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4 **EFFECT OF ORGANIC AMENDMENTS ON THE RETENTION AND MOBILITY**
5 **OF IMAZAQUIN IN SOILS.**

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2 **OF IMAZAQUIN IN SOILS.**

3

4 **Abstract**

5 The influence of two organic amendments consisting of an urban waste compost (SUW)
6 and a commercial amendment from olive-mill wastes (OW) was assessed on the sorption
7 properties and leaching of the ionisable herbicide imazaquin on four soils with different
8 physico-chemical characteristics. A loamy sand soil (CR), a loam soil (P44), a silt loam soil
9 (AL) and a clay soil (TM), with low-medium organic matter contents were chosen.
10 Sorption-desorption experiments were performed on the original soils and on a mixture of
11 these soils with the organic amendments at a rate of 6.25% (w/w). These mixtures were
12 used just after preparation and after aging for 3 months. Imazaquin adsorption was higher
13 on AL soil because of its high content of amorphous iron oxides, whereas it was related to
14 their organic matter (OM) contents on TM and CR soils and to its acid pH on P44 soil.
15 Addition of exogenous OM to soils caused a decrease in the adsorption of the herbicide
16 with the only exception of CR soil, due to blocking of adsorptive surfaces and/or
17 equilibrium pH rise. The extent of this decrease was only dependent on the nature of the
18 added amendment on AL soil. The adsorbed amounts of imazaquin on aged organic
19 fertilized soils were usually pretty close to that on original soils. Results of soil column
20 experiments indicate that addition of exogenous organic matter cannot be considered as a
21 regular practice for retarded movement of imazaquin.

22

1 **Introduction**

2 Concerns about groundwater contamination by the use of pesticides have risen during the
3 last years as a consequence of the increased pesticide application as well as the use of more
4 mobile pesticides (1). In USA it was estimated that in 1990, 92% of the nearly 300 million
5 ha used for agricultural production received herbicide applications and 31% of the acreage
6 received insecticide treatments (2). A survey on the occurrence of pesticides in
7 groundwater tested across the USA during that year stated that 1.2% of community water
8 system wells and 2.4% of rural domestic wells contained pesticides (3). Recent studies
9 indicate that this trend is increasing. Troiano et al. (4) detected residues for 16 active
10 ingredients and breakdown products in California groundwater as a result of legal
11 agricultural use. Spalding et al. (5) reported detection of 14 pesticides and their
12 transformation products in groundwater of the central Platte Valley of Nebraska. In a
13 monitoring study, Barbash et al. (6) detected pesticides in groundwater within 1 year
14 following application.

15 Several strategies have been considered for preventing herbicide leaching, such as adapting
16 appropriate crop management practices, modifying application techniques, and developing
17 slow release formulations (7, 8). An important management strategy for reducing leaching
18 is to manipulate the sorption potential of the soil by incorporating organic residues because
19 a strong correlation is usually observed between soil organic C content and adsorption of
20 pesticides (9, 10). Retarded movement by the application of organic amendments has been
21 often described for widely-used herbicides: clopyralid (11); diuron (12); linuron (13);
22 metolachlor (14); etc.

23 Studies about the effect of addition of exogenous organic matter to soils on the adsorption
24 and leaching of anionic herbicides are really scarce. There are very few studies indicating

1 an increase in the adsorption of some anionic herbicides when applied to amended soils
2 (15, 16).

3 Imazaquin is a selective imidazolinone herbicide used for broad-spectrum weed control in
4 soybean [*Glycine max* (L.) Merr.] and other legume crops. Imazaquin is an amphoteric
5 molecule that has both an acidic carboxyl and a basic quinoline functional groups with pKa
6 values of 3.8 and 2.0, respectively (17), and therefore it exists predominantly as an anion at
7 typical soil-suspension pH values. Several authors have reported to be mobile (18-20),
8 being the time between its application and the first rainfall a crucial factor in imazaquin
9 leaching (21).

10 Because pH and organic matter are the soil properties that most significantly affect the
11 sorption of imazaquin (22-24), the aim of the current study was to evaluate the application
12 of two organic waste amendments, consisting of a commercial product from olive mill
13 wastewater and other plant residues and an urban waste compost, on the sorption and
14 leaching of imazaquin by soils. In addition, the influence of aging of the exogenous
15 organic matter added to the soil on imazaquin adsorption was also assessed because
16 transformation of organic amendments applied to soils can modify the further interaction of
17 xenobiotics with the amended soils (10).

1 **Materials and Methods**

2 *Herbicide*

3 Technical grade imazaquin (97% purity) was obtained from AGAN Chemical
4 Manufacturers (Ashdod, Israel). Its molecular structure and ionization is shown in Scheme
5 I.

6

7 *Soils*

8 The soils used were sampled from the surface horizon (0-20 cm) and were classified as
9 Typic Xeropsamment (CR soil), Aquic Haploxeralf (P44 soil), Typic Eutrochrept (AL soil)
10 and Entic Pelloxerert (TM soil). The soils were dried and crushed to pass a 2 mm sieve, and
11 were analyzed for pH in saturated paste, total carbonate content and particle size
12 distribution. Organic carbon content (OC) was determined by the dichromate oxidation
13 method and organic matter content (OM) was calculated as follows: $OM(\%) = 1.724 \times$
14 $OC(\%)$.

15 The chemical composition of the soils was determined by dissolving the samples using a
16 three-acid method (25); and amorphous and organically bound iron, manganese and aluminum
17 oxides were determined by the ammonium oxalate-oxalic acid method (26).

18 The mineralogical composition of the soil clay fraction was determined by X-ray
19 diffraction (XRD) using Cu K α radiation. Semiquantitative estimation of the minerals was
20 performed using characteristic XRD reflections and their relative intensities according to
21 Schultz (27).

22 The determined physico-chemical properties of the original soils are listed in Table 1.

23

1 *Amended soils*

2 Two organic amendments were used: a commercial product manufactured from olive mill
3 wastewater and other plant residues (OW), and an urban waste compost from Villarasa (SW
4 Spain) (SUW). The organic amendments were dried at 70 °C for 48h, homogenized and
5 crushed to pass a 4 mm sieve. The composition of the amendments is given in Table 2.

