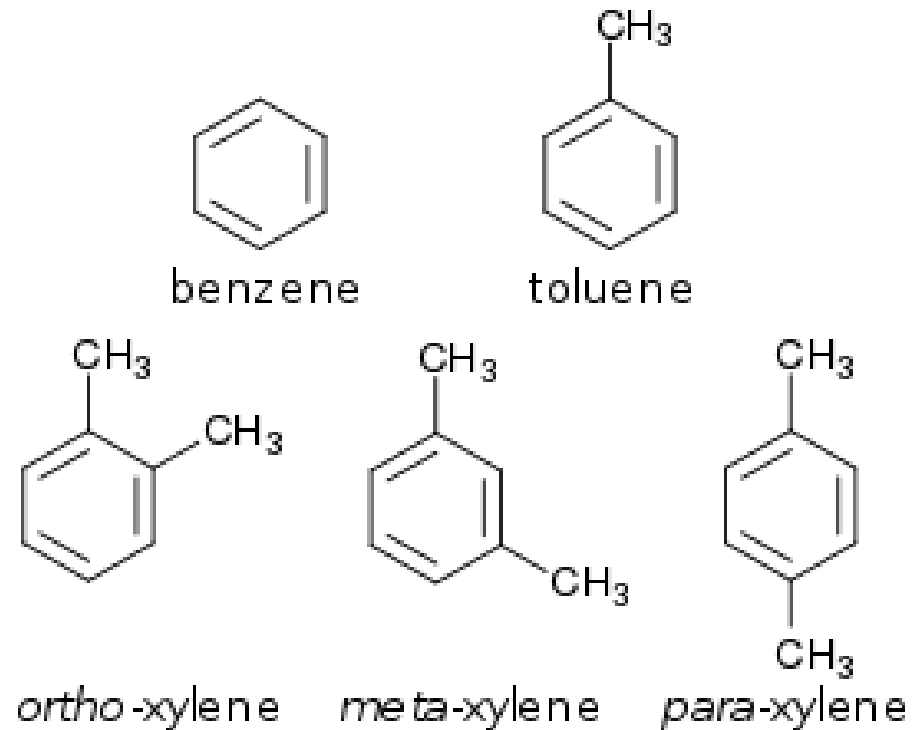
BTEX

BTEX refers to the chemicals benzene, toluene, ethylbenzene and xylene.

These compounds occur naturally in crude oil and can be found in sea water in the vicinity of natural gas and petroleum deposits. Other natural sources of BTEX compounds include gas emissions from volcanoes and forest fires.

The primary man-made releases of BTEX compounds are through emissions from motor vehicles and aircrafts, and cigarette smoke. BTEX compounds are created and used during the processing of petroleum products and during the production of consumer goods such as paints and lacquers, thinners, rubber products, adhesives, inks, cosmetics and pharmaceutical products.

BTEX compounds are among the most abundantly produced chemicals in the world.



Material and Methods

Water and sediment sampling in Saranda port

Seven drinking water samples were taken in the network and three samples from the underground water (wells which is used for drinking water) of Ballshi city and surrounding habitants. The water sampling were realized in September 2023. A quantity of 2 litre of drinking water were taken from each station in Teflon bottles. The sampling method was based on ISO 5667-3: 2018. Water samples were transported and conserved at +4°C prior to their analvze.

