Dynamics of Glyphosate and Aminomethylphosphonic Acid in Soil Under Conventional and Conservation Tillage

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Abstract
This study investigates the adsorption and dissipation of glyphosate and the formation/dissipation of AMPA in non-tilled (NT) and conventionally tilled (CT) soil at 0–5 and 5–20 cm depth. Glyphosate adsorption was mainly related to the different NT and CT soil properties (clay and amorphous Al oxides), whereas an effect of the soil management could not be identified. Glyphosate dissipation was initially fast, and it slowed down later. The initial glyphosate concentration in NT soil at 0–5 cm was significantly lower than the dose applied due to the interception by the weeds and crop residues. AMPA began to form early after treatment and persisted longer than glyphosate. The DT50 range was 8–18 days for glyphosate and 99–250 days for AMPA. Longer glyphosate and AMPA DT50 were observed in NT soil compared to CT soil but, for glyphosate, the difference was significant only at 5–20 cm. Higher glyphosate and AMPA concentrations were detected in NT than in CT soil at the end of the study at 0–5 cm. The differences in glyphosate and AMPA DT50 and persistence were mainly attributable to the influence of different NT and CT soil characteristics. However, other factors could have contributed to the different glyphosate and AMPA dynamics between the soils, like glyphosate wash-off from crop residues on NT soil with the rainfall, the delayed glyphosate return to the soil by weed root exudation or weeds decomposition, and the NT soil compaction which may have reduced the microbial degradation of glyphosate at low concentrations.

Graphic abstract

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Introduction

Glyphosate (N-phosphonomethylglycine) is a non-selective, systemic, broad-spectrum, post-emergence herbicide. Its applications include weed control on transgenic glyphosate-resistant crops, pre-harvest desiccation of cereals and total weed control in agricultural fields. It is the most used herbicide worldwide, with an estimated use of 826 million kg in 2014 (Benbrook 2016).

Although glyphosate is not intentionally applied directly to the soil, a significant portion of the herbicide may reach the soil surface during pre-seeding or early-season applications. Once glyphosate reaches the soil, several processes can influence its environmental fate, such as runoff, leaching, wind erosion, adsorption and degradation (Borggaard and Gimsing 2008; Bento et al. 2016; Silva et al. 2018). Some of the factors influencing the fate of glyphosate in the soil are related to the intrinsic properties of the herbicide (e.g., molecular structure, adsorption, solubility, and persistence), whereas others depend on the physicochemical and biological characteristics of the soil (e.g., organic carbon content, pH, moisture, microbial biomass, pore connectivity, clay fraction, and cation exchange capacity) (Okada et al. 2016; Soracco et al. 2018). The soil properties are also affected by the climate, as well as by crops and soil management (Holland 2004; Okada et al. 2016). Glyphosate tends to adsorb strongly to soil components, particularly iron and aluminium oxides (Sprankle et al. 1975; Morillo et al. 2000; Gimsing et al. 2004b). On one hand, the high solubility of glyphosate (10.5 g/L at 20 °C) may increase the risk of being transported into the aqueous phase (Lewis et al. 2016). On the other hand, the strong adsorption tendency of glyphosate can lower the potential to contaminate surface waters or groundwater, but it contributes to the accumulation of glyphosate in soil (Gimsing et al. 2004a; Vereecken 2005; Sidoli et al. 2016).

Among the factors influencing the environmental behaviour of a herbicide, dissipation is a key process because it determines the persistence of the herbicide in soil and, consequently, the potential for reaching off-target environments. Glyphosate is moderately persistent in soil, with a DT50 value (time for dissipation of 50% of the initial concentration) ranging from 1 to 197 days (Giesy et al. 2000; Laitinen et al. 2006; Lewis et al. 2016; Bento et al. 2016). Glyphosate is primarily degraded by biological activity, although evidence of an abiotic pathway via metal interaction has been reported (Ascolani Yael et al. 2014). Aminomethylphosphonic acid (AMPA) is the main degradation product of glyphosate (Sprankle et al. 1975; Giesy et al. 2000). It is chemically similar to glyphosate and has similar properties in terms of environmental behaviour and toxicity (Lewis et al. 2016). Similarly to the parent molecule, AMPA is polar and well soluble in water (1467 g/L at 20 °C) (Lewis et al. 2016), but it is more persistent in the environment than glyphosate (DT50 = 23–958 days) and tends to accumulate in the soil (EPA. US 1993; Laitinen et al. 2006; Yang et al. 2015; Bento et al. 2016). Given the widespread contamination by glyphosate and AMPA (Battaglin et al. 2014; Lupi et al. 2015; Silva et al. 2018, 2019), there is a growing need to identify and understand the mechanisms that control the fate of glyphosate in the soil as a source of environmental contamination.

