

Supplementary Material

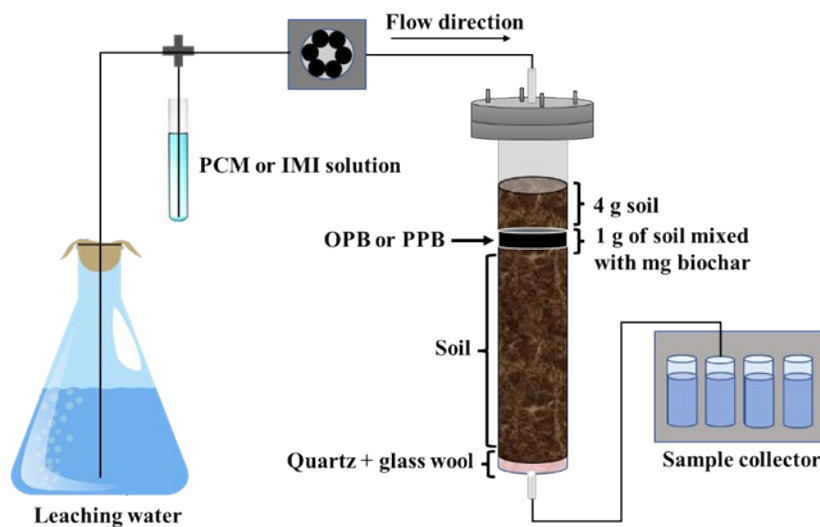


Fig. S1. Soil column experiment to evaluate PCM and IMI vertical transport (total mass of soil=100 g)

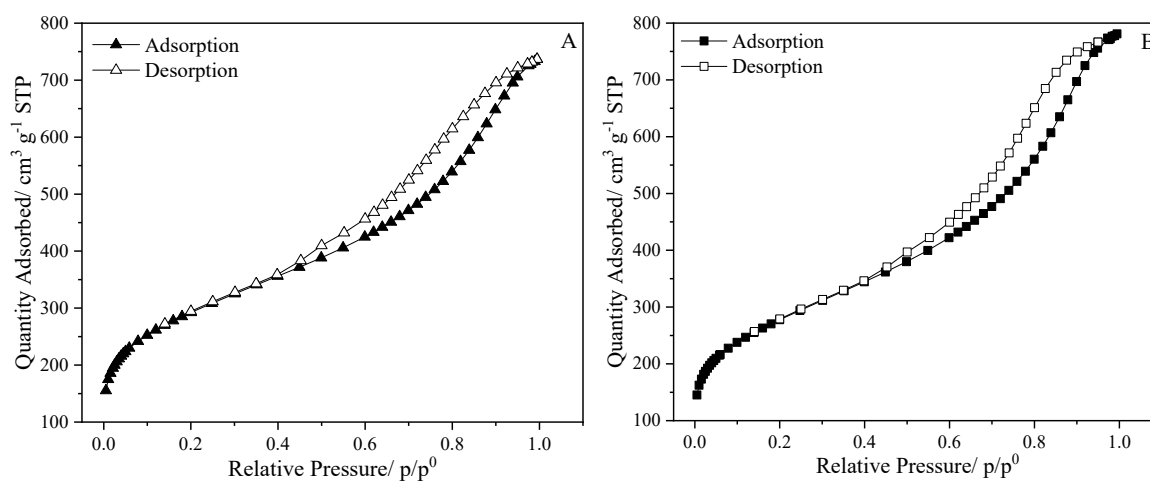


Fig. S2. N₂ adsorption–desorption isotherm of: A) OPB and B) PPB.

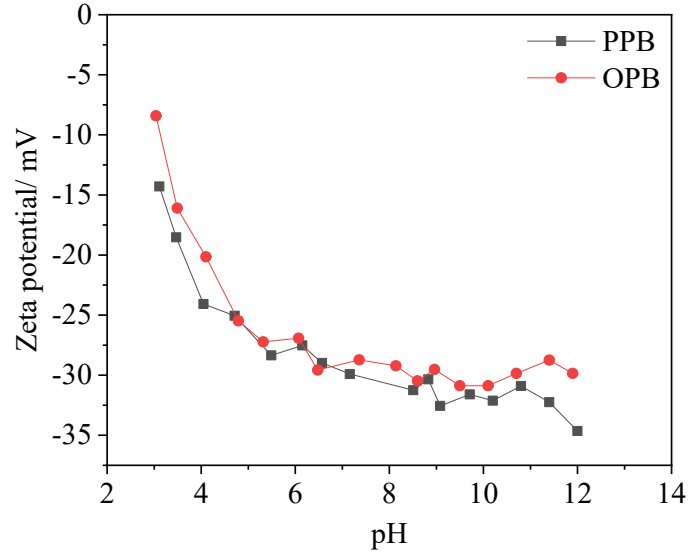


Fig. S3. Zeta potential of adsorbents as a function of pH solution: (●) OPB; (■) PPB.

