**Supplementary content**

**Assessing the dissipation of pesticides of different polarities in soil samples**

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**Figure S1.** Effect on the percentage of analyte recovered in the filtration of: (a) the type of filter; and (b) passing 0.5 mL of methanol after the sample with the cellulose filters. Concentration of the analytes, 200 ng/mL for TRT and TFL, and 50 ng/mL for ACL and BF. Recoveries calculated by comparing the peak areas obtained for the extracts with those obtained when processing unfiltered solutions containing the same concentrations of the analytes. For other conditions, see text.



**Figure S2.** Effect on the peak areas of: (a) the proportion of MeOH to water (v/v) in the extract; (b) the volume of extract containing 33.3 % (v/v) of methanol loaded into the IT-SPME. Concentration of the analytes, 200 ng/mL for TRT and TFL, and 50 ng/mL for ACL and BF. For other details, see text.

**Table S1.** Chemical structures and some properties of the studied compounds compiled from different databases.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Compound** | **Chemical structure** | **Molecular weight**  **(g/mol)** | **Solubility in water, at 20 0C**  **(mg/L)** | **pKa** | **Log Ko/w** | **Half life**  **(lab studies)**  **(days)** | **Data on adsorptiond** |
| Tritosulfurona |  | 445.3 | 78.3 at 20 0C | 4.69 | 0.62 | 29.6-110.4 | Low adsorption (very mobilea)/  Kf = 0.05-0.204 |
| Triflusulfuron-methyl a,b, |  | 492.4 | 260 | 4.4 | 0.96 | 4-20.9 | Low adsorption (mobile)/  Kf = 0.36-1.28 |
| Aclonifena | **A190200 Chemical Structure** | 264.66 | 1.4 | -3.15 | 4.37 | 29.5-96.3 | High potential for particle bound/  Kf = 58.5-265.3 |
| Bifenox a,c |  | 342.1 | 0.1 | - | 4.48 | 4-18 | Medium potential for particle bound/  Kf = 0.93-169 |

Data bases): aPPDB: Pesticide Properties DataBase, <http://sitem.herts.ac.uk/aeru/ppdb/> (accessed on March 2024); bCLH report on triflusulfuron-methyl <https://echa.europa.eu/documents/> (accessed on March 2024); c<https://pubchem.ncbi.nlm.nih.gov> (accessed on March 2024); d Freundlich sorption coefficient, Kf (mL g-1).

**Table S2.** References of the procedures applied to the determination of the moisture content, pH and organic matter content in the soil samples.

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Principle** | **Source** |
| Moisture content | Heating at (105 ± 5) 0C until constant mass | Food and Agriculture Organization  <https://www.fao.org/3/cc4831en/cc4831en.pdf>  (accessed on December 2023) |
| pH | Measurement of the pH of liquid phase after treating the soil with water | Food and Agriculture Organization  <https://www.fao.org/documents/card/es?details=CB3637EN>  (accessed on December 2023) |
| Organic matter | Reaction with chromic acid and measurement of the absorbance at 600 nm | Food and Agriculture Organization  <https://www.fao.org/3/ca7471en/ca7471en.pdf>  (accessed on December 2023) |

**Table S3.** Variation of the responses obtained for three injections of a sample extract and for three sample extracts obtained for three replicates of a soil (each injected by triplicate).

|  |  |  |
| --- | --- | --- |
| **Compound** | **Variation of responses, RSD,**  **(%)** | |
| **The extract obtained for a single soil portion, (n=3)** | **Three extracts obtained from three soil portions, each extract injected by triplicate**  **(n=9)** |
| TRT | 3 | 3 |
| TRF | 2 | 3 |
| ACL | 4 | 3 |
| BF | 0.4 | 4 |