Glyphosate is a very effective option for weed control in conservation agriculture. Conservation agriculture is defined by the Food and Agriculture Organization (FAO) as agriculture that improves the livelihoods of farmers through the application of three main principles: minimal soil disturbance (reduced tillage or no-tillage), permanent soil cover, and crop rotation (Corsi 2019). Some studies have shown how the elimination of tillage operations in no-till systems leads to a change in the soil’s physical, chemical and biological properties. Kreiselmeyer et al. (2020) observed recognizable differences in the soil structure and hence soil hydraulic properties between tilled and non-tilled soil, and an improvement in the soil chemical and microbial properties after 6 years of conservation tillage was observed by Qin et al. (2010). The annual input of crop residues on the soil surface increases the organic matter content (Doran 1982; Levanon et al. 1994). Furthermore, the lack of physical soil mixing results in the stratification of soil organic matter content, with the top few centimetres of soil usually having the highest contents (Karlen et al. 1989; Lal et al. 1994; Reicosky...
An improved redistribution and stabilization of soil organic carbon with the adoption of no-till were shown by Du et al. (2015) and Sheehy et al. (2015). The increased organic matter content promotes the retention of certain pesticides and increases the number and activity of microbial populations (Levanon et al. 1994; Novak et al. 1996). Glyphosate degradation in the soil is strongly controlled by microbial activity (Franz et al. 1997; Schuette 1998). Consequently, glyphosate environmental fate is potentially altered relatively to conventional tillage systems. The dissipation of glyphosate and the formation/dissipation of AMPA in the no-till system must therefore be evaluated and compared with that in conventional agriculture to determine whether and to what extent the altered soil properties affect their persistence. Glyphosate dissipation and AMPA formation/dissipation in agricultural soils have been extensively evaluated both in laboratory (Gimsing et al. 2004b; Accinelli et al. 2005; Prata et al. 2005; Stenröd et al. 2006; Weaver et al. 2007; Simonsen et al. 2008; Zablotowicz et al. 2009; Lancaster et al. 2010; Aslam et al. 2015; Cassigneul et al. 2016; Bento et al. 2016; Góngora-Echeverría et al. 2019; Okada et al. 2019) and field studies (Mamy et al. 2008; Syan et al. 2014; Bandana et al. 2015; Yang et al. 2015; Guijarro et al. 2018; Bento et al. 2019; Brindhavani et al. 2020). Among the above-cited papers, the studies of Aslam et al. (2015) and Bento et al. (2019) regarded non-tilled soils exclusively. The studies of Prata et al. (2005) and Zablotowicz et al. (2009) conducted in laboratory conditions compared the dissipation of glyphosate under no-till and conventional tillage systems. More recently, Okada et al. 2019 compared glyphosate dissipation and AMPA formation/dissipation in no-till and conventional tillage systems under laboratory conditions. No differences in the dissipation of glyphosate between the two tillage managements were observed by Zablotowicz et al. (2009) and Okada et al. (2019), whereas Prata et al. (2005) observed acceleration of the glyphosate mineralization in non-tilled compared to the conventionally tilled soil. However, studies comparing glyphosate dissipation and AMPA formation/dissipation in no-till and conventional systems under field conditions are still lacking.

This study aims to investigate the effect of conservation agriculture (NT) and conventional tillage (CT) on glyphosate dissipation and AMPA formation/dissipation in a field experiment. The year of the study was the fifth year of conservation tillage for the NT field. Because soil properties and the potential herbicide dissipation under conservation agriculture can be different in the surface layer compared to lower depths (Zablotowicz et al. 2007), a component of this study was to evaluate glyphosate dissipation in upper (0–5 cm) and lower (5–20 cm) soil depths. The effect of NT and CT soil management practices on the adsorption of glyphosate was also investigated.

Materials and Methods

Study Site Description

This study was conducted between October 2018 and April 2019 at the Padova University Experimental Farm in the Po Valley (Veneto Region, NE Italy 45°21′N; 11°58′E; 6 m a.s.l.). The local climate is sub-humid with a mean annual temperature of 13.6 °C and annual precipitation of about 837 mm (value calculated as the average of the monthly mean temperatures and annual precipitation from January 1994 to December 2020). Rainfall is evenly distributed throughout the year, with maximums during autumn and
spring. Daily rainfall in the experimental period of October 2018 through April 2019 is illustrated in Fig. 1. The meteorological station of the Regional Agency for Environmental Protection (ARPA), situated on the experimental farm, was used to measure rainfall events. The meteorological station is located 300 and 250 m from the NT and CT field, respectively, and is equipped with a rain gauge recording every 5 min.