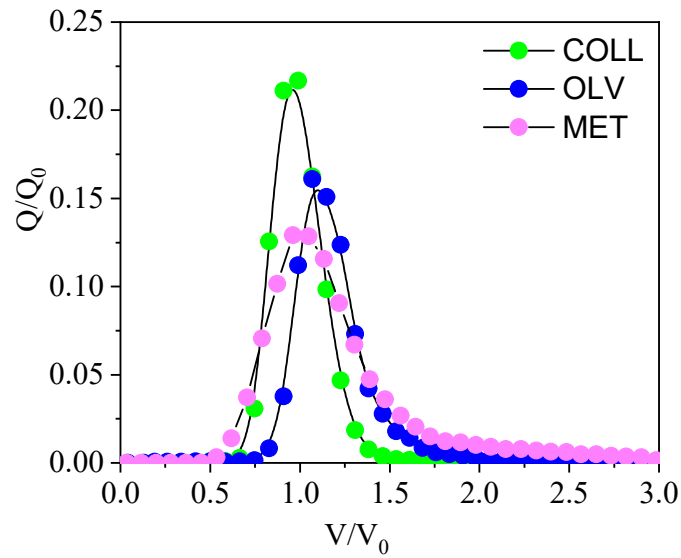
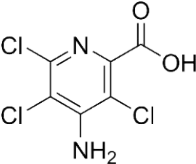
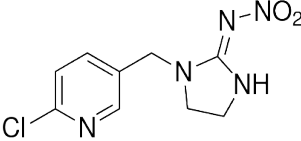


Fig. S4. Breakthrough curves (BTCs) of ³H₂O transport in unamended soil columns.

Table S1. Properties of Picloram and Imidacloprid.

| | Pesticides | |
|---|---|---|
| | Picloram (PCM) | Imidacloprid (IMI) |
| |  |  |
| IUPAC name | 4-amino-3,5,6-trichloropyridine-2-carboxylic acid | 1-[(6-Chloro-3-pyridinyl)methyl]-N-nitro-4,5-dihydro-1H-imidazol-2-amine |
| Solubility in water (20 °C) (mg L ⁻¹) | 488 | 610 |
| K _{ow} (pH 7, 20 °C) | -1.92* | 0.57 |
| pKa at 25 °C | 2.3* | not available |

*Data obtained from <https://chemicalize.com/app/calculation>

Table S2. Coded and natural values of the Doehlert design and results obtained for Picloram on OPB.