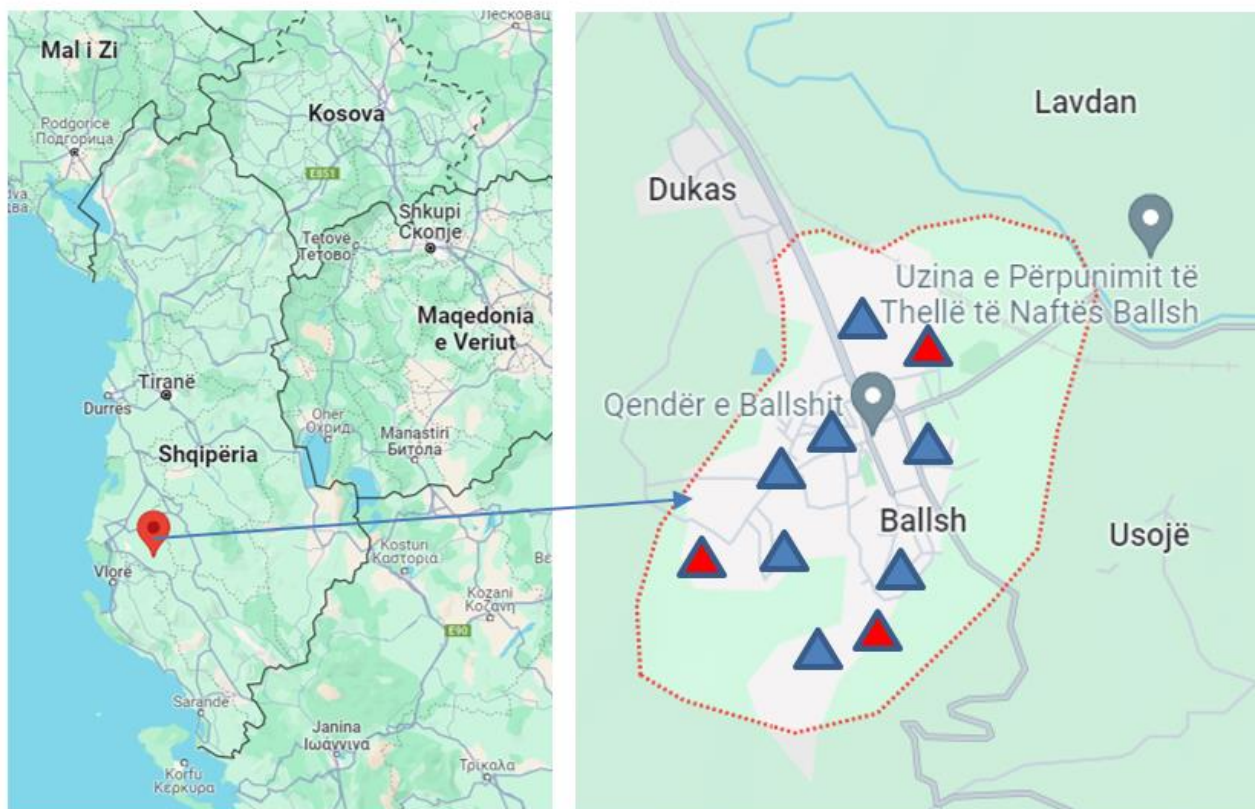
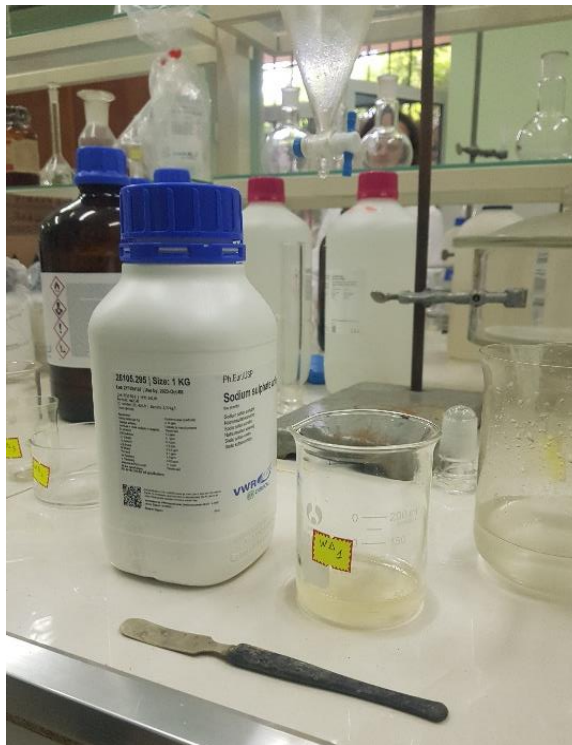
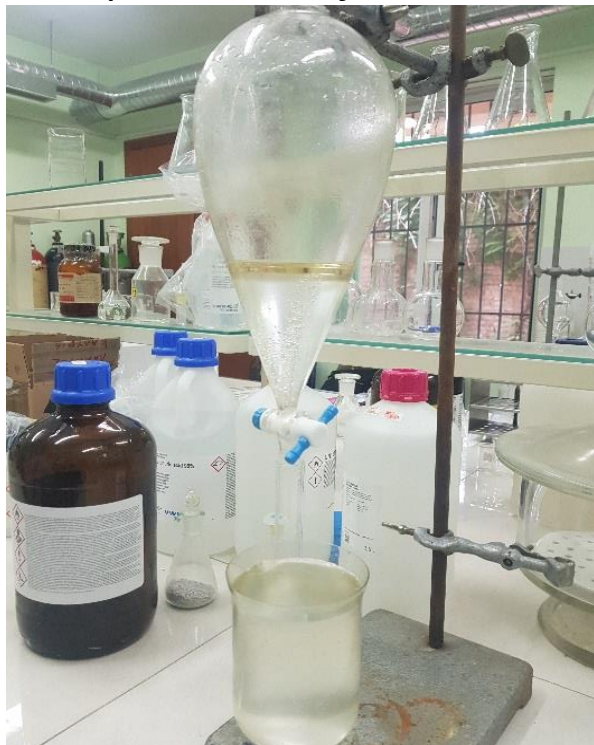


Figure 1. Drinking water sampling by network tap (▲) and wells (▲) of Ballshi area

Treatment of water samples for pesticide, PCB and PAH analyzes

Two times Liquid-liquid extraction was used for extraction of organochlorine pesticides, their degradation products, polychlorinated biphenyls and polycyclic aromatic hydrocarbons from water samples. One liter of water and firstly 40 ml Dichloromethane and after that 40 ml n-Hexane as extracting solvent were added in a separatory funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removal. A florisil column was used for the sample clean-up. 20 ml n-hexane/dichloromethane (4/1) was used for elution. After concentration to 1 ml, the samples were injected in GC/ECD.



Gas chromatography analysis of pesticides, PCB markers and PAHs

Organochlorine pesticides and PCBs were analyzed simultaneously using capillary column model Rtx-5 (30 m long x 0.25 mm i.d. x 0.25 μ m film thicknesses) on a gas chromatograph Varian 450 GC with ECD detector. The organochlorine pesticides detected were DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), HCHs (α -, β -, γ - and δ -isomers), Heptachlor's (Heptachlor and Heptachlorepoxide); Aldrin's (Aldrine, Dieldrine and Endrin) and Endosulfanes (Endosulfan α , Endosulfan β and Endosulfan sulfat). Analysis of PCBs was based on the determination of the seven PCB markers (IUPAC Nr. 28, 52, 101, 118, 138, 153 and 180). PAH according EPA 525 were analyzed using a capillary column model VF-1ms (30 m long x 0.25 mm i.d. x 0.25 μ m film thicknesses) on a gas chromatograph Varian 450 GC with FID detector.

