RESEARCH ON RISK ASSESSMENT OF CONTAMINATED SOILS

Comisu Oana Mădălina [1] Pricop Iulian [2]
[1;2]"Gh. Asachi" Technical University of Iasi, Blvd, D. Mangeron 67, 700050 Iasi, Romania
daria_1804@yahoo.com

Abstract
The work includes a study presents an analysis of the soil model involving both physical parameters and chemical environment and dispersion of chemical contaminants in soil.
Data entry computer program and estimate the chemical behavior of contaminants in soil are: chemical name, molar mass, temperature (°C), solubility, water, and vapor pressure, partition coefficient organic carbon – water (K_{oc}), *partition coefficient octanol – water* $(\log K_{ow})$, *coefficient of the partition mineral matter – water* (K_{mv}), *degradation half-life in soil, surface and depth soil, diffusion in the vertical distance from the middle of the surface soil layer, fractional volume of air, water and roots, leaching rate, thickness of air separation, molecular pore diffusion, air and pore water density of water, organic matter, minerals and roots, the mass fraction of organic carbon in dry soil and organic matter fraction of lipids in roots, the quantities of chemicals applied.*
In the examined model, the roots of plants are included as a fractional volume of soil and are considered to be in equilibrium with other phases of the soil.
As a case study presented an analysis of an aria planted with carrots which was polluted with benzene.
Using the program, analyzing the results and effects, offers assistance in a timely and correct the imbalances of any soil, caused by the presence of chemicals.

Keywords: soil, chemical, dispersion, model

1. INTRODUCTION

The study refers to a model of soil analysis. It involves both physical and chemical environmental parameters of dispersion and of chemical contaminants in soil.
With this model analysis of soil can study the behavior of chemicals in the soil root layer. It allows the realization of simulations, which may change, both environmental properties of dispersion and chemical properties taken in the analysis [1], .
A specific model is that the root system of plants is considered as an integral part of soil composition [2].

2. MODEL DESCRIPTION

This analysis model allows the study to determine the potential reaction exerted on the soil of different chemicals. Chemical partition coefficients of air, water, organic matter and mineral part in a single layer of soil are calculated as a function of physico-chemical properties [3], [4]. The roots are included as a fractional volume of soil and are considered to be in equilibrium with other phases of the soil. By its nature, the model is not dynamic, but is steady state condition [5], [6].
The input data and estimate calculation program are:
a. Chemical properties: chemical name, molar mass, temperature (°C), solubility, water, and vapour pressure, partition coefficient organic carbon – water (K_{oc}), partition coefficient octanol – water $(\log K_{ow})$, coefficient of the partition part matter – water (K_{mv}), degradation half-life in soil [7],[8].
b. The environmental properties of dispersion: surface and depth soil, diffusion in the vertical distance from the middle of the surface soil layer, fractional volume of air, water and roots, leaching rate, thickness of air separation, molecular pore diffusion, air and pore water density of water, organic matter, minerals and roots, the mass fraction of organic carbon in dry soil and organic matter fraction of lipids in roots, the quantities of chemicals applied [9],[10].
The output data includes the following elements: all input data, soil characteristics, Z values for all phases, the quantities and

concentrations for all phases, D and flow values for all processes, a summary chart.

Some comments on the environmental properties of dispersion are listed below:

$$f_{om} = {f_{oc}}/{f_{ocm}} \quad (1)$$

$$f_{mm} = 1 - f_{om} = 1 - \left({f_{oc}}/{f_{ocm}}\right) \quad (2)$$

where: f_{om} - organic matter content, f_{mm} - mineral matter content, f_{ocm} - fractional mass of organic carbon in the mineral part, f_{oc} - organic carbon in dry soil.

The fractional volume of the system is:

$$V_{f\ system} = V_{f\ sol} + V_{f\ root\ layer}\ (m^3) \quad (3)$$

$$V_{f\ system} = 1\ (m^3) \quad (4)$$

In calculations, the 5 elements of soil composition note: air (1), water (2), organic matter (3), mineral matter (4), roots (5).

For the following elements $i = 1 \div 4$, we have:

$$M_{(i)} = V_{(i)} \times \rho_{(i)} \quad (5)$$

$$M_{soil} = \sum M_{(i)} \quad (6)$$

where: $i = 1 \div 4$ M, $M_{(i)}$ – mass of each element in soil composition (kg).

$$M_{(5)} = V_{(5)} \times \rho_{(5)} \quad (7)$$

$$M_{system} = M_{soil} \times M_{(5)} \quad (8)$$

$$M_{dry\ soil} = M_{(3)} + M_{(4)} \quad (9)$$

where: $M_{(3)}$ – mass of soil organic matter (kg), $M_{(4)}$ – mineral matter of soil mass (kg).