| | Coded Values | | | | Natural values | | | | PCM adsorbed $\mu\text{g mg}^{-1}$ |
|-----|--------------|--------|--------|--------|----------------|-----------|------------------------------|-------------|---------------------------------------|
| | A | B | C | D | pH | OPB mg | PCM $\mu\text{g mL}^{-1}$ | Time min | |
| 1** | 0 | 0 | 0 | 0 | 5.5 | 10 | 27.5 | 60 | 21.2 |
| 2* | 1 | 0 | 0 | 0 | 9 | 10 | 27.5 | 60 | 20.2 |
| 3 | 0.5 | 0.866 | 0 | 0 | 7.2 | 15 | 27.5 | 60 | 16.4 |
| 4* | 0.5 | 0.289 | 0.817 | 0 | 7.2 | 11.7 | 50 | 60 | 30.7 |
| 5 | 0.5 | 0.289 | 0.204 | 0.791 | 7.2 | 11.7 | 33.1 | 107 | 23.0 |
| 6* | -1 | 0 | 0 | 0 | 2 | 10 | 27.5 | 60 | 26.1 |
| 7 | -0.5 | -0.866 | 0 | 0 | 3.7 | 5 | 27.5 | 60 | 30.5 |
| 8* | -0.5 | -0.289 | -0.817 | 0 | 3.7 | 8.3 | 5 | 60 | 5.6 |
| 9 | -0.5 | -0.289 | -0.204 | -0.791 | 3.7 | 8.3 | 21.8 | 12 | 21.8 |
| 10* | 0.5 | -0.866 | 0 | 0 | 7.2 | 5 | 27.5 | 60 | 26.1 |
| 11 | 0.5 | -0.289 | -0.817 | 0 | 7.2 | 8.3 | 5 | 60 | 5.2 |
| 12 | 0.5 | -0.289 | -0.204 | -0.791 | 7.2 | 8.3 | 21.8 | 12 | 18.9 |
| 13 | -0.5 | 0.866 | 0 | 0 | 3.7 | 15 | 27.5 | 60 | 16.7 |
| 14 | 0 | 0.577 | -0.817 | 0 | 5.5 | 13.3 | 5 | 60 | 3.6 |
| 15 | 0 | 0.577 | -0.204 | -0.791 | 5.5 | 13.3 | 21.8 | 12 | 14.5 |
| 16 | -0.5 | 0.289 | 0.817 | 0 | 3.7 | 11.7 | 50 | 60 | 34.5 |
| 17 | 0 | -0.577 | 0.817 | 0 | 5.5 | 6.7 | 50 | 60 | 38.9 |
| 18* | 0 | 0 | 0.613 | -0.791 | 5.5 | 10 | 44.3 | 12 | 31.4 |
| 19 | -0.5 | 0.289 | 0.204 | 0.791 | 3.7 | 11.7 | 33.1 | 107 | 24.0 |
| 20 | 0 | -0.577 | 0.204 | 0.791 | 5.5 | 6.7 | 33.1 | 107 | 28.9 |
| 21* | 0 | 0 | -0.613 | 0.791 | 5.5 | 10 | 10.6 | 107 | 9.7 |

*, ** Values correspond to the mean values of 2 and 3 replicates, respectively to account for experimental errors

Table S3. Coded and natural values of the Doehlert design and results obtained for Imidacloprid on PPB.

| | Coded values | | | Natural values | | | IMI |
|-----|--------------|--------|--------|----------------|------------------------------|-----------------------------------|-----------------------------------|
| | A | B | C | PPB mg | IMI $\mu\text{g mL}^{-1}$ | Temperature $^{\circ}\text{C}$ | adsorbed $\mu\text{g mg}^{-1}$ |
| 1** | 0 | 0 | 0 | 10 | 27.5 | 20 | 25.3 |
| 2* | 1 | 0 | 0 | 15 | 27.5 | 20 | 17.7 |
| 3 | 0.5 | 0.866 | 0 | 12.5 | 50 | 20 | 35.8 |
| 4 | 0.5 | 0.289 | 0.817 | 12.5 | 35 | 30 | 26.1 |
| 5* | -1 | 0 | 0 | 5 | 27.5 | 20 | 42.0 |
| 6 | -0.5 | -0.866 | 0 | 7.5 | 5 | 20 | 6.2 |
| 7 | -0.5 | -0.289 | -0.817 | 7.5 | 20 | 10 | 23.5 |
| 8 | 0.5 | -0.866 | 0 | 12.5 | 5 | 20 | 3.8 |
| 9 | 0.5 | -0.289 | -0.817 | 12.5 | 20 | 10 | 15.1 |
| 10 | -0.5 | 0.866 | 0 | 7.5 | 50 | 20 | 52.3 |
| 11* | 0 | 0.577 | -0.817 | 10 | 42.5 | 10 | 37.9 |
| 12 | -0.5 | 0.289 | 0.817 | 7.5 | 35 | 30 | 39.4 |
| 13* | 0 | -0.577 | 0.817 | 10 | 12.5 | 30 | 12.0 |

*, ** Values correspond to the mean values of 2 and 3 replicates, respectively to account for the experimental error.

Calibration parameters and figures of merit

Two calibration ranges were established for PCM and IMI. The 0.08 – 1.00 $\mu\text{g mL}^{-1}$ calibration curve was used to determine the method's limits of detection (LOD) and quantification (LOQ), as well as to quantify analyte concentrations in samples within this range. The 1.00 – 20.00 $\mu\text{g mL}^{-1}$ calibration curve was used to assess linearity and to quantify the analyte concentration in samples exceeding the lower range. All calibration standards were injected in duplicate. Reproducibility was determined at three concentration levels by injecting the corresponding standards 5 times and results were expressed as coefficient of variation (CV%).

