Assessment of Pollution with Organochlorine Substances in the Accumulation Lakes on the Olt River, Using the Fugacity Model

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This aims of this paper is to studying the transfer of organochlorine substances (1, 2-dichloroethane, trichlorethylene, perchlorethylene, benzen and 1,2,4 -trichlorobenzene) in the environmental water, sediment and biota using calculation MacKay model. In order to study the transfer of organochlorine substances in the environmental compartments (water, sediment, biota), was chosen as the study area, the lakes of Zavideni (Z), Dragasani (D) and Strejesti (S) on the River Olt. In this study, sections studied are located downstream from the chemical platform Ramnicu Valcea. Zavideni section is located approx. 40 km to the paltform, Dragasani section situate approx. 20 km to the Zavideni section while the Strejesti section is located approx. 10 km to the Dragasani section. The utilization of this model has highlighted the transfer in the air as environmental component of the 1, 2 dichloroethane, trichlorethylene and benzene, are known in fact that the volatile compounds. However, based on the modelling, there is a significant transfer of the perchlorethylene and 1, 2, 4 -trichlorobenzene pollutants in biota as environmental component in amounts which may generate medium to long term by taking over risks to human health.

Keywords: organochlorine substances, MacKay model, fugacity, environmental compartments

In order to study distribution of chemicals in various environmental matrices (air, sediment and biota) was required and a qualitative description of the types of matrices, highlighting some of the most important properties of them. In this sense, there is put together *the averages model* that could be used later in the calculations. The volatile organic compounds (VOC) are considered among the most dangerous indoor pollutants because of their diffusion properties and their continuous emission from many sources, predominantly from organic compounds and chlorinated and non-chlorinated solvents. Some of the main sources of VOC associated to the indoor pollutions are as follows: human activities inside buildings using VOC based compounds, emissions from building materials containing VOC compounds and the contaminated air from outside introduced inside the buildings through ventilation processes, the pollutant concentration depending largely on the location, construction materials, and the activities that occur inside [1,2].

In the decision No. 1038/2010 on *the approval of the measures against pollution with chemicals*, the organochlorine substances: 1, 2-dichloroethane, trichlorethylene, 1, 2, 4 trichlorobenzene, benzene and perchlorethylene are included into the *List I* of the priority substances, the most dangerous chemicals. Justification for selection and classification of these substances in the environment resides in their behaviour. Above mentioned substances are not biodegradable and persist in the environment and accumulate in animal and plant tissues, thus showing, long-term risks to human health and ecosystems. As these substances progresses in the food chain, their concentration increases risks to human and ecosystem following the same trajectory. It is therefore necessary to take control of emissions of these substances, even when they are very small [3-7].

Experimental part

General data regarding the fugacity concept

One way to estimate the level of pollution with hazardous chemicals to environmental matrices (air, sediment and biota) is the MacKay model. This model can give hints conclusive for a rapid risk assessment on which to base conclusions on the preventive measures for the future studied area. Effective management requires understanding of the environment and the ability to analyse quantitative risk transfer mechanism associated health and chemical contamination. The level of contamination resulting from accidental chemical discharges or continuous was usually assessed using transfer models on environmental compartments. These models are mainly based on a single environmental compartment, such as the transfer of a contaminant in water. However, the chemicals that are released into the environment succeed through various compartments of the environment as a result of complex processes physic - chemical and biological [8-12]. One such model is the MacKay model [13-14], which uses patterned backgrounds to explore the possible behaviour of the chemical. For this purpose model generates some equations that can be validated using real environments. A somewhat different assembly equation proves to be convenient for real-world environments, but the basic principles are the same. The Mackay model of *Level I* is based on four basic components: air, water,

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sediment, soil and to, through bio-concentration factors can be added and biota. This calculation model is based on using of the fugacity of the substances and can quickly estimate the level of pollution in the environment with pollutants analysed without carrying out analytical determinations costly in terms of time and money. The fugacity describes the tendency of a chemical transition from one phase to another when they are in contact. It is identical to the concept of ideal gas partial pressure and chemical potential is related to logarithmically, so it varies linearly or non-linearly with concentration. At low partial pressures ideal conditions fugacity is equal to the partial pressure [13, 14].