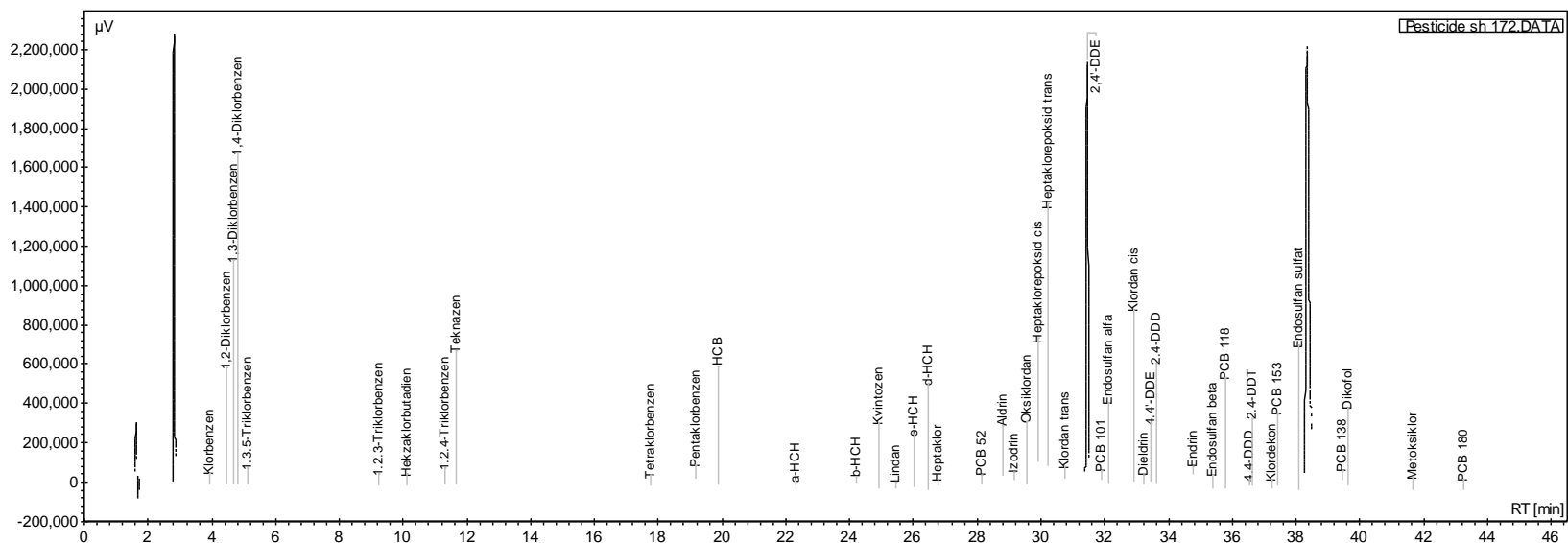


Analyzes of BTEX in water samples

For the determination of BTEX, 5 ml of water samples were taken in analyze in SPME bottles with a volume of 10 ml. The bottles were equipped with Teflon stoppers suitable for their analysis by Head-space technique. The manual SPME syringe equipped with a 100 μm PDMS (Polydimethyl siloxane) fiber was inserted through the Teflon stopper into the top of the sample. The bottle was placed at a temperature of 50°C for 30 minutes. PDMS fiber was transferred to the gas chromatograph injector where desorption process was carried out at 250°C for 10 seconds. For the qualitative and quantitative determination of BTEX, the Varian GC 450 apparatus equipped with a flame ionization detector (FID) and a PTV injector was used. The separation of BTEX was performed in VF-1ms (30m length x 0.33mm internal diameter x 0.25 μm film), suitable for their separation



