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Assessment of organic pollutants in sediments from Maritsa River basin (Bulgaria)

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Sediments were sampled from 5 sites from the Maritsa River basin in the period 2013-2014 with the aim to assess effects of the anthropogenic pressure caused by the pesticides production and by the intensive agriculture. Sites were located in the middle part of the Maritsa River basin (near Plovdiv city) and the watersheds of Chepelarska and Stryama rivers. Methods for analysis of certain priority substances and specific pollutants were applied in order to establish trends in the accumulation in sediments, as required by the Directive 2000/60/EC and Directive 2008/105/EC. The reported data for organic pollutants are the first for the studied river basin.

Key words: sediments, Maritsa River, PCBs, OCPs, PAHs

INTRODUCTION

The Maritsa is the largest river on the Balkan Peninsula; it is the biggest river in terms of discharge volume and the third longest river in Bulgaria. It emerges from springs in the Rila mountain range and its basin is a cross-border watershed for Bulgaria, Greece and Turkey. The number of the tributaries of Maritsa River is about 100. The most significant among them are the rivers Chepinska, Topolnitsa, Luda Yana, Vacha, Chepelarska, Stryama, Sazliyka, Arda, Tundzha, Ergene.

Sediments are by far less variable in time, but much more heterogeneous than waters. Determining organic compounds in river sediments enables the identification of the contaminant origin in local regions. Polychlorinated biphenyls (PCBs) are toxic chemicals, which precipitate in soil and water. They are mixtures of synthetic and organic chemical substances which share similar chemical structure. PCBs had been derived for their very high flash points and were widely deployed as fire-extinguishing agents, electrical insulators and plasticizers mainly in electrical apparatuses. Most often they are introduced into the environment through defective equipment, illegal discharge, scavenge oil from electrical equipment, as well as hazardous waste. They are a family of 209 synthetic molecules composed of a biphenyl nucleus with chlorine at any, or all, of the 10 available sites [1]. The ortho-, meta- and para positions are important in determining the chemical properties of PCB, such as high dielectric constants, nonflammability, hydrophobic quality and chemical stability. The usefulness of these properties led PCBs to be used in mixtures for a wide range of applications from the 1930s onwards [2,]. However, after their toxicity became recognized, PCBs were progressively banned in most developed countries during the 1980s [4]. Due to their large-scale production, extensive use and environmental persistence, these compounds have accumulated in many ecosystems all over the world; in aquatic environments they are trapped in sediments. PCB contamination continues to be a problem as compounds can be transferred from the sediment to the lower trophic levels of an ecosystem through microbial and bottom-feeder uptake.

Organochlorine pesticides (OCPs) have been widely used in the past, but because of their high persistency in environment and accumulation in the food chain, they can still arouse topical concerns about human health.

Polyaromatic hydrocarbons (PAHs) are a large group of organic substances with two or more benzene cores. They are characterized by low solubility in water, but high solubility in fats. The polycyclic aromatic hydrocarbons are produced mainly by incomplete combustion of coal and diesel fuel. There are several hundred PAHs. These compounds are absorbed by organisms mainly through the respiratory system, but may also be assimilated together with water and food. The most thorough study of the carcinogenic effect is that of inhaled benzo[a]pyrene (BaP), essential source of which is tobacco smoke.

The aim of the research was to identify the extent of accumulation of organic pollutants in “sediment” matrix in selected river valleys and monitoring stations along the Maritsa River basin. The study for

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the first time provided information about the organic pollutants and could be a basis for initial examination of the level of pollution in the surveyed water bodies and identification of the sources of anthropogenic pressure. The selection of indicators (priority substances and specific pollutants) provides particular guidelines for planning future monitoring for assessment of their chemical and ecological status. The data from the analysis conducted may be used for the purpose of monitoring the tendencies in the pollution of water bodies in terms of the examined indicators.