6 The organic amendment of the soils was carried out by mixing thoroughly, during 24 hours,
7 300 g of the original soils with 20 g of the two amendments (6.25% of the total) (from now
8 on fresh amended soils).

9 In order to study the exogenous OM evolution, incubation experiments under controlled
10 conditions were also performed. The amended soils were maintained under constant
11 humidity at field capacity during three months in darkness at 30°C (from now on aged
12 amended soils).

13

14 *Sorption-desorption experiments*

15 Triplicate sorption experiments were done by mixing 10 g of the soils with 10 mL of 0.01
16 M Ca(NO₃)₂ solutions, containing various concentrations (0.16, 0.32, 0.96, 1.60, 2.60, 3.20
17 µM) of imazaquin, in 30 mL polypropylene centrifuge tubes. The samples were shaken for
18 3 days at 20 ± 1 °C. Preliminary experiments showed that equilibration was completed
19 within three days. After shaking, the suspensions were centrifuged and the concentration of
20 the herbicide in the supernatant was determined. The difference in pesticide concentration
21 between the initial and final equilibrium solutions was assumed to be due to sorption.

22 Additional adsorption experiments of imazaquin at 1.60 and 3.20 µM were performed on
23 the soils by determining the adsorbed amount at 24 h for an estimation of the percent
24 adsorbed with respect to the total amount after 3 days.

1 Imazaquin analysis was performed by using a Shimadzu HPLC equipped with PDA
2 detector set at a wavelength of 240 nm. The reverse phase column was a 15 cm Kromasil
3 100 C18. The mobile phase was a mixture of 65% water and 35% methanol containing 2%
4 acetic acid. The flow rate was 1.2 mL min⁻¹. The retention time was 18.2 min.
5 Desorption experiments were performed on original and amended soils after sorption
6 equilibrium was reached for the points corresponding to imazaquin initial concentrations of
7 0.96 and 2.60 μM, by removing half of the supernatant after centrifugation, replacing it by
8 5 mL of 0.01 M Ca(NO₃)₂ solution, allowing equilibration for an additional 3 days period,
9 and after that operating as in the sorption experiment. This process was repeated twice
10 more.

11 Sorption-desorption isotherms were fitted to the logarithmic form of the Freundlich
12 equation:

$$13 \quad \log C_s = \log K_f + n \log C_e$$

14 where C_s (μmol kg⁻¹) is the amount of herbicide sorbed at the equilibrium concentration C_e
15 (μmol L⁻¹), and K_f and n are constants that characterise the relative sorption capacity and
16 the sorption intensity, respectively, for the herbicide. The fitted equation was used to
17 calculate sorption distribution coefficients (K_d) at a selected C_e (2 μmolL⁻¹). The organic
18 carbon (OC) normalized distribution coefficient (K_{oc}) was calculated from K_d values.

19 Hysteresis coefficients, H , for the sorption-desorption isotherms were calculated according
20 to:

$$21 \quad H = n_d/n_a$$

1 where n_a and n_d are the Freundlich n constants obtained from the sorption and desorption
2 isotherms, respectively. The ratio n_d/n_a has been used to describe the hysteretic behaviour of
3 desorption from soils (10, 28).

4

5 *Leaching experiments*

6 Leaching experiments were performed in metacrylate tubes of 3.0 cm diameter cut into 4-
7 and 8-cm sections, and five units of 4 cm were glued together with a 8 cm unit at one end to
8 construct a 28 cm column. The column was covered at the end opposite to the 8 cm unit
9 with 1 mm nylon screen padded with a thin layer of glass wool (0.5 g) to hold the soil
10 firmly in the column. Soil was packed from the top of the column (8 cm section), creating a
11 24 cm soil column that could be readily separated into 4 cm segments. A thin layer of glass
12 wool was placed on top of each soil column to maintain the integrity of the surface during
13 leaching.

14 The leaching experiments were carried out in triplicate in CR, P-44 and AL soils, their
15 amount packed in the columns being 0.240, 0.246 and 0.190 kg, respectively. The pore
16 volume of the soils was determined to be 57 ml in CR soil, 66 ml in P-44 soil and 88 ml in
17 AL soil. These soil column experiments were also performed with fresh amended soil by
18 filling the first two upper rings of the columns with the equivalent amount of amended soil
19 instead of the original soil.

20 The columns were treated with 5 pore volumes of a 0.01 M $\text{Ca}(\text{NO}_3)_2$ solution followed by
21 1 pore volume of distilled water before spraying 10 ml of the herbicide at a rate of 140 g
22 *a.i.* ha^{-1} . 25 mL of distilled water was added every 24 h at the top of the column and the
23 leachates were collected and analysed for the herbicide.

1 Each soil column was separated into six 4 cm-segments and the soil was dried at 40°C. A
2 bioassay was used to calculate the residual activity of the herbicide throughout the rings of
3 the soil column by measuring the inhibition of shoot weight of sorghum seedlings. 10 g of
4 soil in triplicate from each segment was mixed with 10 g of the original soil and 4 seeds
5 were planted. The weight of the shoots was measured after 9 days and the inhibition
6 percentage determined by comparison with a control of the untreated soil.

7

8 **Results and Discussion**

9 *Sorption on the original soils.*

10 Figure 1 shows the adsorption isotherms of imazaquin on the original soils CR, P44, AL,
11 and TM, and on these soils after amendment, both used just after mixing and after
12 incubation for three months. The sorption of the herbicide is well described by fitting the
13 experimental data to the linearized Freundlich relationship (Table 3).