RESULTS AND DISCUSSIONS



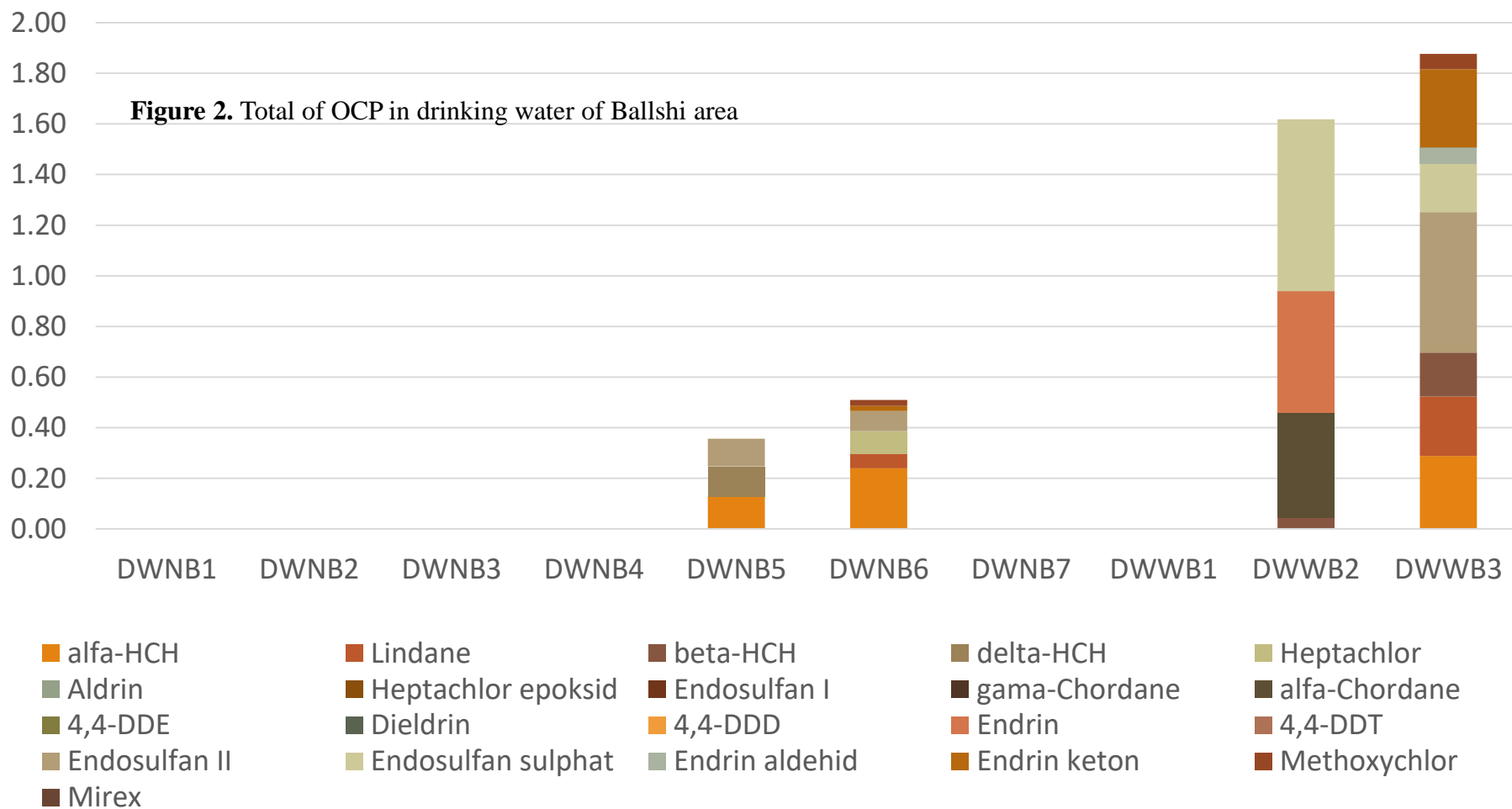


Figure 3. Profile of OCP in drinking