**Table S4.** Relevant features of methods proposed for the determination of the tested herbicides in soil.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Compound** | **Sample treatment** | **Separation/ detection** | **Working concentrations**  **(µg/g)** | **Recovery (%)** | **LOD (ng/g)** | **Degradation studies** | **Reference** |
| TRT and other pesticides | 5 g of soil sieved (2 mm) were mixed with 5 g of NH4HCO3 and treated with acetonitrile acidified with formic acid for 1 hour (end-over-end agitation); the suspension was centrifugated and filtrated, and the obtained solution was processed by LC. | LC/ESI-MS/MS | 0.01-0.25 | 92-103 | 0.5 | - | Bakanov et al. 2023 |
| TRF | 20 g of soil were treated with 25 mL of methanol/water/acetic acid for 1 h. The mixture was then centrifuged for 5 min, and the supernatant was processed by LC. | LC/UV | 1-19.8 | n. r. | n.r. | Study of the degradation of TRF different sterile and nonsterile soils (t1/2 =1.7-9.25 days) | Vega et al, 2000 |
| TRF | 100 g of air-dried soil were sieved (2 mm), treated with 150 mL of methanol and shaken for 60 min. The suspension was centrifuged for 20 min, the supernatant removed, and the procedure repeated with shaking for 30 min. The supernatants were reunited, and TRF was reextracted with dichloromethane, adjusting the pH to 2. Dichloromethane was evaporated to dryness. The residue was redissolved in the mobile phase, filtered, and processed by LC. | LC/UV | 0.060 | 87.8 | n.r. | Study of the degradation of TRF in microbially active soil (t1/2 = 17-18 days) | Gigliotti et al, 2005 |
| TRF and other sulfonylurea herbicides | 0.5 g of soil were mixed with 1.0 mL of acetonitrile/formic acid and sonicated for 2 min. The suspension was centrifuged for 10 min, and then the supernatant was filtered through 0.45 mm membrane; the procedure was repeated. The filtrates were combined and evaporated to dryness with nitrogen. The residue was dissolved with 5 mL ultrapure water; the pH water was adjusted to 5.0. Finally, 5 mL of the extract were processed by magnetism-reinforced IT-SPME coupled online to LC. | LC /UV(DAD) | 0.005-0.30 | 80.4-111 | 1.5 | - | Pang et al, 2020 |
| TRF and other sulfonylurea herbicides | 0.5 g of soil were mixed with 1 mL of acetonitrile and vortexed for 2 min. The suspension was centrifugated and the supernatant was filtrated. The procedure was repeated. The combined fractions were evaporated to dryness with nitrogen. The residue was redissolved in 20 mL of water. The pH value was adjusted to 4.0. Then, homemade multiple monolithic SPME fibres were immersed in the sample extract for 50 min under agitation to extract analyte. Next, the analyte was desorbed from the fibers with 400 µL of acetonitrile/formic acid using stirring for 20 min. The liquid phase was evaporated to dryness. The dried residue was dissolved in 0.1 mL methanol and processed by LC. | LC/UV(DAD) | 0.002-0.3 | 78.9-118 | 0.61 | - | Pei et al, 2018 |
| ACL | 50 g of soil samples were treated 80 mL of water:methanol, shaken for 30 min, then centrifuged for 10 min and the supernatant was separated. This procedure was repeated three times. The combined extracts were reextracted in dichloromethane (3 x 50 mL). The organic phase was evaporated to dryness. The residue was dissolved in acetonitrile:water acidified to pH 3 and processed by LC. | LC/UV(DAD) | 4 | 94 | n. r. | Study of the degradation of ACL in unamended and amended soils  (t1/2 = 13-30 days) | Abbate et al, 2007 |
| ACL and other herbicides | 10 g of soil samples were extracted into 20 mL of acetonitrile-water by sonication (time not specified) and then centrifuged for 10 min. Next, 2 mL of the supernatant were filtered; the filtrate was processed by LC. | LC/UV(DAD) | 1 | 81-95  (n.s.) | n. r. | Study of the degradation of ACL in an amended and unamended loam soil (t1/2 =433-990 days) | Perez Lucas et al, 2020 |
| ACL | 50 g of soil were mixed with 50 mL of methanol and shaken for 24 hours; the extract was centrifuged for 10 min and then filtered. The filtrate was processed by LC. | LC/UV(DAD) | ≈11000 - 21000 | 84.9-118.1  (n.s.) | n. r. | Study of the degradation of ACL in different agricultural soils (t1/2 =3.2-20 days) | Sharipov et al, 2021 |
| TRT, TRF, ACL and BF | 0.5 g of soil are treated with 5 mL of methanol-water and vortexed for 10 min. A 1 mL aliquot of the supernatant was passed through prewashed filters, followed by 0.5 mL of methanol. Next, 1.5 mL of water were added to the combined extract, and 1 mL of the resulting solution was processed by IT-SPME coupled online to capLC. | CapLC-UV(DAD) | 0.2-4 µg/g | 90-101 | 25-100 | Study of the degradation of the herbicides in soil exposed to different conditions (t1/2 = 24.8 days for TRT in soil exposed to outdoor conditions). | This work |

n. r. – not reported; n,s,- exact value not specified