

## Assessment organochlorine pesticides in Velipoja ground waters

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### Abstract

Due to their lipophilic nature, hydrophobicity, and low chemical and biological degradation rates, organochlorine pesticides (OCPs) have led to their accumulation in the biological tissues and subsequent magnification of concentrations in the organisms due to the progression up the food chain. A survey for the possible contamination of underground water by organochlorine pesticides (OCPs) was carry out in the year 2015. The water samples were collected 11 domestic wells in the area. The water samples were collected in cleaned glass bottles and refrigerated at 4 °C until chemical analyses. The samples were extracted by using L/L extraction. The chemical analyses were performed in gas chromatograph equipped with micro electron capture detector (GC- $\mu$ ECD). A number of pesticides as heptachlor, HCB, DDTs were detected. In general, the levels of some individually OCPs in the study area for groundwater are still within EU Directive for ground water. The hexachlorobenzene and lindane were the most problematic pollutants with higher concentrations. The total concentration of the OCPs ranged from 0.5-3.1  $\mu$ g/L.

**Keywords:** HOPs, OCPs , HCB, DDTs, L/L extraction

### Introduction

Velipoja lies in the north of Albania and south of Shkodra, with an area of 72,40 km<sup>2</sup> and at a distance of 25 km from the city of Shkodra. In the north is bordered by the commune of Dajç, in the south with the Adriatic Sea, in the east with the prefecture of Lezha and in the west by the river Buna, the river that separates it from the Republic of Montenegro. The surveyed area extends close to the coast which has negative effects on the quality of groundwater of the whole area of Velipoja since the aquifers are regularly polluted by the salt water of the Adriatic Sea. The accumulation of residues of urban, agricultural origin also has an impact on groundwater which is of great importance because a part of the population is not connected to the water supply system and uses drilling water as drinking water.

Chemicals including many pesticides polychlorinated biphenyls (PCBs), phthalates, lead, mercury and cadmium do not necessarily remain were they are released into the environment, but may be transported in water or in air currents throughout the globe. (Moga et al.2011) The potential risks they pose to the environment and to human health are so serious that international treaties, e.g. the United Nations Aarhus Protocol and the Stockholm Convention aimed at elimination or restriction of their production and use have been established. Although the uses of

OCPs were banned about three decades ago, the elevated concentrations of OCPs residues were still observed in the environments due to their persistency (Meijer et al. 2003). The WHO and EU recommendations set a limit on total pesticide content in drinking water of up to 0.5 µg in agriculture can cause the exceedance of environmental quality standards and adverse effects on species and ecosystems in the neighborhood farms. (Teodorescu&Cristin 2002). Groundwater is considered to have a good chemical status when: measured or predicted of active pesticide ingredients, their metabolites and reaction products do not exceed 0.1 µg/l (a total of 0.5 µg/l for all pesticides measured), (EU Directive, 2006). The aim of this study was to characterize the nature and content of the persistent organic pollutants, during 2015 by analyzing the ground water from the Velipoja area.



**Figure 1.** The map of studied area

## Materials and Methods

In the 9 (pumping wells) were collected a total of 18 water samples during the year 2015 (Table 1). The "in situ" parameters as conductivity, temperature and pH were measured by using AQUALYTIC multiparameter device. The water samples were collected in 1 liter glass bottles and stored in 4°C.

prior chemical analyses. The water samples were processed the Liquid- Liquid extraction by using 1 L separatory funnel. The water samples were spiked with 10 µl PCB 29 as internal standard with concentration 2.5 ng/ul and extracted with 40 ml n-hexane. The organic phase (n-hexane) were dried by using 10g Na<sub>2</sub>SO<sub>4</sub>. The cleaning of the extracts were done in a glass column filled with deactivated with