EXPERIMENTAL

The monitoring of sediments was accomplished in accordance with Guidance document No. 25 on chemical monitoring of sediment and biota to the common implementation strategy for the Water Framework Directive (WFD) 2000/60/EC.

The research was conducted at 5 monitoring stations located in the Maritsa River basin and two of its major tributaries – Chepelarska River and Stryama River (Fig 1). The selection of the stations was made in compliance with the key criteria and the best practices of the strategy for sampling of sediments specified in Guidance document No. 7 [5] of the WFD. Thus, stations were selected upon a preliminary analysis of the information about the anthropogenic pressure from point and diffuse sources of organic pollutants, the typological characteristics of the rivers, the composition of the bottom substrate (pebbles, gravel, sand, slime, clay), the hydrological characteristics (water runoff, water level) and accessibility for sampling. The geographic characteristics of the monitoring stations (watershed, river, location, geographic coordinates) were specified below.

Stryama river, the village of Slatina (42.6902; 24.56917**)** has been selected as a potential reference site for national type R5 Semi-mountain rivers in Ecoregion 7, slightly influenced by anthropogenic pressure and limited impact on the quality elements: extensive agriculture and forestry in the vicinity of the monitoring station; low pressure from domestic discharges in the catchment area of the site (the town of Klissura); limited automobile traffic; good chemical and good to high ecological status identified as a reference point for type R5 in the RBMP of East Aegean River Basin district. Substratum was consisted mainly by pebbles, gravel and sand, and organic slime where the current is sluggish. Moderate to significant water runoff, moderate to high current velocity, water level was 0.2-0.4 m.

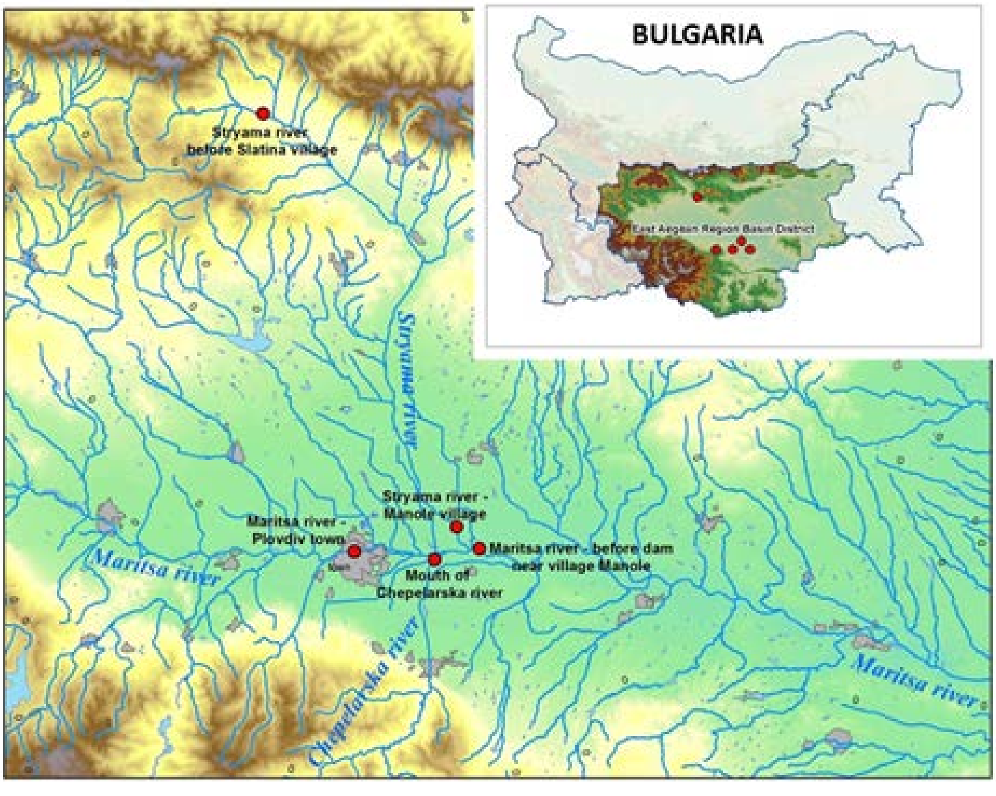

Fig. 1. Map of the studied region.

