Journal of Environmental Protection and Ecology 17, *No 1*, *102–107* (*2016*)

Water pollution

DISTRIBUTION OF POLYCHLORINATED BIPHENYLS AND ORGANOCHLORINATED PESTICIDES IN THE ALBANIAN PART OF THE DRIN AND BUNA RIVERS

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Abstract. The organochlorinated pesticides (OCP) and polychlorinated biphenyls (PCB) are the widest class of organic compounds and the most problematic in environment. The objective of this paper is to compare the presence of OCP and PCB in surface waters of Drin and Buna rivers at the most probably affected sites from anthropogenic pollution. Different sites through river flow were chosen for pesticide concentration measurement. Water was sampled in 10–25 cm depth in these sites. Samples were taken every six month during 2012–2015. The liquid–liquid (L/L) water extraction followed gas chromatography (GC) with micro electron-capture detector (μ-ECD) were applied for pesticide residue analyses. The quantified pesticides were α-HCH, β-HCH, HCB, Lindan, Heptachlor, 2,4-DDE, 4,4-DDE, DDT, DDD representing organochlorinated pesticides and PCB 28, PCB 101, PCB118, PCB 153, PCB 138 for polychlorinated biphenyls. The other identified pesticides were Aldrin, Endrin, Heptachlorepoxide, γ-HCH, δ-HCH and Metoxichlor. The most polluted site Zuswhich is located in the Albanian part of Buna River.

Keywords: Drin River, Buna River, organochlorinated pesticides, polychlorinated biphenyls.

AIMS AND BACKGROUND

Agriculture is a major user of land and water resources and has significant environmental impacts. It is an essential source of pollution[1]. The use of pesticides in agriculture deteriorates environmental quality standards and causes adverse effects on species and ecosystems in the neighbouring farms[2]. Pesticides affect all fauna depending on peculiarity of toxics and permanence. Human beings are the most sensitive targets in this interaction[3]. The Drin River basin represents a very complex water system where rivers, lakes, wetlands and groundwater interact with each other and create a very rich ecosystem in terms of natural resources[4]. It is

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the longest river in Albania. It is formed near the Albanian border from two main branches: White Drin originating from Kosovo and Black Drin originating from the Ohrid Lake in FYROM. After merging the river passes across the northern part of Albania and at the lower part most of its waters flow to Buna River.

The aim of this study is the distribution of pollution with organochlorinated pesticides (OCP) and polychlorinated biphenyls (PCB) in different locations through the river flow. Alpha-HCH, Beta-HCH, HCB, Lindan, Heptachlor, 2,4-DDE, 4,4-DDE, DDT, DDD were chosen as representatives of organochlorinated pesticids and PCB-28, PCB-52, PCB-101, PCB-118, PCB- 138, PCB-153 and PCB-180 as representatives of polychlorinated biphenyls.

EXPERIMENTAL

Study area. The following sampling points were chosen: Morine (White Drin), Zall Rec (Black Drin), Fierze and Vau Dejes (Drin) and Zus (Buna) (Fig. 1). Samples of surface waters were taken in six months intervals from October 2012 to September 2015.

Fig. 1. Sampling points

Sampling technique. Samples were collected using grab sampler bottle UWITEC, transferred in 1-l glass bottles and stored at 4°C prior to chemical analyses.

Extraction and measurement. Water samples were processed with liquid–liquid extraction by using 1-l separator funnel. Samples were spiked with 10 µl PCB 29 as internal standard in 2.5 ng μl^{-1} concentration and extracted with 40 ml *n*-hexane. The organic phase (*n*-hexane) was dried by using 10 g Na_2SO_4. The cleaning of the extracts was done in a glass column filled with deactivated 5% water fluorosil (100–200 mesh or 0.075–0.150 mm). The column was rinsed out with 8 ml mixture of 4:1 *n*-hexane and DCM. The extract was evaporated till 1 ml extract by rotary evaporator (Laborota 4000, Heidolph) and N2 evaporator (Thermo Scientific). The