The experimental site is constituted of two fields, NT and CT, about 350 m apart from each other (Fig. 2). The NT field measures 0.70 ha, whereas the CT field has an area of 1.17 ha. The NT field has been managed under conservation agriculture since 2014, whereas the CT field has been managed under conventional tillage. The NT and CT fields are dedicated to the cultivation of non-GMO crops in a maize-wheat-soybean rotation, which includes cover crops for the no-till system. The last crop on both fields prior to the experimental period was maize, harvested on 17/09/2018. On the NT field, maize residues were left on the surface after harvesting. On the CT field, seedbed preparation had been done according to local practices consisting of mouldboard ploughing (10/10/2018) followed by harrowing (16/10/2018).

Since 2014, glyphosate-based herbicides have been applied 1–2 times per year on the NT field using a conventional rear-mounted boom sprayer at application rates ranging between 1.3 and 1.8 kg/ha of the active ingredient. The last glyphosate treatment on the NT field was performed 6 months before the study period began using the product Taifun MK (glyphosate isopropylamine salt) at a dose of 1.8 kg/ha of the active ingredient, whereas the CT field was treated with glyphosate 14 months before the start of the study period using the product Taifun MK at a dose of 1.6 kg/ha of the active ingredient.

Soil Characterization

NT and CT soil samples were collected on 17/10/2018 to analyse soil characteristics and determine background concentrations of glyphosate and AMPA. Soil samples were collected with a soil auger (3.5 cm i.d. × 25 cm length) at two depths, 0–5 and 5–20 cm. Five sub-samples per field were randomly collected and combined to obtain a single composite sample. The samples were placed in labelled plastic bags, sealed and transported to the laboratory, where they were air-dried, homogenised, crushed with mortar and pestle to break up clods, and sieved at Ø 2 mm within 1 day. After each sample was sieved, the sieve was cleaned by brushing the two sides and the borders with a small brush until no visible particles remained, then it was rinsed three times with deionized water and one with acetone. After sieving, the samples were stored at room temperature in the dark in sealed plastic bags until analysis. Residual soil moisture of each sample after air-drying was determined by weight difference before and after drying at 105 °C three aliquots of 20 g of soil. Moisture value was used to express the results of the analyses on a dry weight (d.w.) basis.

Soil properties of the CT and NT soils are presented in Table 1, and both soils are classified as silt loam.

Determination of Soil Adsorption of Glyphosate

Glyphosate adsorption isotherms were determined under laboratory conditions for the NT and CT soil samples collected on 17/10/2018 at 0–5 and 5–20 cm depth. Before performing the adsorption experiments, a pre-test on adsorption kinetics was carried out. It was found that 24 h was a sufficient time to reach the adsorption pseudo-equilibrium of glyphosate in soils. Adsorption of glyphosate to the soil was measured for five different concentrations (1, 5, 10, 50 and 100 µg/g of soil d.w.) in three replicates. The selected concentrations
Table 1

| Soil Depth (cm) | NT | CT |
|----------------|----|----|
| 0–5            | 45.2 | 51.2 |
| 5–20           | 41.2 | 51.2 |

Physical and chemical characteristics of the non-tilled (NT) and conventionally tilled (CT) soils used in the adsorption and dissipation experiments.

### Particle Size Distribution (% by weight)

- **Sand**: 45.2% in NT, 51.2% in CT
- **Silt**: 23.4% in NT, 29.4% in CT
- **Clay**: 31.4% in NT, 19.4% in CT

### Exchangeable Cations (meq/100 g d.w.)

- **Ca**: 18.4a in NT, 18.8a in CT
- **Mg**: 0.62a in NT, 0.32a in CT
- **K**: 0.04a in NT, 0.03a in CT
- **Na**: 2.27a in NT, 2.23a in CT

### pH

- NT: 7.07a in 0–5 cm, 7.17a in 5–20 cm
- CT: 7.07a in 0–5 cm, 7.17a in 5–20 cm

### Organic Carbon (OC) (% d.w.)

- NT: 15.5a in 0–5 cm, 15.6a in 5–20 cm
- CT: 11.7a in 0–5 cm, 11.4a in 5–20 cm

### Assimilable Phosphorus (Olsen P) (mg/kg d.w.)

- NT: 1549a in 0–5 cm, 895a in 5–20 cm
- CT: 1717a in 0–5 cm, 1060a in 5–20 cm

### Determination of the particle size distribution through wet sieving and with the use of the hydrometer.

### Determination of the exchangeable cations with barium chloride and triethanolamine.

### Determination of organic carbon and total nitrogen with an elemental analyser (organic carbon by separation of temperatures at 550 °C).

### Determination of assimilable phosphorus with Olsen method.

### Extraction of noncrystalline (amorphous) and organically bound Fe (Feo) and Al (Alo) oxides with acid ammonium oxalate in the dark and determination with inductively coupled plasma-optical emission spectroscopy, based on Violante (2000).