Stryama river, the village of Manole (42.1871; 24.91314**)** – type R13 Small and medium-sized lowland rivers in Ecoregion 7, located in a region with settlements in the catchment area of the of monitoring station; intensive agriculture; cumulative pressure from small settlements (<2000 p.e.); automobile traffic; good chemical and moderate ecological status; substrate – mostly sand and at places where the current is sluggish – organic slime. Moderate to significant water runoff, moderate to low current velocity, water level was 0.3-0.6 m.

Mouth of Chepelarska river, Kemera bridge area (42.1457; 24.87722**)** – type R5 Semi-intensive rivers in Ecoregion 7, a site of significant anthropogenic pressure from industrial plants producing pesticides and metals (Agria AD, KCM AD); discharge of untreated waste water from large settlements (Assenovgrad >1000 p.e.); intensive agriculture; automobile traffic; poor chemical status (metals) and poor ecological status; substrate – mostly gravel and sand, and where the current is sluggish – organic slime. Moderate to significant water runoff, moderate to low current velocity, water level: 0.3-0.5 m.

Maritsa river upstream of Plovdiv city (42.1608; 24.95124**)**– type R12 Large lowland rivers in Ecoregion 7, site of combined point and diffuse pressure from the upper and middle part of the catchment area of the Maritsa river, before discharge of waste water from the city of Plovdiv; discharge of treated waste water from large settlements in the catchment area on the monitoring station (Pazardzhik >1000 p.e., Stamboliyski town 2000-10000 p.e.); advanced industry (pulp and paper, food and flavor industry); intensive agriculture; intensive automobile traffic; good chemical and moderate to good ecological status; substrate – mostly sand and gravel with depositions of organic slime at places of sluggish current; significant water runoff, moderate to low current velocity, water level: 0.4-1.2 m.

Maritsa river, dam near the village of Manole (42.1529; 24.74322**)**– type R12 Large lowland rivers in Ecoregion 7; a monitoring station of significant cumulative anthropogenic pressure from all the sources in the catchment area of the other monitoring stations (discharge of waste water from large settlements, industrial enterprises and intensive agriculture; discharge of treated waste water) from large settlements in the catchment area of the monitoring station (Plovdiv – 300000 p.e., Assenovgrad >10000 p.e., a large number of settlements <2000 p.e.); combined pressure from developed industry (industrial zones of the city of Plovdiv, Agria AD, KCM AD); intensive agriculture in the catchment areas of the surveyed rivers – the Maritsa, Stryama and Chepelarska rivers; limited automobile traffic; good chemical and moderate ecological status; substrate – massive deposition of organic slime in the area of the monitoring station before the dam near the village of Manole, sand; significant water runoff, low velocity of the current, water level: 1.0-3.0 m.

Samples were collected from their upper layer, which indicates the actual materials deposited and the actual extent of pollution. Furthermore, the sediment topmost layer forms the habitat of the benthic organisms, which are part of the biological quality elements for the assessment of the status of water bodies. The sediments are composed of particles varying from very fine clay (< 2 µm) to larger pebbles and stones with a size of several mm. Their surface is often covered with organic substances which have the effect of binding element for many pollutants and other compounds. The smaller the particle is, the greater the relative surface area is, which means that the majority of monitored substances are contained in the fine fractions of the sediments, which are the main source of nutrients for the biota. The size of the particle is one of the most important factors, which controls the distribution of natural and anthropogenic components in sediments, along with the content of organic substances. The clay-silt fraction of particle size < 63 µm was analyzed. Volume (quantity) of sample for analysis was 200 mL.

The sampling was done in compliance with the ISO 5667-12:2002 standard [6]. Stainless steel blades were used in order to minimize contamination.

