Adsorption of metsulfuron-methyl on soils under no-till system in semiarid Pampean Region, Argentina

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ABSTRACT

Adsorption isotherms of metsulfuron-methyl (MM) on thirty soils from the semiarid Pampean Region of Argentina were determined. The effect of total organic carbon (TOC) content on the adsorption was the main focus, but the effects of clay content, specific surface area and pH were also analyzed. pH is a very important factor that affects the adsorption. In fact, this article demonstrates that a good pH control is necessary to investigate the effects of TOC, otherwise results are obscured by changes in pH. Under pH controlled conditions (pH 6.0 ± 0.2), a significant and positive correlation between MM adsorption and TOC was observed for a large range of concentrations (up to 40 mg L^{-1}). There was no significant correlation between adsorption and inorganic components or specific surface area. The potential mobility of MM in soils was estimated by calculating the groundwater ubiquity score (GUS), using K_{OC} values calculated from adsorption isotherms and appropriate half-times. MM can be ranked as leacher in all the studied soils. The results suggest that MM would be rather mobile and transported by water flows.

1. Introduction

Sulfonylurea herbicides, such as metsulfuron-methyl (MM), tria-sulfuron, chlorsulfuron, etc., are widely used in a variety of crops because they can control a broad spectrum of weeds with low acute and chronic animal toxicity (Fletcher et al., 1993). For these reasons, they were thought to be the ideal candidates for replacing some highly polluting compounds such as atrazine, in efforts to reduce soil and groundwater contamination (Fletcher et al., 1993). Thus, sulfonylurea herbicides have widespread use in fields around the world, e.g. Europe (Walker and Jurado-Exposito, 1998), U.S.A (Ukrainczyk and Ajwa, 1996), Australia (Nyström et al., 1999). They are also widely used in the semiarid Pampean Region of Argentina, especially for broadleaf weed control in winter wheat and soybean (Castro et al., 2002; Bazzigalupi and Cepeda, 2005; Bedmar et al., 2006).

Although sulfonylurea herbicides have low animal toxicity at normal application rates, there are reports indicating that they may affect plant reproduction and crop yields (Fletcher et al., 1993, 1996; Kjær et al., 2006). Moreover, as stated by Bedmar et al. (2006), these herbicides can persist in the soil throughout more than one growing season and may affect rotational crops. These possibilities indicate that an important research effort is necessary to gain a clearer understanding of the behaviour of sulfonylurea herbicides in soils.

One of the main processes controlling the behaviour of herbicides in soils is their sorption on soil components (Walker and Jurado-Exposito, 1998; Berglöf et al., 2003). Herbicides in soils can be found as dissolved molecules in the aqueous phase and/or as molecules bound to the solid phase (minerals, refractory organic matter, plants residuals, etc.). As indicated by Sparks (2003), the affinity of herbicides for the solid phase controls the extent of the sorption and thus their availability and their capacity to remain immobilized, to be trans-formed, or to be transported in the environment. Gaining information on the sorption process can be valuable to understand and predict the activity, mobility and fate of herbicides in the soil system and, consequently, their potential effect in crop yields and the potential risk for contamination of water resources.

Many articles have appeared in the literature regarding the sorption of sulfonylurea herbicides on soil or soil components. Pusino et al. (2004), for example, studied the adsorption of primisulfuron on different soils, an amorphous Fe oxide, a montmorillonite exchanged with different cations, a humic acid and a Ca^{2+}-humate. Except for Ca^{2+}- and Na^+-exchanged montmorillonites, all the solids adsorbed the herbicide, including Fe^{3+}- and Al^{3+}-exchanged montmorillonites. In all the cases, the pH was a key factor in controlling the adsorption, which decreased as pH increased. For the three soil samples studied by these authors, it was also observed that adsorption increased as the organic matter content increased. Although this number of samples is not enough to achieve unquestionable conclusions, the results suggest that the content of organic mater is also important in determining the adsorption. Very similar results were found by Pusino et al. (2003) for the adsorption of triasulfuron on the same solids.

