Determination of Rainwater Concentrations and Wet Deposition Fluxes of the Selected Current-Use Pesticides (CUPs) in Bursa, Turkey

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Introduction

As the legacy pesticides were banned by the Stockholm Convention or underwent significant reduction of usage, use of some current-use pesticides (CUPs) have increased significantly. Although most CUPs were designed to have reduced environmental persistence in comparison with the older organochlorine pesticides (OCs), they are generally detected in various environmental compartments such as air and the aquatic environment in agricultural or urban areas. Exposure to pesticides can be through contact with the skin, ingestion, or inhalation. The numerous negative health effects that have been associated with chemical pesticides include, among other effects, dermatological, gastrointestinal, neurological, carcinogenic, respiratory, reproductive, and endocrine effects. Furthermore, high occupational, accidental, or intentional exposure to pesticides can result in hospitalization and death.

Pesticides are able to enter the atmosphere through volatilization from soils and vegetation after application, and also from wind erosion of soil particles, and the commercial application powders on which the pesticide is sorbed. Once a chemical is airborne, atmospheric transport depends on both meteorological conditions and pesticide physical-chemical properties. Pesticides may be removed from the atmosphere both via physical mechanisms (dry and wet deposition) and photochemically-driven reactions. Pesticides which are susceptible to photochemical removal processes typically have relatively short residence times in the atmosphere, and normally are subject to only a nominal transport from their application area. Chemical species which are less susceptible to photochemical reaction are transported over much longer distances, as their atmospheric residence times range from several hours to days. As the importance of chemical removal processes decreases, deposition from the atmosphere becomes a controlling factor in determining long range atmospheric transport (LRAT)[1].

Common CUPs such as trifluralin, chlorpyrifos and chlorothalonil have K_{WA} values which make them subject to removal from the atmosphere mainly by wet gaseous deposition. This means that the occurrence of precipitation may have a much greater effect on the LRAT potential of CUPs than for compounds such as polyaromatic hydrocarbons (PAHs) polychlorinated biphenyls (PCBs) and OCs, which have much lower K_{WA} values and are removed from the atmosphere by rain with much less efficiency [2].

The aim of this study was to determine occurrence of selected CUPs in precipitation and wet depositon fluxes in Bursa province of Turkey by using a modified wet deposition sampler.

Materials and Methods

Bursa city, with a population over 2.5 million has 13 large industrial zones (including Turkey's first industrial zone) in addition to 19 small-scale industrial zones, one free-trade zone and also a technology development center which provides services to industry. In Bursa, home to Turkey's second largest Export Union, production has been focused on the textile, automotive, automotive spare parts, ready-to-wear garments, machinery and metal industries, dry-fresh and frozen foods, agriculture and service sectors. Bursa province is heavily cultivated with vegetables and fruits (especially olive, peach, pear and apple). The high population growth and rapid industrialization and urbanization during the last decades have resulted in significant environmental problems, including CUPs contamination.

Precipitation samples were collected between October 2017 and January 2018. Modified wet deposition sampler (WDS, Teknosem TYN-400 Model, Turkey), were placed on a platform (2.5 m height) located in an urban sampling location which is at BUTAL (TUBİTAK Bursa Test and Analysis Laboratory). All components of the WDS are made of stainless steel and Teflon The WDS has an active cover, and it works with the command received from a rain sensor. Surface dimensions of sampler where the sampling is carried out is 40 cm×40 cm (0.16 m^2) and 70 cm in depth. A collection hole is (0.5 cm diameter) located under the sampling section[3]. Dissolved CUPs in rainwater are captured on an XAD-2 resin column, and treated rain water is collected in a large reservoir after the resin column. The duration of rainy periods is recorded by time counter located on the WDS. In addition, a resistant heater is located in the sampler to prevent freezing in cold air conditions. The WDS was exposed to the atmosphere for about 15 days and wet deposition samples were collected after this period.

The XAD-2 resin was extracted twice in an ultrasonic bath with 150 mL of an ACE/HEX (1:1) mixture for 30 min. The solvent extracts were filtered through sodium sulfate (Na2SO4) to remove any residual water. The After the sample extraction, the solvent extracts were reduced to 1 mL using a rotary evaporator. Then 5 mL of Methanol was added to the sample, and the volume was again reduced to 1 mL to exchange the solvent to Methanol. Shimadzu CBM-20A, 8040 model LC-MS-MS was used for analysis of CUPs in multiple reactions monitoring (MRM+) mode. In the selection of target chemicals, pesticide species used in the production of agricultural products such as peaches, olives, apples and pears, which are frequently grown in Bursa province, have been considered. Benomyl, Dichlorvos, Dimethoate, Imidacloprid, Monocrotophos and Pymetrozine were the targeted compounds.

