Movement of pesticides in tropical soils
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Pesticides can move through soil but can also volatilize, can be adsorbed by soil particles (clay fraction) or organic matter, can decompose itself being less effective, can be photodegradated, can be adsorbed or broken by microorganisms and can also be converted in other compounds. Several environmental factors can affect the compounds, such as pressure and temperature. This academic review presents movement of solutes and pesticides in soils considering only the adsorption by soil. Comprehension of pesticides behavior in soils is very important to estimate its effectiveness as well as its potential for groundwater contamination.

Several water quality models have been proposed to help such understanding. Besides that, a mathematical treatment can be used to solve the governing equations under different initial and boundary conditions. A good example is the Groundwater Screening Index (Bishop, 1986):

$$GSI = LN\left[\frac{St_{1/2}}{Kow}\right]$$

Where S is the solubility (ppm), $t_{1/2}$ is the chemical half life (time in days for the product to reach half of its concentration), and Kow is the octanol/water partitioning coefficient, relating the fraction of pesticides that can be adsorbed to octanol in relation to that adsorbed to water. Compounds more adsorbed to octanol are known as lipophilic while the opposite is hydrophilic or aqueous. Solubility, chemical half life and Kow values for some compounds are presented at table 1.

Table 1: Water solubility of selected compounds

Compound	Water solubility(ppm)	t1/2 (days)	Log(Kow)
DDT	0.003	3850	6.2
Simazine	0.3	75	4.8
Parathion	24	2	3.8
Atrazine	32	60	2.8
Carbofuran	320	40	2.3
Aldicarb	6000	70	1.6

For example, for aldicarb the GSI can be calculated as:

$$GSI = LN\left[\frac{(6000)(70)}{Log^{-1}(1.6)}\right] \qquad GSI = 9.4$$

For comparison purposes,

GSI < 1 : unlikely contamination
1 < GSI < 3 : possible contamination but not significant groundwater contaminant (ex: atrazine)
GSI > 3: probable contamination
GSI > 5: contaminant should be treated with special consideration

Mass transport (convective transport) of pesticides (Jm)

$$J_m = qC$$

where C is concentration and q is soil flux (Darcy´s velocity): $q = -k\frac{dH}{dx}$

H is the total potential (hidraulic or matrix potential + gravitational) and x is the distance

Difusion transport (Jd)

$$J_d = -\theta D_m \frac{\partial C}{\partial x}$$

θ is the volumetric soil water content, D_m is the molecular diffusion coefficient.

$$D_m = D_o \tau$$

where τ is the tortuosity factor (0,3 a 0,7)

Dispersion Transport (Jh)

$J_h = -\theta D_h \frac{\partial C}{\partial x}$ where Dh is the mechanical dispersion coefficient.

$D_h = \lambda V^n$ where λ is the dispersivity and n is an empirical coefficient equal to approximately 1.0 and v is the real velocity of water in soil

$$v = \frac{q}{\theta}$$

The dispersivity (λ) is larger on undisturbed soils than in disturbed soils.

Given the similarity between D_h and D_m, the Hydrodynamic dispersion coefficient was created (D), being

$$D = D_m + D_h$$

Total Transport (J)

$$J = qc - \theta D \frac{\partial C}{\partial x} \qquad \text{Eqn. 1}$$

Continuity equation or mass conservation equation

$$\frac{\partial J}{\partial x} = -\frac{\partial C_t}{\partial t} \qquad \text{Eqn 2}$$

Ct = water dissolved solute + solute present in solid particles

This equation states that any variation of transported solutes (J) from one point to another (for example from entrance to exit) will be a result of accumulation or depletion of concentration (C) per unity of time.