Walker et al. (1989) studied the adsorption of chlorsulfuron and MM on different soils. Soil pH was the dominant factor controlling adsorption, which decreased by increasing pH. They also found a positive correlation with soil organic matter content. However, since

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the pH was not the same for all the soils studied, this positive correlation was not unambiguously established because both variables (pH and organic matter content) changed simultaneously in the experiments. This is the case of most adsorption studies with soil materials where the effects of organic matter content are investigated. The studies are usually performed at natural soil pH, which can vary by several pH units from one soil to another, and thus the effect of organic matter content cannot be well established. In order to solve this problem, Pusino et al. (2004) artificially modified the pH of four soil dispersions aiming to obtain a relatively constant pH (5.9–6.2) for the adsorption of azimsulfuron. They found that in most cases the organic matter content was very important to determine the adsorption at constant pH, although other factors such as clay content were also important. The conclusions of Pusino et al. (2004) were obtained for only one herbicide (azimsulfuron) and four soils. More experiments are still needed for other herbicides and soils, in order to establish unambiguously the effects of organic matter on the adsorption of sulfonylurea herbicides.

Factors other than pH, organic matter and clay content may influence the adsorption of herbicides on the soil phase. The specific surface area (SSA) may be one of them. In fact, if adsorption sites are rather homogeneously distributed at the surface of the soil particles there will be a significant positive correlation between adsorption and SSA. In addition, the tillage system used in farming may also modify the soil characteristics. No till system, for example, has grown in popularity in recent years and this practice seems to affect not only the organic matter content but also the quality of this organic matter. It has been reported that adoption of no till in Pampas soils can increase by 12% the total organic carbon, TOC, (Galantini and Rosell, 2006).

In this article a study of MM sorption on thirty different Argentinean soils is reported. All of them are located in the semiarid region of the Argentinean Pampas and in all cases the croplands are under no till practice. Adsorption isotherms at constant pH are reported and the effects of TOC, SSA and clay content are investigated. Although MM is broadly used in Argentina, information regarding its sorption on Argentinean soils is very limited. Therefore, the aims were a) to investigate the effects of several parameters on the sorption of MM on soils under no till, and b) to provide information on the adsorption behaviour of sulfonylurea herbicides on Argentinean soils.

2. Materials and methods

2.1. Chemicals

The herbicide used was a commercial formulation of MM (Trimet, origin: China, company: Tamer, 60% a.i.) and an analytical grade sample (Riedel-de-Häen, Pestanal 99.3%, Germany). All other chemicals (CaCl$_2$, HCl, NaOH) were analytical grade chemicals. MM is a weak acid with pK_a = 3.5 (Berglöf et al., 2003). The protonated species, which is dominant at pH < 3.5, is a neutral molecule (Fig. 1). The deprotonated

species, which is dominant at pH > 3.5, is a negatively charged ion, which results from deprotonation of the nitrogen atom in the –SO$_2$NHCO– group.

2.2. Soils

Thirty agriculture soils under no-till practice were used. Surface soils (0–5 cm) were collected from the semiarid Pampean Region of Argentina, and they were distributed over an area of 10,000 km^2 in the south of the province of Buenos Aires, east central Argentina. Selected physical and chemical properties of soils are listed in Table 1. Soils of this region contain mainly quartz, feldspars and plagioclase in the sand fraction, and illite, interstratified illite-smectite, quartz, feldspars and mica in the silt and clay fraction, being Ca^{2+} and Mg^{2+} the main exchangeable cations (Blanco and Stoops, 2007). Soils were Typic Haplustolls (soils 1, 5, 6, 7, 9, 12, 13, 17, 19, 22, 23, 25), Typic Argiustolls (soils 2–4, 8, 10, 11, 14) and Typic Argiudolls (soils 15, 16, 18, 20, 21, 24, 26–30). They were selected to cover a rather ample range in TOC (from 0.98% to 4.85%). For comparison, two of these soils with intermediate TOC (soils 20 and 22) were treated with H$_2$O$_2$ in order to remove most of their TOC. Samples were air dried and passed through a 2 mm sieve. Soil pH was determined in a 1:2.5 soil/water suspension using a glass pH electrode. Particle size distributions were evaluated using the hydrometer method (Gee and Bauder, 1986). TOC was measured by dry combustion using a LECO CR-12 Carbon System Analyzer, model 781–600. The SSA was determined from N$_2$ adsorption isotherms at 77 K using the BET equation with a Quantachrome NOVA 1200e surface area analyzer. Samples were dried in vacuum at room temperature before these measurements.

