ADSORPTION OF POLYCHLORINATED BIPHENYLS BY SOILS

Mihaela Preda[1], Radu Lăcătuşu[2], Dumitru Marian Motelică[1],
Nicoleta Vrînceanu[1], Veronica Tănase[1]
[1]National Research and Development Institute for Soil Science, Agrochemistry and Environment
Marasti, nr. 61, 011464, Bucharest, Romania
[2] "Al. I. Cuza" University of Iaşi, Carol I, Nr.11, 700506, Romania
E-mail: mishapreda@yahoo.com

Abstract
The behavior of polychlorinated biphenyls (PCBs) in soil is determined by several factors including adsorption, mobility and degradation. Adsorption, directly or indirectly, influences the other factors. Adsorption process is generally evaluated by using adsorption isotherms representing the relationship between the quantity of substance adsorbed per unit weight and concentration of the substance in solution at equilibrium. They allow determination of the adsorption constant, which is directly proportional to the adsorption of PCBs in soil. PCBs are very insoluble in water, so they tend to accumulate in the lipids. This is the reason why polychlorinated biphenyls are more strongly adsorbed in soils with higher organic matter content. To obtain the adsorption isotherm were used standard solutions of PCB 101with initial concentrations: 0.05, 0.1, 0.5, 1 and 2 μg/ml. The adsorption constants were in order: 3072 ml/g for chernozem, 2943 mg/l for chromic luvisol, 998 mg/l for aluviosol and 1443 mg/l for anthrosol. The values of adsorption constants depend on the organic matter and clay content.

Keywords: PCBs, adsorption, soil

1. INTRODUCTION

Soil adsorption is a major process affecting the interaction between substances and solid phase. This process is influenced primarily by the nature of the substance and by the soil characteristics. Regarding the nature of the substance, essential for the adsorption process are:

- The size of the molecule;
- Hidrophobicity;
- Spatial structure [4].

Size of organic molecules is significant for its potential for adsorption. Within a homologous series, such as PCBs, as the molecule is larger, the probability of staying in the adsorbed state is larger [2]. Also, as the molecule is larger, the contribution of Van der Waals forces on the adsorption potential is higher. Van der Waals forces are relatively weak forces resulting from electrostatic attraction between atoms and molecules. They are the weakest of the molecular interactions and they occur because, at some point, all molecules have an asymmetric electronic distribution that creates small dipoles that can induce complementary dipoles in the adjacent surface [3]. A large number of organic molecules, including PCBs are adsorbed in the soil due to these forces [1].

Hydrophobicity of the molecule, or in other words, its repulsion for water, refers to its preference to migrate in organic solvents or to accumulate on hydrophobic surfaces such as soil organic matter. PCBs are insoluble in water, soluble in organic solvents. It must be pointed out that even the organic matter from soil has the major contribution to adsorption, other soil constituents such as clay, play also an important role. The contribution is dependent on the extension of organic matter covering the clay particles. In such cases, these interactions may be stronger than those between contaminant and organic matter; thus, it was found that the PCBs adsorption is stronger in soils with high clay content and low organic carbon content than in soils with high organic carbon content.

In some cases, substitution of the molecular fragments may affect the planaritaty of the molecules. Thus, in the case of PCBs in the absence of the ortho substitution, the two phenyl rings are in the same plane. By increasing substitution at positions ortho increases congestion around the rings, which leads to their twisting. Therefore, non-ortho substituted PCBs are adsorbed in greater quantity; for example, the adsorption coefficient of 2,2'- dichlorobifenyl is five times lower than in the case of 2,4-dichlorobifenyl [8].

Adsorption process is generally evaluated by using adsorption isotherms representing the relationship between the quantity of the adsorbed substance per unit weight and concentration of the substance in solution at equilibrium. PCBs adsorption is described by Freundlich adsorption isotherm, which was first presented by Herbert Max Finley Freundlich în 1906 [5]. It can be described by the following equation :

$$\frac{x}{m} = KC^{1/n} \qquad (1)$$

where:

x/m is the ratio between the compound and the adsorbent mass;

C – the substance concentration in solution upon achieving equilibrium;

K, n – constants.

The equation is used in linear form:

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log C \qquad (2)$$

A plot of log x/m against logC should give a straight line which determine the origine ordinate, respectively the adsorption constant K. This constant is a measure of adsorption and it increases with the adsorption potential of the molecule.

2. MATERIALS AND METHODS

The adsorption experiments were realized by chosen 4 types of soils with different physical and chemical properties:

- chernozem, from Fundulea area;
- chromic luvisol, from Tâncăbeşti;
- aluviosol, sampled from Albota;
- anthrosol, from Bucharest, Ghencea area.