5% water fluorosil (100-200mesh ose 0.075-0.150 mm). The column was rinse out with 8 ml of a mixture of (4:1 v/v) n-hexane and DCM. The extract was evaporated by using Rotary Evaporator (LABOROTA 4000, HEIDOLPH) and N<sub>2</sub> evaporator (Thermo Scientific), till 1 ml extract. The 1ml extracts were transferred in the chromatographic vials. Gas chromatographic analyses were performed with an Agilent 7890 gas chromatograph equipped with a micro <sup>63</sup>Ni electron-capture detector and a split/splitless injector and autoinjector. The column used was a HP-5 [low/mid polarity, 5% (phenyl methyl siloxane)] (30 m x 0.32 mm I.D., 0.25µm film). The split/splitless injector and detector temperatures were set at 280°C and 300°C, respectively. Carrier gas was N<sub>2</sub> at 3.5 ml/min and make-up gas was nitrogen 29 ml/min. The initial oven temperature was kept at 60°C for 15min, which was increased, to 200°C at 20°C/min, held for 10min, and then increased to 250°C at 4°C/min for 20min. The temperature was finally increased to 300°C, at 10°C/min, held for 7 min. Injection volume was 1µl, when splitless injections were made. OCP quantification was performed by internal standard method. Nitrogen was used both as the carrier gas (3.5 ml min<sup>-1</sup>) and makeup gas (29 ml min<sup>-1</sup>). The system was calibrated with a standard OCP mixture containing 7 OCPs.

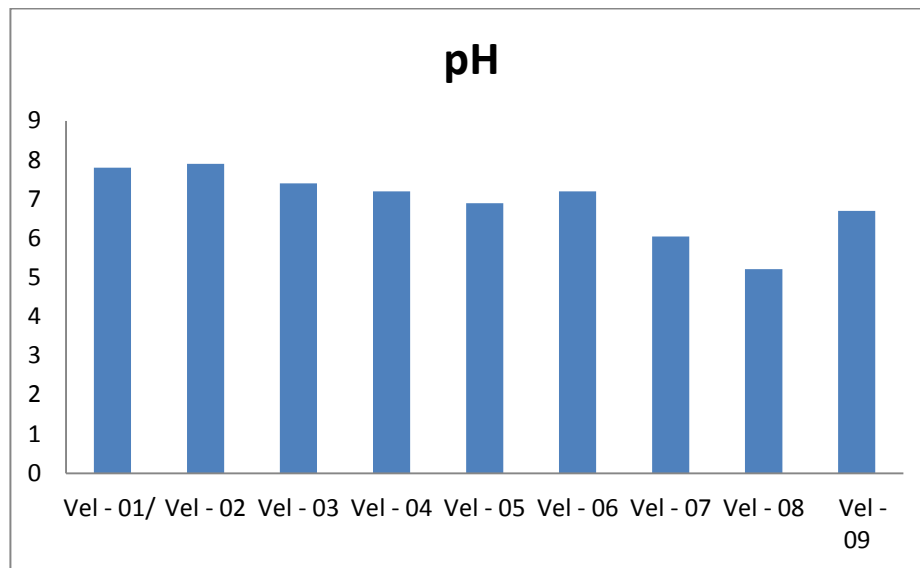
Table 1. The data of sampling sites.

No Wells	Coordinates		Depth (m)
	X	Y	
Vel-01	4636414	03 68323	5m
Vel-02	4635933	03 69151	4m
Vel-03	4637852	03 68002	8 m
Vel-04	4637865	03 67977	7 m
Vel-05	4640925	03 68188	10 m
Vel-06	4635596	03 73544	6m
Vel-07	4635788	03 73694	7m
Vel-08	4635922	03 70248	8 m
Vel-09	4949238	03 68595	10 m