Based on the concept of fugacity, one can postulate a nearly linear relationship between fugacity dependence and concentration of the chemical in each environmental compartment (eq.1):

$$C = Zf \tag{1}$$

where Z is a constant of proportionality called *fugacity capacity* with the units mol / m^{3}Pa. This equation implies that C always varies linearly with f. Nonlinearity can be adapted by consideration of Z as a function of C or f.

Fugacity (Z) for air components

The basic equation for the fugacity for a substance in the state of the vapor (eq.2):

$$F = y \times \phi \times P_T \tag{2}$$

where y is the mole fraction of chemicals and fugacity coefficient ϕ is P_T is the pressure (atmospheric) total.

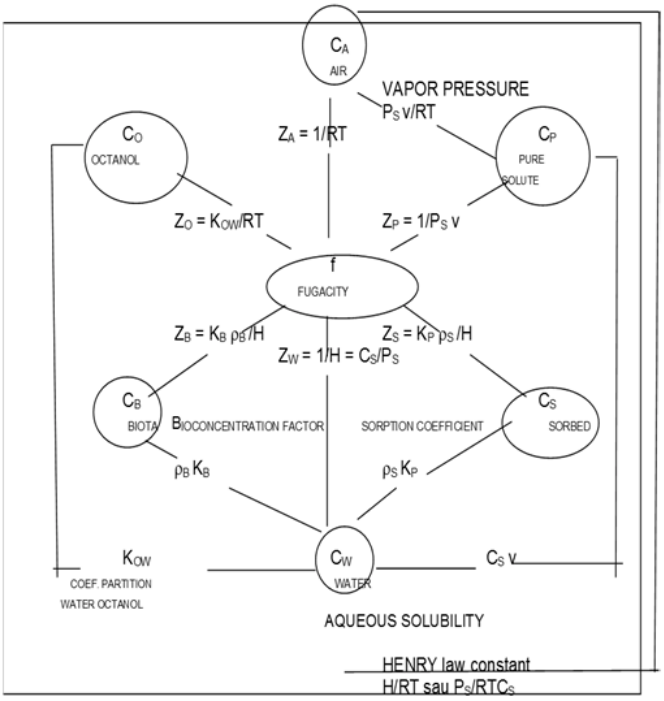


Fig. 1. Conceptual Diagram of the Fugacity Model, source [14]

If the law of gases (eq.3):

$$P_T \quad V = nRT \tag{3}$$

where n is the total number of moles of air and chemicals present, and T is the absolute temperature, chemical concentration C (solute) will be that (eq.4-6):

$$C = \frac{yP_T}{RT} = \left(\frac{1}{\phi RT}\right) f \tag{4}$$

Thus Z is $\frac{1}{\phi RT}$ or (5)

$\frac{1}{RT}$ when the $\Phi = 1$. (6)

Fugacity (Z) for water components

Fugacity equation for a compound i dissolved in water or another solvent is given in terms of mole fraction xi activity coefficient γi and reference fugacity fR based on Raoult law as (7-14):

$$f_i = x_i \gamma_i fR \tag{7}$$

$$C_i = \frac{n_i}{(V_w + V_i)} \approx \frac{n_i}{V_w} \tag{8}$$

$$V_w = n_w v_w \tag{9}$$

$$x_i = \frac{n_i}{n_i + n_w} \approx \frac{n_i}{n_w} \tag{10}$$

"I" - solute, and "w" - water

$$C_i \approx \frac{x_i}{v_w} \approx \frac{x_i}{(18 \times 10^{-6} m^3 / mol)} \tag{11}$$

$$f_i = C_i v_m \gamma_i fR \quad \text{or} \tag{12}$$

$$C_i = \frac{1}{(v_w \gamma_i fR) f_i} \tag{13}$$

$$Z_i = \frac{1}{v_w \gamma_i fR} \tag{14}$$

For a solution in water Z_W may be inferred as (eq. 15-17):

$$Z_w = \frac{1}{v_W \gamma_i P_{SL}} \tag{15}$$

$$K_{AW} = \frac{Z_A}{Z_W} = \frac{H}{RT} = \frac{P_S}{C_S RT} \tag{16}$$

$$Z_w = \frac{Z_A RT}{H} = \frac{1}{H} = \frac{C_S}{P_S} \tag{17}$$

because

$$Z_A = \frac{1}{RT},$$

C_S and P_S situation where are values for liquids and solids status.