14 As inferred in Figure 1, the sequence of sorption of imazaquin on the original soils was:
15 AL>P44>TM>CR.

16 The soil properties found to be better correlated with imazaquin sorption are the organic
17 matter content and the soil-solution pH (19, 24, 29). However, positively charged Fe and Al
18 oxyhydroxides contribute to sorption of the herbicide on soils with low organic matter
19 content (23, 30). Gennari et al.(31) found a positive correlation between Kf values of
20 imazaquin and extractable amorphous iron oxides in addition to organic matter content. The
21 high affinity of imazaquin for oxyhydroxides was the basis for the development of slow
22 release formulations of this herbicide (32). The highest adsorption of the herbicide on AL
23 soil can be explained based on its high iron oxides content, especially of amorphous oxides
24 (Table 1). This is illustrated by comparing imazaquin adsorption on AL and TM soils

1 where the content of the iron amorphous oxides is about 13-fold higher on AL soil than on
2 TM soil, but the differences between the organic matter contents and equilibrium pH are
3 negligible (Table 4). At the equilibrium pH, the iron oxides will exhibit partially positive
4 charge since their zero point charge values are around pH 8.5 (33), and therefore these
5 surfaces will interact with the anionic molecules of the herbicide.

6 The high adsorption of imazaquin on P44 soil is related to the low pH of this soil during the
7 adsorption experiments, which amounts to more than 2 units lower than in the rest of soils
8 (Table 4). In spite of the fact that more than 99% of the imazaquin molecules are predicted
9 to be ionized at the lowest solution pH found in this study (pH 5.42) according to Stougaard
10 et al. (19), the effective acidity at soil colloid surfaces can be 2 or 3 units lower than
11 solution pH due to cation distribution in the diffuse double layer and higher hydrogen
12 concentrations near weakly ionized organic functional groups and mineral edges.

13 Imazaquin affinity for soil surface will increase with a pH decrease because of a larger
14 decrease in the percentage of herbicide molecules remaining as anion, and there will be a
15 decrease in the electrostatic repulsion of herbicide molecules from negatively charged soil
16 surfaces. At the effective pH of the colloidal surfaces of P44 soil, imazaquin adsorption will
17 be favoured because of strong interactions with the humic substances (22). In addition, a
18 semiquantitative estimation of the clay minerals present in the clay fraction of P44 soil
19 indicated the presence of clay minerals such as kaolinite and illite, whose percents with
20 respect to the total layer silicate content were 42 and 58%, respectively. These clay
21 minerals are able to develop a small amount of positive charge on the edges under acidic
22 conditions (34), with a subsequent enhancement on imazaquin adsorption.

23 No influence of pH is expected on the sorption of the herbicide on the original TM and CR
24 soils because of identical equilibrium pH (Table 4). Adsorption of the herbicide on TM soil

1 is higher than on CR soil (Figure 1) which is related to the organic matter content. Kf
2 values are 2.5-fold higher on TM than on CR soil (Table 3). When the Kf values are
3 normalized to the organic carbon content (Koc values), there is no statistical difference
4 between the calculated values for both soils (Table 5), indicating the organic matter as the
5 main soil property controlling the sorption of the herbicide on these soils. These Koc values
6 are within the range of the calculated values (8.1-30.6) from the data in the work by Loux
7 et al. (29) for soils with a pH round 7.8, where imazaquin adsorption was stated to be
8 correlated with the organic matter content. A few deviations from that range in that work
9 may arise from the fact that additional sites can be performing on the adsorption, probably
10 amorphous iron oxides whose influence was not examined.

11

12 *Sorption on amended soils.*

13 The adsorption of imazaquin on fresh and aged amended soils shows different patterns
14 depending on the type of amendment and on the soil (Figure 1). As commented above, the
15 pH of the soil solution and the content of organic matter have been reported as the most
16 important factors for determining the adsorption of imazaquin on soils, in addition to their
17 amorphous iron oxides content. The supply of amendments to the soil will influence both
18 the pH and the organic matter content. The pH of the adsorption experiments on amended
19 soils are shown in Table 4 where there is almost no difference between the equilibrium pH
20 of fresh and aged amended soils. These values are also identical to those of equilibrium of
21 the herbicide on the original soils because of the buffer effect of the soil, except on P44 soil
22 because of its quite initial low pH value. In consequence, adsorption of the herbicide on the
23 amended soils with the exception of P44 soil, will be mainly determined by the content and
24 the properties of their organic matter (original and from amendment). The organic matter

1 contents of the original and amended soils are also listed in Table 4. A decrease in the
2 percent of the organic matter content is notorious after incubation of the amended soils for
3 three months due to the increase in the microbial activity of the soil with a subsequent
4 decomposition of the organic matter, but the final values are always higher than those of the
5 original soils.

6 In general, the addition of fresh amendments on the soil decreases the adsorption of the
7 herbicide because much of the mineral and organic soil surfaces become blocked, with the
8 exception of the sandy soil which has originally very few adsorptive surfaces. Moreover,
9 except for AL soil, the type of amendment did not influence on the adsorption of the
10 herbicide on the amended soils.

11 In AL soil, the addition of fresh exogenous organic matter causes a decrease in the
12 adsorption of the herbicide because of covering by the added organic matter of the iron
13 oxide surfaces, which are the main responsible for the high adsorption of the herbicide on
14 this soil. The contribution of the sorptive surfaces supplied by the amendments is negligible
15 compared with that of blocked iron oxide surfaces and the overall adsorption of imazaquin
16 is decreased. Similar pattern was observed by Leone et al. (35) in their study on imazaquin
17 adsorption of ferrihydrite and ferrihydrite-humic acid associations.

18 In addition, there is a notorious difference in the reduction of the amount sorbed of the
19 herbicide depending on the source of the amendment. SUW produces a two-fold decrease
20 in the amount adsorbed of imazaquin when compared to the use of OW. Similar Koc values
21 are expected if the organic matter is controlling its adsorption on the fresh amended soils.

22 However, Koc values are about three-fold higher in AL soil amended with OW than with
23 SUW (Table 5), and therefore the nature of the exogenous organic matter is an important
24 factor determining the extension of adsorption of herbicides on soils with a high content of

1 iron oxides. The protonated iron oxide surfaces will interact with the carboxylate groups of
2 the exogenous organic matter resulting in the formation of inner-sphere complexes
3 according to the scheme in (35). Cox et al. (16) obtained a lower humification index by
4 fluorescence measurements for SUW than OW. In consequence, SUW amendment with a
5 higher content of carboxylic groups will block in a larger extension the iron oxides surfaces
6 responsible for imazaquin adsorption on this soil.