1-ml extracts were transferred in the chromatographic vials. Gas chromatographic analyses were performed with an Agilent 7890 gas chromatograph equipped with a micro^{63}Ni electron-capture detector and a split/splitless injector and auto-injector. The column used was a HP-5 [low/mid polarity, 5% (phenyl methyl siloxane)] (30 m × 0.32 mm I.D., 0.25 μm film). The split/splitless injector and detector temperatures were set at 280 and 300°C, respectively. Carrier gas was N_2 at 3.5 ml/min and make-up gas was nitrogen 29 ml min^{-1}. The initial oven temperature was kept at 60°C for 15 min, which was increased to 200°C at 20°C min^{-1}, held for 10 min and then increased to 250°C at 4°C min^{-1} for 20 min. The temperature was finally increased to 300°C at 10°C min^{-1} and held for 7 min. Injection volume was 1 μl, when splitless injections were made. The organochlorinated pesticides and polychlorinated biphenyls quantification was performed by internal standard method. Nitrogen was used both as the carrier gas (3.5 ml min^{-1}) and make-up gas (29 ml min^{-1}). The system was calibrated with a standard mixture containing organochlorinated pesticides and polychlorinated biphenyls.

The system was calibrated with a standard OCP and PCB mixture containing each of the chosen chemical compounds to evaluate. Values of each component were expressed in ng/l.

At the end of study mean concentration during the year for each component was calculated.

RESULTS AND DISCUSSION

The sea, rivers, dams or lakes have become the immediate environmental reservoirs for all possible organic pollutants[5]. The organochlorine pesticides group includes DDT (dichlorodiphenyltrichloroethane), Methoxychlor, Aldrin, Dieldrin, Chlordane, Toxaphene, Endrin, Heptachlor, and Lindane (gamma isomer of benzene hexachloride (BHC)). These are trade names for closely related hydrocarbon compounds to which several chlorine atoms have been joined[6]. Due to their environmental persistence, these pollutants can cause contamination of surface water and underground water[7]. Persistent organic pollutants including OCP are of global concern because of their toxicity, resistance to degradation, potential for long-term transport and their tendency to accumulate in fatty tissues (lipophilicity), the latter of which renders them likely to bioaccumulate through food chain[8].

Mean concentrations of each PCB for the five sample points are presented in the figures below. PCB-52 and PCB-180 were not detectable at all in either sample point. In another study on the same time period, Nuro and Marku have found these two PCB in considerable level in sediment samples near the delta of Drin river[9].

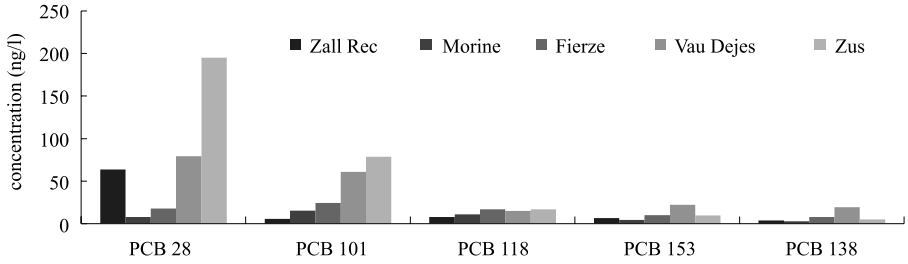

Fig. 2. Distribution of PCBs

In descending scale the higher concentrations of PCB-28 were detected in Zus, Vau Dejes and Zall Rec. Two other points, Fierze and Morine have lower levels. PCB-101 concentrations result to be higher in Zus, Vau Dejes, Fierze and lower in Morine and Zall Rec. PCB-118 result to have only small differences between these five points. PCB 153 and PCB 138 have slightly higher levels in Vau Dejes. The other sample points have only small differences ranging 4.5–22.12 ng/l for PCB 153 and 3.07–19.5 ng/l for PCB 138 (Fig. 2). The values of OCP vary on the range of ten to a few hundreds of ng/l for α-HCH, β-HCH, Lindan, Heptachlor, DDE, DDT and DDD. Only HCB values range is in thousands of ng/l. Figure 3 shows the distribution of HCB in the five sampling points while Fig. 4 – the distribution of all the other OCPs.

