

CRITICAL KEY BUFFER CAPACITY POINTS IN THE SOIL PESTICIDE TOLERANCE

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Abstract: The bioavailability and mobility of a compound is not only influenced by concentration and quantity, but also by the ability of soil to recharge the compounds that plants have taken up from soil solution or removed by the moving ground water. The effective diffusion and mass flow of the compounds depends on the soil's buffer capacity for that compound. The buffer capacity in function of equilibrium concentration (EBC) can be calculated as the first derivative of sorption isotherms. Using the measured and modelled multi-step isotherms for this calculation we could get wave-shaping functions where the maximums are bigger even ten times than the minimums in the 5-10% interval of the whole soluble pesticide concentration. This result is highlighting some problems what we have never been taken into account before: Very small difference in the measured concentration can cover even ten times more or less amount of pesticide in the soil and the capacity of the soil to tolerate disturbance may also change even a magnitude in the aforementioned interval.

Keywords: pesticide, adsorption, buffering capacity

Introduction

As the importance of pesticide and toxic organic chemical soil sorption for environmental fate has become apparent, it has been studied intensely for the last 22 years (R Don Wauchope et al., 2002). The soil science and agricultural chemistry literature describe that the buffer capacity mainly used the phosphorus availability and pollution problems as a solution.

The buffer capacity is measured from either adsorption or desorption isotherms and the equilibrium buffer capacity - function B - can be written as:

$$B = \frac{\partial q}{\partial c}$$

Specifically at the Langmuir isotherms the following formula can describe the equilibrium buffering capacity as a function of equilibrium concentration:

$$B = \frac{A}{(1 + kc)^2}$$

(Rattan, 2006). The buffer capacity of the soil's P system may be described by the phosphorus adsorption isotherm. As a result of differentiating the adsorption equation, the equilibrium buffer capacity at any concentration (EBC) can be calculated as:

$$EBC = \frac{dP_{ads}}{dc} = \frac{1}{3} \cdot \frac{k}{\sqrt[3]{c^2}}$$

assuming that the adsorption reduces exponentially according to the Freundlich isotherm with a 1/3 exponent (Tolner and Füleký 1995). The advantage of using Q/I relationships is that they allow the prediction of both P retention and release in soils (Kpombekou and Tabatabai, 1997). The P-buffering capacity of a soil is its ability to

resist a change in the P concentration of the solution phase. Phosphorus-buffering capacities of soils can be related to both plant nutrition and environmental pollution. The Q/I model can be applied to either adsorption or desorption experiments (Yaobing et al., 2000). Results showed that Q/I parameters (the intercept labile P, a; the equilibrium buffering capacity, EBC; and the equilibrium P concentration, EPC) varied significantly between and within sites for the studied cropping systems.

Materials and methods

The herbicides as solutes resulted in two- or more step isotherms on soils and quartz. This phenomenon has not been observed yet concerning on the trace compounds in the environment. In this case the so-called Distributed Reactivity Model (DRM) is used to suggest the total sorption is given as the sum of the local adsorption isotherms (Czinkota et al., 2002; Konda et al., 2002).

$$q = \sum_{i=1}^s \left\{ \frac{q_{Ti} \cdot K_i \cdot (c - b_i + |c - b_i|)^{n_i}}{2^{n_i} + K_i \cdot (c - b_i + |c - b_i|)^{n_i}} \right\}$$

In the cited work the adsorption isotherm was measured in different compounds using one soil sample, or one compound in different soil samples. The exact descriptions of experiments are in the cited articles.

Results and discussion

Using the isotherms the Equilibrium Buffering Capacity was calculated with help of the derivative function.

$$B = \frac{\partial}{\partial c} \left\{ \sum_{i=1}^s \left\{ \frac{a_i \cdot k_i \cdot [(c - b_i) + \text{abs}(c - b_i)]^{n_i}}{2^{n_i} + k_i \cdot [(c - b_i) + \text{abs}(c - b_i)]^{n_i}} \right\} \right\}$$

The straightforward derivation of the above function is impossible because of the break point of abs function. *However, if we know that the abs function is just needed for negative (c-b) data that is not to be taken into account*. It means we can make the derivative function as the sum of single Langmuir isotherm in every x region. Therefore the following function can be used as the Equilibrium Buffering Capacity of multistep adsorption isotherms:

$$B = \sum_{i=1}^s \left\{ \frac{2^{n_i} \cdot a_i \cdot k_i \cdot n_i \cdot [(c - b_i) + \text{abs}(c - b_i)]^{n_i - 1}}{\left\{ 2^{n_i} + k_i \cdot [(c - b_i) + \text{abs}(c - b_i)]^{n_i} \right\}^2} \right\}$$

Using the given parameters the Equilibrium Buffering Capacity function was calculated. *But because the larger error of derivative function was fitted on the differentiate data of original measurement result*.

Generally/In other cases we calculated the new parameters (Tolner, 2008) (it is a little bit different from the original sorption isotherm parameters, because of the new fitting weighting points). The values of the parameters are given in Table 1.

