SORPTION BEHAVIOR OF SELECTED PESTICIDES IN ALLUVIAL AQUIFERS

Nevena Živančev[1], Marina Radišić[2], Srđan Kovačević[1], Marija Perović[3], Mila Laušević[2], Milan Dimkić[3]

[1] *University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering and Occupational Safety and Health, Trg Dositeja Obradovića 6, Novi Sad, Serbia; e-mail: nevenazivancev@uns.ac.rs; srdjankovacevic@uns.ac.rs*

[2] *University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia; e-mail: marinar@tmf.bg.ac.rs, milal@tmf.bg.ac.rs*

[3] *Jaroslav Černi Institute for the Development of Water Resources, Jaroslava Černog 80, Belgrade, Serbia; e-mail: okukamarija@gmail.com; milan.dimkic@jcerni.co.rs*

Abstract: There are approximately 1000 registered products for plant protection with over 300 different active ingredients in Serbia. Due to their extensive use in agriculture, they may be detected in all environmental mediums. Therefore, they're monitored in air, water and soil, but also in food and tissues. Concentrations of 15 pesticides in surface and groundwaters in Serbia have been monitored from the year 2009 to 2014, in sampling campaigns conducted by the Jaroslav Černi Institute for the Development of Water Resources. The results showed that the selected pesticides were detected in almost 34% of surface water samples, and in 33% of groundwater samples. All of the detected pesticides had very low concentrations in both surface and groundwater samples (lower than 0.1 µg/L), with a few exceptions. The most frequently detected pesticides were carbendazim and atrazine. These two pesticides have been selected for further analyses of sorption behavior in the sediment, with one additional pesticide for these experiments: carbofuran. In this paper, sorption coefficients for Danube sediment samples collected in Kovin-Dubovac area were analyzed. Sorption coefficient in these samples was highest for carbofuran, and lowest for atrazine. Lack of information on organic matter content and pH of the sediment used in sorption experiments lead to the further research of sorption behavior dependence on various factors of the three selected pesticides in literature data. Regression analysis with a large number of literature data was carried out, with regression equations as results. These results were compared to the ones gained in sorption experiments.

Keywords: pesticides, sorption coefficient, multiple regression analysis

INTRODUCTION

The consequence of growing agricultural production is the increased use of pesticides for plant protection, which leads to the potential contamination of soils, sediments and water resources. The behavior of a pesticide in the environment depends on its structure and physicochemical properties. Other important aspects affecting pesticides' environmental fate are the form, intensity and frequency of application (Meiwirth, 2003). Characteristics of a region, such as climate, geology, morphology and hydrology also have an important impact on the fate of these chemicals.

The research of sorption behavior of a pesticide is of great importance, due to its effect on other processes determining their fate in the environment, such as transport, degradation, volatilization and bioaccumulation (Gao et al., 1998; Krishna and Philip, 2008). Pesticides that are not effectively retained in the soil by sorption processes may reach the groundwater. Shallow groundwater tables are especially vulnerable for pesticide contamination (Meiwirth, 2003). Pesticide sorption processes greatly depend on the soil's organic matter, particle-size characteristics, but also pH values of the soil (Gao et al., 1998; Krishna and Philip, 2008; Meiwirth, 2003, Weber et al., 2004).

Several surface and groundwater sampling campaigns were performed from the year 2009 to 2014, by the Jaroslav Černi Institute for the Development of Water Resources. The samples were collected from Danube, Sava, Tisa and Great Morava and corresponding wells and piezometers. Total of 188 samples (74 surface

water samples and 114 groundwater samples) were analyzed in the laboratory at the Faculty of Technology and Metallurgy in Belgrade. Out of 15 targeted pesticides, only 6 of them were detected, including one that was detected in only two samples, with concentrations under the limit of quantification. The most frequently detected pesticide was carbendazim, which was detected in more than 29% of the surface water samples, and more than 16% of the groundwater samples. The second most frequently detected pesticide was atrazine, that was banned several years ago, but can still be detected because of its persistent nature. It is important to emphasize that the detected pesticides had very low concentrations, below 0.1 µg/L, with a few exceptions in Morava river samples, when concentrations were 0.165 µg/L (atrazine, May 2010) and 0.269 µg/L (carbendazim, June 2011).

The main focus of this paper is the sorption behavior of the two most frequently detected pesticides: atrazine and carbendazim. The sorption experiment of these two pesticides has been conducted on the alluvial sediment of the Danube river, in the Kovin-Dubovac area. The reason for choosing this area is the fact that it has a lot of agricultural fields. Also, during the sampling campaigns, 46 both surface and groundwater samples were collected from this area with very low concentrations of selected pesticides. It is possible that these low concentrations are a consequence of sorption processes on aquifer materials. The sorption experiment was also performed for carbofuran, even though it was detected in only a few samples. This pesticide was chosen, due to its rare detection and also the fact that the detected concentrations were very low, which can be a result of sorption processes.