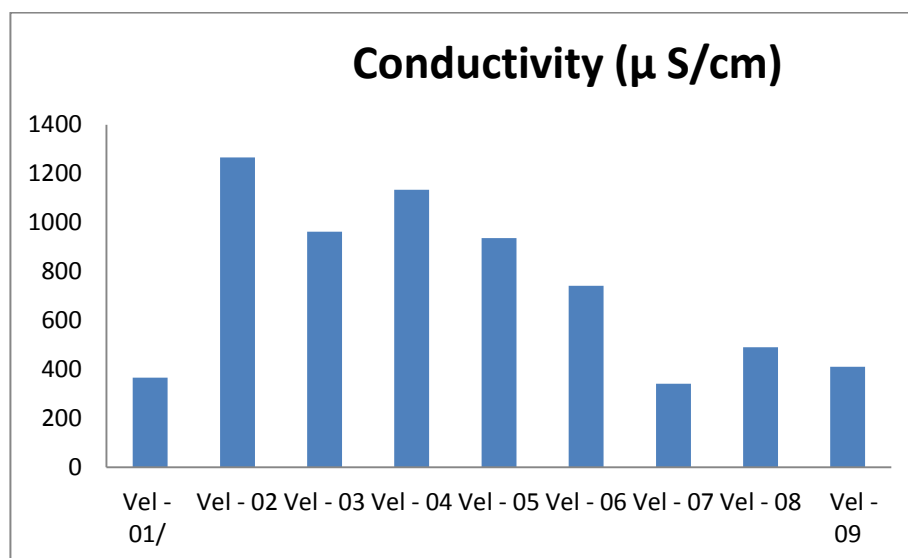
## Results and discussion

Physical chemical "in situ" parameters were determined by using of potable pH meter and conductimeter ACQUALYTIC. From the pH values shown in Figure 2 it is noticed that most wells have pH values close to 7 indicating that the water is in optimal parameters. Regarding conductivity, most of the samples have high values especially wells near the sea shore due to the impact of saltwater in the aquifer of this area. Even the values of solids dissolved are presented with the same trend as conductivity and indicate the presence of salts in these wells (Fig 3-4).

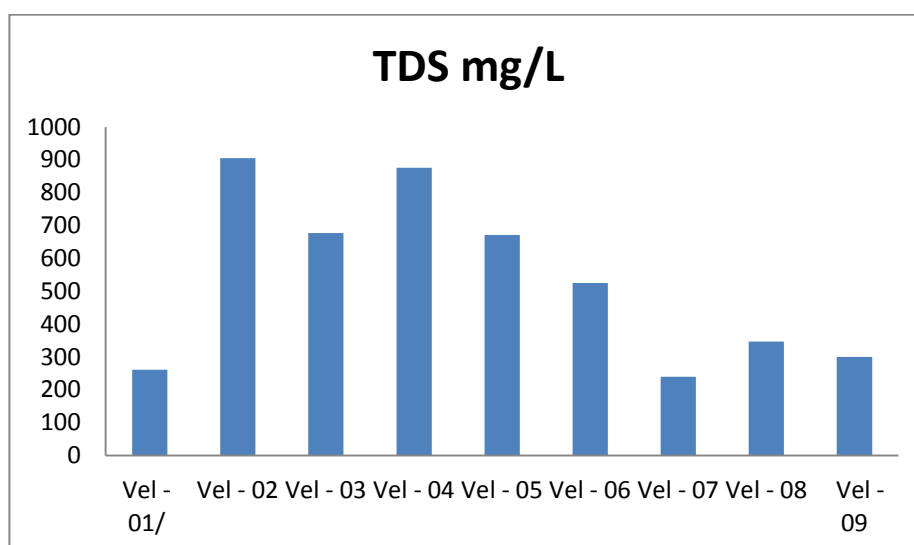
The total OCP concentration ranges between 0.5 - 3.1 µg /L see Fig 9. The average heptachlor concentration and HCB is higher than other OCPs and exceeds EU norms especially in developed agricultural areas where concentrations of them are about 2 times higher than other wells. The main source of OCP pollution is from agriculture. The concentrations of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane – p,p'-DDT and metabolites in the study area still within EU Directive and ranged from