### Mean of three replicates. Means within a column followed by the same letter are not statistically different at \( p < 0.05 \).

**Dissipation Experiment Under Field Conditions**

Before glyphosate application, the soil cover percentage of crop residues on the NT field was visually estimated from aerial photography of three 2 x 5 m plots. The aerial photography was taken on 10/10/2018 using a camera carried by a drone at the height of 15 m. The soil cover of crop residues was estimated to be 15–20%. The mass of crop residues on the NT field was estimated on 10/10/2018 by sampling and weighing the crop residues from the three plots. Then, three samples of 500 g each were oven-dried at 75 °C for 48 h and weighed to determine the dry matter content. Subsequently, the crop residues were evenly redistributed on the plots. The mass of crop residues was estimated to be 4736 kg/ha, corresponding to 1485 kg/ha of dry matter. After this procedure, the plots area was bordered with pickets, and no soil samples were taken from this area for the dissipation experiment.

A visual survey conducted on 17/10/2018 on the NT field revealed that weeds covered 20–30% of the NT field area, with an estimated height of 5–10 cm. The main weeds were Cardamine hirsuta, Poa annua, Stellaria media, Capsella bursa-pastoris, Taraxacum officinale, Veronica persica, Sonchus oleraceus, Senecio vulgaris and Rumex spp. There were no weeds in the CT field.

On 18/10/2018, a pre-sowing treatment was applied on both the NT and the CT fields with glyphosate as a formulated product (Roundup Power 2.0, glyphosate potassium salt, Monsanto, St. Louis, MO, USA) using a conventional rear-mounted boom sprayer at 200 kPa pressure. The applied dose was 4 L/ha for both NT and CT fields, which corresponds to 1.44 kg/ha of the active ingredient. On 26/10/2018, the fields were sown with wheat. Six hours after treatment, soil samples were taken to assess the initial concentration of glyphosate and AMPA (soil
concentration at 0 days after treatment, DAT), then at increasing times from spraying to evaluate the field dissipation kinetics (1, 4, 7, 13, 19, 29, 50, 90, 126, 161 and 182 DAT). For the case of the NT soil, the sampling also regarded the soil covered by crop residues and weeds. The sampling strategy, the sample processing, the determination of residual soil moisture, and the storage conditions before the analysis was the same as described in “Soil Characterization”.

**Glyphosate and AMPA Analysis**

**Chemicals**

Analytical-grade standards of glyphosate and AMPA were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The compound purities were 98 and 99%, respectively. Isotope-labelled glyphosate (1,2-13C, 15N) and isotope-labelled AMPA (13C, 15N), used as internal standards (IS), were purchased from Toronto Research Chemicals (North York, Canada). Reagent-grade sodium tetraborate decahydrate was obtained from Honeywell Riedel-de Haën [Sigma-Aldrich Co. Ltd. (Steinheim, Germany)]. Hydrochloric acid (37%) was obtained from VWR International (Leuven, Belgium). Hydrochloric acid (37%) was obtained from Sigma-Aldrich Co. Ltd. (Steinheim, Germany). UPLC-MS-grade acetonitrile was supplied by Honeywell Riedel-de Haën [Sigma-Aldrich Co. Ltd. (Steinheim, Germany)] and UPLC-MS-grade water from Scharlau (Barcelona, Spain). Ultrapure water was obtained by an Arium® basic system (Sartorius Stedim Biotech GmbH, Goettingen, Germany). Formic acid for mass spectrometry (~98%) was purchased from Honeywell Fluka (Seelze, Germany). The AccQ-Tag™ Ultra Derivatization Kit (AccQ-Tag™ Ultra Reagent Powder, AccQ-Tag™ Ultra Borate Buffer, and AccQ-Tag™ Ultra Reagent Diluent) was purchased from Waters Corporation (Milford, MA, USA). Because glyphosate tends to bind to glass (Goscinny et al. 2012), all used labware was of polystyrene.

Standard stock solutions of glyphosate and AMPA were prepared by dissolving 1 mg of powder, accurately weighed, in 10 mL of ultrapure water, obtaining a final concentration of approximately 100 mg/L. A 20-mg/L standard-mix solution was prepared in ultrapure water by mixing and diluting the individual standard stock solutions. The working calibration standard and fortification solutions of glyphosate and AMPA were prepared by serial dilution of the standard-mix solution in ultrapure water. All standard solutions were stored in polystyrene tubes at 4 °C.

The isotope-labelled glyphosate and AMPA were purchased as 1 mL of 100-µg/mL stock solution in water. A 10-µg/mL standard-mix solution was prepared by mixing 1 mL of each stock solution in 10 mL of ultrapure water. Standard working solutions were prepared by diluting the intermediate standard solution in water to reach a concentration equal to 1 µg/mL of both glyphosate and AMPA.