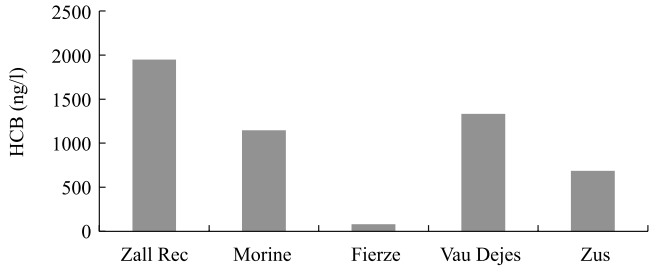

Fig. 3. Distribution of HCB

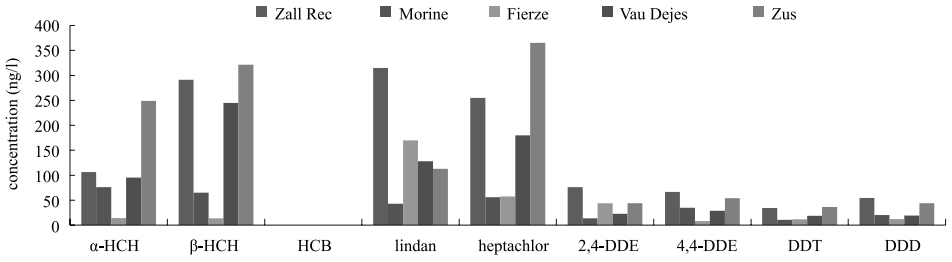

Fig. 4. Distribution of OCPs except HCB

Zus, Zall Rec and Vau Dejes resulted to have the higher levels of α-HCH. Zus, Zall Rec and Vau Dejes were more polluted by β-HCH, while Fierze and Morineare less polluted. The concentrations of HCB were considerably higher than the other pesticides. HCB ranged from 1146.27 ng/l in Morineto, 1948.42 ng/l in Zall Rec. Lindan results to be in a higher level in Zall Rec and Fierze. Vau Dejes and Zus have comparable values, respectively 127.93 and 113.03 ng/l. Heptachlor results to be in higher levels at Zall Rec and Vau Dejes. The values of Lindan and Heptachlor are comparable. 2,4-DDE 4,4-DDE, DDT and DDD have small differences between locations.

Zus (Buna) results to be more polluted than Zall Rec (Black Drin), Vau Dejes, Fierze (Drin) and Morine (White Drin) and for each OCP. The highest concentration of PCB – 28 was found in Zusand, the lowest in Morine. A study concerning similar substances performed for the Ohrid Lake where Black Drin originates, has reported levels 12–24 ng/l for Lindan and 19–32 ng/l for HCH (Ref. 10). These are very low compared to our results in Zall Rec, the end point of this river branch, respectively in the range 300 ng/l for Lindan and 400 ng/l for total HCH. Slightly higher levels are detected in our study even for 4.4-DDE, DDT and DDD compared with Velianovska et al.[10] This discrepancy may be a testimony of agricultural pollution in north-eastern Albania where this river branch passes and collects smaller branches. Pollution from municipal, industrial, and agrochemical sources remains a major threat to Balkan freshwater ecosystems. Mining mainly affect Bulgarian and Albanian rivers, industrial pollution is important in Bulgaria, FYR Macedonia and Bosnia and Herzegovina, agricultural pollution is widespread in Greece, Bulgaria and Albania, while municipal waste water pollution prevails in all countries except Greece[11].

CONCLUSIONS

In our study Zus and Zall Rec are the most polluted locations of Drin and Buna River. HCB is the most problematic substance. Other pollutants with high levels are Lindan, HCH and Heptachlor. Based on the UNECE classification of natural waters individual DDT levels are lower than the EU norms but their total concentration is higher than these norms in some sample points namely: Zus and Zall Rec. The other identified pesticides: Aldrin, Endrin, Heptachlorepoxide, γ-HCH, δ-HCH and Metoxichlor were detected in low levels.

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Received 15 December 2015
Revised 18 January 2016