METRIBUZIN ADSORPTION ON A SILTY-CLAY SOIL OF ALGERIA : EFFECTS OF FERTILIZER AND pH

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Introduction

Pesticides used on crop production soils could lead to environmental fate and be transfered towards ground waters, depending on the soil properties and addition of other treatments.

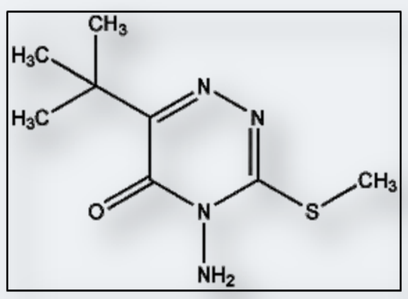
- Herbicides are commonly used around the world.
- In Algeria, Metribuzin , a triazin herbicide, is frequently used in agriculture, even in regions with subjacent ground waters utilized for drinking and irrigation.
- Soil properties and content play a key role in the dispersion of the herbicide in the environment.
- Addition of other treatments to the soil could modify the retention of the herbicide on the soil.

Objectives:

- Evaluate, in laboratory batch experiments , the retention of Metribuzin through adsorption isotherms on a silty-clay agricultural soil of the Algiers region with subjacent ground waters.
- Study the influence of the addition of an NPK fertilizer (15-15-15) on the adsorption of Metribuzin on the soil.
- Study the effect of the variation of the soil pH, linked to the addition of the fertilizer, on the adsorption of Metribuzin.

Material

Metribuzin



- Triazinone
- Solubility in water = 1.05 g L^{-1} at 20 C
- pK_a = 1
- Pestanal (99.3% purity) from RDH

Soil

- From the 30 cm surface layer
- Dryed in air, crushed and sieved at 2mm → Analyzed

Table 1: Physicochemical characteristics of the soil

Texture	% Clay	39.45
	% Silt	40.33
	% Sand	20.22
% Organic matter		3.01
% Organic carbon		1.75
pH_{water}		7.45

Fertilizer

Granular NPK fertilizer (N, P_2O_5, K_2O) (15-15-15) is from Fertial SPA (Annaba – Algeria)

Methods

❖ **Laboratory batch experiments:**

○ **Adsorption studies of Metribuzin on the soil:**

- T = 25 2 C
- Mass of soil (or soil + fertilizer) : **5 g**
- Volume of Metribuzin solution : **10 mL**
- Initial Metribuzin concentrations:
  Co : 2.5- 5- 10- 15- 17.5- 20- 25 mg L^{-1} in $CaCl_2$. 2 H_2O (0.01M)

. Rotative shaking for 8 hrs continuously
. Centrifugation for 15 min
. Filtration under vacuum
. NPK fertilizer added to the soil : **0% , 1% , 2%**
. K_d deduced from the linear part of the isotherms

○ **pH effect studies:**

- Real pH of the soil / Metribuzin suspensions: **6.67 ; 6.18 and 5.86** after addition of **0%, 1% and 2%** of fertilizer respectively
- Artificially modified pH without fertilizer by addition of HCl or NaOH to the soil / Metribuzin in $CaCl_2$. 2 H_2O (0.01M) suspensions → **pH= 5.02 – 6.05 – 6.97 – 8.09**

❖ **Analysis:**

- HPLC-DAD (WATERS 600 controller, detector DAD WATERS 2996)
- Column NUCLEOSIL **C18** (250 x 4.6 mm; 5µm)
- Eluant: **methanol / water** 65 /35 (V/V) ; flow rate :1 mL min^{-1}
- Detection of Metribuzin at **λ = 294.7 nm**

Results

Adsorption isotherms of Metribuzin on the soil and effect of fertilizer

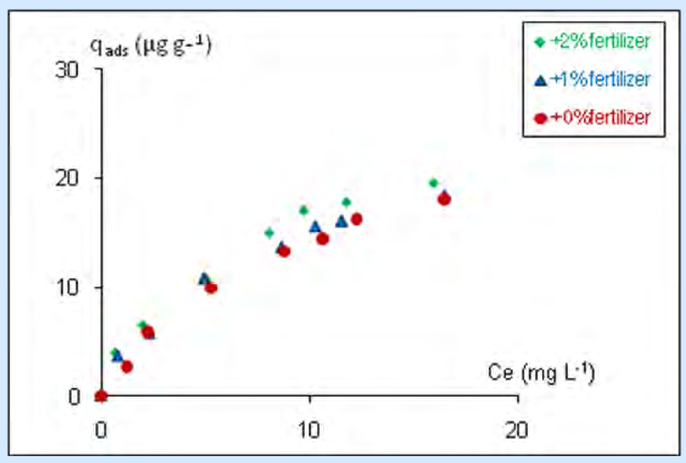


Figure 1 : Adsorption isotherms of Metribuzin on the soil with 0%, 1% and 2% of the NPK fertilizer at T = 25 2 C

➢ Metribuzin is moderately adsorbed on the soil without fertilizer (q_{ads} < 20 µg g^{-1})

➢ Metribuzin is also moderatly adsorbed on the soil with the fertilizer (q_{ads} < 20 µg g^{-1})

But : adsorption is slightly higher and increases with increase of % of fertilizer

➢ Addition of the fertilizer decreases the pH of the soil:

✓ 0% fertilizer pH = 6.67
✓ 1% fertilizer pH = 6.18
✓ 2% fertilizer pH = 5.86

Effect of pH on the adsorption of Metribuzin on the soil without fertilizer

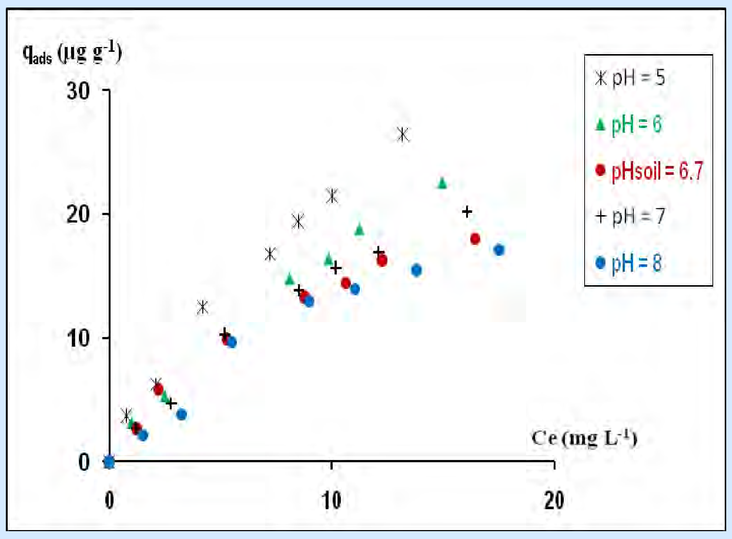


Figure 2 : Adsorption isotherms of Metribuzin on the soil without fertilizer at different pHs, at T = 25 2 C

➢ pH of the soils is a factor known to influence the adsorption of pesticides on the soil.

➢ This is confirmed with Metribuzin that shows a decrease of the adsorption on the soil without fertilizer as the pH increases from 5 to 8.

Effect of the ajustement of the pH of the soil containing 2% fertilizer

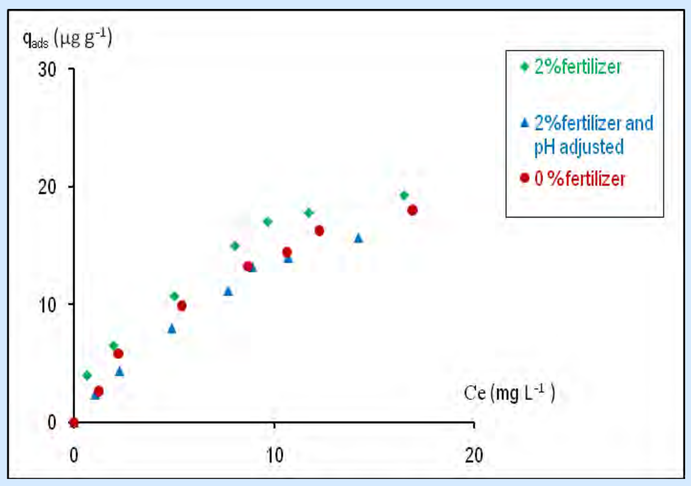


Figure 3: Adsorption isotherms of Metribuzin on the soil containing 2% of the NPK fertilizer and pH adjusted at 6.67, at T = 25 2 C

➢ To verify if the change of adsorption is due to the fertilizer itself or to the induced modification of pH:

pH of the soil containing 2% of fertilizer was artificially adjusted by addition of NaOH 0.1 N to **pH 6.67** (natural pH of the soil / Metribuzin suspensions without fertilizer).

➡ Both adsorption isotherms look quasi-superposed

Table 2: Adsorption parameters of Metribuzin on the soil (Freundlich model)

	1/n	K_F ($g^{1-1/n}$ kg^{-1} $L^{1/n}$)	R^2	K_d (L kg^{-1})	K_{oc}
0% NPK (pH = 6.67)	0.70	2.81	0.96	1.9 0.8	109 46
1% NPK (pH = 6.18)	0.58	3.97	0.99	1.9 0.5	109 29
2% NPK (pH = 5.86)	0.52	4.83	0.99	2.4 1.4	137 80
2% NPK at pH = 6.67	0.75	2.36	0,99	1.8 0.7	103 46
pH = 5.02	0.71	4.17	0.99	3.1 1.7	177 97
pH = 6.05	0.75	2.93	0.99	2.1 0.9	120 51
pH = 6.97	0.80	2.35	0.98	1.8 0.4	103 29
pH = 8.09	0.89	1.57	0.96	1.4 0.3	80 17

➢ 1 / n < 1 ➡ Non linear adsorption
➢ K_F values between 1.57 and 4.83
➢ K_d between 1.4 and 3.1 ➡ Low
➢ K_d increases slightly with the fertilizer

❖ **Parameters:**

$q_{ads} = K_F\ Ce^{1/n}$
$K_d = q_{ads} / Ce$
$K_{oc} = (K_d / \%\ OC)\ 100$

Conclusion

- Metribuzin was expected to be very mobile in soils due to its high solubility in water and its K_{oc} values.
- Metribuzin has been found indeed moderately adsorbed on the studied soil (q_{ads} < 20 µg g^{-1} and K_d between 1.4 and 3.1).
- Addition of the NPK fertilizer lowers the pH of the soil and increases the adsorption of Metribuzin. Addition of 2% of fertilizer leads to a decrease of pH of 0.81.
- Adsorption increases with the amount of fertilizer added and decreases at higher concentrations of Metribuzin.
- Apparently, there is no effect due specifically to the fertilizer on the adsorption of Metribuzin but it is a pH effect.
- K_F varies from 2.35 (for the soil at pH 6.97) to 4.83 (for 2% fertilizer).
- K_d varies slightly and the 1/n values are small.
- Modifications of the adsorption of Metribuzin on the soil containing the NPK fertilizer are probably not due to the agricultural practices.

Adsorption of Metribuzin is low, even in the presence of the NPK fertilizer, despite the high clay content of the soil, suggesting risks of percolation of the herbicide in the subjacent ground waters.

Perspectives:

Adsorption studies in soil columns in the dynamic mode and computer modeling of the risks of transfer.

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