**Extraction and Derivatisation**

A schematic representation of the sample preparation procedure can be found in Online Resource 1. Aliquots of 2 g of soil were transferred to polypropylene centrifuge tubes (50 mL). 122 µL of isotope-labelled glyphosate and AMPA (1 µg/mL), used as internal standards, were added before extraction of the target analytes to account for all uncontrollable losses of analytes. Samples were extracted by shaking with 0.6 M KOH (10 mL) on a mechanical shaker for 1 h at 280 rpm (IKA yellow line RS 10 control orbital shaker) and then centrifuged at 6000 rpm for 10 min at 6 °C. An aliquot of the supernatant (4 mL) was filtered at room temperature (about 20 °C) using a regenerated cellulose membrane filter with 0.20-µm pore size. The first attempt to determine glyphosate and AMPA without any sample clean-up gave poor absolute recoveries (less than 30%, data not shown) for both the analytes in all the tested soils. A clean-up step with Oasis® HLB Plus light cartridges (30 mg sorbent per cartridge, 30 µm particle size) was performed to limit matrix interference to the maximum extent. When loaded with the extract, glyphosate was expected to pass through the cartridge, whereas some matrix components such as amino compounds, which could compete with the analytes in the derivatisation, were retained on the cartridge. No cartridge conditioning was performed. A 1-mL syringe was connected for clean-up to the cartridge. A sample (2 mL) was manually delivered by syringe to obtain dropwise flow through the cartridge. A portion of 1 mL of sample was collected after the sample passed through the cartridge and transferred to a 2-mL polypropylene tube. Then, 85 µL of 6 M HCl was added to adjust the pH to approximately 9 before derivatisation. An aliquot of 200 µL of the sample was introduced into a 1.5-mL polypropylene vial. The sample was then derivatised according to our previously reported procedure (Carretta et al. 2019) using the AccQ-Tag™ Ultra Derivatisation Kit. The AccQ-Tag™ Ultra Reagent Powder, which consists of 6-aminoquinolyl-n-hydroxysuccinimidyl carbonate (AQC), was reconstituted with 1 mL of AccQ-Tag™ Ultra Reagent Diluent in a 1.5-mL glass vial. The vial was vortexed for 10 s and heated on a heating block at 55 °C for 15 min until the powder was dissolved. A 5% borate buffer solution was included in the derivatisation kit; however, because the kit was designed for amino acids analysis, which requires a different ratio between derivatising agent and buffer, the quantity of buffer solution was not enough. Thus, when necessary, an additional buffer solution was
prepared by dissolving 5 g of sodium tetraborate decahydrate in 100 mL of ultrapure water. A 5% borate buffer solution (225 µL) was added, followed by the addition of 25 µL of freshly prepared derivatising reagent. The vials were capped, vortexed for 10 s and placed in a water bath at 55 °C for 15 min. The glyphosate and AMPA concentrations were then analysed by UHPLC–ESI–MS/MS. The reaction products were stable for 5 days. Every sample was extracted and derivatised in triplicate and analysed for glyphosate and AMPA.

**LC–MS/MS Analysis**

The analysis was conducted with a triple quadrupole mass spectrometer system (TSQ Quantiva, Thermo Scientific, Waltham, MA, USA) equipped with an electrospray ionization (ESI) source and coupled to an UltiMate 3000 UHPLC System (Thermo Scientific, Waltham, MA, USA). The LC analysis was performed with a reversed-phase C18 column of 2.1 mm × 100 mm, 2.5 µm, 100 Å particle size (XSelect HSS T3 XP, Waters Corporation, Milford, MA, USA). The LC system was operated with mobile phase A (UPLC-MS-grade water) and mobile phase B (UPLC-MS-grade acetonitrile), both with 0.1% formic acid. The LC gradient and instrumentation conditions of the UHPLC-MS/MS (i.e., column temperature, flow rate, MS method optimization, and source parameters) were as described by Carretta et al. (2019). The limit of detection (LOD) and the limit of quantification (LOQ) were 15 and 50 µg/kg, respectively, for glyphosate and 6 and 20 µg/kg, respectively, for AMPA. A detailed description of the method validation and quality control can be found in Online Resource 2.

**Data Analysis**

Adsorption data of glyphosate were fitted by nonlinear regression to the Freundlich adsorption isotherm (Eq. (1)) using RStudio Version 1.4.1106 (RStudio Team 2021).

\[ Q_e = K_f C_e^{(1/n)} \]  

(1)

where \( Q_e (\mu g/g) \) is the adsorbed amount, \( C_e (\mu g/mL) \) is the concentration in the aqueous phase, \( K_f (\mu g^{1-1/n} (mL)^{1/n} g^{-1}) \) is the Freundlich adsorption coefficient, and \( 1/n \) is the exponent of nonlinearity.