2.3. Adsorption isotherms

MM adsorption isotherms were measured at 25 ± 2 °C with all soils. The advantage of measuring adsorption isotherms as compared to the customary one-point measurement is that information can be obtained in a range of adsorbate concentrations, strengthening the conclusions. For each soil, batch adsorption experiments were done by weighing 5 g soil sample in 50 ml centrifuge tubes. After that, 10 ml of an aqueous MM solution prepared in 0.02 M CaCl$_2$ as supporting electrolyte were added to each tube. One tube, containing the soil sample and pure 0.02 M CaCl$_2$ was used as blank. The herbicide concentration range was 0.5–60 mg L^{-1}. The tubes were shaken for 15 min and small volumes (a few μL) of either NaOH or HCl solutions were added in order to reach a constant pH = 6.0 in all of them. The shaking (end over end) was continued for 24 h and the pH was again measured. In all cases, the final pH was in the range of 6.0 ± 0.2. The dispersions were then centrifuged at 1700 g for 30 min, and the supernatants were withdrawn and quantified immediately. The amount retained by the soil was calculated from the difference between the initial and final concentration of MM in solution.

In order to obtain information on the influence of pH on the adsorption of MM, adsorption isotherms were measured at two additional pH (pH 4 and 8) for soil 5. The pH was measured with a Consort C231 Electrochemical Multimeter and an Altronix SilverCap combination p/N: PHS-0101-3B pH electrode.

Quantification of MM was performed by UV–Vis spectroscopy, using an Agilent 8453 UV–Vis diode array spectrophotometer equipped with a Hellma 1 cm quartz cell. The spectrum of the commercial sample matched exactly that of the pure analytical grade sample. This indicates that no UV–Vis absorbing impurities are present in the commercial sample, making possible the spectrophotometric quantification of the herbicide. For the quantification, each supernatant was placed into the cell and the UV–Vis spectrum was recorded in the 200–500 nm wavelength range. After the blank subtraction, it was checked that the spectrum corresponded to that of MM, and then the absorbance at 233 nm was used for quantification. Calibration
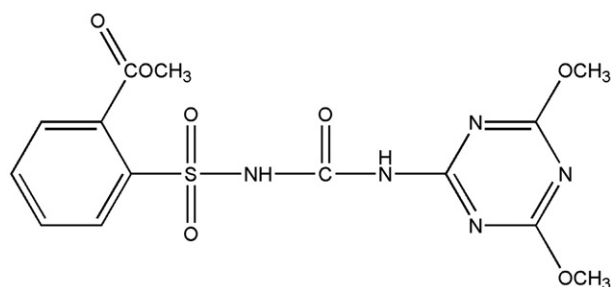

Fig. 1. Molecular structure of the protonated (uncharged) species of MM. This species is dominating at pH < 3.5. The anionic species dominating at pH > 3.5 results from deprotonation of the nitrogen atom in the –SO$_2$NHCO– group.