Total concentration of pesticide in soil

$$Ct = \theta C + \rho S$$

where ρ is the soil bulk density (g solids/cm3) and S is the solute fraction adsorbed to solids (grams of solute/grams of solids). We are not considering pesticides adsorbed to microorganisms

Substituting this equation into equation 2,

$$\frac{\partial J}{\partial x} = -\frac{\partial(\theta C + \rho S)}{\partial t} \qquad \text{Eqn 3}$$

Also derivative of equation 1 in relation to x,

$$\frac{\partial J}{\partial x} = -\frac{\partial}{\partial x}\left[\theta D\frac{\partial C}{\partial x} - qC\right] \qquad \text{Eqn 4}$$

Equations 3 and 4 are the same,

$$-\frac{\partial(\theta C + \rho S)}{\partial t} = -\frac{\partial}{\partial x}\left[\theta D\frac{\partial C}{\partial x} - qC\right]$$

$$\frac{\partial(\theta C + \rho S)}{\partial t} = \frac{\partial}{\partial x}\left[\theta D\frac{\partial C}{\partial x} - qC\right]$$

$$\frac{\partial(\theta C)}{\partial t} + \frac{\partial(\rho S)}{\partial t} = \frac{\partial}{\partial x}\left[\theta D\frac{\partial C}{\partial x}\right] - \frac{\partial(qC)}{\partial x}$$

$$C\frac{\partial \theta}{\partial t} + \theta\frac{\partial C}{\partial t} + \rho\frac{\partial S}{\partial t} + S\frac{\partial \rho}{\partial t} = \theta D\frac{\partial}{\partial x}\frac{\partial C}{\partial x} + \theta\frac{\partial D}{\partial x}\frac{\partial C}{\partial x} + D\frac{\partial \theta}{\partial x}\frac{\partial C}{\partial x} - q\frac{\partial C}{\partial x} - C\frac{\partial q}{\partial x}$$

Considering steady state flux with no spatial variability, θ, D, and q don´t vary with x neither with t. Considering also that S doesn´t vary with x,

$$\theta\frac{\partial C}{\partial t}+\rho\frac{\partial S}{\partial t}=\theta D\frac{\partial}{\partial x}\frac{\partial C}{\partial x}-q\frac{\partial C}{\partial x}$$

Dividing all terms by θ

$$\frac{\partial C}{\partial t}+\frac{\rho}{\theta}\frac{\partial S}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-\frac{q}{\theta}\frac{\partial C}{\partial x}$$

Since $\frac{q}{\theta}=v$ (pore water velocity)

$$\frac{\partial C}{\partial t}+\frac{\rho}{\theta}\frac{\partial S}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}$$

Considering a linear isotherm ($S = K_dC$) ISOTHERM?

$$\frac{\partial C}{\partial t}+\frac{\rho}{\theta}\frac{\partial K_d C}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t}+\frac{\rho K_d}{\theta}\frac{\partial C}{\partial t}+\frac{\rho C}{\theta}\frac{\partial K}{dx}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}$$

Since K doesn´t vary with x,

$$\frac{\partial C}{\partial t}+\frac{\rho K_d}{\theta}\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}$$

$$\left[1+\frac{\rho K_d}{\theta}\right]\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}$$

$$R\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}$$ where R is the Retardation Factor. Eqn. 5

If there is no interaction between solute and soil, $K_d = 0$ and in this case R = 1.0

ISOTHERM

An isotherm is a graphic representation of the amount of solute adsorbed to soil particles related to the solute concentration in soil pores. For example, the quantity of compound adsorbed to soil particles (S) can be written as:

$$S = K_f C^N$$

Where C is the solute concentration (for example micromol/liter), S is the solute adsorbed to soil (micromol/Kilogram of dry soil) and Kf and N empirical constants. The equation above is known as Freundlich equation or Freundlich isotherm. The term isotherm express the fact that the temperature is held constant.

When N = 1, a linear isotherm is reached and equation above is rewritten as:

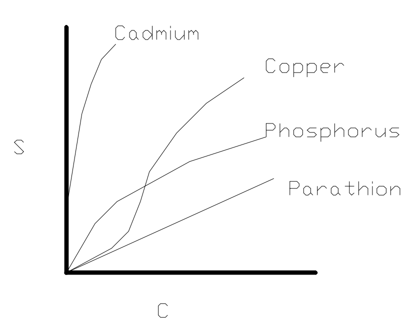
$$S = K_d C$$

For N>1 the graphic is curvilinear upwards while N<1 establishes a curvilinear format downward.