water of Ballshi area

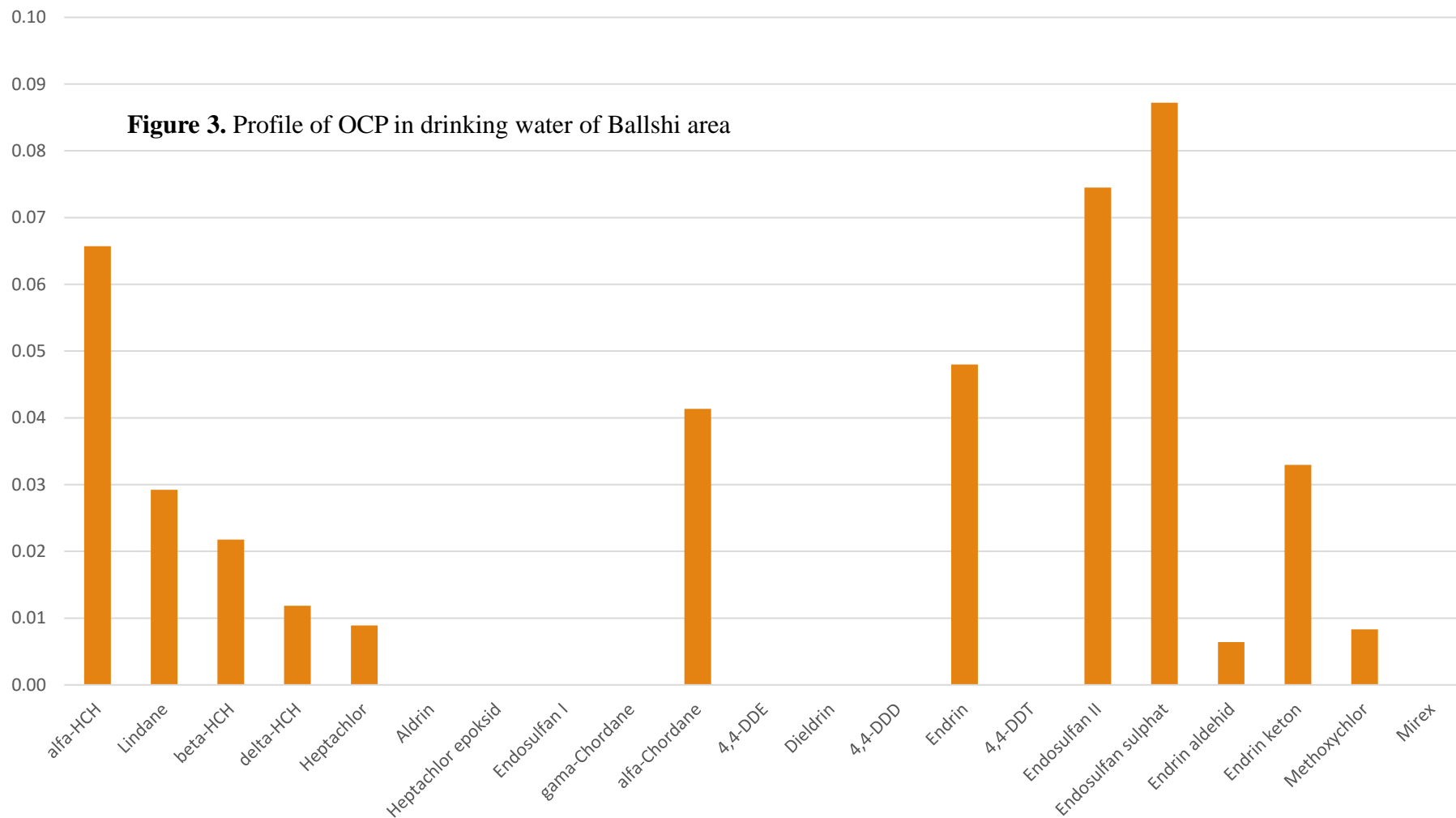
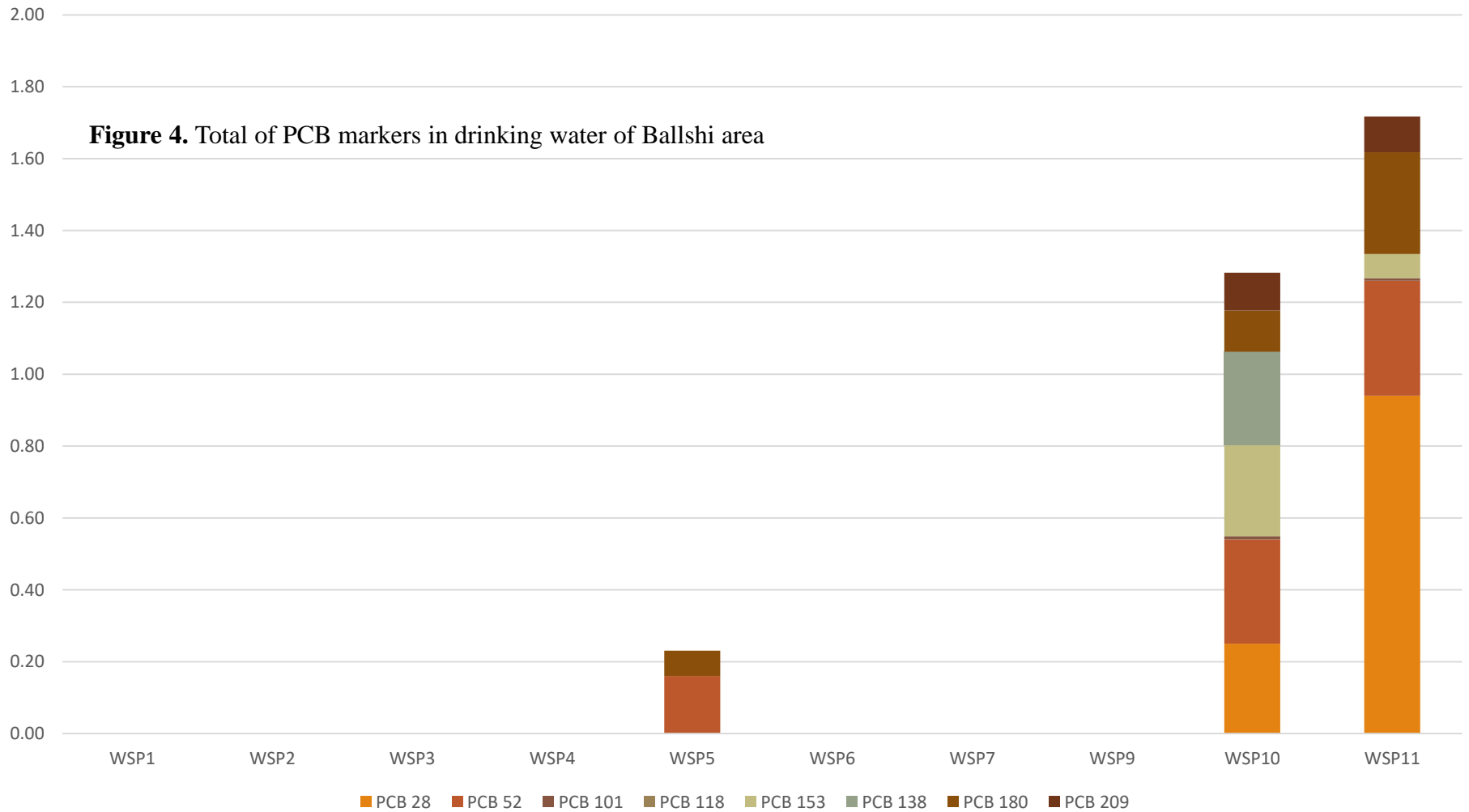