7 The adsorption of imazaquin on TM soil freshly amended with SUW and OW decreases
8 considerably with respect to the original soil (Figure 1). Koc values of the OW and SUW
9 amended soils are 3- and 4-fold lower, respectively, than that of the original soil (Table 5).

10 It seems that the exogenous organic matter has a lower adsorption capacity than the
11 original, and the addition of the amendments impedes in part the herbicide sorption due to
12 the covering and blocking of the more reactive soil adsorptive surfaces in TM soil, mainly
13 the endogenous organic matter.

14 Adsorption of imazaquin on fresh-amended P44 soils also resulted in a high decrease in
15 comparison to the original soil because of their higher pH values (Figure 1), though it could
16 be also due to a blockage of the sorptive sites operating at these solution pH on the original
17 soil by the added organic matter.

18 The incubation of the soils with the organic amendments for three months produced a
19 modification of the exogenous organic matter by modifying its hydrophilic-hydrophobic
20 balance (10). The highest degradation occurred on AL and TM soils amended with OW
21 accounting for about 45% of the OM content of the freshly amended. The sorption
22 behaviour of imazaquin on the aged amended soils shows a clear pattern for TM and CR
23 soils where imazaquin tend to be sorbed in the same extension than on the original soil
24 (Figure 1). In Table 5, the Koc values for the original CR and TM soils where the organic

1 matter was the key parameter governing the adsorption of imazaquin are quite close to
2 those of the aged amended soils, that may indicate a more related nature of the degraded
3 and humified organic amendment to that of the original soils.

4

5 *Desorption experiments.*

6 No general trend of desorption of imazaquin on the original and amended soils is followed
7 from the desorption percentages and hysteresis coefficients in Table 6.

8 In AL soil, the use of both fresh amendments decreased its hysteresis. The addition of fresh
9 amendment blockages the sorptive sites on the original soil and gives additional sites that
10 may be considered of lower affinity, therefore enhancing the desorption of the herbicide as
11 shown by the lower H values than those of the original soil. On AL aged soils, the
12 hysteresis was dependent on the type of the added amendment. Unlike the soil treated with
13 SUW, the use of OW increased the hysteretic behaviour of the herbicide on the aged soil in
14 addition to highly promote its adsorption with respect to the use of fresh amendment
15 (Figure 1). This indicates that the transformed organic matter from OW on AL soil
16 provides more active sites than those of the fresh amendment and/or a release of adsorption
17 sites on the amorphous iron oxides previously blocked.

18 The CR soil presents in general the highest desorption percentages. In the original soil and
19 after amendment with SUW, H values are pretty close to the unity indicating that the
20 adsorption of the herbicide on these soils is almost completely reversible.

21 In P44 soil, the hysteresis coefficients are very low for the original soil unlike the amended
22 soils. The pH in the desorption steps were acid on the original soil whereas on the amended
23 soils they were as those in the adsorption steps (data not shown). On the original soil,
24 imazaquin is adsorbed not only on the organic matter, but also on surfaces exhibiting pH-

1 dependent charges, on which the herbicide is easily desorbed, and therefore H values will
2 be lower than those on the amended soils. This is in agreement with the study by Che et al.
3 (22) who observed that under acidic conditions imazaquin adsorbed on pH-dependent
4 surfaces from clay minerals was completely desorbed after two desorption cycles whereas
5 an important fraction was still remaining adsorbed on humic acids. These pH-dependent
6 surfaces on P44 soil are of lower affinity for the retention of the herbicide than those of the
7 amorphous iron oxides operating on AL soil (31).

8 The original TM soil has a very small amount of amorphous iron oxides and a higher fine
9 fraction (clay+silt) than P44 soil, and in consequence a higher reversibility of the adsorbed
10 imazaquin would be expected. However, this soil has the highest H values showing that the
11 adsorption of the herbicide is not occurring on pH-dependent surfaces such as those of P44
12 soil but mainly on the original organic matter. Molecular modelling of adsorption data of
13 imazaquin on humic acids by Nègre et al. (36) showed that in addition to binding to
14 specific sites of the humic acids, the herbicide was strongly trapped by steric hindrance
15 which would be the reason of the high values of H obtained.

16 The desorption pattern of imazaquin from TM soil is completely different from CR soil
17 despite that adsorption of the herbicide in both soils was mainly determined by the organic
18 matter content, but the hysteresis coefficients show a hysteretic behaviour in imazaquin
19 desorption from TM soil, unlike CR soil, indicating a higher affinity of the herbicide for the
20 original organic matter present in TM soil than that in CR soil. This higher affinity for the
21 original organic matter in TM soil is also clearly deduced when comparing H values of the
22 original soil and those of this soil treated with both fresh amendments. H values decrease in
23 fresh amended soils because adsorption of the herbicide is also occurring on sites of the
24 added organic matter of which imazaquin molecules are easierly detached than those of the

1 original organic matter. *H* values are indicating that the aging of the added OW in this soil
2 produces either a degraded material with a higher affinity for the herbicide than that of the
3 freshly amended, or a release of adsorption sites blocked just after amendment.

4

5 *Leaching experiments.*

6 Leaching experiments were performed on CR, P44 and AL soils but not on TM soil
7 because it has an important fine fraction containing swelling clay minerals that impeded the
8 flow of water through the column.

9 The shape of the elution curves of imazaquin on original and fresh amended CR and those
10 on P44 and AL soils is completely different (Figure 2). The curves are highly symmetric on
11 CR soils whereas on P44 and AL soils the elution curves present a very sharp ascendant
12 part and a longer extended tail.

13 The herbicide is almost completely eluted from the original CR soil and when the SUW
14 amendment is applied, their recovery percentages being $97.2 \pm 0.5\%$ and $92.8 \pm 0.6\%$,
15 respectively. In contrast, the total recovery of the soil where the upper layers were amended
16 with OW was $61.0 \pm 4.9\%$ amounting to a 1/3 reduction in leaching. The lower recovery of
17 the herbicide in CR soil amended with OW may be due to some microbial degradation.