The total number of moles of chemical substance in the soil:

$$m_{s.c.} = m(1) + m(2) + m(3) + m(4) \quad (10)$$

where: m – number of moles of each element of the chemical composition.

The total concentration of chemical substance in the soil (moles/m^3).

$$CT = \frac{M_{s.c.}}{V_{total\ soil}} \quad (11)$$

where: CT – total concentration of chemical substance; $M_{s.c.}$ – number of moles of chemical substance that are in the soil (moles); $V_{total\ soil}$ – total volume of soil (m^3).

The total amount of soil (g):

$$G_{total\ soil} = G_{(air\ pores)} + G_{(water\ pores)} + G_{(mineral\ part)} + G_{(org.\ mat.)} \quad (12)$$

where: G – the weight of each element in soil composition, in grams, without taking into account the weight of root layer.

Calculation of percentage content of soil is calculated with:

$$C\%_{total\ soil} = C\%_{(1)} + C\%_{(2)} + C\%_{(3)} + C\%_{(4)} \quad (13)$$

$$C\%_{system} = C\%_{total\ soil} + C\%_{root\ layer} = 100\% \quad (14)$$

where: $C\%$ - concentration as a percentage of each element of the analyzed system.

Note that the roots is taken into account, only in the total environmental system analysis, although it is seen as a component of the soil.

This model is useful for examining the dispersion of various chemicals in the soil. The importance of soil characteristics in the dispersion of chemicals can be examined by input data modification[11].

3. PROGRAM USAGE

To start simulation, input data must be entered, from top to bottom, starting with the ID simulation (Figure 1). When the entry form is completed, there is a checkmark next to the mark corresponding to the "Main Program

Screen". When all four input buttons are signs of tick becomes available central button "Compute" and pressing the button will perform the simulation calculations. Then, "Model Output" can be viewed.
It can return to any of the forms of entry at any time to make changes to the current simulation because all existing entries are saved. To view entries, select the "Chemical Parameters" or the "Environmental Parameters" under "Model Output". After reselecting any form of entry, the central button "Compute" must be pressed again to recalculate the model with the revised values.
Surfing can be done either with the mouse or by using the Tab key. The cancel button is turned way by removing the current shape on the screen and resetting each field of the form the last set of accepted values. For each form of the program, the Enter key is equivalent to the OK button and the Escape key to the Cancel button.
The "Print Simulation" button allows a copy of the input parameters, output tables with elements of the program and/or the simulation diagram.

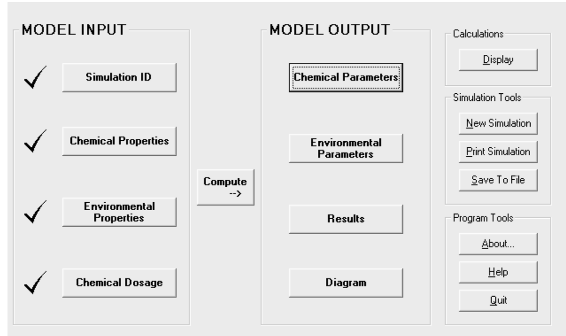

Figure 1. The opening window "Program" of the pattern analysis of the soil

The "Save to File" option saves all the information from the current simulation as a comma separated value file (CSV) with no numeric formatting (ie, no rounding-off). Selecting "Save to File" allows the disk, directory and file name selection [12].

4. OBTAINED RESULTS

An area planted with carrots which was polluted with benzene was analyzed. Input data used in the program are presented in Tables 1÷5, and the results in Tables 6÷10 and in Figure 2.

Table 1. Chemical substance parameters: Benzene

Parameters	Values	Unit	Observations
Molar mass	78,1	g/mole	
Data Temperature	25	^{o}C	298,15 Kelvin
Water Solubility	1780	g/m^3	22,8 moles/m^3
Vapour Pressure	12700	Pa	
Henry's Constant	557	$Pa.m^3/mole$	
Vapour Density	400	g/m^3	
$\log k_{ow}$	2,13	Dimensionless	
Degradation Half-Life in Soil	1200	hour	50 days
Degradation Rate Constant in Soil	$5{,}78 \times 10^{-4}$	hour	0,0139/day

Table 2. Partition coefficients

Partition coefficients	Dimension (L/kg)
Air – water	0,225
Octanol – water	135
Organic carbon – water	83,00
Organic Matter – water	46,50
Mineral Matter – water	1,00 - 2,50

Table 3. Environmental parameters of dispersion

Physical soil parameters	Dimension	Unit	Observations
Area	10000	m^2	
Depth	0,100	m	
Diffusion Path Length	0,05	m	
Leaching Rate	5	mm/day	
Air Boundary Layer Thickness	$4,75 \times 10^{-3}$	m	
Molecular Diffusivity in Air	0,430	m^2/day	0,0498 cm^2/s
Molecular Diffusivity in Water	$4,30 \times 10^{-5}$	m^2/day	$4,98 \times 10^{-6}$ cm^2/s