Figure 4. Total of PCB markers in drinking water of Ballshi area



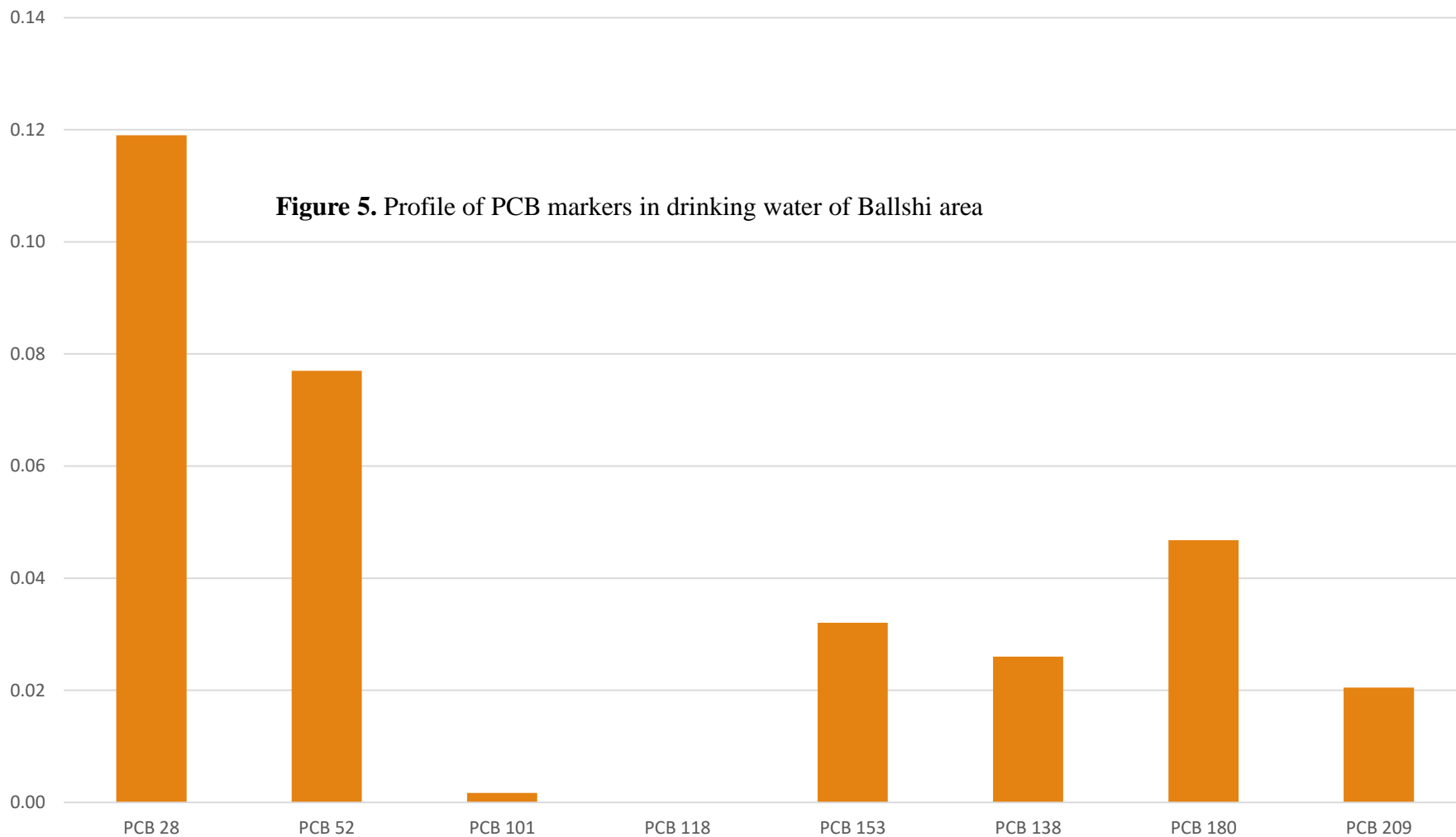


Figure 6. Total of PAH in drinking water of Ballshi area

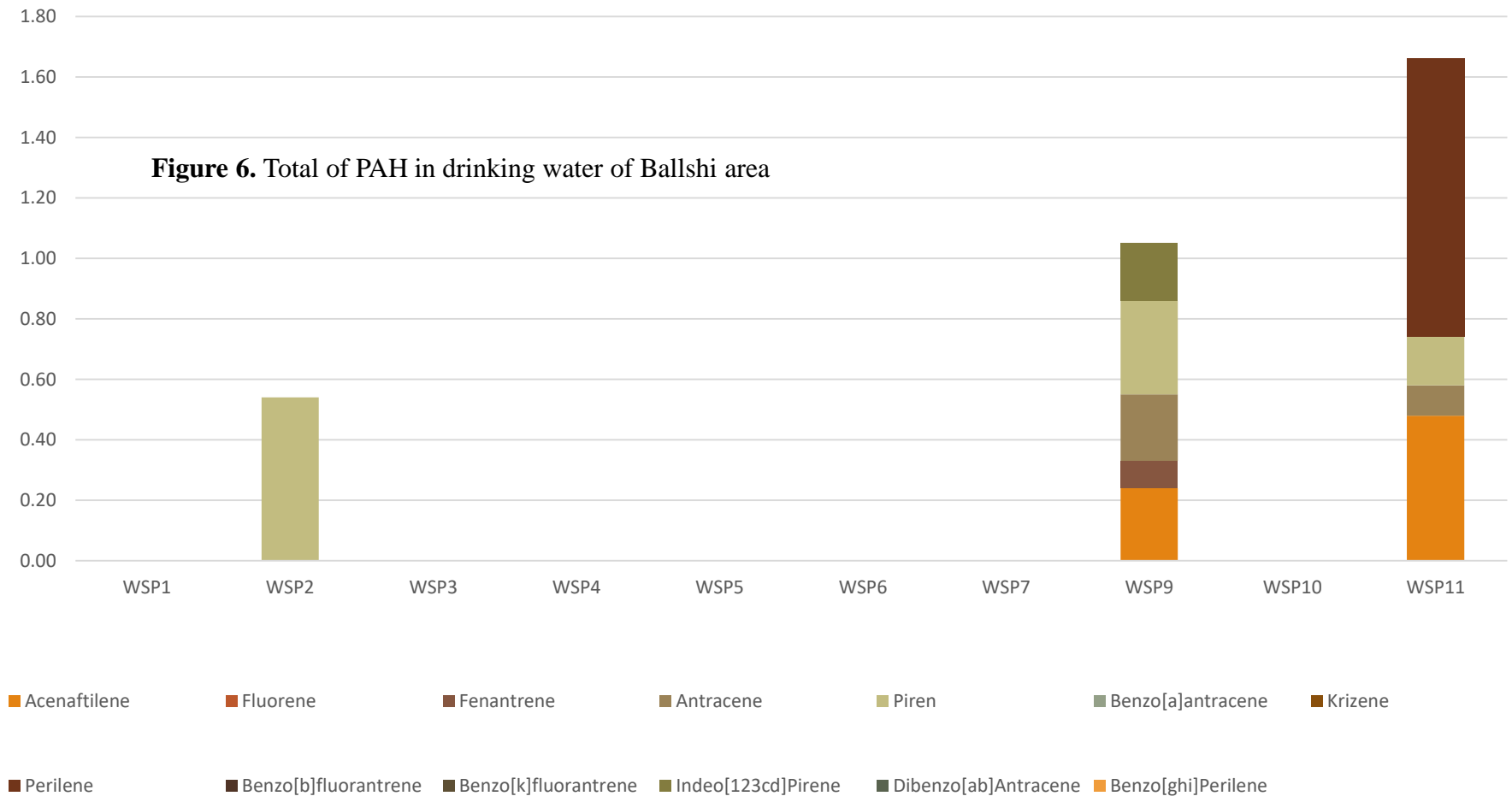


Figure 7. Profile of PAH in drinking water of Ballshi area

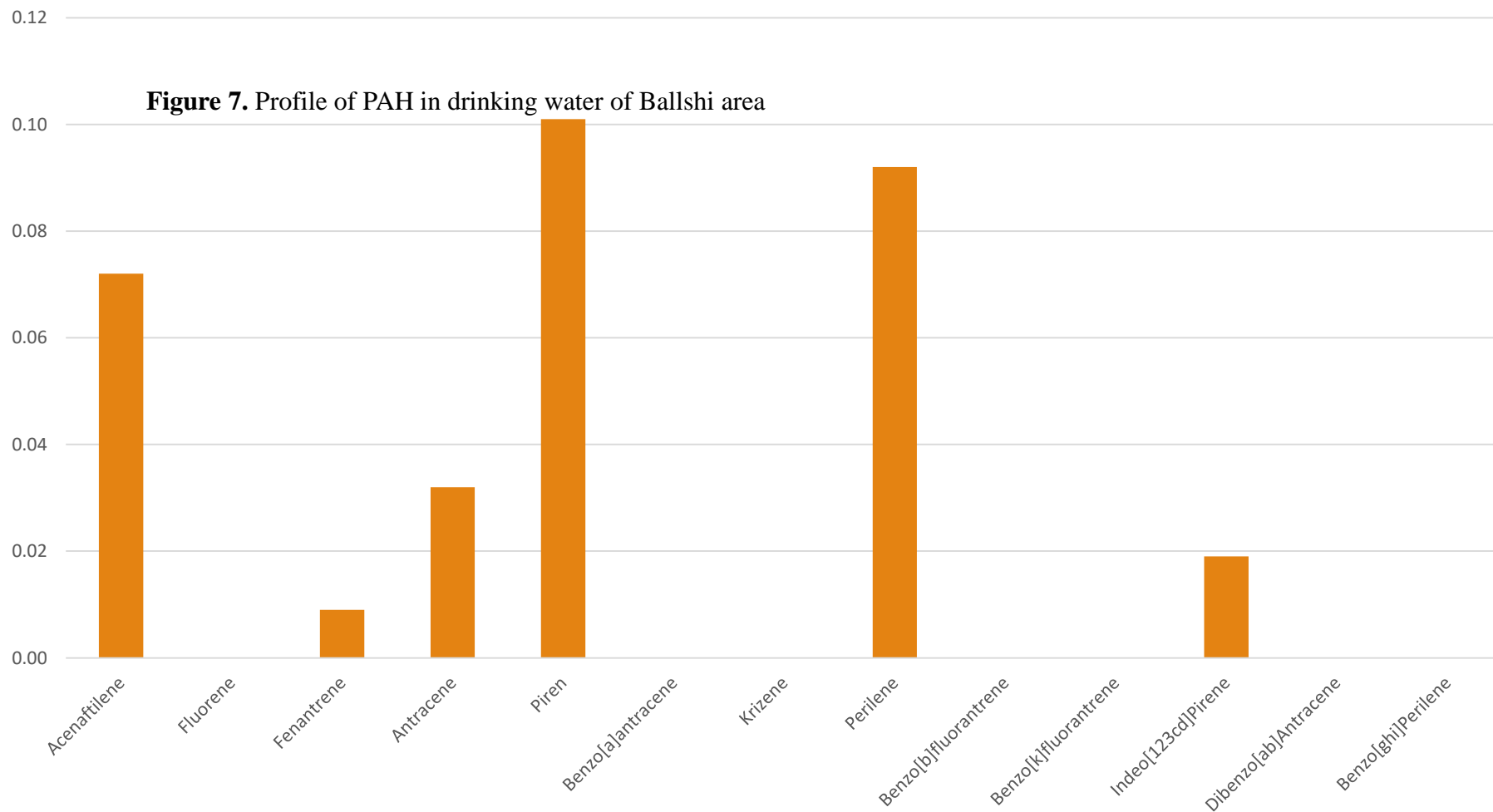
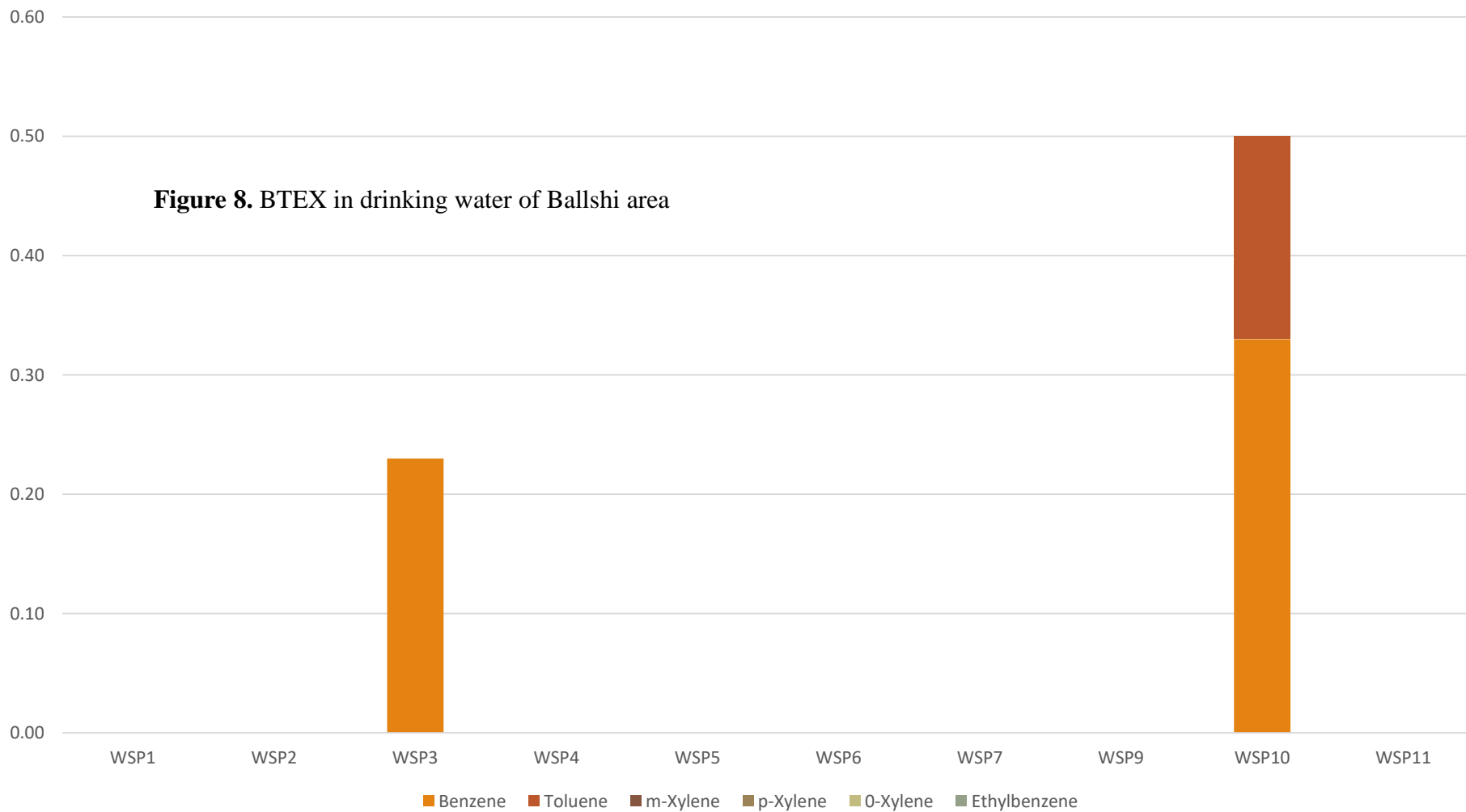
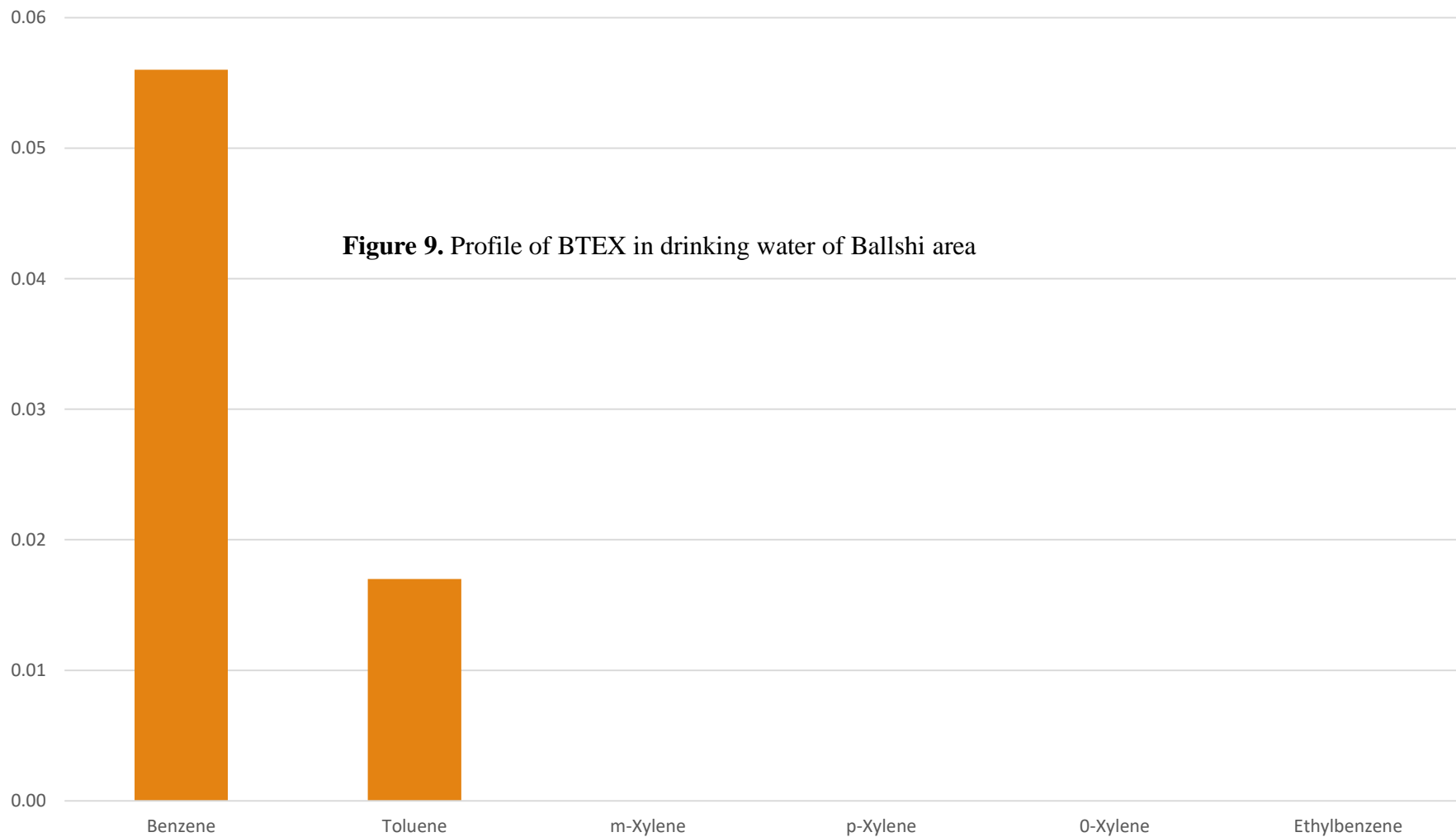


Figure 8. BTEX in drinking water of Ballshi area





CONCLUSION

- ❑ Priority substances were not detected (or were lower than LOD) for more than 70% of drinking water samples. Presence of organochlorine pesticides (4 samples), PCBs (3 samples), PAHs (3 samples) and Benzene (2 samples) could be because of elevated agricultural and industrial activity in this area.
- ❑ Pesticides were found due to their previous uses in agricultural areas near the Ballshi city and surrounding habitans. Degradation products of pesticides were found in higher levels compared to their active products. This fact is connected with the previous use of pesticides in Albania and their degradation process.
- ❑ Presence of PCBs and PAHs in water samples can be related to the extracting/processing/production of oil since 1940. Also, this area is part of Myzeqeja Field (Southeast Albania), which is the main field in Albania for crops, vegetables and fruits. Mechanical activities could be a terrestrial source of PCBs and hydrocarbons in stations of Ballshi area.
- ❑ Levels of individual organochlorine pesticides, PCBs and PAHs in water and sediment samples of Ballshi area were lower than permitted levels for drinking waters according to EU Directive and Albanian norms.
- ❑ Monitoring of organic pollutants in drinking water of Ballshi area should be continuous because of these area could be affected by many sources of pollution.

Thank You!