Table 1
Selected physical and chemical properties of the studied soils

Soils	TOC %	Sand %	Clay %	SSA m^{2}g^{-1}	pH	K_f	$1/n$	R^2	K_{OC} L kg^{-1}	GUS
1	0.98	53.7	28.4	8.3	7.50	0.16 (0.01)[a]	0.95 (0.03)[a]	0.99[b]	16.3	4.98
2	1.28	64.1	25.3	3.4	5.94	0.24 (0.04)	0.91 (0.05)	0.99	18.8	4.87
3	1.29	51.9	38.9	12.0	6.51	0.22 (0.03)	0.98 (0.04)	0.99	17.1	4.94
4	1.40	48.5	33.9	5.2	6.05	0.54 (0.08)	0.74 (0.05)	0.95	38.6	4.31
5	1.43	56.5	28.2	4.5	6.90	0.24 (0.09)	1.02 (0.10)	0.96	16.8	4.95
6	1.44	57.4	33.4	4.9	6.05	0.61 (0.06)	0.70 (0.03)	0.98	42.4	4.24
7	1.58	54.5	33.4	5.4	6.51	0.22 (0.08)	0.86 (0.11)	0.94	13.9	5.10
8	1.76	44.7	41.8	7.3	6.19	0.78 (0.12)	0.55 (0.05)	0.97	44.3	4.20
9	1.82	45.8	39.8	8.4	6.55	0.36 (0.07)	0.86 (0.05)	0.98	19.8	4.83
10	1.88	43.7	44.2	7.9	6.47	0.74 (0.16)	0.68 (0.07)	0.96	39.4	4.29
11	1.91	50.3	41.8	4.6	6.04	0.96 (0.29)	0.40 (0.09)	0.86	50.3	4.10
12	1.94	42.7	39.4	4.6	6.46	0.54 (0.08)	0.74 (0.05)	0.97	27.8	4.56
13	2.06	47.2	39.2	6.1	6.77	0.20 (0.07)	1.02 (0.10)	0.97	9.7	5.38
14	2.07	44.0	38.3	5.8	6.30	0.53 (0.13)	0.88 (0.08)	0.98	25.6	4.63
15	2.10	46.4	38.9	4.8	6.51	0.31 (0.07)	0.85 (0.07)	0.97	14.8	5.05
16	2.18	52.7	28.2	4.6	6.90	0.78 (0.06)	0.69 (0.07)	0.98	35.8	4.37
17	2.46	52.2	35.9	3.7	6.14	0.76 (0.27)	0.77 (0.10)	0.94	30.9	4.48
18	2.50	42.5	36.7	10.6	6.58	0.60 (0.12)	0.98 (0.06)	0.99	24.0	4.68
19	2.56	30.7	49.7	7.7	6.59	1.18 (0.12)	0.55 (0.06)	0.93	46.1	4.17
20	2.59	32.6	44.0	5.6	6.08	0.91 (0.12)	0.69 (0.04)	0.91	35.1	4.38
21	2.75	36.1	40.9	5.6	5.80	0.84 (0.21)	0.65 (0.08)	0.97	30.5	4.49
22	2.88	43.0	35.4	5.2	6.44	0.56 (0.10)	0.92 (0.06)	0.98	19.4	4.84
23	2.93	31.2	48.6	5.2	7.80	0.36 (0.11)	0.80 (0.09)	0.96	12.3	5.20
24	3.07	47.2	33.7	4.3	6.36	1.07 (0.25)	0.67 (0.07)	0.96	34.9	4.39
25	3.10	45.3	33.9	4.4	7.10	0.61 (0.14)	0.69 (0.07)	0.98	19.7	4.83
26	3.34	50.4	30.6	9.0	6.51	0.85 (0.16)	0.89 (0.06)	0.98	25.4	4.63
27	3.91	46.5	31.2	5.5	6.10	1.10 (0.32)	0.79 (0.09)	0.99	28.1	4.55
28	4.02	52.0	28.6	6.1	6.65	0.96 (0.05)	0.83 (0.02)	0.99	23.9	4.68
29	4.62	61.4	25.3	4.0	5.86	0.80 (0.15)	0.93 (0.06)	0.99	17.3	4.93
30	4.85	44.3	32.8	6.0	8.03	1.35 (0.22)	0.77 (0.05)	0.98	27.8	4.56

[a] Values within brackets correspond to standard error.
[b] R^2 corresponds to the fitting with the Freundlich isotherm.

curves at the working pH were constructed with MM solutions having concentrations that ranged between 0.5 and 60 mg L^{-1}.

The Freundlich equation (Stumm, 1992; Sparks, 2003), which is commonly used to describe pesticide adsorption on soils (Valverde-García et al., 1988), was used to fit and analyze the adsorption isotherms. This equation can be expressed as

$$q = K_f C^{1/n} \qquad (1)$$

where q is the amount of MM adsorbed per unit mass of adsorbent (mg of MM per kg of soil in this article), C is the MM equilibrium concentration (mg L^{-1}), and K_f and $1/n$ are constants. According to Sparks (2003), this and other adsorption isotherms are purely descriptions of macroscopic data and do not prove a reaction mechanism. This is especially true in very complex and heterogeneous systems such as the formed by soil particles, where the fit of experimental data with isotherm equations should only be used for comparative purposes and to give some interpretation of the shape of the isotherms. Hence, the Freundlich equation was used here to numerically describe the adsorption of MM in the studied concentration range, and to compare the adsorption capacity of the different soils at selected values of MM concentration.

