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MOBILITY OF SELECTED PESTICIDES IN GROUNDWATER

Nevena Živančev[1*], Srđan Kovačević[1], Boris Obrovski[1], Mirjana Vojinović Miloradov[1], Milan Dimkić[1,2]

[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
[2]Institute for the Development of Water Resources, Jaroslava Černog 80, Pinosava-Belgrade, Serbia
e-mail: nevenazivancev@uns.ac.rs

Abstract
The use of pesticides in plant protection products could result in their occurrence in all environmental mediums. Due to the concern about their environmental impact, the presence of pesticides is monitored in air, soil, water, and also in food and tissues. Jaroslav Černi Institute for the Development of Water Resources has conducted surface and groundwater sampling campaigns, in order to monitor fifteen different pesticides from priority and emerging substances lists. This paper is focused on the results of the groundwater sampling, where the most frequently detected pesticides were herbicide atrazine, fungicide carbendazim and insecticide carbofuran. In this paper, the fact that these pesticides were most frequently detected in groundwater was used for further research of their mobility. The most important process that influences the mobility of pesticides in the environment is the sorption. Therefore, sorption process was observed in the terms of linear sorption coefficient. Multiple linear regressions were used to establish the relationship between the linear sorption coefficient of each pesticide and various soil parameters, that have the highest impact on the sorption process. A thorough understanding of pesticides sorption behavior is crucial for predicting the movement rate of the pesticide in the environment. Information based on these processes will help with predicting the fate of pesticides in the groundwater, but also in the surface waters.

Introduction
Pesticides are substances mostly used in agriculture, to increase the quality and quantity of food. More than 1000 different plant protection products, with over 300 different active ingredients are currently registered for use in Serbia. With increasing the amounts of pesticides being used in the world, the concern about their adverse effects on the environment has also grown. The estimation is that less than 0.1% of the applied pesticide actually reaches the targeted pest, and the rest of the amount enters the environment [1]. The problem with pesticides reaching environmental mediums is also the fact that many of them can persist for long periods of time in an ecosystem.
Information on the quantities of pesticides that reach the environment, and especially the groundwater sources, which are used as sources of drinking water, are extremely important. Therefore, Jaroslav Černi Institute for the Development of Water Resources has monitored the concentrations of fifteen different pesticides in surface and groundwaters of Serbia, from the year 2009 to 2015. In this paper, the results of groundwater sampling campaigns are used. The most frequently detected pesticide in groundwaters in Serbia was herbicide atrazine, with detection in almost 32% of the samples. This herbicide has been banned for use several years ago, but it is still detected in the water samples, due to its persistent nature. It should be highlighted that median concentration of this pesticide in groundwater samples was 3.9 ng L^{-1}, which is a very low concentration. The second most frequently detected pesticide was fungicide carbendazim, which was detected in almost 22% of the samples, and the third most

frequently detected was insecticide carbofuran (in around 6% of the samples). Median concentrations of carbendazim and carbofuran was also very low, 9 and 6 L^{-1}, respectively.
Pesticides may reach the groundwater if they are not effectively retained by the sorption processes in the soil, because these processes are the most influential on the mobility of pesticides. Therefore, the sorption behavior of the three most frequently detected pesticides in groundwaters of Serbia was analyzed in this paper. Sorption process can be represented in the form of sorption coefficient, and in this paper the linear sorption coefficient was chosen for the analysis. The reason for choosing this coefficient is the fact that models predicting pesticides behavior and transport most frequently use this type of coefficient [2]. In this paper, multiple linear regression analysis was conducted, using literature data to set correlation between linear sorption coefficient and soil properties that sorption processes mostly depend on: organic matter content, soil texture and pH of the soil [3-4].

Materials and methods

In this paper, multiple linear regression analysis has been performed for carbendazim, carbofuran and atrazine linear sorption coefficients. This type of analysis is an imporant tool for predicting an uknown value based on the two or more known values.
The multiple linear regression analysis was conducted with a large number of literature data where linear sorption coefficients were gained in the laboratory conditions, and where soil properties values were available, in order to set the correlation between these properties and the sorption coefficient. The database on which this analysis was performed was organized to use only the values where soils had less than 10% of organic matter content, because the main interest of this research are soils in contact with groundwater, where organic content is lower than in the upper layers of soil.
Development of regression equations was performed using Microsoft Excel, with the Solver and Data Analysis Plug-In. The main objective was to develop equations based on the most important soil properties responsible for the sorption behavior of pesticides, that would accurately estimate the linear sorption coefficients for selected pesticides when soil properties are available for a given soil.

Results and discussion

Multiple linear regression analysis for carbendazim showed no significant dependence of linear sorption coefficient on pH, organic matter content or soil texture. It is important to establish which parameters do have an influence on sorption of carbendazim to soil. This should be the subject of further research.
The analysis for carbofuran showed the dependence of linear sorption coefficient (K_d) on pH and organic matter content of the soil, represented as % organic carbon. The following equation (1) is the result of the literature data analysis [5-8], where the coefficient for multiple correlation is 0.66:

$$K_d = -1.80 + 0.33 \cdot (pH) + 0.43 \cdot (\%OC) \pm 0.80 \quad (1)$$

Figure 1. represents the difference between literature data and the values calculated using the previously mentioned equation (1).

