

Selected Current Use Pesticides in sediment and water samples from Buyuk Menderes River, Turkey

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Introduction

Buyuk Menderes River is located in south-west of Turkey and surrounded by Izmir, Manisa, Usak, Mugla, Afyon, Burdur provinces. It flows to Aegean Sea in west part of Turkey. The river basin of 24873 m² covers 3.2% of Turkey's total area. Total length of Buyuk Menderes River is 584 km and it is the longest river of Aegean region of Turkey. The land use in the watershed is dominated by forestry activities (45%) followed by agricultural use (40%), grassland (10%), urban (1 %), surface water (1%). Cotton, fig and olives are the main agricultural products. The area is one of the most important geothermal water resource of Turkey. The main point source of pollution to the Buyuk Menderes River are domestic and industrial wastewater discharges as well as geothermal discharges. Diffuse pollution sources mainly originate from agricultural practices (fertilizers, pesticide applications, irrigation etc). Tourism and touristic facilities are also an important source of pollution to the watershed [1].

Agricultural use of pesticides is a subset of the larger spectrum of industrial chemicals used in modern society. The American Chemical Society database indicates that there were some 13 million chemicals identified in 1993 with some 500 000 new compounds being added annually. The adverse effects of pesticides to human and wild lives are known for a long time and still is a concern due to persistence of these chemicals in environmental compartments. Consequently, many highly toxic and persistent pesticides have been banned worldwide gradually. Turkey, as a signatory of Stockholm Convention, banned all organochlorine pesticides in the country [2]. Therefore, current-use pesticides (CUPs) are of concern in the country since use of these chemicals are widespread and agricultural practices are one of the main economical income resource for Turkey. Turkey adopted Europe's Water Framework Directive and has started strict control of use of selected current-use pesticides as well as de-registration of selected CUPs listed in Annexes of Directive, many others are still in use in the country and therefore environmental compartments should be monitored for occurrence, levels and effects of these chemicals.

In this study, we present occurrence and levels of current use pesticides in surface water samples and sediment samples (collected in August 2015) from Buyuk Menderes River of Turkey.

Materials and methods

Sampling

Surface water and sediment samples were collected at 8 points from Buyuk Menderes River (Figure 1). Water samples were collected from 10 cm below the water surface. Surface sediment samples (0-30 cm) were collected using a grab sampler. Water samples (5 L) were immediately placed in solvent rinsed amber bottles and kept in a cooler. Sediment samples were kept in solvent rinsed aluminum foil bags, sealed in zipper bag and kept in a cooler during the sampling. Samples were transferred to the laboratory in -20°C until extraction and analysis. A total of 16 samples (8 water samples and 8 sediment samples) were collected in April 2015 (before the rainy season).



Figure 1. Sampling Locations

Chemicals and Solvents

Standards for the OCPs and CUPs were purchased from Ehrendorfer GmbH, Germany at analytical grade. All solvents used were GC/HPLC quality. Glassware were carefully washed with solvents, baked at 450 °C when possible to remove any organic substances on the surface.

Extraction and Sample Preparation

Solid phase extraction of the CUPs from water samples was achieved using the method given by Turgut (2003) [3]. Briefly, 500 mg/ml was injected into a Varian 24 SPE System that was conditioned using a flow of 1 ml/min and pre-cleaned with 3 × 3 ml hexane/acetone, 3 ml methanol, and flushed with 3 ml distilled water. Five liters of the water samples were drawn through the conditioned octadecyl column at 400 mbar pressure. After drying for 1 h, the substances in column were dissolved in hexane/acetone mixture, the solution collected concentrated to 2 ml solvent in vacuum dryer. The 2-ml samples were cleaned on an alumina–silicic acid column containing 3 g silicic acid and 2 g alumina according to Sofuoglu et al. (2001) [4] and eluted with 20 ml dichloromethane. The collected eluent was further concentrated 1 ml in vacuum dryer. Sediment samples (~10 g) were kept in 1:1 acetone:dichloromethane mixture overnight at dark and then extracted using an ultrasonic bath for 60 minutes. Extraction process was repeated two more times and all of the eluants were combined in a round bottom flask. Volume reduced to approx. 1 mL using a rotary evaporator and to approx. 0.5 mL using a gentle stream of nitrogen gas. Clean up of the extracts were done on a Pasteur pipette column containing 0.7 g of 70-230 mesh silica gel (baked overnight at 450 °C). Column was conditioned using 10 mL Hexane. After introducing the sample to the column, the column eluted using 8 mL of methanol:dichloromethane. Volume of the extract was reduced to 0.5 mL in iso-octane.

Instrumental Analysis

Pesticides were determined on an LC-MS-MS instrument (Schimadzu, 8030-triple quadrupole), equipped with a binary pump and C18 column. Flow rate was 0.4 mL/min, oven temperature was 40°C, interface voltage was 4.5 kV, drying gas flow was 15 L/min. Electron spray ionization (ESI) was used to ionize samples. Ultra pure distilled water (containing %0.03 (w:V) ammonium formate buffer) (A) and methanol (containing %0.03 (w:V) ammonium formate buffer) (B) used as mobile phases. The mobile phase program was: 95% B+5% A (for 8 min.); 95% A+5% BA (for 4 min.).