Due to the fact that information on the soil properties responsible for sorption of pesticides are not available for the selected sediment, except the particle-size (from 63 µm to 1 mm in diameter), some further analyses have been conducted. In this paper, multiple linear regression of sorption coefficients has been performed, using the literature data to set correlation to pH, texture and organic matter content.

MATERIALS AND METHOD

Sorption Experiments

Adsorption experiments for the three selected pesticides were conducted at the Faculty of Technology and Metallurgy in Belgrade. In this paper, the experiment was carried out for the sediment material collected from the Danube river, for the particles with 63µm to 1mm in diameter. This particle-size is specific for sand particles. This is highly important, because the results of the adsorption isotherms on these particles will give a good perspective on the sorption behavior of selected pesticides in the alluvial aquifer sand.

Adsorption experiments were performed using the previously optimized 1 g: 20 ml rate of sediment mass and water solution volume, and the optimal time for the sediment/solution contact was 24h. Sediment samples were dried prior to adsorption experiments at a room temperature, in the dark. Specific volume of the standard pesticide solution was added to 1 g of sediment mass, and then the deionized water was added to the volume of 20 ml, so the solution concentrations in contact with the sediment were 10, 25, 50, 75, 100, 250 and 500 ng/mL. After the addition of soil samples, the reaction mixtures were agitated in a shaker at 300 rpm for 24 h, and then centrifuged for 10 minutes at 4000 rpm. The solution was decanted, and the pH value of the solution was adjusted to the optimal value for determination of selected pesticides (pH=6). Simultanously with the samples, for every value on the adsorption isotherm, the specific standard was prepared, and for every sediment sample, a blank probe was conducted. Decanted solution was extracted on Oasis HLB cartridges. Cartridges were preconditioned with 5 mL of methanol-dichloromethane (1:1) mixture and 5 mL of deionized water. Eluate was evaporated in a stream of nitrogen in a water bath at 25°C. Sample, standard and blank were reconstructed with 1 mL of methanol and analyzed using an optimized and validated method on HPLC-MS2 for these pesticides (Dujaković et al., 2010).

The sorption of pesticides is most frequently described using linear, Langmuir or Freundlich isotherms for equilibrium (Dimkić et al., 2008; Köhne et al., 2009; Weber et al., 1991). The linear sorption isotherm is based on the following equation (equation 1):

$$A = K_d \cdot C_e \tag{1}$$

Where A is the amount of pesticide sorbed at equilibrium, ng/g; K_d is the linear sorption coefficient, mL/g; C_e is the equilibrium solute concentration, ng/mL.

The Langmuir sorption isotherm is described using an equation with two parameters (equation 2):

$$A = A_{max} \frac{b \cdot C_e}{1 + b \cdot C_e} \tag{2}$$

Where A_{max} is the maximum sorption capacity at the given conditions, ng/g; b is the Langmuir constant related to energy of adsorption, mL/ng.

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Coefficient of multiple correlation is 0.73, p-values are lower than 0.0001 for all parameters in the equation. The resulting equation cannot be compared with the result gained in the sorption experiments on the Danube river sediment, because there is no information about these parameters for the sampled sediment. Due to these results, it is important to continue the research on sorption behavior of carbofuran and to include the analysis of these parameters in the experiments.

CONCLUSIONS

The sorption experiment presented in this paper showed that among the three selected pesticides, carbofuran has the highest affinity for the sediment used in this study. This conclusion is significant, because it explains the results of surface and groundwater monitoring studies, more precisely, why carbofuran was detected to a lesser extent than carbendazim and atrazine. The other important conclusion is that sorption behavior of atrazine, carbendazim and carbofuran on Danube river sediment can be predicted with linear, Langmuir and also Freundlich sorption isotherm, with determination coefficients close to 1, when initial concentrations of these analytes are below 250 ng/mL (lower than 100 ng/mL for carbendazim). Multiple linear regression analysis showed that the sorption behavior of atrazine and carbofuran are influenced by the pH and organic matter content of the solid material. The linear sorption coefficient of atrazine was also dependent on clay content. The multiple linear regression analysis of linear sorption coefficient for carbendazim could not be calculated only using the pH value, organic matter content and the texture of the solid material. Further research is acquired to establish the parameters on which this sorption coefficient is dependent on. The sorption behavior of these pesticides has to be researched even further. It would be significant to discover what sorption mechanisms are the most important for retaining these pesticides in soil and prevailing them from entering the groundwater and other environmental compartments.