3. Results and discussion

3.1. Effects of pH

Fig. 2 shows the adsorption isotherms of MM on soil 5 at pH 4, 6 and 8. MM adsorption decreases as the pH increases, in agreement with the general trend observed for sulfonylureas (Beyer et al., 1988; Hay, 1990). This behaviour is usually explained in terms of charge development at the surface of soil particles and speciation of the herbicide in aqueous solutions as a function of pH (Berglöf et al., 2003). Since the surface charge of soil particles becomes more

negative as the pH increases, the adsorption of the negatively charged MM species becomes less favored by increasing pH as a consequence of electrostatic repulsion. In addition, although the adsorption of the neutral MM species should not be affected by electrostatics, its concentration decreases by increasing pH, leading also to a less favorable adsorption as the pH increases.

Fig. 2 shows that changes in pH can significantly affect the adsorption of MM ($p<0.05$), as reported for other sulfonylureas. Therefore, if correlations between herbicide adsorption and other parameters such as TOC are looked for, it is desirable to have a relatively good control of pH in order to avoid ambiguous conclusions. In agreement with Kah and Brown (2006), an artificial control of pH may have different drawbacks, such as impossibility of obtaining results that reflect the real condition of the studied soils or modification of other soil characteristics during pH adjustments. However, this is necessary in order to evaluate the effects of factors other than pH.
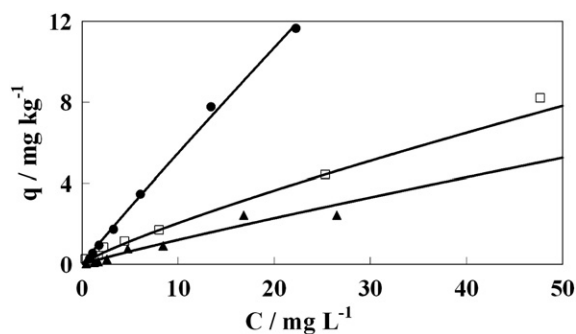

Fig. 2. Adsorption isotherms at (●) pH=4, (□) pH=6, (▲) pH=8 for soil 5. Lines have been drawn according to the Freundlich isotherm with the following parameters: (●) K_f=0.60, $1/n$=0.96; (□)K_f=0.24, $1/n$=1.02; (▲)K_f=0.15, $1/n$=0.91.
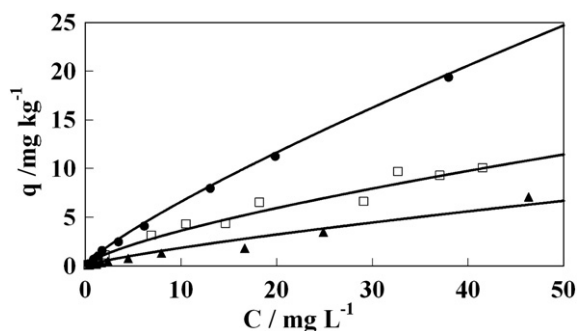
Fig. 3. Adsorption isotherms at pH=6 for samples with different TOC. (●) 4.02%, soil 28; (□) 2.08%, soil 16; (▲) 0.98%, soil 1. Lines have been drawn according to the Freundlich isotherm with the parameters in Table 1.

3.2. Adsorption on soils at constant pH

Adsorption isotherms at pH 6.0±0.2 were measured for the 30 studied soils. Fig. 3 gives an example for three selected soils (soils 1, 16 and 28). These soils have relatively similar SSA and clay contents but rather different TOC (0.98%, 2.18% and 4.02% respectively). In addition, since all the studied soils are subject to similar farming practices (no till and production of the same kind of crops), the quality of the soil organic matter is expected to be similar, and thus the adsorptive differences among soils should be mainly given by differences in TOC. Fig. 3 indicates that adsorption of MM increases significantly ($p<0.05$) with increasing TOC.