Quality Control/Quality Assurance

Blank samples were prepared for water and sediment samples using distilled water and solvent extracted sediment samples, respectively. None of the target analytes were determined in blank samples. Therefore, it is assumed that IDL=MDL. IDL values ranged between 0.002 ppb to 0.01 ppb for target chemicals for both sediment and water samples. Recovery of target analytes from spiked water and sediment samples ranged between 72% to 90%.

Results and discussion

Results showed that the levels of selected CUPs were at detectable levels in water and sediment samples from Buyuk Menderes river. Concentrations of CUPs in surface water samples ranged between 0.01 ppb and 3.206 ppb depending on the analyte. Buprofezin, cyprodinil, indoxacarb and triadimefon showed the lowest concentration in water samples while pyrimethanil (3.206 ppb) showed the highest concentration.

Table 1. Ratio between concentrations of sampling sites normalized to background site (Site 8) (Surface water)

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
Acetamiprid	8.1	0.5	0.4	0.2	0.6	1.8	1.8	1.0
Buprofezin	1.0	1.2	1.7	1.5	0.6	0.3	0.3	1.0
Carbendazim	0.1	0.1	0.2	0.2	0.6	0.9	0.8	1.0
Chlorpyrifos	2.5	2.0	0.8	0.8	2.8	0.3	0.4	1.0
Cyprodinil	1.9	28.2	3.6	2.0	47.9	1.4	1.5	1.0
Dimethoate	11.3	0.8	0.4	0.3	1.7	6.1	5.2	1.0
Imidacloprid	11.4	1.3	1.3	0.2	1.6	4.8	3.4	1.0
Indoxacarb	85.8	1.4	1.0	2.2	4.7	0.2	0.1	1.0
Triadimefon	2.3	0.2	0.6	0.5	0.4	0.2	0.2	1.0
Pyrimethanil	3.2	349.3	1.3	1.0	343.6	7.3	2.0	1.0

In sediment samples, tebufenozide showed the lowest concentration (0.062 ppb) while fenvalerate (4.367 ppb), fluvalinate (4.730 ppb) showed higher concentrations. Carbendazim, chlorpyrifos, triadimefon and pyrimethanil were present both in sediment and water samples. Average concentrations of these CUPs in sediments were significantly higher compared to levels in water environment.

Table 2. Ratio between concentrations of sampling sites normalized to background site (Site 8) (Sediment)

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
Fenvalerate	1.1	0.8	0.8	0.8	0.7	0.7	0.8	1.0
Fluvalinate	2.4	1.4	0.8	0.5	1.3	1.4	2.5	1.0
Azoxystrobin	0.1	0.1	0.2	0.0	0.6	0.2	0.0	1.0
Carbendazim	0.1	0.1	0.2	0.2	1.1	0.2	0.0	1.0
Chlorpyrifos	2.5	0.2	0.4	0.5	0.2	0.1	0.1	1.0
Triadimefon	0.7	0.4	0.7	0.4	0.7	1.4	0.1	1.0
Pyrimethanil	2.0	0.8	1.2	2.8	0.3	0.2	0.3	1.0
Tebufenozide	4.3	1.6	1.4	2.4	1.9	34.7	17.1	1.0

Although the number of samples collected in this study is limited and may not be representative for the whole Buyuk Menderes watershed and/or river environments in Turkey. Results showed in the current study is important to emphasize the occurrence of CUPs in environmental compartments of Turkey. Also, results can serve as a preliminary data set for future monitoring and/or watershed contaminants management studies in terms of detection of candidate CUPs contaminants to be focused on.