Research projects carried out at UFLA revealed that the linear form of isotherm fits well with atrazine and thiamethoxam in tropical soils, as published by Castro (2005) and Lima (2004). For example, Kd values for atrazine varied from 11.4 go 16.6 in oxisols. For thiamethoxam, the Kd value was slightly larger than 1.0.

To measure the Kd, a laboratory procedure is required and very useful to better understand the sorption behavior. In this case, a batch experiment is used. Several flasks with different solute concentration are filled with same amount of dry soil. Under constant temperature and a brief period (2 hours at most), the concentration of solution is measured again. The difference corresponds to the quantity of compound absorbed by soil particles. The amount absorbed versus the initial concentration will establish a graph called isotherm and it is valid only for the temperature used during the experiment.

Different formats for isotherms are presented at figure below:



The linear distribution coefficient can also be estimated considering that the compound adsorption is directly related to the organic content of soil. In this case the coefficient would be referred as Koc as:

$K_d = K_{oc} f_{oc}$

Where foc is the organic carbon fraction (varying from 0 to 1).

The main limitation of this technique is that it considers that adsorption is restricted only to the organic components of soil. Values of Koc are available in the literature for many compounds.

When Koc values are not available, a common procedure is to estimate it from Kow. For example, Rao and Davidson (1982) suggested for 13 compounds the approximation:

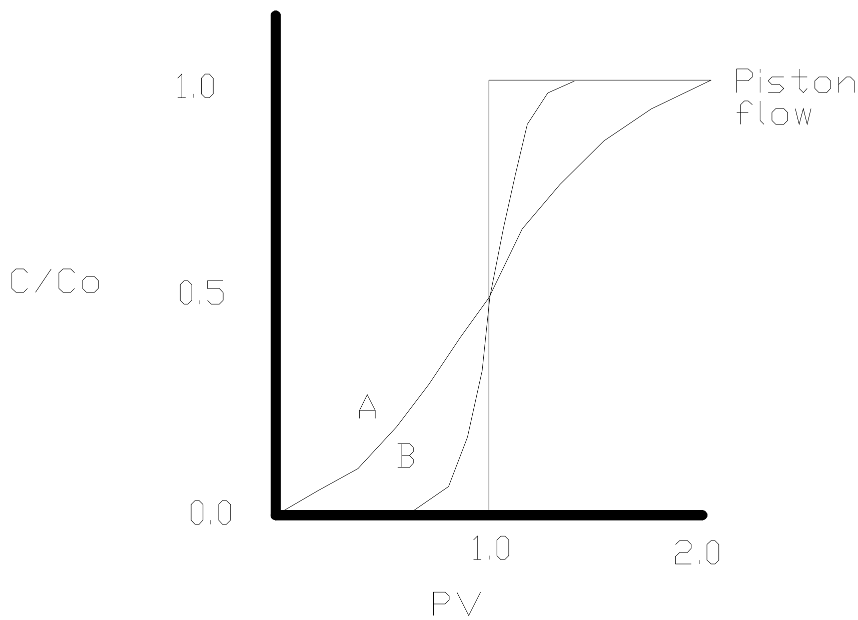
$\text{Log Koc} = \text{Log Kow} - 0.317$