A more quantitative analysis of the effects of TOC and other parameters on the adsorption of MM on all the studied soils can be done with the Freundlich equation. The values of K_f and $1/n$ that resulted from the fitting are presented in Table 1. The value of K_f, which represents the adsorption of MM in mg kg^{-1} when the equilibrium MM concentration is 1 mg L^{-1}, is positively and significantly correlated to TOC (R^2 0.48, $p<0.05$), but not significantly correlated to either clay content (R^2 0.01, $p>0.60$) or SSA (R^2 0.025, $p>0.57$). Except for soils 3, 5, 7 and 18 that have $1/n$ values close to 1 indicating linear isotherms under the studied conditions, $1/n$ is lower than 1 for all the other soils and thus their isotherms are L-shaped (Sparks, 2003). This kind of shape was also found by Pusino et al. (2004) for the adsorption of primisulfuron on soils, suggesting that the affinity of surface sites for MM is decreasing as the surface is becoming

populated with MM and/or a decrease in vacant adsorption sites as MM concentration increases (Sparks, 2003).

Values of K_f and $1/n$ together with the Freundlich equation were used to calculate the adsorption of MM at four different equilibrium concentrations (10, 20, 30 and 40 mg L^{-1}), in order to cover the concentration range investigated. The plots for the 30 soils are presented in Fig. 4. A positive and significant relationship between q and TOC is observed for all concentrations (R^2 between 0.68 and 0.78, $p<0.05$). Results for soils 20 and 22 after removing part of their TOC are also in agreement with this relationship. The results show that TOC is a very important factor that affects MM adsorption in the whole MM concentration range investigated. Although this is known for several herbicides (Kah and Brown, 2006; Weber et al., 2004), it has not been well established for MM adsorption on soils. For example, in a study of MM adsorption, Walker et al. (1989) worked with seven soils whose organic matter content varied from 1.64% to 4.98% and a sample (Arthur Rickwood) with a very high organic mater content (from 26.5% to 35.1% depending on the depth of the investigated horizon). They found a positive correlation between MM adsorption and organic matter content when all the samples were considered. However, as the authors state (Walker et al., 1989), the linear regression was strongly influenced by the Arthur Rickwood sample, which contained an unusual amount of organic matter and the lowest pH. When this sample was excluded from the regression analysis, the correlation between MM adsorption and organic matter content was negative and had not statistical significance (Walker et al., 1989). This is presumably due to the fact that the working pH varied more than two pH units (5.6 to 7.9) for the different solids. In addition, since only one-point measurements were performed by these authors, the equilibrium concentration was different for each experiment, which also complicates the comparison of adsorption data if adsorption isotherms are not linear.

Comparable results were informed by Cranmer et al. (1999) for the adsorption of MM in Colorado Soils. As the authors state, there was no obvious influence of soil organic matter on adsorption, and the adsorbed amount showed weak correlation coefficient with organic matter content (Cranmer et al., 1999). Therefore, the significant correlations shown in Fig. 4 as compared to the no significant or weak correlations informed respectively by Walker et al. (1989) and Cranmer et al. (1999) demonstrate that a good pH control is needed when effects of TOC are investigated. The need of a good pH control can be also deduced by analyzing data in Figs. 3 and 4. For example,
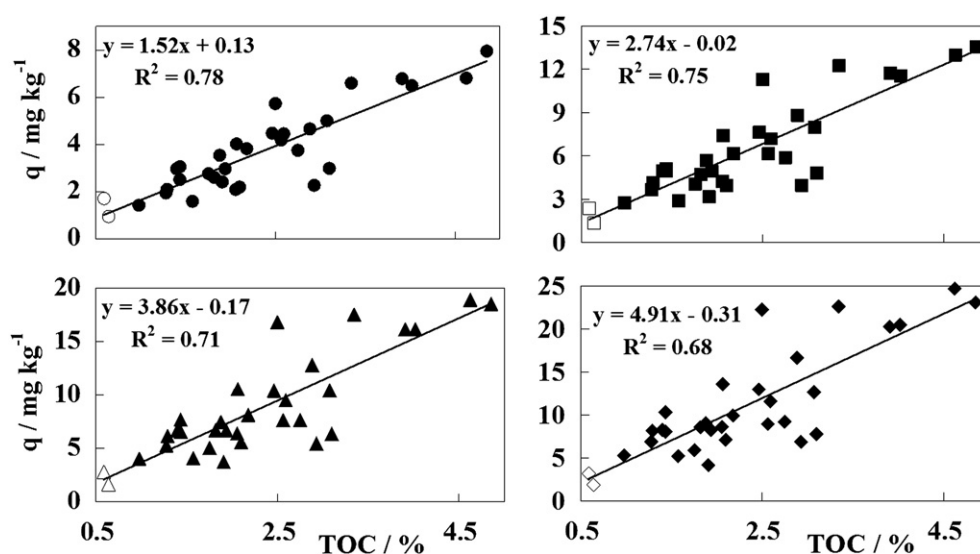