Table 1. The fitted parameter values of the measured Equilibrium Buffering Capacity data.

compound	R ²	a ₁	a ₂	a ₃	k ₁	k ₂	k ₃	b ₁	b ₂	b ₃	e ₁	e ₂	e ₃
Isoproturon	0,9993	9,29	9,93	4,42	0,30	3,79	1,47	0	4,57	13,16	0,45	0,55	3,11
Diazinon	0,9998	31,73	31,89	0,00	0,51	0,28	1,00	0	3,86	1,00	1,84	2,67	1,00
Atrazin	0,9980	9,26	10,97	0,00	0,28	0,49	1,00	0	4,16	1,00	0,95	2,46	1,00
Imidacloprid	0,9960	4,22	9,82	6,01	2,41	0,14	0,01	0	2,33	5,67	1,00	3,00	6,00

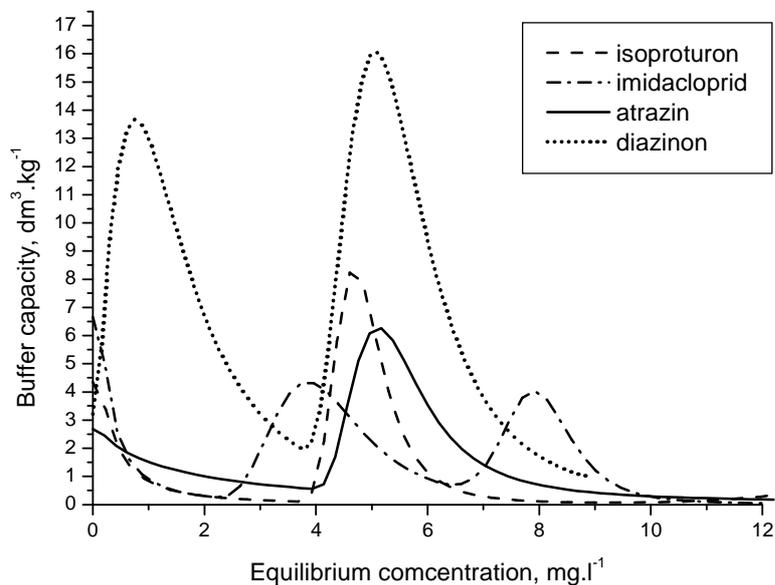


Figure 1. Equilibrium Buffering Capacity functions of different compounds.

Fig1. shows the calculated functions, as it can be seen, there are very big differences in the EBC values with relatively small equilibrium concentration differences, *and in some cases these are almost periodical*.

Conclusions. How to use these results?

If we know the water content of soil, based on the buffering capacity value we can calculate the ratio of adsorbed and dissolved amount of given compound. *In the analytical and monitoring practice we measure the concentration change of liquid phase, and we draw the conclusion that it is proportional to the changing of pollution amount and it is not true in aspects of our research*. The suggested calculation method step by step is the following:

To calculate the changing of pollution amount of a compound in solid phase in a given water content of soil the following formula can be used:

$$dQ = \frac{1-\Theta}{\Theta} \cdot EBC \cdot dc$$

where dQ is the change of the pollution amount in solid phase, [mg*kg⁻¹]

dc is the change of the concentration of solution, [mg*dm⁻³]

EBC is the Equilibrium Buffering Capacity, [dm³*kg⁻¹]

Θ is the water content of soil, [dm³*dm⁻³].

To calculate the total amount in milligrams of compound in the soil we must add the solid phase and liquid phase content,

$$dQ = \frac{1-\Theta}{\Theta} \cdot V_{soil} \cdot \rho_{soil} \cdot EBC \cdot dc + \frac{\Theta}{1-\Theta} \cdot V_{soil} \cdot dc$$

If we have got one hectare soil and 25 cm plugged layer, *and calculate total amount in kilograms*:

$$dQ = 10^{-6} \cdot \left(\frac{1-\Theta}{\Theta} \cdot \rho_{soil} \cdot EBC + \frac{\Theta}{1-\Theta} \right) \cdot V_{soil} \cdot dc$$

where ρ_{soil} is the density of solid phase, about 2.6 [kg*dm⁻³];

V_{soil} is the volume of soil, in this case 2500000 [dm³]

dQ is the change of the pollution amount in given soil area, [kg].

An example about the measurement or monitoring causation of this results:

Let the soil water content be 0.2. Based on the isoproturon curve if the equilibrium solution concentration increases from 2 mg*dm⁻³ to 2,1 mg*dm⁻³, the EBC is 0.35 dm³*kg⁻¹. The change of the total isoproturon content is 0.1 kg. With the same water condition and isoproturon buffer function if the equilibrium solution concentration increases from 4.5 mg*dm⁻³ to 4.6 mg*dm⁻³, the EBC is 8.18 dm³*kg⁻¹. The change of the total isoproturon content is 21 kg.

To the contrary, let's suppose 20 kg*ha⁻¹ isoproturon added into the soil, presumably as a plant protection activity. If the original equilibrium solution concentration was 2 mg*dm⁻³ it is increasing by 2 mg*dm⁻³, i.e. 100 % increase, but if the original equilibrium solution concentration was 4,5 mg*dm⁻³ it would increase by 0,1 mg*dm⁻³, i.e. 2 % increase. Based on these results we must redefine our original contamination assessment methods to avoid even a magnitude error. *In addition to the equilibrium solution concentration measurement the Equilibrium Buffering Capacity (EBC) function for assessing the real amount of contaminants*.

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