Table 4. Mass fractionation in dry soil:

Organic carbon	0,0200
Organic Matter	0,0357
Mineral Matter	0,9640
Mass Fraction of OC in Organic Matter	0,560
Volume Fraction of Roots	0,0100
Fraction of Lipid in Root	0,0250

Table 5. Physical soil properties („Z" values)

Phase	Density (kg/m^3)	Volume (m^3)	Fractional volume	Mass (kg)
Pore Air	1,19	220	0,220	261
Pore Water	1000	310	0,310	$3,10 \times 10^5$
Organic Matter	1000	39,0	0,039	38983
Mineral Matter	2500	421	0,421	$1,05 \times 10^6$
Total dry soil	-	-	-	$1,09 \times 10^6$
Total organic carbon	-	-	-	21831
Bulk soil	1416	990	0,990	$1,40 \times 10^6$
Roots	1000	10,0	-	10000

Table 6. Chemical substance data.

Chemical Dosage	1,00 kg/ha	
Mass of Chemical	1000g	
Concentration in Bulk Soil	1,000g/m^3	0,706 µg/g
Concentration (amount/mass of dry soil)	-	0,907 µg/g
Pressure exerted by chemical in soil (Fugacity soil)	2,19 Pa	

Table 7. Quantities and concentrations for all soil phases.

Soil phase	"Z" values ($mole/m^3Pa$)	Quantity (mole)	Quantity (g)	Conc. (%)	Conc. ($mole/m^3$)	Conc. (g/m^3)	Conc. (µg/g)
Pore Air	$4,03 \times 10^{-4}$	0,194	15,2	1,52	$8,84 \times 10^{-4}$	0,069	58,2
Pore Water	$1,79 \times 10^{-3}$	1,22	95,2	9,52	$3,93 \times 10^{-3}$	0,307	0,307
Organic Matter	0,0834	7,12	556	55,60	0,183	14,3	14,3
Mineral Matter	$4,49 \times 10^{-3}$	4,14	323	32,30	$9,83 \times 10^{-3}$	0,767	0,307
Bulk Soil	-	12,7	990	99,00	0,0128	1,000	0,706
Roots	$6,05 \times 10^{-3}$	0,133	10,4	1,04	0,0133	1,04	1,04
System Totals	-	12,8	1000	100,0			

Table 8. Loss and transfer processes. "D" values

Diffusions	"D" values (mole/Pa.h)
Air Diffusion	0,0331
Water Diffusion	$4,62 \times 10^{-5}$
Air Boundary Layer	15,2

Table 9. Soil processes, "D" values, and their flows

Processes	"D" values (mole/Pa.h)	Flow (mol/h)	Flow (g/h)	Flow (μg/day)	Flow (%)
Volatilization	0,0331	0,0724	5,65	1,36 x 10^{8}	82,3
Leaching	3,74 x 10^{-3}	8,19 x 10^{-3}	0,64	1,53 x 10^{7}	9,31
Reaction	3,38 x 10^{-3}	7,40 x 10^{-3}	0,578	1,39 x 10^{7}	8,41
Overall	0,0402	0,0880	6,87	1,65 x 10^{8}	100

Table 10. Half-life time and the persistence of benzene in soil

Processes	Half-life Time		Persistence Time of benzene in soil	
	hour	day	hour	days
Volatilization	123	5,11	177	7,37
Leaching	1084	45,2	1564	65,2
Reaction	1200	50,0	1731	72,1
Overall	101	4,2	146	6,06