The dissipation of glyphosate and the formation/dissipation of AMPA were studied by modelling the experimental data according to the FOCUS work group guidance document on degradation kinetics (FOCUS 2006). Both parent and metabolite dissipation data were expressed in µmol/kg soil d.w. RStudio was used to estimate the kinetic model’s parameters for both glyphosate and AMPA. Initially, the single first-order model (SFO, Eq. (2)) and the first-order multicompartment model, also known as Gustafson and Holden (FOMC; Eq. (3)), were tested to describe glyphosate dissipation kinetics:

\[ \frac{dC}{dt} = -kC \]  

(2)

\[ \frac{dC}{dt} = - \frac{a}{\beta} C \left( \frac{t}{\beta} + 1 \right)^{-1} \]  

(3)

where \( C \) is the glyphosate concentration at time \( t \), \( k \) is the rate constant (SFO), and \( a \) and \( \beta \) are respectively the shape and location parameters for the variation of the degradation rate over time (FOMC). For the selection of the models best describing the dissipation of glyphosate, the criteria proposed by FOCUS (2006) for assessing the goodness of fit and comparing different models were used, i.e., visual assessment of fitted and observed data versus time and of the residuals plot, chi-square (\( \chi^2 \)) model errors, and \( t \) test.

The model for the metabolite AMPA was composed of an FOMC degradation model for glyphosate and an SFO degradation model for AMPA. The rate equation for the AMPA was Eq. (4):

\[ \frac{dM}{dt} = - \frac{dC}{dt} \times ff \times k_2 M \]  

(4)

where \( M \) is the metabolite concentration at time \( t \), \( ff \) is the formation fraction of AMPA and \( k_2 \) is the constant degradation rate for the metabolite.

Differential equations were integrated numerically using the Runge–Kutta methods (Runge 1895; Kutta 1901) with a time-step equal to 0.1 days. Integrated models were fitted to the observed data using maximum likelihood, based on the BFGS (Broyden–Fletcher–Goldfarb–Shanno) algorithm and log-normal likelihood. Standard errors were derived by the Hessian of the objective function at maximum likelihood.

The parameter \( ff \) was constrained to \( 0 \leq ff \leq 1 \) to avoid unrealistic values (\( ff > 1 \)), as recommended by FOCUS (2006). The goodness of fit for the metabolite was assessed by visual assessment of fitted and observed data versus time and of the residuals plot, chi-square (\( \chi^2 \)) model errors, and \( t \) test.

The estimated trend of concentrations over time for both glyphosate and AMPA were used to derive the DT50 for glyphosate, the maximum concentration value for AMPA and the DT50 for AMPA. Standard errors for these estimates were obtained using the delta method (Weisberg 2005).

**Statistical Analysis**

The statistical analysis was performed using RStudio Version 1.4.1106. To test for significant differences (\( p < 0.05 \)) of the soil characteristics reported in Table 1 between different...
soil managements (NT and CT) and soil depths (0–5 and 5–20 cm), a two-way ANOVA followed by Tuckey post hoc tests was performed. For the adsorption experiment, best-fit $K_f$ values for glyphosate were compared across treatments using a heteroscedastic t test (Motulsky and Christopoulos 2003), and $p$ values < 0.05 were considered statistically significant. A heteroscedastic t-test can be used to compare one parameter of the same model between different treatments. The t ratio is calculated as:

$$t = \frac{|\text{Parameter}_{\text{treatment} A} - \text{Parameter}_{\text{treatment} B}|}{\sqrt{SE^2_{\text{treatment} A} + SE^2_{\text{treatment} B}}}$$

(5)

In addition, Pearson correlation of $K_f$ with selected properties of NT and CT soils at 0–5 and 5–20 cm depths were evaluated ($p = 0.05$ and $p = 0.01$). The DT50 values of glyphosate and AMPA were compared across treatments using a heteroscedastic t-test (Motulsky and Christopoulos 2003), and $p$ values < 0.05 were considered statistically significant.

**Results and Discussion**

**Adsorption of Glyphosate in Tilled and Non-tilled Soil**

Glyphosate adsorption isotherms are shown in Fig. 3. The fit of the data was generally good ($R^2 \geq 0.98$), indicating that the data for all soils and depths are described well by the Freundlich equation, which defines the multilayer adsorption processes that occur on heterogeneous surfaces and assumes an exponential change in the distribution of energy among adsorption sites (Saleh et al. 2017). The $1/n$ values, which were consistently < 1, indicated non-linear adsorption. The estimated parameters ($K_f$ and $1/n$) and $R^2$ values for the adsorption isotherms of glyphosate in the NT and CT soils at 0–5 and 5–20 cm depth and the results of the heteroscedastic t tests on the $K_f$ values are summarised in Table 2. The values of $K_f$ ranged from 22 to 55. In general, they are in accordance with others reported in the literature (Yu and Zhou 2005; Mamy et al. 2005; Sidoli et al. 2016; Lewis et al. 2016).