The LOD ($3.3S_{y/x}/m$) and LOQ ($10S_{y/x}/m$) were calculated based on the regression standard deviation ($S_{y/x}$) and the slope (m) of the calibration curve. Soil matrix effects were evaluated by confirming the identity of the analyte using the UV spectrum obtained for each analytical standard and by verifying the absence of co-eluting interferences using the Empower 3 Chromatography Data System software from Waters. No matrix interferences were observed.

Results are presented in Table S4.

Table S4. Calibration parameters and figures of merit for the IMI and PCM quantification methods.

| Calibration parameters and linearity of the method | | |
|--|----------------------|---------------------|
| Parameter | Value | |
| | PCM | IMI |
| Concentration range ($\mu\text{g mL}^{-1}$) | 0.08 – 1.00 | 0.08 – 1.00 |
| Regression equation | $y = 99751x - 652$ | $y = 100613x - 738$ |
| Coefficient of determination (R^2) | 0.999 | 0.999 |
| Regression standard deviation (Sy/x) | 859.3 | 616.4 |
| LOD ($\mu\text{g mL}^{-1}$) | 0.026 | 0.018 |
| LOQ ($\mu\text{g mL}^{-1}$) | 0.086 | 0.061 |
| Concentration range ($\mu\text{g mL}^{-1}$) | 1.00 – 20.00 | 1.00 – 20.00 |
| Regression equation | $y = 101081x - 4006$ | $91521x - 3635$ |
| Coefficient of determination (R^2) | 0.999 | 0.999 |
| Reproducibility parameters of the method (n=5) | | |
| Concentration ($\mu\text{g mL}^{-1}$) | *CV (%) | |
| 0.08 | 2.68 | 2.54 |
| 1.00 | 2.52 | 2.32 |
| 20.00 | 0.30 | 0.56 |

*CV= (standard deviation/media) x 100

Table S5. Preliminary study of the adsorption process of Picloram onto OPB and PPB.

| Biochar | Adsorbent mass (mg) | Initial Concentration $\mu\text{g mL}^{-1}$ | Q adsorbed $\mu\text{g mg}^{-1}$ | Adsorption % |
|---------|------------------------|---|-------------------------------------|--------------|
| OPB | 5 | 5 | 9.3 | 93 |
| | 10 | 5 | 4.7 | 95 |
| | 15 | 5 | 3.2 | 97 |
| | 5 | 20 | 29.4 | 74 |
| | 10 | 20 | 15.6 | 78 |
| | 15 | 20 | 10.8 | 82 |
| | 5 | 50 | 45.1 | 45 |
| | 10 | 50 | 39.4 | 79 |
| | 15 | 50 | 28.5 | 85 |
| PPB | 5 | 5 | 9.2 | 92 |
| | 10 | 5 | 4.7 | 95 |
| | 15 | 5 | 3.2 | 97 |
| | 5 | 20 | 29.9 | 74 |
| | 10 | 20 | 15.8 | 79 |
| | 15 | 20 | 11.0 | 83 |
| | 5 | 50 | 47.1 | 47 |
| | 10 | 50 | 39.8 | 80 |
| | 15 | 50 | 28.7 | 86 |

Table S6. Preliminary study of the adsorption process of Imidacloprid onto OPB and PPB.

| Biochar | Adsorbent mass (mg) | Initial Concentration $\mu\text{g mL}^{-1}$ | Q adsorbed $\mu\text{g mg}^{-1}$ | adsorption % |
|---------|------------------------|---|-------------------------------------|--------------|
| OPB | 5 | 5 | 9.8 | 99 |
| | 10 | 5 | 4.9 | 100 |
| | 15 | 5 | 3.3 | 100 |
| | 5 | 20 | 36.3 | 91 |
| | 10 | 20 | 19.5 | 97 |
| | 15 | 20 | 13.1 | 98 |
| | 5 | 50 | 65.6 | 65 |
| | 10 | 50 | 42.5 | 84 |
| | 15 | 50 | 30.7 | 91 |
| PPB | 5 | 5 | 9.8 | 98 |
| | 10 | 5 | 5.0 | 100 |
| | 15 | 5 | 3.3 | 100 |
| | 5 | 20 | 36.2 | 90 |
| | 10 | 20 | 19.5 | 97 |
| | 15 | 20 | 13.1 | 98 |
| | 5 | 50 | 64.3 | 64 |
| | 10 | 50 | 42.5 | 84 |
| | 15 | 50 | 30.8 | 92 |