18 Addition of compost to soils has been reported to enhance microbial degradation of the
19 herbicides (9, 37). The possibility that some amount of the herbicide was degraded instead
20 of remaining adsorbed was checked by applying the sterilization method of the soil as in
21 (38). No statistical difference was observed in the eluted amounts of the herbicide when
22 compared to those of the non-sterilized soil. The retained herbicide in non-sterilized OW-
23 amended CR soil was available for plants since bioassays performed along the rings of the

1 soil columns showed in the 1st and 2nd upper layers of the soil column, respectively, a
2 18.2 ± 1.1 and $11.0 \pm 0.7\%$ of inhibition expressed as percent of the control.

3 A different trend is noted in P44 soil where there is no statistical difference between the
4 elution percentages of imazaquin in the amended and the original soil. The elution
5 percentages were 95.3 ± 7.6 for the original soil, 96.5 ± 0.3 and 81.8 ± 6.7 for SUW- and OW-
6 amended soils, respectively. In the case of both amended soils, these results are again in
7 agreement with those from the adsorption experiments where similar values of K_{oc} and K_d
8 were obtained by the use of fresh amendments (Table 5). However, the retention of the
9 herbicide in the columns filled with only the original soil is too low and comparable to
10 those by using amendments, despite of its much higher adsorption (Figure 1). This trend
11 opposite to the batch adsorption data may be explained because of a slower kinetics for the
12 retention of the herbicide in the leaching experiments. Similar results were obtained by
13 Worrall et al. (39) on their adsorption study of the herbicide isoproturon on soils and
14 subsoils showing that different methodologies such as batch and column techniques will
15 reflect different kinetic processes. To assess the influence of the kinetics on imazaquin
16 adsorption, the amount of herbicide adsorbed after 24 and 72 h was determined in batch
17 experiments. As seen in Table 7, only a very small fraction of the total adsorbed amount
18 occurred during the first 24 h on the amended P44 soils, and despite the adsorption on the
19 original soil occurring practically within the first 24 hours, the hysteresis coefficients in
20 Table 6 are very low indicating almost total reversibility in the desorption of the herbicide
21 on this soil. In consequence, the elution pattern of the herbicide on P44 soils is well-
22 explained by the high reversibility of imazaquin from the original soil, and on the amended
23 soils by the low amount adsorbed in the layers filled with amended soil during the lapsed
24 time between every elution event.

1 In AL soil, the elution peak is shifted to a higher elution volume indicating a higher
2 retention on AL soil when compared to CR and P44 soils. At the top of the elution peaks,
3 the cumulative amounts of imazaquin eluted were $43.0 \pm 2.4\%$ for the original soil; $87.9 \pm$
4 1.0 and $54.2 \pm 3.0\%$ for the SUW and OW amended soils, respectively, amounting to a
5 significant reduction in leaching in the case of the original soil and after OW amendment
6 when compared to SUW. This sequence in the elution pattern agrees with the sorption data
7 of the herbicide (Figure 1) on these soils and their H values (Table 6) where a higher
8 retention is expected on the original soil and after OW amendment because of its higher
9 adsorption and hysteretic behaviour than after SUW amendment. After 400 mL, the total
10 leaching percents were $85.4 \pm 2.6\%$, $100.6 \pm 4.8\%$ and $97.9 \pm 4.2\%$ for the original, SUW-
11 and OW-amended soils, respectively.

12 Leaching experiments indicate that the application of organic amendments for retarded
13 movement of the herbicide is limited to sandy soils such as CR because of their originally
14 very low adsorptive surfaces. Consequently, the application to soils of the organic
15 amendments used in the present study cannot be accepted as a general practice to reduce
16 herbicide losses due to leaching processes.

17

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1 **Figure legends.**

2 Scheme I. Ionization of imazaquin.

3

4 Figure 1. Adsorption isotherms of imazaquin on original (■), fresh amended (●) and aged
5 amended (▲) soils with SUW and OW.

6

7 Figure 2. Breakthrough curves of imazaquin on CR (a), P44 (b) and AL (c) soils. The soils
8 used were original (■) and freshly amended with OW (●) and SUW (▲).

Table 1. Some characteristics of the original soils used.

	CR	P44	AL	TM
	(loamy sand)	(loam)	(silt loam)	(clay)
OM (g kg⁻¹)	7.9	14.0	19.0	17.6
CEC (cmol_c kg⁻¹)	4.8	7.8	17.2	39.0
Carbonates (g kg⁻¹)	69.0	<0.1	<0.1	241.0
pH	8.0	5.5	7.6	8.0
Sand (%)	87.6	49.8	16.4	2.7
Silt (%)	4.0	34.5	61.2	31.5
Clay (%)	8.4	15.7	22.6	65.9
Total Fe₂O₃ (g kg⁻¹)	11.4	46.1	241.7	43.9
Amorphous Fe₂O₃ (g kg⁻¹)	0.4	1.9	10.8	0.8
Total Al₂O₃ (g kg⁻¹)	53.2	111.8	161.0	116.4
Amorphous Al₂O₃ (g kg⁻¹)	0.2	1.0	9.4	3.5
Total MnO (g kg⁻¹)	<0.1	0.6	35.8	0.7
Amorphous MnO (g kg⁻¹)	<0.1	0.1	9.8	0.2

Table 2.- Some chemical characteristics of the organic amendments.

	OW	SUW
pH	8.6	8.0
Organic matter (g kg⁻¹)	315.0	441.0
Kjeldahl N (g kg⁻¹)	9.6	13.5
C/N	19.0	18.9
P (g kg⁻¹,P₂O₅)	8.7	10.3
K (g kg⁻¹,K₂O)	32.3	5.1
Ca (g kg⁻¹)	65.0	60.4
Mg (g kg⁻¹)	13.0	3.7
Na (g kg⁻¹)	2.0	2.6
Cu (mg kg⁻¹)	70.0	283
Pb (mg kg⁻¹)	19.0	134
Mn (mg kg⁻¹)	240	217
Zn (mg kg⁻¹)	67.0	373

OW: Olive mill Wastewater; SUW: Solid Urban Wastes.

Table 4. Organic matter content (g kg^{-1}) and equilibrium pH of the original and amended soils after treatment with the initial solutions of imazaquin in the adsorption experiments.