Transportation and sieving

In order to minimize the possibility of disturbing the sediment/water equilibrium, wet sieving was done at the point of sampling with water from the environment. The samples (upon sieving) were transferred into preliminary cleaned brown glass containers for organic pollutants. The containers for samples were filled up to the brim (allowing a minimum space for the stopper), in order to minimize the probability of oxidation and loss of acid-volatile sulfide during transportation. The samples were transported in a cooled state to the laboratory (at T 4°C) within a period not exceeding 6 hours. Cooling was accomplished by using cool boxes and freezer block inserts.

Storage

Temperature is the most important factor concerning samples from the time of sampling, throughout their handling and processing to the moment of final analysis. Another source of contamination is the adsorption of pollutants from the laboratory air. Decomposition and evaporation of contaminants might also be a source of analysis error. The sifted samples of sediments were kept in containers freeze dried in accordance with the EN ISO 16720:2007 standard [7] and deep frozen at -20°C.

Analytical methods

Validated standardized methods as per: ISO 18287-1; EN 16167; SD/CEN/TS 16181; EN 16179 were used for the analyses [8-11].

Sample preparation

A 10 g sample was extracted with organic solvent Hexane:Acetone (1:1), by microwave decomposition under a programmed furnace temperature of 120°C detainment time 25. The extract obtained was concentrated, then subjected to a purification procedure with silica gel and again concentrated. The sample was analyzed using Gas chromatography – mass spectrometry (GC-MS) equipment.

Quality control

The procedures for quality assurance include validation of the methods by routine in-house procedures and independent external procedures (participation in inter-laboratory tests). Use was made of certified reference materials: Certified Reference Material PAHs, PCBs, and Pesticides in Fresh Water Sediment CNS391, Fluka and Standard Reference Material NIST- SRM 1944.

Period and frequency of sampling

As a result from the limited rate of deposition (typically within the range of 1-10 mm/year) and the physical и biological blending of surface sediments, the composition of sediments is usually quite stable in comparison to the concentration of the pollutants in the aquatic ecosystem. The sediment sampling was accomplished three times in the period 2013-2014 and corresponded to the expected changes in the sediments, taking into account the seasonal changes in the hydrological regimes of the rivers.

Selection of organic pollutants to be monitored

Analysis of synthetic compounds was made (pesticides, medicinal preparations, industrial pollutants), dissociated in the event of pollution from point and diffusive sources, atmospheric depositions, which are taken into account in the assessment of the chemical and ecological status of the water bodies (e.g. priority substances according to Directive 2008/105/EO and Directive 2013/39/EC), and specific pollutants in compliance with the approved list and the EQS of the Bulgarian legislation [12].

RESULTS AND DISCUSSION

All six PCBs (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) studied were below the limit of quantification (<0.001 mg kg^{-1}) at all monitoring stations, probably due to the ban imposed on the manufacture thereof for decades.

Results for 17 OCPs showed that exceeding the limit of quantification have been detected for chlorbenzene, α-HCH, β-HCH, α-Endosulfane, endrine, o,p-DDE, p,p-DDE, o,p-DDD (Table 1). The lowest concentrations were detected in the Stryama River, Slatina village – a site slightly influenced by anthropogenic pressure.

Table 1. Detected minimum, maximum and average values of studied OCPs in sediments, mg kg^{-1} d.w.

OCP	**min** (n=15)	**max**	**average**
Pentachloro benzene	<0.001	-	-
ChBenzene	0.001	0.0023	
α-HCH	0.002	0.05	0.0093
β-HCH	0.002	0.015	0.0028
γ-HCH	<0.002	-	-
α-Endosulfane	0.003	0.068	0.0388
β-Endosulfane	<0.003	-	-
Aldrin	<0.002	-	-
Dieldrin	0.002	0.024	0.0106
Endrin	<0.002	-	-
Heptachlor	<0.001	-	-
o,p-DDE	0.001	0.035	0.0113
p,p-DDE	0.002	0.047	0.0192
o,p-DDT	<0.001	-	-
p,p-DDT	<0.001	-	-
o,p-DDD	0.001	0.007	0.0034
p,p-DDD	<0.003	-	-

Table 2. Minimum, average and maximum concentrations of 16 measured PAH in sediments, mg kg^{-1} d.w.