Data on physical and chemical characteristics of soils are presented in tables 1 and 2.

Table 1. Physical properties of soils used in adsorption isotherms experiments

Soil type	Grain size fraction (mm) %											Texture class
	Coarse sand				Fine sand				Dust	Clay		
	total	*2,0-1,0*	*1,0-0,5*	*0,5-0,2*	*total*	*0,2-0,1*	*0,1-0,05*	*0,05-0,02*	*0,02-0,002*	*<0,002*	*<0,01*	
Chromic luvisol	0,6	0,2	0,1	0,3	32,2	1	0,9	30,3	30	37,2	53,8	Loamy clay
Chernozem	0,2	0	0,1	0,1	34	0,7	1,5	31,8	29,5	36,3	50,5	Loamy clay
Aluviosol	11,3	2,1	3,5	5,7	40	5,5	3,8	30,7	25,8	22,9	35,4	Loamy clay
Anthrosol	9,7	2,5	1,9	5,3	29,9	3	1,7	25,2	27,3	33,1	46,4	Loamy clay

Table 2. The main chemical properties of soils used in adsorption isotherms experiments

Soil Type	pH	Organic carbon content (%)	Clay content (%)	Total nitrogen (%)	Mobile phosphorus (mg/kg)	Mobile potassium (mg/kg)	Percentage base saturation (%)	Cation exchange capacity (me/100g)
Chromic luvisol	6,29	2,25	55,4	0,104	61	318	90,6	29,04
Chernozem	6,27	2,69	59,4	0,145	51	318	90,3	28,08
Aluviosol	5,71	1,1	39,7	0,065	15	74	73,1	14,31
Anthrosol	7,75	1,52	49,7	0,132	90	258	112,4	38,24

It can be observed that the content of organic carbon decreases in order: chernozem, chromic luvisol, anthrosol and aluviosol. Also, as it was expected, anthrosol is slightly alkaline, chernozem and chromic luvisol have slightly acid reaction and aluviosol has a moderately acidic reaction.

Regarding to the macroelements content, except aluviosol, which has low content of nitrogen, mobile potassium and mobile phosphorus, the other soils chosen for this experiment have a high content of these elements. Also, chernozem and chromic luvisol have a high percentage of colloidal complex, which means they have a natural fertility better than aluviosol. In conclusion, selected soils have different properties and are suitable for the proposed experiments.

Known volumes of the test substance, at known concentrations in 0.01 M $CaCl_2$ are added to soil samples of known dry weight which have been pre-equilibrated in 0.01 M $CaCl_2$. Five test substance concentrations are used (0,05; 0,1; 0,5; 1 and 2μg/ml), covering preferably two orders of magnitude. The mixture is agitated for an appropriate time. The soil suspensions are then separated by centrifugation and the aqueous phase is analysed.

The PCB 101 was extracted from this phase with petroleum ether:acetone = 2:1 and determined by gas chromatography. The amount of test substance adsorbed on the soil sample is calculated as the difference between the amount of test substance initially present in solution and the amount remaining at the end of the experiment.

One blank run consisting of the system soil and $CaCl_2$ solution (without test substance) must be included, in order to check for artefacts in the analytical method and for matrix effects caused by the soil.

The adsorbed mass per unit mass of soil is plotted as a function of the equilibrium concentration of the test substance. The adsorption constant obtained give important information about the adsorption of PCB 101 on the soils used in the experiment.

3. RESULTS AND DISCUSSION

To obtain the adsorption isotherms were used PCB 101 initial concentrations: 0,05; 0,1; 0,5; 1 şi 2μg/ml. Following the presented procedure it was obtained a chromatogram which provides the concentration in solution at equilibrium. By difference results the quantity of the test substance adsorbed per unit of mass.

The adsorption isotherms (figure 1) are used for determination of the adsorption constants. These values are:

- K = 3072 ml/g – for chernozem
- K = 2943 ml/g - for chromic aluvisol
- K = 1443 ml/g - for anthrosol
- K = 998ml/g - for aluviosol

Adsorption constant is an indicator for the adsorption capacity of the soil. Thus, the higher is the constant, the stronger is the adsorption of the compound.

The adsorption constants values are very high, considering that the literature dates indicate heavy metal values between 1.52 for copper and 0.34 for lead [6] and tens or hundreds for pesticide [4].

However, data from the EPA (Environmental Protection Agency) for PCBs indicate even higher adsorption constant, around 5000 [7].