Table S7. ANOVA parameters of response surface methodology for Picloram adsorption on OPB ($\mu\text{g mg}^{-1}$).

| Source | Sum of Squares | Df | Mean Square | F-Ratio | P-Value |
|-------------------|----------------|----|-------------|---------|---------|
| A: Adsorbent mass | 219.6 | 1 | 219.6 | 456.6 | 0.000 |
| B: Concentration | 2252.6 | 1 | 2252.6 | 4683.2 | 0.000 |
| C: pH | 41.2 | 1 | 41.2 | 85.7 | 0.000 |
| D: time | 0.2 | 1 | 0.2 | 0.4 | 0.500 |
| AA | 1.7 | 1 | 1.7 | 3.6 | 0.0750 |
| AB | 8.4 | 1 | 8.4 | 17.5 | 0.0007 |
| AC | 4.3 | 1 | 4.3 | 9.0 | 0.0083 |
| AD | 0.1 | 1 | 0.1 | 0.2 | 0.624 |
| BB | 9.8 | 1 | 9.8 | 20.5 | 0.0003 |
| BC | 6.8 | 1 | 6.8 | 14.1 | 0.0017 |
| BD | 0.04 | 1 | 0.04 | 0.09 | 0.769 |
| CC | 6.8 | 1 | 6.8 | 14.2 | 0.0017 |
| CD | 0.7 | 1 | 0.7 | 1.5 | 0.2265 |
| DD | 0.6 | 1 | 0.6 | 1.4 | 0.2537 |
| Total error | 7.6 | 16 | 0.4 | | |
| Total (corr.) | 2546.2 | 30 | | | |

R-squared = 99.6 percent

R-squared (adjusted for d.f.) = 99.4 percent

Standard Error of Est. = 0.6

Mean absolute error = 0.4

Durbin-Watson statistics = 2.3 (P=0.3)

Lag 1 residual autocorrelation = -0.1

Quadratic Model Equation

$$\mu\text{g PCM mg}^{-1} = 21.7 - 1.8 \times \text{Adsorbent mass} + 1.2 \times \text{Concentration} - 3.0 \times \text{pH} - 0.07 \times \text{time} + 0.03 \times \text{Adsorbent mass}^2 - 0.02 \times \text{Adsorbent mass} \times \text{Concentration} + 0.1 \times \text{Adsorbent mass} \times \text{pH} + 0.001 \times \text{Adsorbent mass} \times \text{time} - 0.003 \times \text{Concentration}^2 - 0.03 \times \text{Concentration} \times \text{pH} - 0.0001 \times \text{Concentration} \times \text{time} + 0.1 \times \text{pH}^2 + 0.006 \times \text{pH} \times \text{time} + 0.0001$$

Table S8. ANOVA parameters of response surface methodology. Imidacloprid adsorption on PPB ($\mu\text{g mg}^{-1}$).

| Source | Sum of Squares | Df | Mean Square | F-Ratio | P-Value |
|--------------------------|----------------|----|-------------|---------|---------|
| A: Adsorbent mass | 778.0 | 1 | 778.0 | 1347.7 | 0.000 |
| B: Initial concentration | 2301.5 | 1 | 2301.5 | 3987.0 | 0.000 |
| C: Temperature | 0.1 | 1 | 0.1 | 0.2 | 0.641 |
| AA | 41.4 | 1 | 41.4 | 71.7 | 0.000 |
| AB | 50.5 | 1 | 50.5 | 87.5 | 0.000 |
| AC | 0.005 | 1 | 0.005 | 0.01 | 0.920 |
| BB | 5.5 | 1 | 5.5 | 9.6 | 0.0113 |
| BC | 0.03 | 1 | 0.03 | 0.05 | 0.821 |
| CC | 0.1 | 1 | 0.1 | 0.2 | 0.608 |
| Total error | 5.7 | 10 | 0.5 | | |
| Total (corr.) | 3306.9 | 19 | | | |