	CR		P44		AL		TM	
	OM	pH	OM	pH	OM	pH	OM	pH
Original soil	7.9	7.83 (± 0.29)	14.0	5.42 (± 0.36)	19.0	7.69 (± 0.11)	17.6	7.83 (± 0.17)
OW-F	18.6	8.10 (± 0.35)	32.8	8.04 (± 0.26)	35.9	7.57 (± 0.25)	32.1	7.65 (± 0.15)
OW-A	12.1	8.11 (± 0.35)	23.3	8.49 (± 0.22)	28.4	7.98 (± 0.30)	26.4	8.08 (± 0.21)
SUW-F	24.3	7.71 (± 0.24)	37.1	7.95 (± 0.32)	56.2	7.65 (± 0.31)	47.6	7.51 (± 0.31)
SUW-A	16.4	7.96 (± 0.21)	25.5	8.01 (± 0.24)	30.2	8.03 (± 0.25)	26.9	7.91 (± 0.27)

SUW: soils amended with SUW; OW: soils amended with OW; F: fresh amended soils; A: aged amended soils.

Table 7. Percent of imazaquin adsorbed of the total amount adsorbed after 3 d in batch experiments, as a function of time. The initial concentrations of the herbicide were 1.60 and 3.20 μM .

Soil	Time (h)	1.60 μM	3.20 μM
CR	0-24	77.8	95.0
	24-72	22.3	5.0
CR+OW	0-24	76.6	94.7
	24-72	23.4	5.3
CR+SUW	0-24	35.0	26.9
	24-72	65.0	73.1
P44	0-24	88.9	100
	24-72	11.1	0
P44+OW	0-24	16.0	26.5
	24-72	83.0	73.5
P44+SUW	0-24	10.0	13.9
	24-72	90.0	86.1
AL	0-24	87.5	94.4
	24-72	12.5	5.6
AL+SUW	0-24	72.8	82.1
	24-72	27.2	17.9
AL+F	0-24	67.3	81.2
	24-72	32.7	18.8

Table 3. Freundlich adsorption isotherms parameters (K_f and n values) for imazaquin sorption on the soils used (numbers in parentheses are standard errors). The coefficients of determination (R^2) were higher than 0.952 in all cases.

	CR		P44		AL		TM	
	K_f	n	K_f	n	K_f	n	K_f	n
Original soil	0.06 (± 0.02)	0.56 (± 0.14)	0.46 (± 0.03)	1.00 (± 0.06)	0.59 (± 0.02)	1.14 (± 0.03)	0.15 (± 0.02)	0.49 (± 0.06)
OW-F	0.24 (± 0.02)	0.83 (± 0.04)	0.18 (± 0.05)	0.66 (± 0.14)	0.41 (± 0.02)	0.96 (± 0.03)	0.08 (± 0.02)	0.65 (± 0.03)
OW-A	0.06 (± 0.02)	0.48 (± 0.04)	0.22 (± 0.03)	0.88 (± 0.05)	0.46 (± 0.06)	1.52 (± 0.20)	0.16 (± 0.03)	0.57 (± 0.09)
SUW-F	0.13 (± 0.04)	1.79 (± 0.19)	0.21 (± 0.03)	0.71 (± 0.05)	0.27 (± 0.02)	0.50 (± 0.06)	0.10 (± 0.02)	0.55 (± 0.03)
SUW-A	0.08 (± 0.02)	0.69 (± 0.04)	0.25 (± 0.05)	1.20 (± 0.11)	0.35 (± 0.03)	0.91 (± 0.07)	0.14 (± 0.02)	0.63 (± 0.03)

SUW: soils amended with SUW; OW: soils amended with OW; F: fresh amended soils; A: aged amended soils.

Table 5. Distribution (K_d , L kg⁻¹) and organic carbon normalised distribution coefficients (K_{oc}) for imazaquin sorption on the original and amended soils (numbers in parentheses are standard errors).

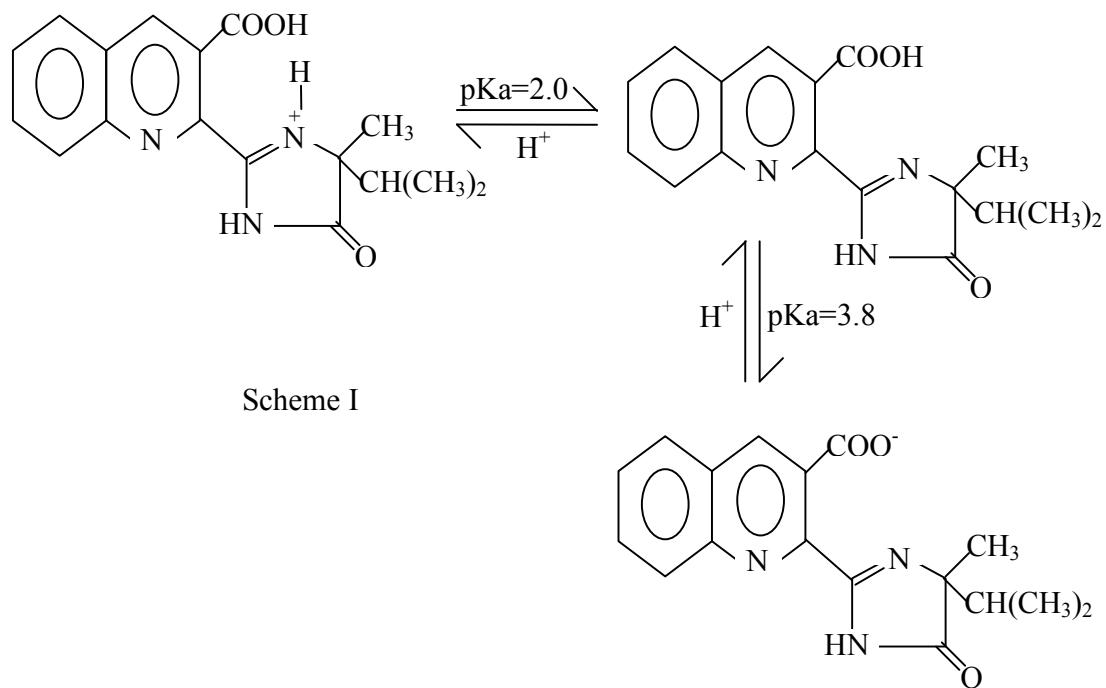
	CR			P44			AL			TM		
	K_d	K_{oc}		K_d	K_{oc}		K_d	K_{oc}		K_d	K_{oc}	
Original soil	0.044 (±0.009)	9.6 (±1.8)	0.463 (±0.041)	57.1 (±4.4)	0.646 (±0.025)	58.6 (±2.7)	0.105 (±0.011)	10.3 (±1.1)		0.062 (±0.008)	3.3 (±0.5)	
OW-F	0.213 (±0.011)	19.7 (±1.0)	0.142 (±0.034)	7.5 (±1.7)	0.396 (±0.019)	19.0 (±1.0)	0.062 (±0.008)	3.3 (±0.5)		0.116 (±0.018)	7.6 (±1.3)	
OW-A	0.043 (±0.009)	6.1 (±1.3)	0.202 (±0.016)	14.9 (±1.1)	0.650 (±0.101)	39.5 (±5.5)	0.073 (±0.023)	2.6 (±0.2)		0.104 (±0.006)	6.6 (±0.4)	
SUW-F	0.228 (±0.048)	16.2 (±3.4)	0.171 (±0.014)	8.0 (±0.7)	0.188 (±0.023)	5.8 (±0.6)	0.073 (±0.023)	2.6 (±0.2)		0.104 (±0.006)	6.6 (±0.4)	
SUW-A	0.066 (±0.004)	6.9 (±0.4)	0.285 (±0.035)	19.3 (±2.4)	0.326 (±0.031)	34.9 (±1.5)	0.104 (±0.006)	6.6 (±0.4)				