DETERMINATION OF HYDRODYNAMIC DISPERSION COEFFICIENT

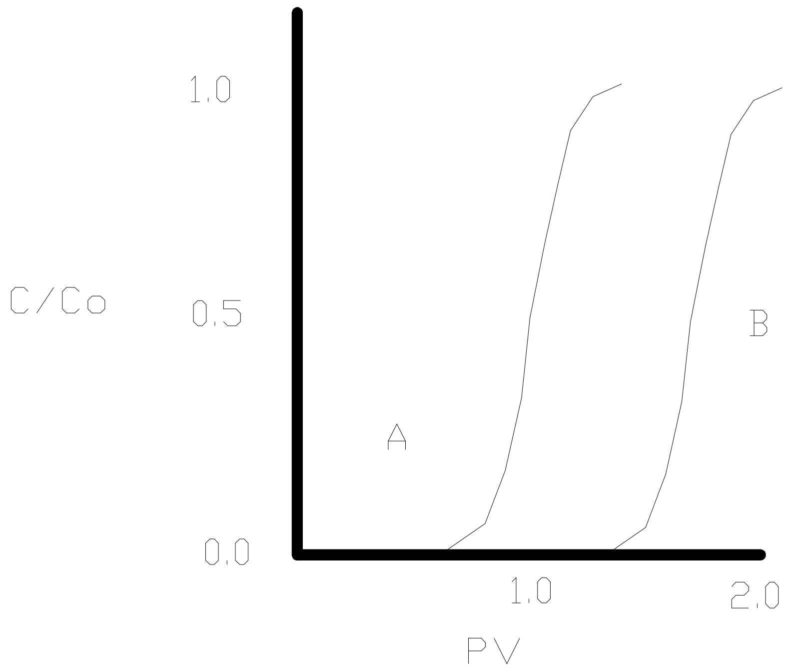
In order to quantify the D value for a given compound, a miscible displacement experiment should be carried out. On these experiments, the objective is to evaluate concentration of the compound as it leaves a soil column versus the volume of effluent. In fact, rather than versus the volume of effluent, such volume is expressed as number of pore volumes, a parameter that expresses the quantity of volumes equivalent to total porosity has passed through the column. For example, for a column with 100 cm3 of porosity, 2 pore volumes would mean that 200 cm3 or 200 ml have passed through the column.

The effluent concentration can also be expressed as the relative concentration (C/Co) where C is the effluent concentration and Co is the concentration of compound at column entrance, held constant as the experiment is carried out.

Figure below shows different formats of curves relating the relative concentration to the number of pore volumes. These curves are called breakthrough curves.



The piston flow curve represents the hypothetical situation where the solute moves as a linear front and the relative concentration ahead of such front is zero and behind the front is 1.0. Such situation doesn´t occur in porous media. Curve A represents a compound with larger dispersion capacity than compound B. At the next figure, the breakthrough curves for two compounds are shown, being compound B with a delayed movement or, in other words, with a larger retardation factor (significant part of B compound had been absorbed to soil) before leaving the column.