Comparing the results obtained for the soils used in the experiments it can be observed that the values of adsorption constants are directly proportional to organic carbon and clay content. Thus, chernozem and chromic luvisol have the highest contents of organic carbon and clay, so they adsorbed the highest quantity of PCB 101. Instead, aluviosol has a low content of organic carbon, so PCB 101 is poorly adsorbed by this soil.

The value of adsorption constant indicates strong adsorption of PCB 101 by the anthrosol. Since PCB compounds were used in industrial urban areas, it is possible to appear a significant pollution in these zones.

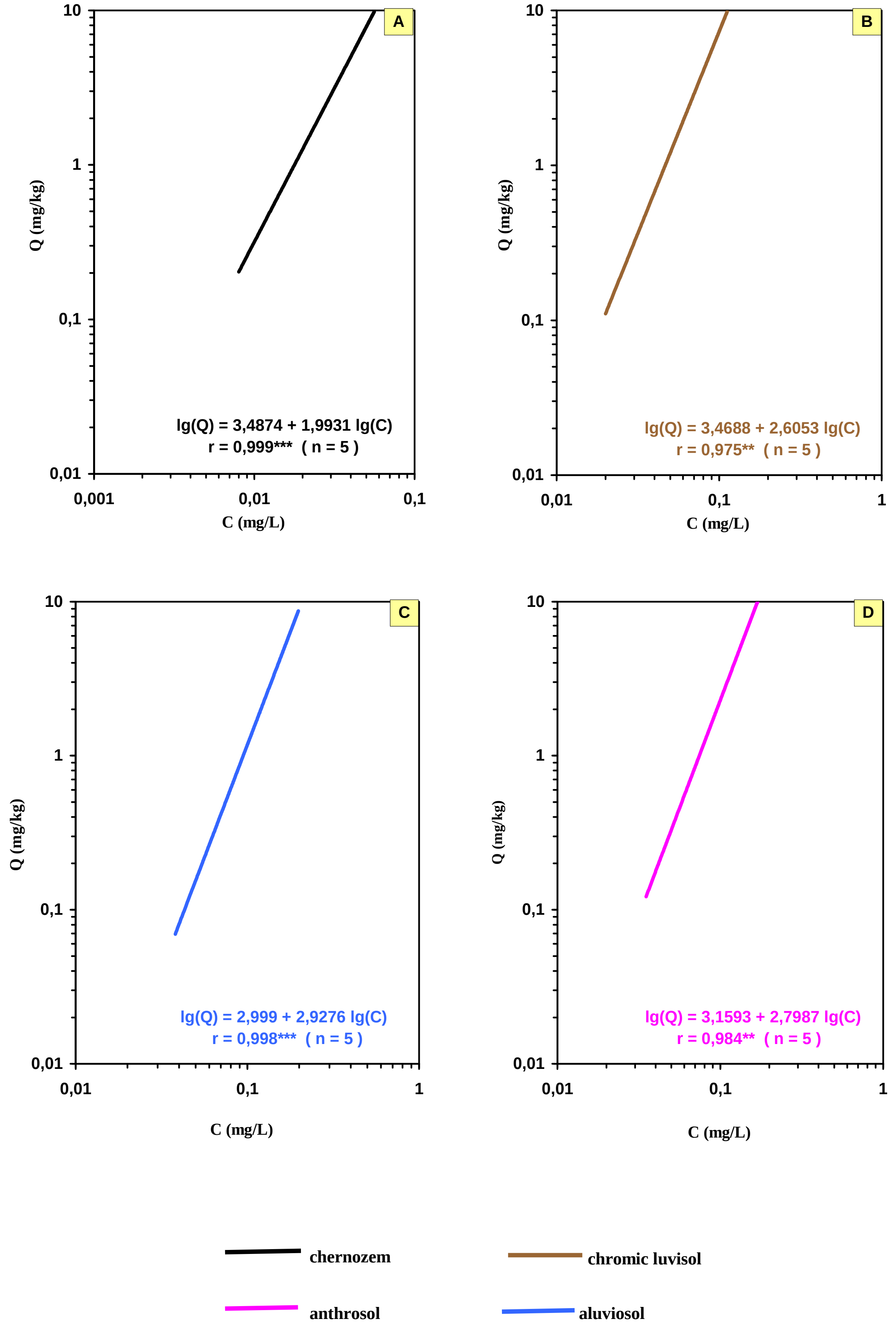

Figure 1 Adsorption isotherms for: A – chernozem, B – chromic luvisol, C – aluviosol, D - anthrosol

4. CONCLUSIONS

- PCB compounds are stongly adsorbed in soil;
- The adsorption constants values decrease in order: chernozem, chromic luvisol, anthrosol, aluviosol;
- The adsorption constant of PCB 101 are dependent by the organic matter and clay content.

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