Fugacity (Z) for the soil or sediment components

The simplest method of deduction of Z is correlating him for Z_{APA} using a dimensionless partition coefficient. This coefficient can be determined from several isothermal equations (linear, Langmuir, Freundlich). In most cases the data may be represented, at least at low concentrations of the linear expression (18):

$$C_s = K_{SW} C_W \tag{18}$$

where C_S is the concentration of adsorbed (mol / m^3 of sorbent), C_W is the water content. The nonlinear equation K_{SW} is a function of concentration. K_{SW} is a dimensionless partition coefficient.

As is known concentrations to adsorbed substances are usually expressed as the amount of solute (sorbent) adsorbed per unit mass. K_p is defined by units of L / kg and

$$K_{SW} = \rho_S K_p \tag{19}$$

$$K_{SW} = \frac{Z_S}{Z_W} \tag{20}$$

$$Z_S = Z_W K_{SW} = \frac{\rho_S K_P}{H} \tag{21}$$

K_{SW} is related to the density of sorbent ρS in l g / L (or g / cm ^{3} or mg / m ^{3}) as follows (19-22):

Fugacity (Z) for biotic phase (fish)

$$Z_B = \frac{\rho_B K_{BW}}{H} \tag{22}$$

ρB equals the numerical density of water and can be ignored. It should be recalled, however, in cases where K_{BW} is defined on a dry weight basis (not wet mass), or the concentration in specific tissues such as fat. In these cases the density is calculated as the mass of biota / dry tissue per unit volume of wet biota.

If you develop procedures for estimating the *Z* values for each environmental situation again, then the equilibrium concentrations can be derived using f as a common criterion of balance.

The studied area

In order to study the transfer of organochlorine substances in the environmental compartments (air, sediment, biota), there was chosen as the study area, the lakes of Zavideni (Z), Dragasani (D) and Strejesti (S) on the River Olt, June- August, 2015. In this study, sections studied are located downstream from the chemical platform Ramnicu Valcea. Zavideni section is located approx. 40 km to the paltform, Dragasani section situate approx. 20 km to the Zavideni section while the Strejesti section is located approx. 10 km to the Dragasani section (fig.2).

Methods of analysis

Determination of organochlorine compounds in water samples

The contents of organochloride compounds were determined by gas chromatography coupled with mass spectrometry (GS-MS).

A sample was taken and discarded glass bottle filled with enough water so that there was no residual sample volume of 200 mL. Add to the sample the extraction solvent (pentane), close and vigorously mix using a magnetic shaker or a mechanical shaker for 5 min to ensure that the extracting has been finely dispersed in the sample in order to obtain a reproducible recovery.

The sample volume was one litter. A volume of 30 mL of extraction solvent (heptane) was added and the solution was stirred for at least 10 min and transferred to a separating funnel with adequate capacity and standing to allow phase separation.

Organochlorine compounds determination in sediment samples

For samples that contain volatile components no any pre-treatment was necessary. Amount of 30 g of wet soil was weighted in a glass iodometrical beaker. 50 mL of methanol were added and stirred 30 min., and then a volume of 50 mL pentane was added and stirred for another 30 min. The liquid phase was filtered through a filter paper with medium porosity and was introduced into a 500 mL separator funnel together with 250 mL distilled water. The soil was washed with 10 mL pentane. The funnel was stirred 5 min allowing separation and discard the organic phase. The organic layer was passed through a filter with anhydrous Na_2SO_4 into a hermetic closed vessel. The

Table 1

DEFINING THE FUGACITY CAPACITIES, source [13]

Compartment	Definition Z (mol/m^3 Pa)
Air	1/RT ; R=8,314 Pa m^3/mol K ; T=Temp (K)
Water	1/H or C^S/P^S C^S = aqueous solubility (mol/m^3) P^S = vapor pressure (Pa) H = Henry law constant (Pa m^3/mol)
Solid sorbent (e.g.: soil, sediment, particulate)	$K_P\ \rho_S/H$ K_P= partition coefficient (L/kg) ρ_S = density (kg/L)
Biota	$K_B\ \rho_B/H$ K_B= bioconcentration factor (L/kg) ρ_B = density (kg/L)
Pure solute	$1/P^S$ v ; v= the molar volume of solute (m^3/mol)