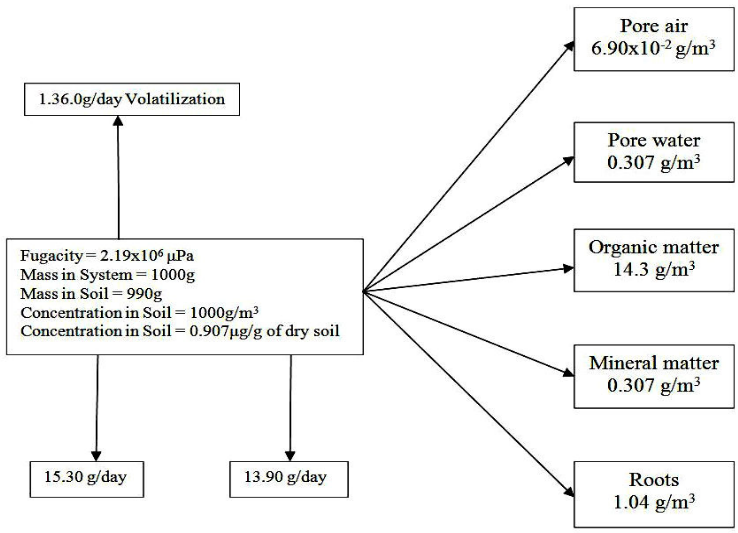

Figure 2. The obtained summary diagram

The study covered and determine the influence of environmental characteristics of dispersion (in this case soil) on the reaction of benzene. Were amended to input data on environmental characteristics of dispersion. The remaining steps of the model remained unchanged.
Research has produced the following results:
Decrease the temperature from 25°C to 16°C had the following effects: reducing the amount of contaminant mass of dry soil, reducing pressure chemical (benzene) exerted on the soil, reducing the volatilization of the chemical process, increase the half-life and the period of persistence in the soil contaminants, remaining constant only during the reaction, since this is the same chemical.
Change the depth to which conducted the analysis, the vertical diffusion and the amount of water leachate revealed the following observations: as depth increases, and reduce the amount of water leachate, leachate concentration diminishes, the pressure exerted on the soil contaminant decreases processes of diffusion and transfer variations bear comparable periods of half-life in soil processes, increase significantly, as the periods of persistence in soil of chemical, in all examples where the chemical is the same reaction time is constant.
Also change the input data partition coefficient octanol-water log K_{ow}, bringing significant change analysis results. To understand the importance of the dimensionless coefficient can

be defined as the ratio of steady state of a substance dissolved in a two-phase system, consisting of octanol-water. Otherwise defined, one can say that is a factor of solubility of the chemical analysis, which was consistent with the requirements of environmental analysis and can range between -3 and 12.

Change the value of this coefficient from 6.19 to 9.90, highlighted the following: the concentration of benzene, both in the liquid phase and solid phase of low pressure chemical on the soil was low but has doubled the concentration of benzene in the roots, loss and transfer processes were intensified.

5. CONCLUSIONS

The model of soil gives a very simple assessment of a chemical reaction in the soil for each of its characteristics and cultivated plants.

Chemical separation of phases air, water, organic matter and minerals in the soil layer is done through their physico-chemical properties. The roots of plants are included as a fractional volume of soil and are considered to be in equilibrium with other phases of the soil.

The analysis model allows simulation of different states of dispersion medium (soil) in the presence of chemicals, in various concentrations and forms and their effects on soil balance (here is included and roots present in soil).

Using the program, analyzing the results and effects, offers assistance in a timely and correct the imbalances of any soil, caused by the presence of chemicals.

6. REFERENCE

1. Mackay, D, Shiu, W.Y., Ma, K.C. 2000. *Physical-chemical Properties and Environmental Fate and degradation Handbook*. CRCnetBASE 2000, Chapman & Hall CRCnetBASE, CRC Press LLC, Boca Raton, FL. (CD-ROM).
2. Conway, R.A., Ed.,*Environmental Risk Analysis for Chemicals*, Van Nostrand Reinhold, 1981.
3. McCall, P.J., Laskowski, D.A., Swann, R.L., and Dishburger, H.J., *Estimation of environmental, partitioning in model ecosystems,* Residue Rev., 1983.
4. Association of Official Analytical Chemists, *Test Protocols for Environmental Fate and Movement of Toxics*, Arlington, VA, 1981.
5. *OECD Test Guidelines for the Testing of Chemicals*, (8000-TS-978-1051), ISBN 92-64-1221-4, OECD Publications Office, Paris, France.
6. U.S. EPA. 1996. *Soil Screening Guidance: Technical Background Document.* Office of Emergency and Remedial Response, Washington, DC. EPA/540/R95/128.
7. Chiou, C.T., Schmedding, D.W., and Manes, M., *Partitioning of organic compound in octanol-water systems*, Environ. Sci. Technol., 16, 4, 1982.
8. Will, M.E. and G.W. Suter II. 1994. *Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Terrestrial Plants, 1994 Revision.* ES/ER/TM-8/R1. Prepared for the U.S. Department of Energy by the Environmental Sciences Division of Oak Ridge National Laboratory.
9. Mackay, D., Stiver, W. (1991), *Predictability and Environmnetal Chemistry*, Chapter 8 in *Environmental Chemistry of Herbicides, Volume II,* Grover, R., and Cessna, A.J. (Eds). CRC Press, Boca Raton, FL.pp 281-297
10. Mackay, D., *Fugacity revisited,* Environ. Sci. Technol., 16, 654A, 1982.
11. Van Wijnen, J.H., P. Clausing, and B. Brunekreef. 1990. Estimated soil ingestion by children. *Environ Research* 51: 47 - 162.
12. http://www.trentu.ca/cemc