SUW: soils amended with SUW; OW: soils amended with OW; F: fresh amended soils; A: aged amended soils.

Table 6. Percentage of imazaquin desorbed (%D) and hysteresis coefficients (*H*) for original, fresh and aged amended soils when treated with the initial concentrations of the herbicide of 0.96 and 2.6 μ M (numbers in parentheses are standard errors).

	Original		SUW-F		SUW-A		OW-F		OW-A		
	0.96	2.60	0.96	2.60	0.96	2.60	0.96	2.60	0.96	2.60	
CR	%D	50.7 (± 10.3)	73.2 (± 8.1)	68.5 (± 3.5)	74.5 (± 6.7)	69.6 (± 1.2)	71.4 (± 1.0)	58.7 (± 1.8)	65.2 (± 0.4)	56.2 (± 2.7)	67.5 (± 5.7)
	H	1.05 (± 0.18)	0.95 (± 0.10)	0.94 (± 0.27)	1.05 (± 0.08)	1.14 (± 0.23)	1.15 (± 0.18)	1.46 (± 0.10)	1.48 (± 0.14)	1.24 (± 0.11)	1.32 (± 0.08)
P44	%D	51.6 (± 4.4)	40.2 (± 8.8)	40.3 (± 3.6)	38.6 (± 2.8)	45.4 (± 4.3)	41.6 (± 3.7)	33.5 (± 1.4)	30.4 (± 3.4)	58.2 (± 3.8)	47.1 (± 7.2)
	H	1.00 (± 0.13)	2.09 (± 0.09)	3.25 (± 0.13)	3.56 (± 0.09)	2.48 (± 0.13)	2.71 (± 0.09)	3.03 (± 0.16)	3.29 (± 0.22)	1.28 (± 0.09)	2.47 (± 0.06)
AL	%D	44.0 (± 1.0)	38.8 (± 1.8)	40.5 (± 2.3)	52.3 (± 6.5)	64.0 (± 4.4)	56.4 (± 2.1)	44.3 (± 9.2)	57.1 (± 0.5)	47.5 (± 4.2)	42.8 (± 5.6)
	H	3.35 (± 0.01)	5.26 (± 0.04)	1.07 (± 0.02)	1.87 (± 0.20)	0.98 (± 0.30)	1.29 (± 0.12)	2.15 (± 0.03)	2.25 (± 0.06)	2.81 (± 0.04)	3.30 (± 0.04)
TM	%D	43.5 (± 8.5)	35.5 (± 3.2)	40.6 (± 2.7)	31.4 (± 4.5)	45.6 (± 2.3)	58.8 (± 5.0)	50.7 (± 0.4)	47.1 (± 6.5)	41.4 (± 10.2)	59.6 (± 5.6)
	H	4.25 (± 0.05)	7.05 (± 0.06)	1.66 (± 0.06)	3.05 (± 0.09)	1.98 (± 0.07)	3.02 (± 0.11)	1.64 (± 0.18)	3.00 (± 0.11)	2.04 (± 0.07)	2.96 (± 0.19)

SUW: soils amended with SUW; OW: soils amended with OW; F: fresh amended soils; A: aged amended soils.