**Figure 2.** pH values in sampling wells.

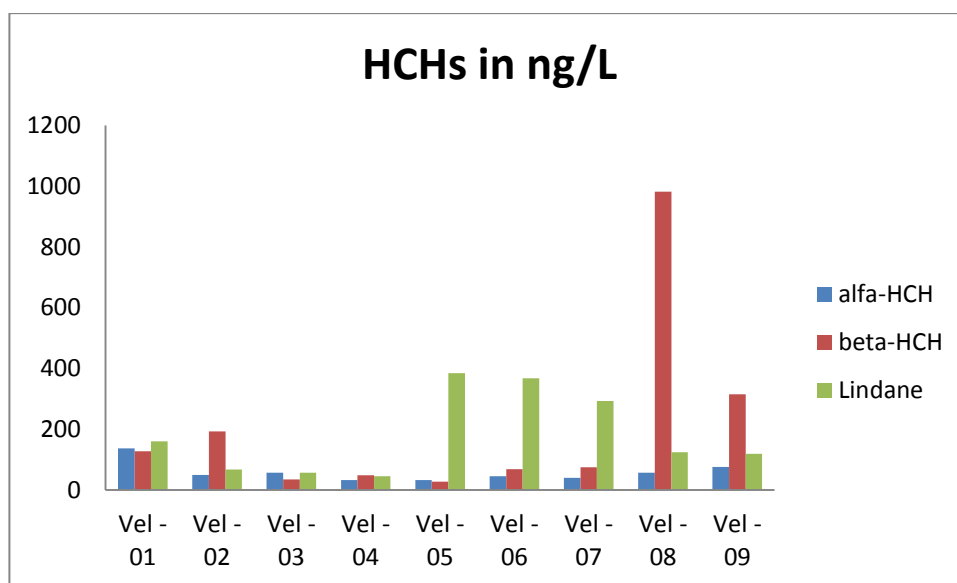


**Figure 3.** Conductivity values in sampling wells.

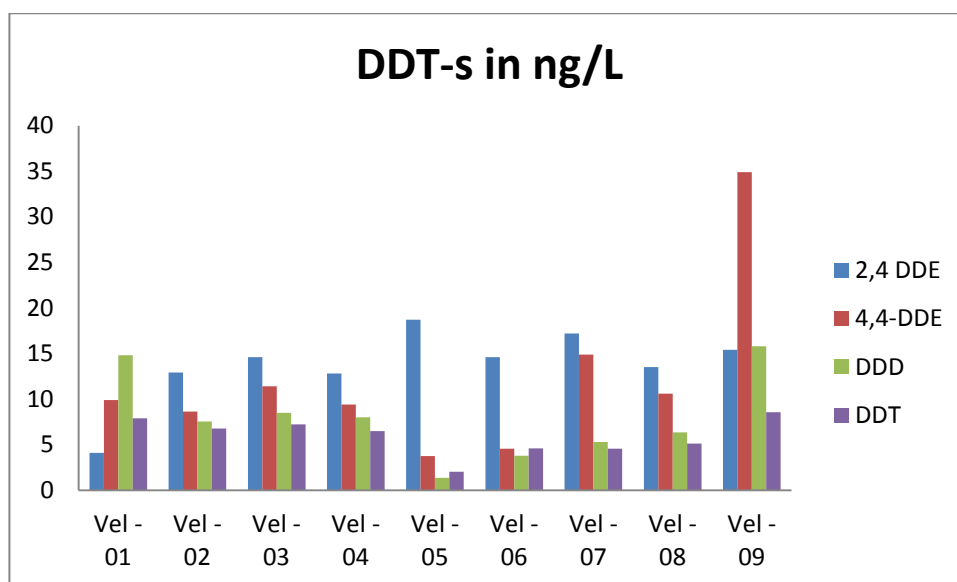


**Figure 4.** TDS values in sampling wells.

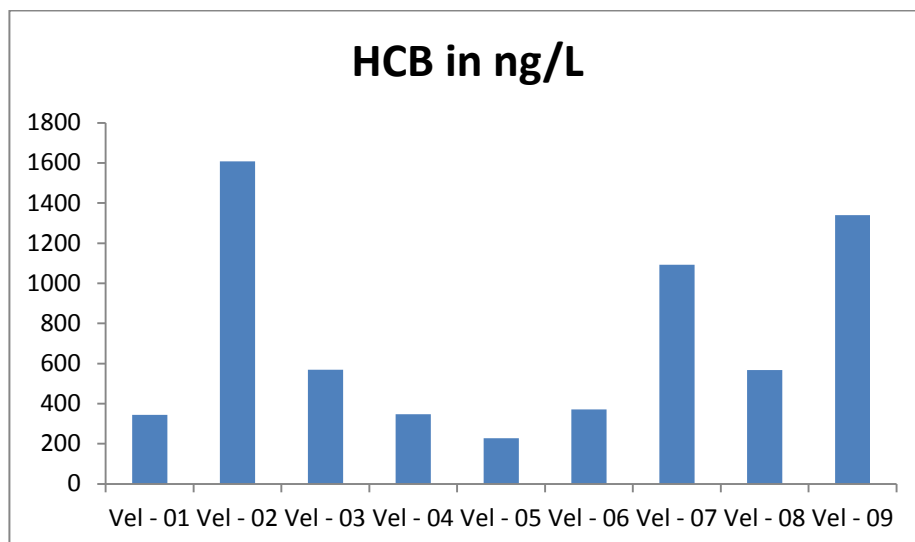
1.3 to 35 ng / L, see Figure 6. Regarding the HCH concentration it is noticed that lindane and beta- HCH have higher concentrations than other metabolites. These concentrations exceed EU norms for lindane and beta -HCH, which are 100 ng / L for individual pesticides, while other metabolites generally meet EU ground water standards. The situation of aquifers worsens, under the influence of anthropogenic agriculture development. Groundwater is usually used for irrigation by residents in the area but some of them are also used as drinking water. Pesticide transport from the soil surface to groundwater is controlled by a number of processes: photo degradation, plant uptake, sorption to solid and possibly colloidal phases, dissolved phase migration, and subsurface chemical and microbial mediated degradation.