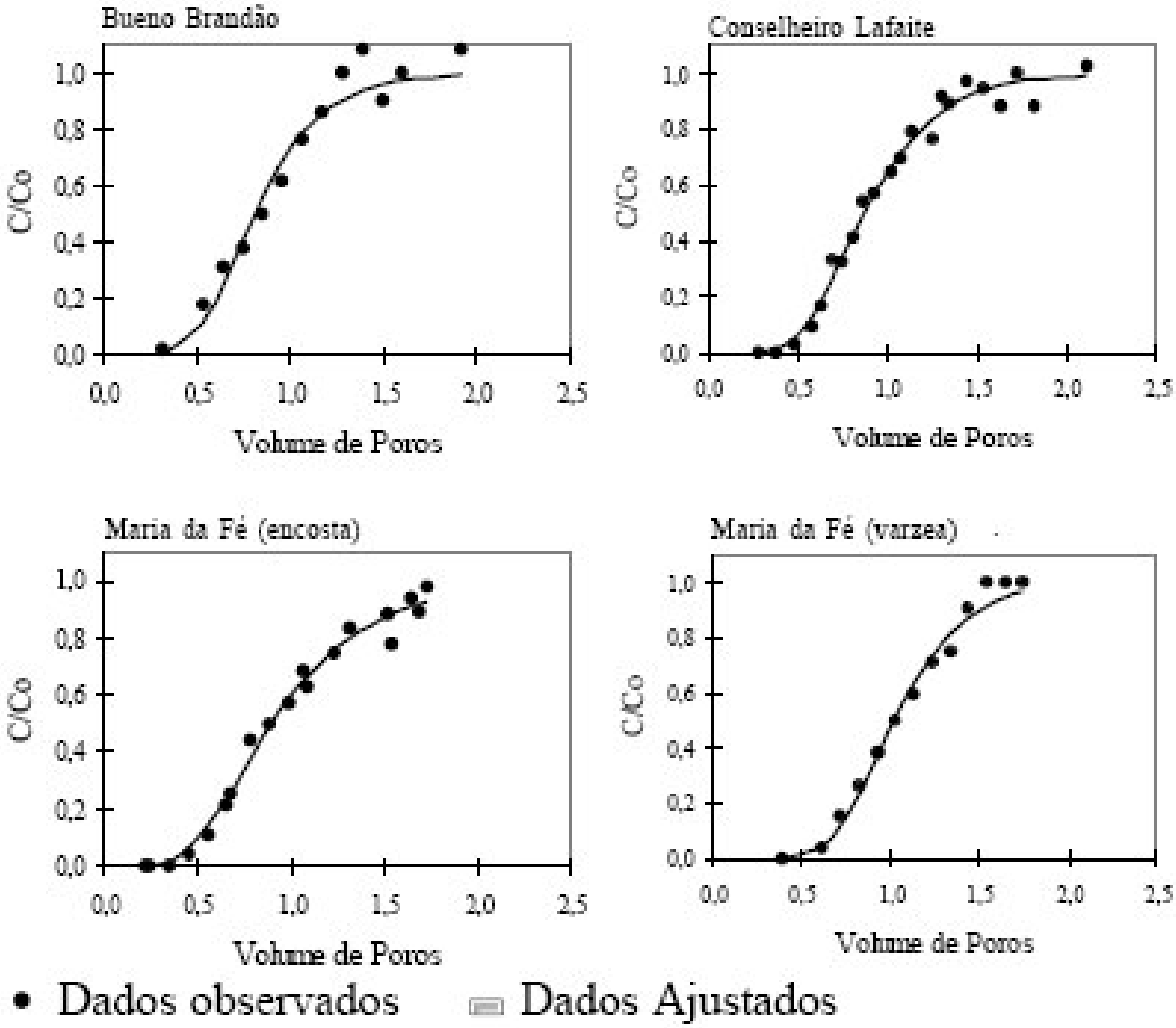


Accordingly to equation 5, the Retardation Factor can be written as:

$$R = \left[1 + \frac{\rho K_d}{\theta}\right]$$

Considering the figure above, compound B would have a larger retardation factor due to more adsorption to soil, represented by its larger K_d value. It is interesting to observe that for Kd = 0, case of no interaction between compounds and soil, the retardation factor is equal to one. In this case, experiments have shown that the breakthrough curve tends to approximate relative concentration equal to 0.5 for one pore volume.

As an example, figures below contain breakthrough curves for aldicarbe sulfone in tropical soils cultivated with potatoes (Correa, 1999).


Bueno Brandão
Conselheiro Lafaite
Maria da Fé (encosta)
Maria da Fé (varzea)
C/Co
1,0
0,8
0,6
0,4
0,2
0,0
0,0
0,5
1,0
1,5
2,0
2,5
Volume de Poros
Dados observados
Dados Ajustados

Analytical solution of the Governing Differential Equation

The solution for equation 5 has been presented by several authors, such as by Lapidus and Amundson (1952), for the following intitial and boundary conditions:

C(0,t) = Co

Which states that the solute concentration entering the column (x=0), for any time value is Co.

$$\frac{\partial C}{\partial x}(\infty, t) = 0$$

Which states that the concentration gradient for larger values of x at any time tends to be zero. In other words, there is a point far away from the inlet position where the concentration doesn´t vary with distance.

The number of pore volumes represented at the horizontal axis of breakthrough curves can be calculated as:

$T = \frac{vt}{L}$ being v the pore water velocity and L the length of the soil column.

Another term (P), defined as the Peclet Number, can be calculated as:

$$P = \frac{vL}{D}$$

Considering the equations above, the relative concentration (C/Co) can be written as:

$$\frac{C}{C_o} = 0.5 erfc\left[\left(\frac{P}{4RT}\right)^{1/2}(R-T)\right] + 0.5\exp(P) erfc\left[\left(\frac{P}{4RT}\right)^{1/2}(R+T)\right]$$

Where erfc is the complementary error function, defined for any variable z, as:

$$erfc(z) = \frac{2}{\sqrt{\pi}}\int_z^\infty e^{-u^2} du$$

with tables provided at the literature, or as a predefined function at mathematical software such as Excel (Office 2008).