R-squared = 99.8 percent

R-squared (adjusted for d.f.) = 99.6 percent

Standard Error of Est. = 0.7

Mean absolute error = 0.4

Durbin-Watson statistics = 2.0 (P=0.1)

Lag 1 residual autocorrelation = -0.02

Quadratic Model Equation

$\mu\text{g IMI mg}^{-1} = 22.2 - 4.1 \times \text{Adsorbent mass} + 1.6 \times \text{Initial concentration} - 0.03 \times \text{Temperature} + 0.1 \times \text{Adsorbent mass}^2 - 0.06 \times \text{Adsorbent mass} \times \text{Initial concentration} - 0.001 \times \text{Adsorbent mass} \times \text{Temperature} - 0.002 \times \text{Initial concentration}^2 - 0.0005 \times \text{Initial concentration} \times \text{Temperature} + 0.002 \times \text{Temperature}^2$

Table S9. Influence of the initial PCM concentration and adsorbent mass of OPB on the adsorption kinetic parameters (n=2).

| Parameters | Initial concentration* | | Adsorbent mass** | |
|---|------------------------|-------------------|--------------------|-------------------|
| | $\mu\text{g/mL}^{-1}$ | | (mg) | |
| | 15 | 35 | 5 | 10 |
| $q_{\text{max. (exp)}} (\mu\text{g mg}^{-1})$ | 17.8 ± 0.4 | 33.1 ± 0.3 | 31.6 ± 0.3 | 22.0 ± 0.5 |
| Pseudo-first-order model | | | | |
| $q_{\text{max.}} (\mu\text{g mg}^{-1})$ | 17.3 ± 0.1 | 31.8 ± 0.1 | 30.2 ± 0.2 | 21.3 ± 0.1 |
| $k_1 (\text{min}^{-1})$ | 1.15 ± 0.07 | 0.87 ± 0.05 | 0.71 ± 0.06 | 1.08 ± 0.07 |
| R^2_{adj} | 0.988 | 0.991 | 0.979 | 0.989 |
| Pseudo-second-order model | | | | |
| $q_{\text{max}} (\mu\text{g mg}^{-1})$ | 17.9 ± 0.06 | 32.8 ± 0.1 | 31.5 ± 0.1 | 22.0 ± 0.07 |
| $k_2 (\text{mg } \mu\text{g}^{-1} \text{ min}^{-1})$ | 0.16 ± 0.00 | 0.073 ± 0.006 | 0.0651 ± 0.004 | 0.145 ± 0.009 |
| R^2_{adj} | 0.997 | 0.997 | 0.996 | 0.998 |
| $h (\text{mg } \mu\text{g}^{-1} \text{ min}^{-1})$ | 51.3 | 78.5 | 66.6 | 70.2 |
| Intraparticle diffusion model | | | | |
| $C_1 (\mu\text{g mg}^{-1})$ | 13.8 ± 0.2 | 22.8 ± 0.9 | 22.2 ± 0.2 | 16.83 ± 0.2 |
| $K_{\text{int } 1} (\mu\text{g mg}^{-1} \text{ min}^{1/2})$ | 1.20 ± 0.09 | 3.44 ± 0.4 | 2.58 ± 0.09 | 1.63 ± 0.07 |
| R^2_{adj} | 0.957 | 0.876 | 0.988 | 0.928 |
| $C_2 (\mu\text{g mg}^{-1})$ | 16.3 ± 0.2 | 29.9 ± 0.7 | 28.4 ± 0.4 | 20.2 ± 0.3 |
| $K_{\text{int } 2} (\mu\text{g mg}^{-1} \text{ min}^{1/2})$ | 0.283 ± 0.06 | 0.776 ± 0.1 | 0.564 ± 0.09 | 0.309 ± 0.07 |
| R^2 | 0.835 | 0.910 | 0.963 | 0.905 |

*7.5 mg OPB; **25 $\mu\text{g mL}^{-1}$

Table S10. Influence of the initial IMI concentration and adsorbent mass of PPB on the adsorption kinetic parameters (n=2).