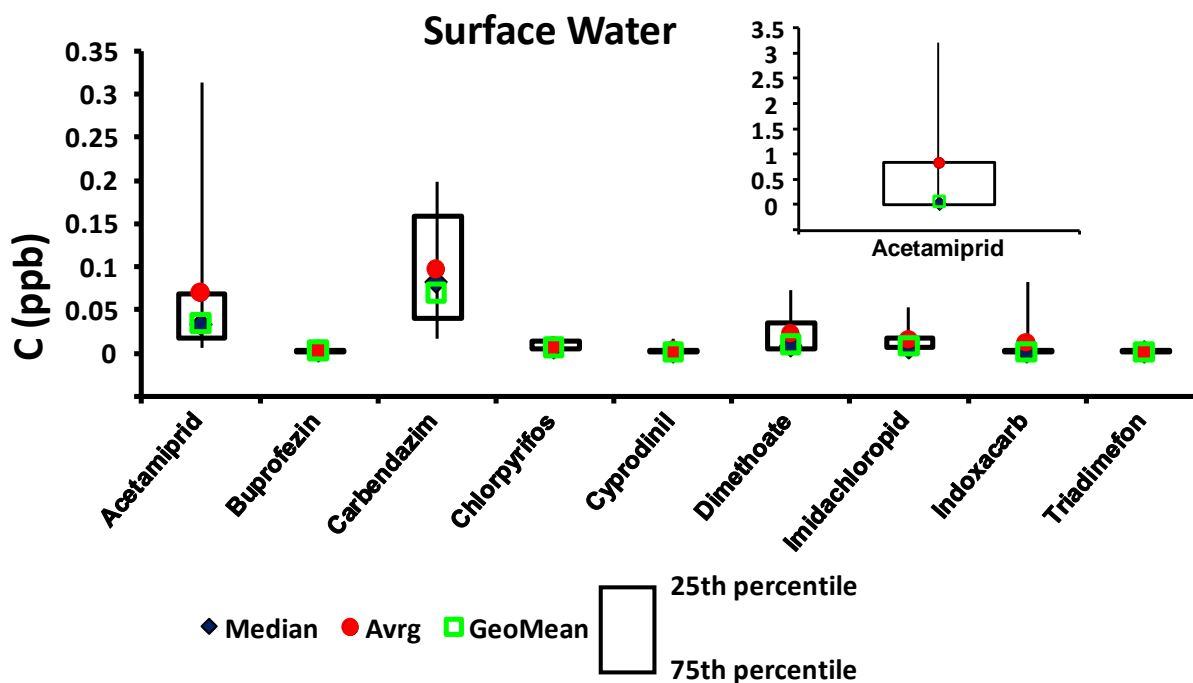


Figure 2. Levels of CUPs detected in surface water samples from Buyuk Menderes River

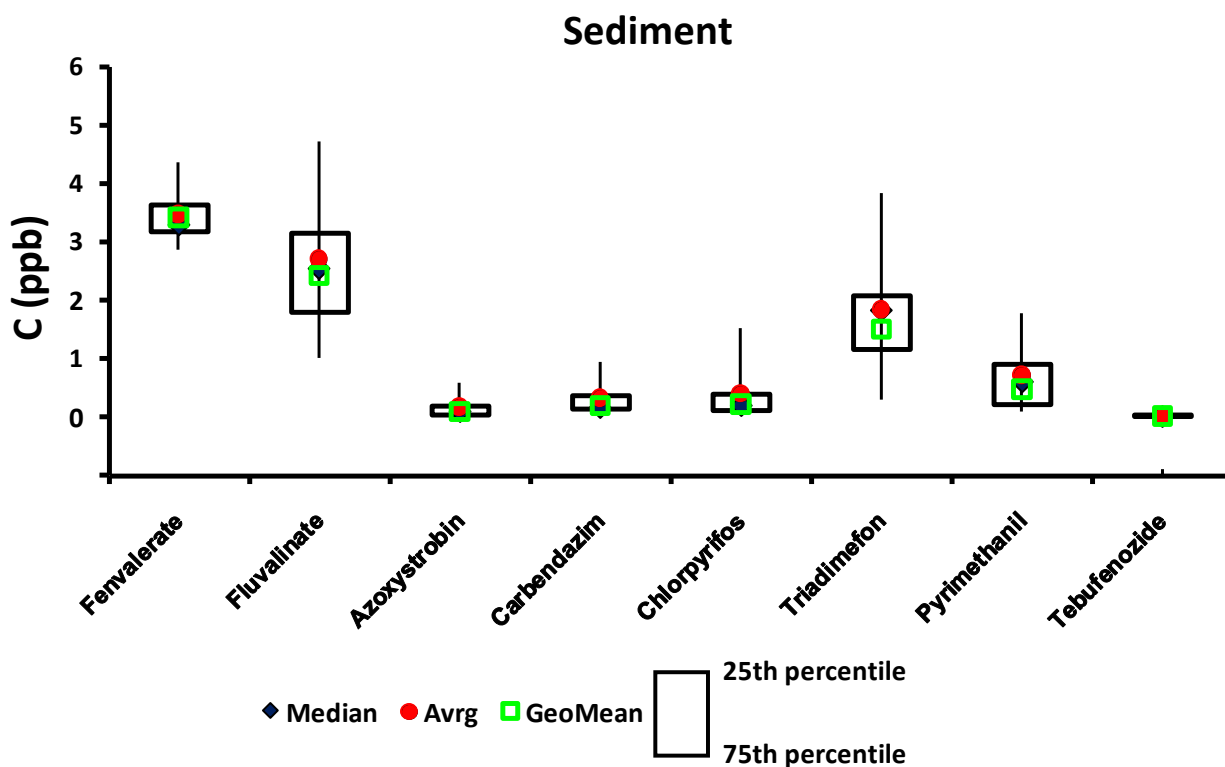


Figure 2. Levels of CUPs detected in sediment samples from Buyuk Menderes River

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