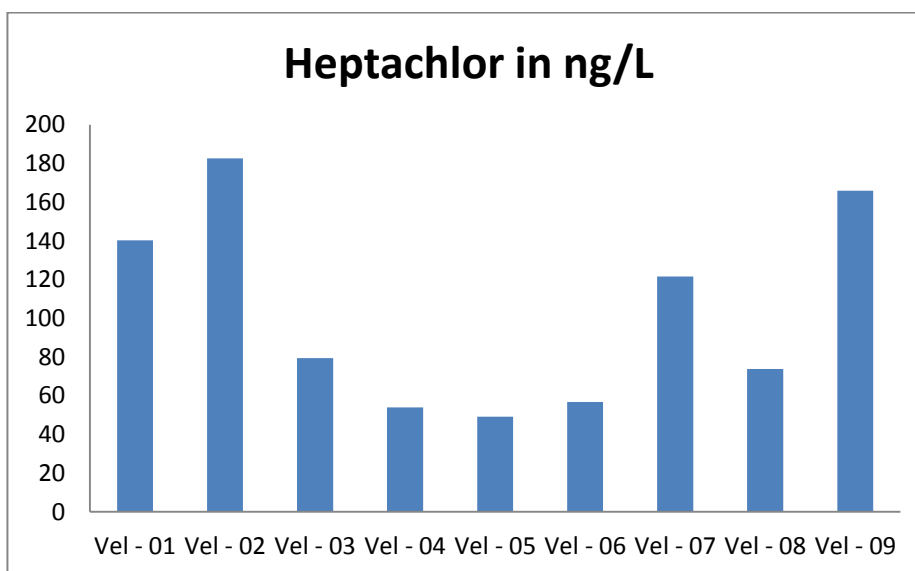
**Figure 5.** Mean concentration of HCH-s.



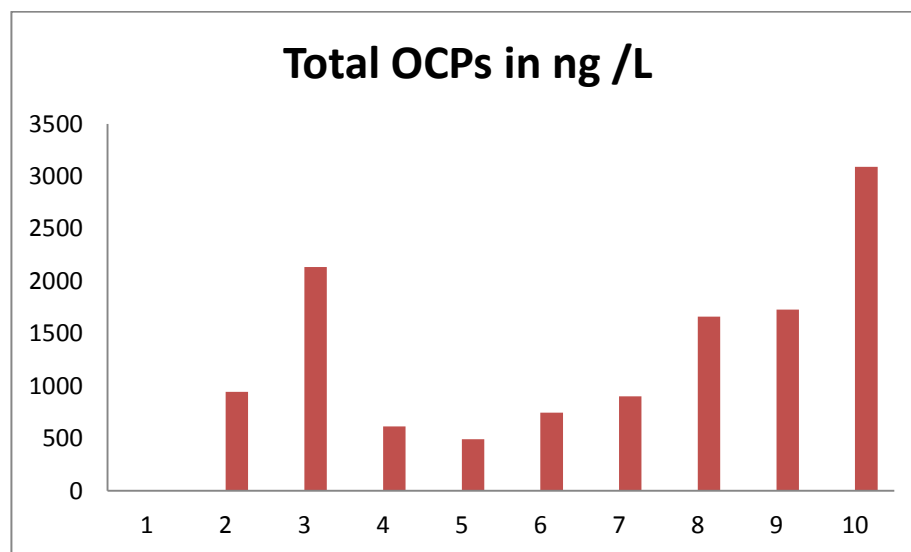
**Figure 6.** Mean concentration of DDT-s.



**Figure 7.** Mean concentration of HCB.



**Figure 8.** Mean concentration of heptachlor.



**Figure 9.** Total concentration of OCP –s.

The levels of some individually OCPs in the area for groundwater are still within EU Directive for ground water. The hexachlorobenzene (HCB) and heptachlor concentrations are higher than other OCPs and exceeds EU norms especially in developed agricultural areas. From the total OCP values we judge that the impact of the use of these chemicals in past decades is still felt in the groundwater, thus reducing the quality of the groundwater. Considering the fact that these waters are used by some residents as drinking water, one can conclude that the risk of OCP presence is evident even though they have many years that are not used. Organochlorine pesticides as organic pollutants with high persistency, bioaccumulation and toxicity represent quite high risk for the human in the studied area.

## References

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