| Parameters | Initial concentration* | | Adsorbent mass** | |
|---|------------------------|--------------------|--------------------|------------------|
| | $\mu\text{g/mL}^{-1}$ | | (mg) | |
| | 15 | 35 | 5 | 10 |
| $q_{\text{max.}}(\text{exp}) (\mu\text{g mg}^{-1})$ | 19.1 ± 0.4 | 41.5 ± 0.6 | 41.6 ± 0.4 | 23.5 ± 0.8 |
| Pseudo-first-order model | | | | |
| $q_{\text{max}} (\mu\text{g mg}^{-1})$ | 18.7 ± 0.07 | 39.8 ± 0.2 | 39.1 ± 0.3 | 22.7 ± 0.1 |
| $k_1 (\text{min}^{-1})$ | 1.19 ± 0.06 | 0.912 ± 0.06 | 0.836 ± 0.07 | 1.17 ± 0.09 |
| R^2_{adj} | 0.993 | 0.984 | 0.972 | 0.988 |
| Pseudo-second-order model | | | | |
| $q_{\text{max.}} (\mu\text{g mg}^{-1})$ | 19.1 ± 0.03 | 41.4 ± 0.1 | 41.1 ± 0.2 | 23.4 ± 0.08 |
| $k_2 (\text{mg } \mu\text{g}^{-1} \text{ min}^{-1})$ | 0.208 ± 0.01 | 0.0524 ± 0.002 | 0.0429 ± 0.003 | 0.150 ± 0.01 |
| $h (\text{mg } \mu\text{g}^{-1} \text{ min}^{-1})$ | 75.9 | 89.8 | 72.5 | 82.1 |
| R^2_{adj} | 0.999 | 0.998 | 0.994 | 0.997 |
| Intraparticle diffusion model | | | | |
| $C_1 (\mu\text{g mg}^{-1})$ | 15.3 ± 0.2 | 28.2 ± 0.8 | 28.1 ± 0.8 | 19.2 ± 0.1 |
| $K_{\text{int } 1} (\mu\text{g mg}^{-1} \text{ min}^{1/2})$ | 1.24 ± 0.1 | 4.23 ± 0.4 | 3.55 ± 0.3 | 1.13 ± 0.05 |
| R^2_{adj} | 0.964 | 0.951 | 0.966 | 0.979 |
| $C_2 (\mu\text{g mg}^{-1})$ | 17.8 ± 0.06 | 36.0 ± 0.2 | 34.1 ± 0.4 | 21.9 ± 0.07 |
| $K_{\text{int } 2} (\mu\text{g mg}^{-1} \text{ min}^{1/2})$ | 0.250 ± 0.01 | 1.00 ± 0.05 | 1.35 ± 0.07 | 0.282 ± 0.01 |
| R^2_{adj} | 0.956 | 0.966 | 0.968 | 0.967 |

*7.5 mg OPB; **25 $\mu\text{g mL}^{-1}$

Table S11. Transport of Picloram and Imidacloprid in agricultural soils with and without amendment. Experimental conditions and results.

| Soil | Added Biochar (mg) | Pore Volume (mL) | PCM μg recovered at 5 PV | IMI μg recovered at 8.5 PV | Total recovered μg | % adsorbed |
|--------------|--------------------|------------------|-------------------------------------|---------------------------------------|-------------------------------|------------|
| Picloram | | | | | | |
| Metrenco | 0 | 31 | 184 | - | 190 | 5 (6.5) * |
| | 150 | 32 | 0 | - | 0 | 100 (6.0) |
| | 100 | 34 | 47 | - | 51 | 75 (5.8) |
| Olivar | 0 | 29 | 181 | - | 187 | 7 (8.6) |
| | 100 | 29 | 40 | - | 62 | 69 (9.6) |
| Collipulli | 0 | 29 | 180 | - | 186 | 7 (7.0) |
| | 100 | 31 | 37 | - | 52 | 74 (7.5) |
| Imidacloprid | | | | | | |
| Metrenco | 0 | 32 | - | 189 | 189 | 5 (9.6) |
| | 100 | 33 | - | 0 | 0 | 100 (10) |
| | 20 | 32 | - | 23 | 23 | 89 (8.5) |
| Olivar | 0 | 28 | - | 170 | 174 | 13 (11.5) |
| | 20 | 31 | - | 48 | 57 | 72 (10.3) |
| Collipulli | 0 | 32 | - | 121 | 149 | 25 (14.4) |
| | 20 | 31 | - | 57 | 59 | 71 (10.6) |

* Values in parenthesis correspond to the total pore volumes collected.