At both sampling depths, the $K_f$ value was significantly higher in the NT soil (41.1 and 54.5 μg 1−1/n (mL)1/n g−1 for 0–5 and 5–20 cm, respectively) than in the CT soil (22.4 and 29.8 μg 1−1/n (mL)1/n g−1 for 0–5 and 5–20 cm, respectively). The $K_f$ value was higher at 5–20 cm than at 0–5 cm for both the NT and CT soils, indicating higher adsorption of glyphosate in the 5–20 cm layer of the investigated soils.

From our results, it was not possible to say that there are effects on glyphosate adsorption due to the different soil management practices. The adsorption behaviour of glyphosate in the studied soils seems to be related in large part to the different intrinsic soil properties of NT and CT soil. In particular, as shown in Table 3, the $K_f$ values found in the present study were positively correlated to the clay content ($r = 0.976; p < 0.05$) and $A_{lu}$ content ($r = 0.962; p < 0.05$) and negatively correlated to the sand content ($r = −0.974; p < 0.05$). Contrary to some previous studies (Gimsing et al.)

![Fig. 3 Freundlich adsorption isotherms of glyphosate in NT and CT soil at 0–5 and 5–20 cm depth. The lines represent the fitting curves, and the symbols represent the observed values. The measured data points represent triplicate samples for each glyphosate concentration](image-url)

**Table 2** Freundlich parameters ($K_f$, 1/n and $R^2$ values) for the adsorption of glyphosate in NT and CT soil at 0–5 and 5–20 cm depths (±SE) and the results of the heteroscedastic t tests on the $K_f$ values used to compare this parameter between different soil managements and depths

| Soil | Depth     | 1/n       | $K_f$ (μg 1−1/n (mL)1/n g−1) | $R^2$ |
|------|-----------|-----------|-----------------------------|-------|
| NT   | 0–5 cm    | 0.45 (±0.027) | 41.1 (±1.02) b<sup>a</sup> | 0.992 |
|      | 0–5 cm    | 0.69 (±0.071) | 22.4 (±0.89) d  | 0.984 |
| NT   | 5–20 cm   | 0.44 (±0.038) | 54.5 (±2.17) a  | 0.982 |
|      | 5–20 cm   | 0.59 (±0.026) | 29.8 (±0.49) c  | 0.997 |

A $K_f$ values followed by the same letter are not statistically different at $p < 0.05$ based on the heteroscedastic t test.

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Clay is not the only soil component that can adsorb glyphosate. It is known that soil minerals can play an important role in this process. The pH of the studied soils is only slightly above the pH range of the most agriculturally important soils, which is 4–8. In this pH range, glyphosate is ionic, and its sorption is mainly controlled by amorphous iron and aluminium oxides, poorly ordered aluminium silicates, and edge-layer silicates are probably the most important soils, which is 4–8. In this pH range, glyphosate is ionic, and its sorption is mainly controlled by amorphous iron and aluminium oxides, poorly ordered aluminium silicates, and edge-layer silicates are probably the most important.

A positive correlation between glyphosate sorption coefficient and aluminium oxides content in soil was also reported by Morillo et al. (2000), Prata et al. (2007), Albers et al. (2009), Paradelo et al. (2015), Sidoli et al. (2016), and Maqueda et al. (2017). To identify the reasons for the higher Feo and Alo content between CT and NT exceeded the objectives of this study. However, according to Borggaard et al. (1990) and Börling et al. (2001), we can hypothesise the role of OC content, which was slightly higher in NT than CT soil, in inhibiting mineral crystallisation and enabling the formation of poorly crystalline Fe and Al oxides. As pointed out by Borggaard and Gimsing (2008), soil organic matter can stabilise oxides with high adsorption capacity, then affecting glyphosate adsorption.

Considering the influence of soil depth, our results agree with what was observed by Zablotowicz et al. (2009), who detected higher glyphosate adsorption at 2–10 cm than at 0–2 cm. Moreover, they found significantly higher glyphosate adsorption in non-tilled soil compared to conventionally tilled soil, although the difference was statistically significant only at 2–10 cm. However, although the authors found a higher OC content in non-tilled than in conventionally tilled soil, they detected no correlation between glyphosate adsorption coefficients and OC and hypothesized that the increase in OC content in non-tilled soil is likely to have no substantial effect on glyphosate adsorption and that iron and aluminium oxide, poorly ordered aluminium silicates, and edges of layer silicates are probably the most important factor controlling glyphosate adsorption in the investigated soil. Unlike what was observed in the present study and in the study of Zablotowicz et al. (2009), Okada et al. (2016) observed a tendency towards higher adsorption of glyphosate in conventionally tilled soil compared to non-tilled soil. The authors stated that the observed tendency was not motivated by the different physicochemical properties of tilled and non-tilled soils under each management system. Despite that, they observed a strong correlation between $K_f$ and clay content and, to a lesser extent, between $K_f$ and OC.