Another solution, provided by Lindstrom et al (1967), published by Methods of Soil Analysis (Part 1) can be written as:

$$\frac{C}{C_o} = 0.5 erfc\left[\frac{Rx - vt}{\sqrt{4DRt}}\right] + \left(\frac{v^2 t}{\pi DR}\right)^{1/2} \exp\left[-\frac{(Rx - vt)^2}{4DRt}\right] - 0.5\left(1 + \frac{vx}{D} + \frac{v^2 t}{DR}\right)\exp\left(\frac{vx}{D}\right) erfc\left[\frac{Rx + vt}{\sqrt{4DRt}}\right]$$

Table A1 registers the collected data for a miscible displacement experiment run for teaching purposes at UFLA, using the above equation for a soil column as displayed.

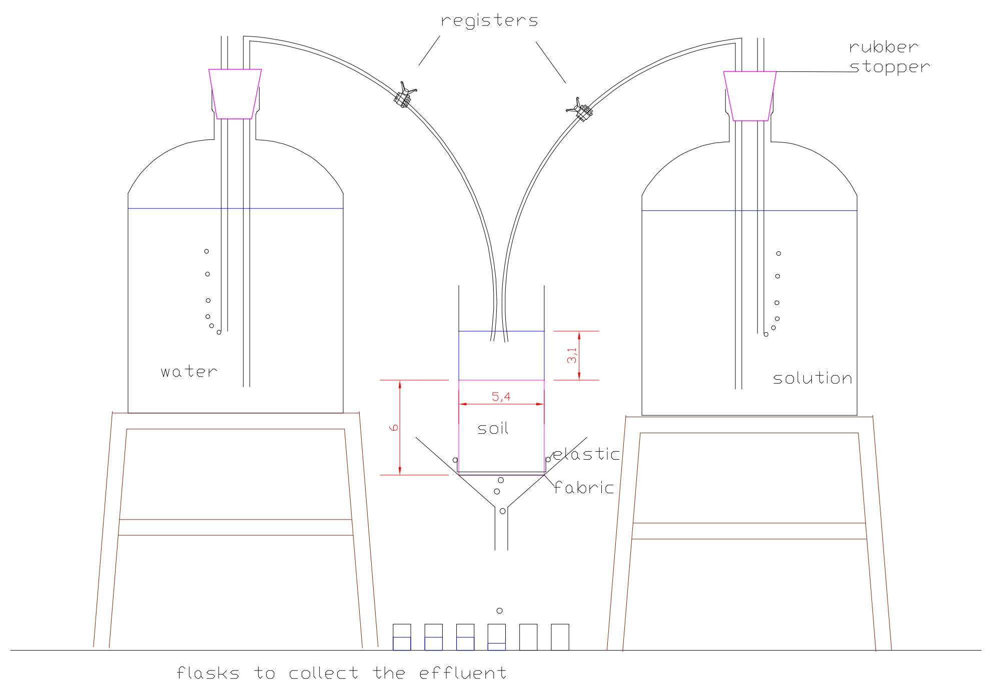


Figure A1: Miscible displacement apparatus

Table A1 was prepared at Excel, using the Solver tool. The file can be found at www.lalima.com.br/lalima/paginas/pos_graduacao.htm as Planilha de Deslocamento Miscivel (Miscible Displacement Worksheet).

The following data was registered during the experiment:

Experimental data	Value
Column diameter (cm)	5.4
Column height (cm)	6
Water on top of column (cm)	3.1
Bulk density (g/cm3)	1.05
Particle density (g/cm3)	2.65
Total porosity (%)	60.38
1 pore volume (cm3)	82.97
Fraction volume (cm3)	10.36
Fraction (Pore volume)	0.1249
Solute inlet conc(mg/l)	500
Soil water movement	
Flow rate (l/h)	0.040
Darcy flux - q(cm/h)	1.74
Hidraulic Conductivity (cm/h)	1.15
v (cm/h)	2.89

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