PAH	**min** (n=15)	**max**	**average**
Naphthalene	0.01	0.03	0.02
Acenaphthene	<0.01		
Acenaphthylene	<0.01		
Fluoranthene	<0.02		
Phenanthrene	0.02	0.046	0.014
Anthracene	0.002	0.008	0.002
Flurene	0.002	0.05	0.015
Pyrene	0.001	0.038	0.013
Benzo(a)anthracene	0.001	0.022	0.002
Chrysene	0.001	0.022	0.004
Benzo(b)fluoranthene	0.001	0.09	0.013
Benzo(k)fluoranthene	0.001	0.08	0.012
Benzo(a)pyrene	0.001	0.04	0.009
Indeno(1,2,3cd)pyrene	<0.003		
Dibenz(a,h)anthracene	<0.003		
Benzo(g,h,i)perylene	<0.003		

Exceeding the limit of quantification for 16 PAHs analyzed was recorded for Naphthalene, Phenanthrene, Anthracene, Flurene, Pyrene, Benzo(a)anthracene, Chrysene Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene (Table 2).

The lowest concentrations were ascertained again in the Stryama River, Slatina village, while the highest concentrations were in the Chepelarska River, Kemera village – a site of significant anthropogenic pressure due to discharge of waste waters from settlements (Assenovgrad) and industrial enterprises (KCM AD and Agria AD).

CONCLUSION

At none of the monitoring stations PCBs (used in the past as pesticides in agriculture) have been detected since production thereof has been discontinued for decades. At all monitoring stations OCPs and PAHs above the LOQ have been detected, which was probably due to diffuse and point pollution in the area of the surveyed river sections.

Eight substances from the group of OCPs were established (persistent organic pollutants used as pesticides in agriculture and forestry). Moreover, six of them were found constantly in all five monitoring stations (α-HCH, α-Endosulfane, Dieldrin, o,p-DDE, p,p-DDE, o,p-DDD).

Nine substances from the group of PAH were also established (pressure from industry and traffic). The lowest number of substances were found in sediments from provisionally selected reference point of Stryama River before Slatina (Naphthalene and Anthracene), in concentrations close to the limit of quantification (LOQ). In the rest of the stations they were detected continuously in different concentrations depending on the anthropogenic pressure.

The highest concentrations of OCPs and PAHs were detected just upstream of the mouth of Chepelarska River, which are in consequence of the combined pollution caused by industry, intensive agriculture and automobile traffic.

The results from the conducted for the first time survey of organic pollutants in sediments from Maritsa River basin could be used for the purpose of monitoring the trends in pollution of water bodies in terms of the examined indicators in accordance with the requirements of Directive 2008/105/EC.

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ОЦЕНКА НА ОРГАНИЧНИ ЗАМЪРСИТЕЛИ В СЕДИМЕНТИ ОТ БАСЕЙНА НА РЕКА МАРИЦА (БЪЛГАРИЯ)

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(Резюме)

В периода 2013-2014 е извършено пробовземане от седименти в 5 мониторингови станции в басейна на река Марица с цел оценка на ефектите от антропогенния натиск, причинен от производството на пестициди и интензивно земеделие. Станциите са разположени с средната част на басейна на река Марица (в района на гр.Пловдив) и водосборите на р.Чепеларска и р.Стряма. Използвани са методи за анализ на приоритетни вещества и специфични замърсители за установяване на тенденции при акумулацията в седименти в съответствие с изискванията на Директива 2000/60/ЕС и Директива 2008/105/ЕС. Представените данни за органични замърсители са първите за изследвания речен басейн.

***Ключови думи**: седименти, река Марица, PCBs, OCPs, PAH*