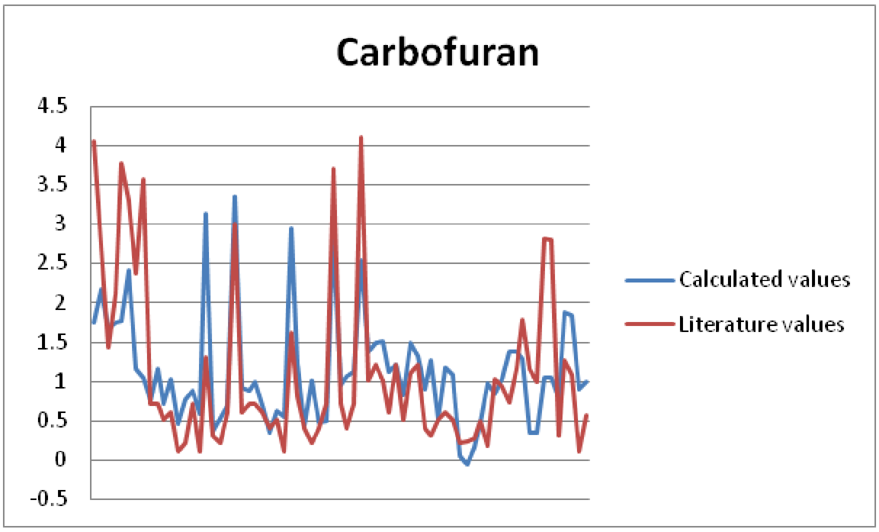

Figure 1. Comparison of calculated and literature data for carbofuran

The multiple linear regression analysis for atrazine showed better results than for carbendazim and carbofuran. The coefficient for multiple correlation was 0.89. The result of the multiple linear regression with literature data [9-11] is the following equation (2):

$$K_d = 1.97 - 0.28 \cdot (pH) + 0.93 \cdot (\%OC) \pm 0.40 \quad (2)$$

Figure 2. represents the difference between literature data and the values gained using the abovementioned equation (2).

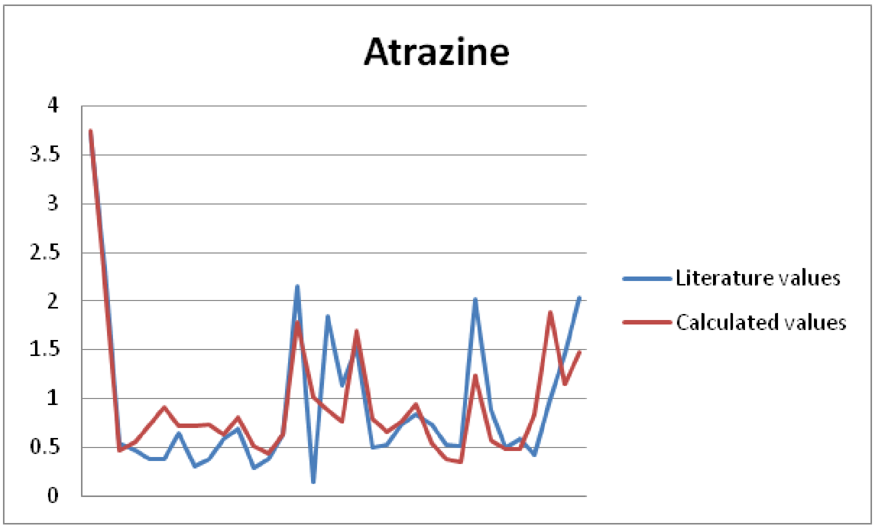

Figure 2. Comparison of calculated and literature data for atrazine

Instead of conclusion

Mobility of pesticides in the groundwater mostly depends on their sorption behavior in the soil. The research of their mobility in the groundwater is highly important in terms of estimating the potential contamination. Due to the fact that movement of pesticides can be slower as the consequence of the sorption processes has resulted in the research of these processes.

In this paper, multiple linear regression was used to correlate the linear sorption coefficient of three selected pesticides to the various soil parameters responsible for sorption. This analysis showed that carbendazim sorption behavior cannot be predicted using a multiple parameter linear equation, because the dependence of the K_d values on soil properties (pH, soil texture

and organic matter content) was insignificant. However, the analyses showed dependence of sorption coefficients on pH and organic matter content (displayed in equations (1) and (2) as % organic carbon) for carbofuran and atrazine. The coefficient for multiple correlation for carbofuran was only 0.66, which is not enough for some serious estimations and predictions. Even more literature data must be examined, but also, some further research should be conducted to establish the connection of sorption coefficent and soil properties.
The best prediction of K_d values through soil properties was for atrazine, where coefficient for multiple correlation was 0.86. However, it is important to continue with the research of atrazine sorption, to better understand the sorption mechanisms and to get even better predictions, which could be used in the assessment of their mobility.
Further research should be focused on establishing the dominant mechanisms for retaining these three pesticides in the soil. This would lead to a better understanding of their mobility in the environment, and more importantly in the groundwater. After gaining a better insight on the sorption of these pesticides, it could be easier to estimate their concentrations in groundwater, and the potential risk for population that gets drinking water from the groundwater sources.

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