All samples were spiked with CUPs surrogate standards prior to extraction. Certified CUPs standard solutions (including the deuterium-labeled surrogate and internal standards) were purchased from TRC (Toronto Research Chemicals). Five deuterated CUPs (dichlorvos-d6, imidcloprid-d4, atrazine-d5, simazine-d1 and diuron-d6) were used as surrogate standards to determine analytical recovery efficiencies. Dimethoate-d6 was used as an internal standard for volume correction. 80 ng of each chemical was added to samples to determine the recovery efficiencies. Average recovery values were determined between 88, 93, 95, 87 and 96 % for dichlorvos-d6, imidcloprid-d4, atrazine-d5, simazine-d1 and diuron-d6, respectively.

Results and discussion:

The concentrations of selected CUPs in the rainwater samples are given in Table 1.

Table 1. Concentration values of CUPs determined in rainwater samples (ng/L)

Sampling Time	Collected Rainwater (L)	Duration (Day)	Benomyl	Dichlorvos	Dimethoate	İmidachloropid	Monocrotophos	Pymetrozine
4.10.2017	15.1	4.4	2.46	nd	nd	nd	nd	0.84
18.10.2017	2.6	1.6	15.06	nd	0.50	nd	nd	3.56
8.11.2017	16.7	7.48	2.05	nd	0.05	nd	nd	0.90
22.11.2017	7.1	3.8	4.43	nd	0.09	nd	nd	1.40
6.12.2017	12.4	3.28	3.67	nd	0.23	nd	nd	1.92
20.12.2017	9.91	4.31	14.52	nd	2.12	nd	nd	16.71
3.01.2018	8.3	3.69	2.07	nd	nd	nd	nd	1.16
17.01.2018	6.1	2.65	2.17	nd	nd	nd	nd	nd

nd: not detected

Benomyl. dimethoate and pymetrozine were the most commonly detected CUP species in the collected rainwater samples. Average rainwater concentration values for Benomyl. Dimethoate and Pymetrozine were determined as 5.8. 0.59 and 3.78 ng/Ll. respectively. When the monthly rainwater concentration value changes investigated highest concentration values were obtained in October for Benomyl. and in December for Dimethoate and Pymetrozine. respectively.

Pesticide concentrations in a precipitation sample are influenced by the total amount of rainfall received in that particular event. Rain concentrations are likely to be highest at the beginning of a rain event. with decreasing concentrations as the air is scavenged of airborne residues[4]. Hence. it is more informative to use mass fluxes of pesticides in precipitation to compare trends.

Deposition fluxes of PAHs were determined by considering real rainy time periods recorded by the timer in the WDS. The CUPs amount in the rain sample was divided by the rainy period and collection area to calculate the wet deposition flux. Calculated wet deposition flux values of CUPs were given in Table 2.

Table 2. Wet deposition fluxes of CUPs determined in rainwater samples (ng/m^2-day)

Sampling Time	Collected Rainwater (L)	Duration (Day)	Benomyl	Dichlorvos	Dimethoate	İmidachloropid	Monocrotophos	Pymetrozine
4.10.2017	15.1	4.4	0.088	nd	nd	nd	nd	0.030
18.10.2017	2.6	1.6	0.139	nd	0.005	nd	nd	0.033
8.11.2017	16.7	7.48	0.032	nd	0.001	nd	nd	0.014
22.11.2017	7.1	3.8	0.065	nd	0.001	nd	nd	0.020
6.12.2017	12.4	3.28	0.124	nd	0.008	nd	nd	0.065
20.12.2017	9.91	4.31	0.261	nd	0.038	nd	nd	0.300
3.01.2018	8.3	3.69	0.036	nd	nd	nd	nd	0.020
17.01.2018	6.1	2.65	0.039	nd	nd	nd	nd	nd

nd: not detected

As it seen from the Table 2. Benomyl was the most detectible CUP compounds in the collected samples and average flux value of this compound during the sampling campaign was determined as 0.098 ng/m^2-day. respectively.

Dichlorvos. Imidacloprid and Monochrotophos could not be determined in the collected samples because they were below the detection limit.

Herbicides and insecticides respond differently to rainfall patterns. reflecting their chemical properties and application patterns. Herbicide fluxes illustrate a higher influence by the timing of application as well as the frequency and distribution of rainfall events relative to application.

Pesticide concentrations in air and precipitation generally are highest in spring and summer. coinciding with pesticide application times and warmer temperatures. which increase re-volatilization from soil and plant surfaces[6]. These results highlight the importance of year-round monitoring to improve estimates of pesticide deposition rates to high-elevation environments.

By using atmospheric concentration values washout ratios of the CUPs from the atmosphere can be calculate. Calculated flux values can be used to determine the amount of pesticide involved in large water bodies.

To our best knowledge, this is the first study reporting precipitation concentrations of CUPs and wet deposition fluxes of these chemicals in an urban area in Turkey. Therefore, it will be act as a baseline for the upcoming studies in other areas of the country.

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