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The Freundlich sorption isotherm is dependent on the two parameters expressed in the equation (3):

$$A = K_f \cdot C_e^{1/n} \quad (3)$$

Where K_f is the Freundlich isotherm constant and n is the Freundlich exponent.

Multiple Regression Analysis

Multiple regression analysis is a valuable tool for predicting an unknown value of a variable from the known value of two or more variables. In this paper, multiple regression analysis was performed for predicting the linear sorption coefficient from the main characteristics of solid materials that have an influence on sorption behavior of pesticides: pH, solid material texture and organic matter content. Literature data for linear sorption coefficient of atrazine, carbendazim and carbofuran were used, choosing only those values where data on previously mentioned parameters of soil were available.

RESULTS AND DISCUSSION

The results obtained in sorption experiments showed high affinity of pesticide carbofuran for sediment particles, resulting in high concentrations of this pesticide on solid material at equilibrium. Atrazine and carbendazim showed very low affinity for the sediment used in the experiments.

Linear, Langmuir and Freundlich equations were used for describing the sorption behavior of atrazine, carbendazim and carbofuran on the 63 μm to 1 mm particle-size Danube sediment,. The most accurate prediction for all three pesticides had the Langmuir model, with coefficient of determination, R^2, around 0,9. The least accurate was the linear sorption model. Better predictions for all three types of isotherms are possible if the values observed are results of sorption equilibrium for initial concentration of these pesticides in the solution under 250 ng/mL (100 ng/mL for carbendazim) (Table 1). The best equilibrium sorption isotherms are for carbofuran, with coefficient of determination higher than 0.98, which means that all of the presented equation coefficients can be used in modeling of the pesticide transport in alluvial aquifer, containing 63 μm to 1 mm particles.

Multiple linear regression was performed for linear sorption coefficient, due to the fact that models commonly use this type of equation for predicting transport and determining the fate of pesticides in the environment (Köhne et al., 2009). Correlation between soil properties (pH, texture and organic matter content) and linear sorption coefficient was analyzed. Regression analysis for carbendazim showed no significant dependence of linear sorption coefficient on pH, organic matter content or soil texture. Multiple linear regression for atrazine showed dependence of linear sorption coefficient on organic matter content, pH and clay content, which is in agreement with the literature results reported by Weber et al. (2004). Coefficient of multiple correlation was 0.85, but the p-values were higher than 0.05 for pH and clay content, so the regression equation is not presented in this paper.

Pesticide	Type of sorption isotherm	Sorption isotherm parameters	R^2
Atrazine	Linear	K_d = 0.3941mL/g	0.9394
	Langmuir	A_{max} = 372.97 ng/g b = 0.001343 mL/ng	0.9544
	Freundlich	K_f = 0.7651 (ng/g)(mL/g)$^{1/n}$ 1/n = 0.8729	0.9509
Carbendazim	Linear	K_d = 2.226 mL/g	0.9281
	Langmuir	A_{max} = 653.39 ng/g b = 0.002712 mL/ng	0.9606
	Freundlich	K_f = 0.6964 (ng/g)(mL/g)$^{1/n}$ 1/n=1.272	0.9512
Carbofuran	Linear	K_d = 15.68 mL/g	0.9847
	Langmuir	A_{max} = 21971.54 ng/g b = 0.0007801 mL/ng	0.9866
	Freundlich	K_f = 19.09 (ng/g)(mL/g)$^{1/n}$ 1/n = 0.958	0.9858

Table 1. Sorption isotherm parameters and R^2 values for atrazine, carbendazim and carbofuran for initial concentrations in the solution lower than 250 ng/mL (100 ng/mL for carbendazim).

Multiple linear regression performed for carbofuran showed that the linear sorption coefficient is dependent on pH and organic matter content. Regression equation for carbofuran, calculated using the literature data (Hsieh and Kao, 1998; Liyanage et al., 2006; Yazgan et al., 2005) (equation 4):

$$K_d = 0.4611 \cdot (pH) + 0.2529 \cdot (\%OM) - 2.7029 \pm 0.7448 \quad (4)$$

Supporting Organizations

Serbian Academy of Sciences and Arts

Government of the Republic of Serbia Ministry of Education, Science and Technological Development

United Nations Educational, Scientific and Cultural Organization - International Hydrological Programme (IHP)

The International Association of Hydrogeologists

International Association of Water Supply Companies in the Danube River Catchment Area

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