Fig. 4. q as a function of TOC for data at pH=6 and four different equilibrium concentrations (a) 10 mg L^{-1}, (b) 20 mg L^{-1}, (c) 30 mg L^{-1}, (d) 40 mg L^{-1}. Open symbol correspond to soils 20 and 22 after removing part of their organic matter (TOC 0.59% and 0.64% respectively).
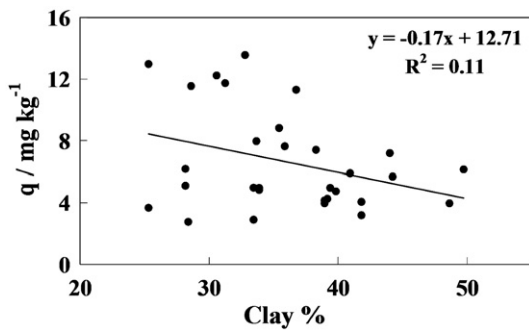
Fig. 5. q (at 20 mg L^{-1} equilibrium concentration) as a function of the clay content.

MM adsorption for soil 5 is predicted to increase around 3.6 times by changing the pH from 8 to 4 at 30 mg L^{-1} MM concentration (Fig. 3). At the same MM concentration and constant pH 6, the maximum difference in TOC found between soils 1 and 30 produces a 4.6-fold increase in adsorption (Fig. 4). Thus, the effects of pH are comparable to the effects of TOC and cannot be neglected.

Fitting lines in Fig. 4 have very small y-axis intercepts. They suggest that inorganic soil components have a weak effect on the adsorption of MM on the set of soils studied. This is also suggested by the plot of q vs. clay content (Fig. 5), which gives a no significant correlation ($p > 0.05$). This is not always the case for the adsorption of sulfonylureas. Pusino et al. (2004), for example, reported that inorganic solids such as amorphous Fe oxides and Al^{3+}- and Fe^{3+}-exchanged montmorillonites were active in adsorbing primsulfuron, but that Ca^{2+}- and Na$^+$-exchanged montmorillonites were ineffective in the adsorption of this herbicide. The absence of important amounts of Fe oxides and smectites exchanged with trivalent cations in the studied soils (Blanco and Stoops, 2007) might explain the weak effect that inorganic components have on the adsorption of MM. Although not shown here, a no significant correlation was also found with SSA (R^2 0.003, $p > 0.77$). It seems that the inorganic fraction, which represents more than 95% of the studied soil samples, is controlling the SSA. Since this fraction is not significantly active in adsorbing MM, no correlation between adsorption and SSA is found.