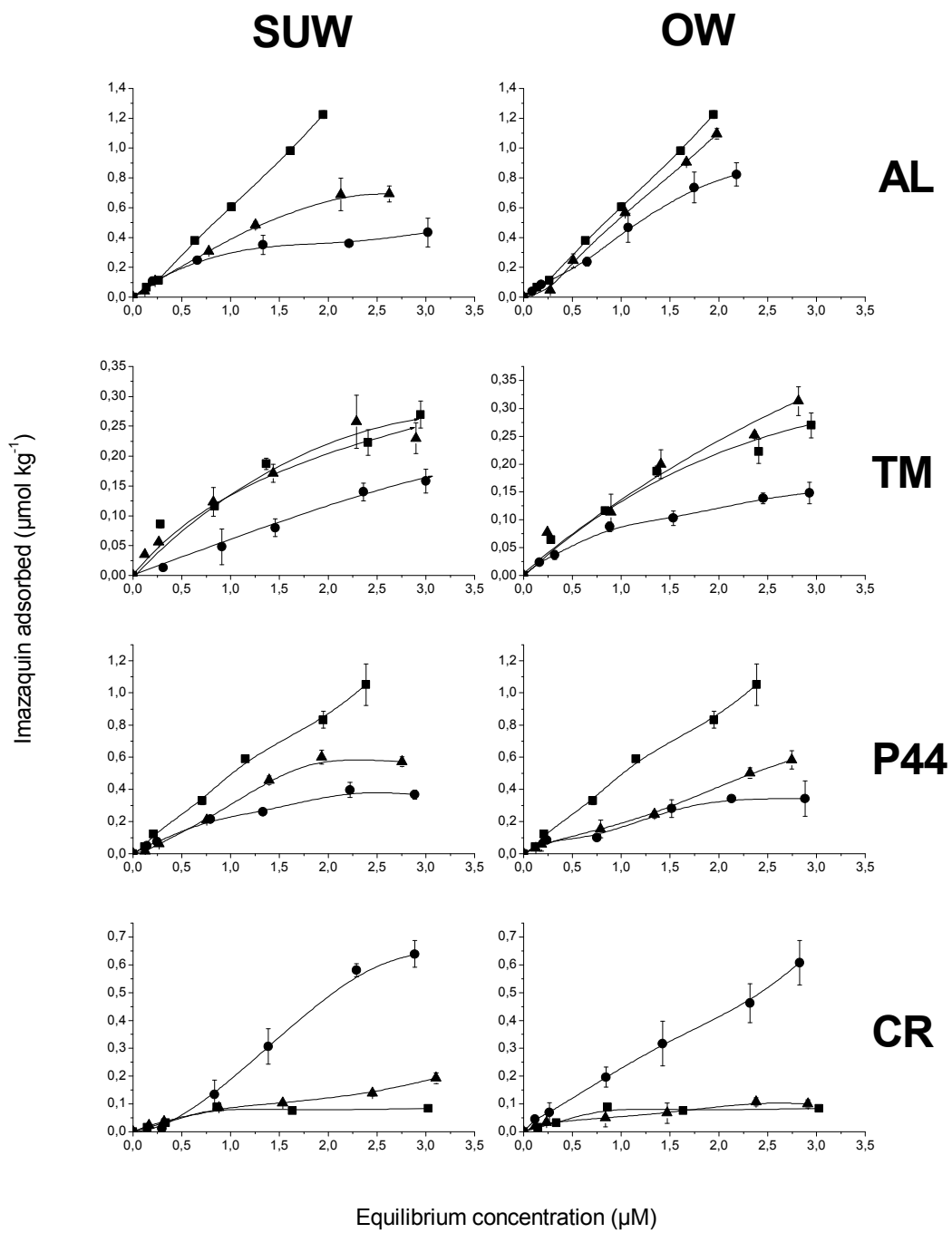


Figure 1

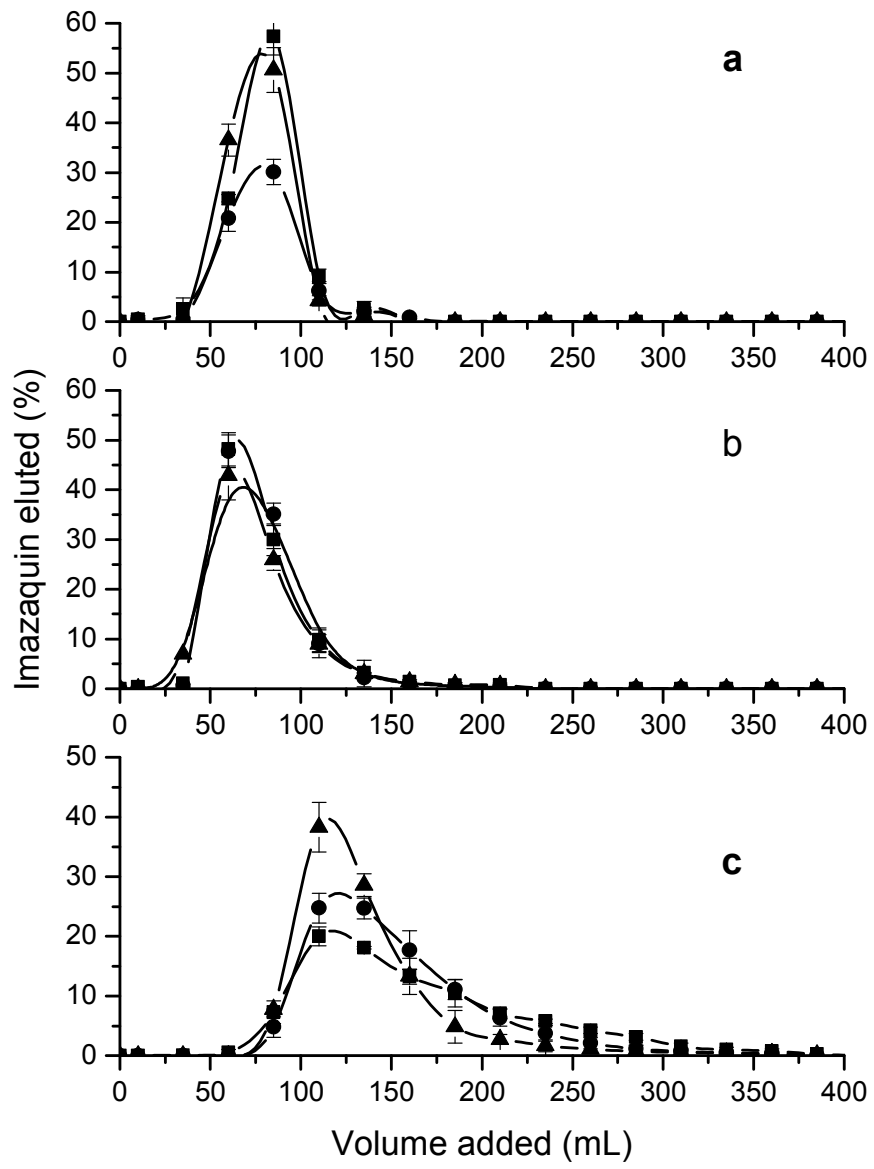


Figure 2