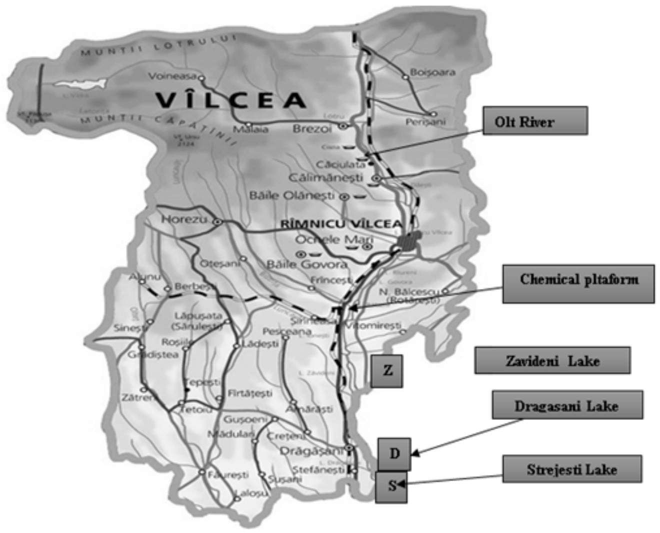
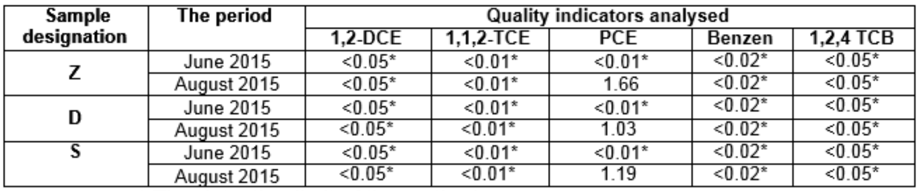


Fig. 2. Localization points, Vilcea County

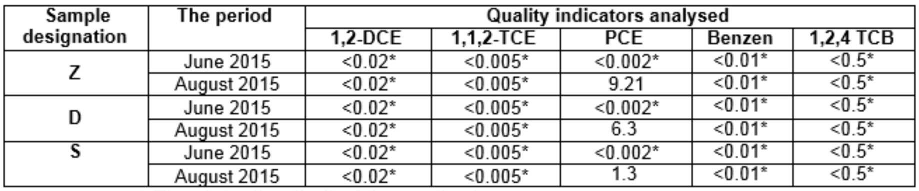
Table 2
THE CONTENT OF ORGANOCHLORINE COMPOUNDS IN WATER OF THE ZAVIDENI (Z), DRAGASANI (D) AND STREJESTI (S) ACCUMULATION LAKES (µg/L)



Sample designation	The period	Quality indicators analysed				
		1,2-DCE	1,1,2-TCE	PCE	Benzen	1,2,4 TCB
Z	June 2015	<0.05*	<0.01*	<0.01*	<0.02*	<0.05*
	August 2015	<0.05*	<0.01*	1.66	<0.02*	<0.05*
D	June 2015	<0.05*	<0.01*	<0.01*	<0.02*	<0.05*
	August 2015	<0.05*	<0.01*	1.03	<0.02*	<0.05*
S	June 2015	<0.05*	<0.01*	<0.01*	<0.02*	<0.05*
	August 2015	<0.05*	<0.01*	1.19	<0.02*	<0.05*

* The detection limit of the method

Table 3
THE CONTENT OF ORGANOCHLORINE COMPOUNDS IN WATER OF THE ZAVIDENI (Z), DRAGASANI (D) AND STREJESTI (S) ACCUMULATION LAKES, (mg/kg D.W.)