According to the presented results, almost all the adsorption of MM can be ascribed to the presence of organic matter at constant pH. Soil organic matter is a heterogeneous mix of molecules presenting plant and animal residues in different stages of decomposition. These molecules contain hydrophobic regions due to the presence of aliphatic and aromatic segments. They also contain hydrophilic regions, which in the case of humic substances are mainly represented by the presence of carboxylic, phenolic and other functional groups that can become protonated or deprotonated depending on the pH. High pH induces deprotonation and leads to an increase in the negative charge of the molecules. Although the mechanisms by which pesticides and other chemicals of similar characteristics are retained by organic matter are not clearly understood yet, there is a general consensus in that these chemicals can bind organic matter via different interactions such as van der Wall forces, π-bonding, hydrophobic interactions, H-bonding, and others (Yang and Koopal, 1999; Sparks, 2003; Kah and Brown, 2006). Although MM is predominantly anionic under the studied conditions, it has hydrophobic regions that may be able to bind hydrophobic regions of organic matter molecules through this kind of interactions provided the electrostatic repulsion is not too high. The presence of divalent or trivalent cations acting as bridges between negatively charged groups in organic matter and MM could be another possibility for binding. In addition, the decrease in the negative charge of organic matter functional groups might explain some of the increase in adsorption with decreasing pH as a consequence of decreased electrostatic repulsion (Berglöf et al., 2003).

3.3. Mobility assessment

Adsorption is one of the main processes controlling herbicide mobility in soils. An indirect estimation of this mobility can be obtained from the groundwater ubiquity score, GUS (Gustafson, 1989), defined as:

$$GUS = \log t_{1/2}(4 - \log K_{OC}) \tag{2}$$

where GUS is a dimensionless index, $t_{1/2}$ is the herbicide half-life in soil and K_{OC} is the soil organic carbon adsorption coefficient. According to Oliveira et al. (2001), herbicides with GUS < 1.8 are ranked as non-leachers, those with GUS > 2.8 are leachers, whereas those with 1.8 < GUS < 2.8 are considered transitional. A $t_{1/2}$ value of 61 days, which is intermediate between the values (range 38–84 days) measured by Bedmar et al. (2006) for MM in soils of the Buenos Aires province, was used in calculations. K_{OC} was calculated as (Raturi et al., 2005):

$$K_{OC} = \frac{K_f}{0.01 TOC} \tag{3}$$

The values of K_{OC} and GUS are listed in Table 1. There is a considerable variation in K_{OC}, ranging respectively from 9.7 L kg^{-1} for soil 13 to 50.3 L kg^{-1} for soil 11. This leads to a respective variation in GUS from 5.38 to 4.10. Besides these considerable variations, GUS values are larger than 2.8 in all cases indicating that MM can be ranked as leacher in all studied soils.

Although leaching indexes such as GUS are valuable as a tool to estimate mobility of herbicides in soils, it must be remarked that a $t_{1/2}$ value of 61 days is relatively high as compared to other values informed in the literature for other soils. Juhler et al. (2008), for example, informed an average $t_{1/2}$ of 20 days (range 3–135 days). By using this average value for $t_{1/2}$ and K_{OC} values from Table 1, GUS becomes smaller, ranging from 3.91 for soil 13 to 2.99 for soil 11. Even in this case, MM can still be ranked as leacher in all the studied cases. It is also necessary to remember that most of the isotherms found in this work were L-shaped isotherms, and thus K_{OC} decreases and GUS increases by increasing C. The values of K_{OC} and GUS informed in Table 1 correspond to $C = 1$ mg L^{-1}. For higher MM concentrations K_{OC} is lower and GUS is larger, indicating that MM can be considered as leacher in all the concentration range investigated.

4. Conclusions and significance of the results

MM adsorption isotherms on 30 soil samples indicate that TOC and pH are important factors affecting adsorption. The adsorption increases by increasing TOC and decreasing pH. The effects of TOC were mentioned previously but the correlation between this parameter and MM adsorption was always obscured because of pH changes in the experiments. In fact, this article demonstrates that a good pH control is necessary to investigate the effect of TOC. Under pH controlled conditions (pH 6.0 ± 0.2), a significant and positive correlation between MM adsorption and TOC was observed for a large range of concentrations (up to 40 mg L^{-1}). The results also show that adsorption is not significantly affected by inorganic components and SSA.

Even though adsorption occurred on all soils, adsorption was relatively low and GUS was larger than 2.8 in all cases, indicating that MM would be rather mobile and transported by water flows. Since MM binds mainly the organic matter of soils, the mobility of the herbicides in soils will be also affected by the mobility of the organic matter. Conditions that favor desorption and/or dissolution of organic matter, such as high soil pH or low Ca^{2+} concentration (Weng et al., 2002; Brigante et al., 2007), might also favor the mobility of the herbicide.

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