Sample designation	The period	Quality indicators analysed				
		1,2-DCE	1,1,2-TCE	PCE	Benzen	1,2,4 TCB
Z	June 2015	<0.02*	<0.005*	<0.002*	<0.01*	<0.5*
	August 2015	<0.02*	<0.005*	9.21	<0.01*	<0.5*
D	June 2015	<0.02*	<0.005*	<0.002*	<0.01*	<0.5*
	August 2015	<0.02*	<0.005*	6.3	<0.01*	<0.5*
S	June 2015	<0.02*	<0.005*	<0.002*	<0.01*	<0.5*
	August 2015	<0.02*	<0.005*	1.3	<0.01*	<0.5*

* The detection limit of the method

funnel and the layer with Na_2SO_4 was rinsed with 5 mL of pentane and added to the organic layer.

Results and discussions

The mathematical model was developed for analysis of organochlorine substances (1, 2-dichloroethane, trichloroethylene, perchlorethylene, benzene and 1, 2, 4-trichlorobenzene). In order to compare the results of the modelling, we used the experimental values presented in table 2 and 3. The values of the modelling are presented in figure 3 - 7. Starting from the measured values for these pollutants in environmental factor *water* was achieved transfer of these hazardous pollutants modelling environments *sediment*, *biota* and *air*. To validate this model were considered values obtained for *sediment*, as these types of evidence have been worked. The following are presented point for each sampling point was studied, the results and conclusions highlighted. Biota are approximate quantity of 1 part / m^3 = 7.83 x 1 million 107/106 = 78.3.

Transfer of 1, 2-dichloroethane

The values obtained for the environmental component *sediment* in the modelling transfer of 1, 2-dichloroethane in water was very similar to those determined experimentally: ex. 0.013 mg / kg to <0.05 mg / kg (the detection limit of the method). The modelled values is clearly observed tendency of this pollutant transfer in the environmental component *air* (3.67 ng / m^3), but is also observed that a large amount is taken from the environmental component *biota*, 0.068 mg / kg.

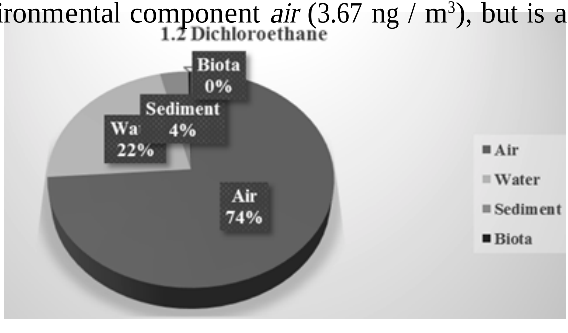


Fig. 3. The transfer of 1, 2 - dichloroethane in the environmental components: air, water, sediment and biota

Transfer of trichloroethylene

The values obtained for the environmental component sediment in the modelling of water the transfer trichloroethylene are slightly higher than the experimentally determined value of 0.024 mg / kg compared to <0.005 mg / kg (limit of detection of the method).The modelled values is a tendency for the transfer of this pollutant in the environmental component *air* (9.98 ng / m^3), but is also observed that a large amount is taken from the component *biota*, 0.126 mg / kg, which has in conjunction with the degree of toxicity of this compound and should be an alarm signal about the level of environmental pollution in the area.

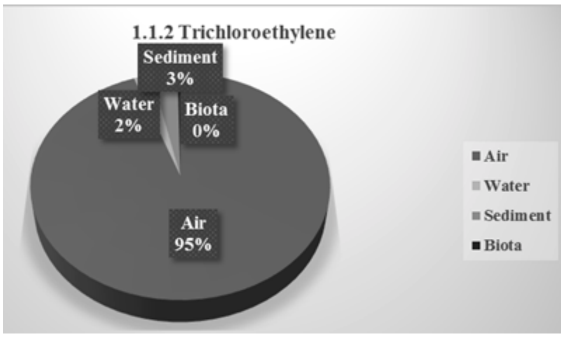


Fig. 4. The transfer of trichloroethylene in the environmental components: air, water, sediment and biota

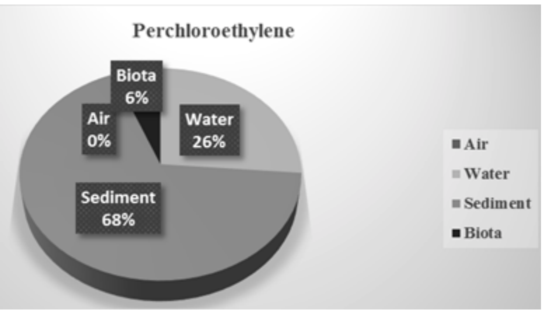


Fig. 5. The transfer of perchlorethylene in the environmental components: air, water, sediment and biota

Transfer of perchlorethylene

In campaign from June 2015, the values obtained for the environmental *sediment* in the modelling transfer of perchlorethylene in water, are slightly higher than those determined experimentally: 0.043 mg / kg compared to <0.002 mg / kg (limit of detection method). In campaign from August 2015 for values obtained for the environmental component *sediment* in modelling the transfer of perchlorethylene in water, are close to the experimentally determined as follows: Zavideni Lake (Z), 7.13 mg / kg to 9.21 mg / kg; Dragasani Lake (D), 4.4 mg / kg to 6.3 mg / kg; Strejesti Lake (S), 11 mg / kg compared to 1.3 mg / kg. The modelled values is observed that a large amount is taken over by the environmental component *biota*, 0.225 mg / kg for the campaign from May and 37.3 mg / kg (Zavideni Lake), 23.1 mg / kg (Dragasani Lake) and 26.7 mg / kg (Strejesti Lake) for the campaign from August, which corroborated the with the degree of toxicity of this compound and should be an alarm signal about the level of environmental pollution in the area.

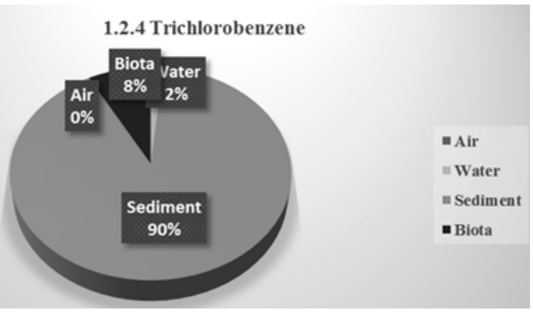


Fig. 6. The transfer of 1, 2, 4- trichlorobenzene in the environmental components: air, water, sediment and biota

Transfer of 1, 2, 4 - trichlorobenzene

The values obtained for the environmental component *sediment* in the modelling transfer of 1, 2, 4-trichlorobenzene in water are close to those determined experimentally: 1.879 mg/kg mg/kg to the value of <0.5 mg/kg (the detection limit of the method). The modelled values is observed that a large amount is taken over by the environmental component *biota*, 9.824 mg / kg, which corroborated the with the degree of toxicity of this compound.

Transfer of benzene

The values obtained for the environmental component *sediment* in the modelling transfer of benzene in water was similar to those determined experimentally: 0.023 mg / kg to <0.01 mg / kg (the detection limit of the method). The modelled values is clearly observed tendency of this pollutant transfer in the environmental component *air* (5.281 ng / m^3), but is also observed that a large amount is taken from the environmental component *biota*, 0.121 mg / kg.

Conclusions

The model based on fugacity or the MacKay model generated realistic values to environmental compartments of interest: air, sediment and biota. Modelled values obtained for the environmental component "sediment" are comparable and compatible with the values obtained by analytical measurements. The modeling has highlighted clear trend a transfer of the volatile compounds: 1,2 dichloroethane, trichloroethylene and benzene into the environmental component *air*. However, based on modeling, there is a significant transfer of pollutants as perchloroethylene and 1, 2, 4 - trichlorobenzene into the environmental component *biota* in amounts which may generate medium to long term by taking over risks to human health in the food chain.

Using the MacKay model, that imply a small number analytical measurements, the authors have determined the pollution footprint, having conclusive indications for the rapid risk assessment to underpin the actions and preventive measures.

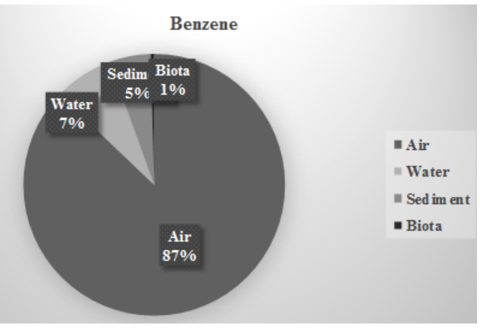


Fig. 7. The transfer of benzene in the environmental components: air, water, sediment and biota

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