**Glyphosate Dissipation in Tilled and Non-tilled Soil**

The FOMC model was the best fit for glyphosate dissipation in both NT and CT soils at 0–5 and 5–20 cm depths, whereas the SFO model did not provide satisfactory results on the basis of visual assessment of curve fits and residual plots, $t$ test, and $\chi^2$ test ($\chi^2$ error values > 20% in all cases for SFO model, data not shown). The estimated parameters for the fitting curves and the DT50 of glyphosate and the metabolic
product AMPA in the NT and CT soils at 0–5 and 5–20 cm depth are presented in Table 4.

In the NT soil samples, the glyphosate concentration measured 1 day before the treatment was 45 µg/kg (< LOQ) at 0–5 cm depth, whereas at 5–20 cm, glyphosate was < LOD. In the CT soil samples, the glyphosate concentrations measured 1 day before the treatment were < LOD for both sampling depths. The measured concentration of glyphosate 0 DAT at 0–5 cm depth was four times higher in the CT soil than in the NT soil (8.37 and 2.09 µmol/kg for CT and NT soil, respectively, corresponding to 1414 and 353 µg/kg for CT and NT soil, respectively), whereas, in the 5–20 cm layer, the concentrations were similar in both soils (0.51 and 0.50 µmol/kg for CT and NT soil, respectively, corresponding to 86 and 84 µg/kg for CT and NT soil, respectively) and markedly lower than those in the surface layer. The lower concentration detected in deeper soil layers can be motivated by the fact, observed by Ratcliff et al. (2006) and Stratton (1990), that glyphosate movement in soil is limited by chemical adsorption to the surface centimetres, although actual penetration can differ somewhat depending on the soil type (Sprankle et al. 1975). In terms of percentage of applied glyphosate, estimated assuming an average bulk density for a silt loam soil of 1.30 g/cm³ (USDA NRCs 2019), the glyphosate concentrations found at 0 DAT at 0–5 cm depth corresponded to 16.3 and 65.3% for NT and CT soil, respectively, whereas at 5–20 cm depth corresponded to 11.7 and 11.9% for NT and CT soil, respectively. The glyphosate concentration at 0 DAT found in NT soil at 0–5 cm was much lower compared to the values estimated by Bento et al. (2019) at 0–1 cm depth in soybean cultivation areas, whereas the result in CT soil at 0–5 cm is comparable to the value estimated by these authors. It has to be noted that Bento et al. (2019) carried out the soil samplings only in bare patches of soil; therefore the spray interception by maize residue cover was not expected to significantly affect the estimated average concentration of glyphosate in the soil soon after the application. However, in the present study, the NT soil sampling strategy regarded also the soil covered by maize crop residues and weeds, which could, therefore, have intercepted a fraction of glyphosate applied, determining the lower concentration of glyphosate detected in the NT soil at 0 DAT. Several studies have observed that crop residues distributed on the soil surface, as is done in conservation agriculture, can intercept a considerable amount of the applied herbicide, thus reducing the amount of chemical reaching the soil (Ghadiri et al. 1984; Gaston et al. 2001; Chauhan et al. 2006; Khalil 2018). According to Chauhan et al. (2006), crop residues, which physically separate herbicides from the soil surface, can intercept from 15 to 80% of the applied herbicide, affecting herbicide persistence and fate. The potential interception of herbicides by crop residues may depend on the biomass of the residues as well as on their surface area. Once intercepted by the residues, herbicides can be adsorbed on them or subsequently washed off by rainfall (Unger and Kaspar 1994; Gaston et al. 2001). The observed effect of crop residues on its interception is important because glyphosate is the most used herbicide in conservation agriculture, where the distribution of crop residues on the field is a fundamental practice.

In both tillage systems and depths, an immediate dissipation response was observed to the glyphosate applied without any lag phase (Fig. 4), and this is in agreement with what was reported by Gimsing et al. (2004b), Many et al.
In our soils, the initial dissipation was fast, and 30–38% of the applied glyphosate was degraded within the first 4 days. The fast initial decrease in glyphosate concentration was followed by a slower decline. Several studies reported that a readily available form of glyphosate (either soluble or desorbed into the soluble soil phase) allows for its fast initial dissipation but that it decreases at a later stage, resulting in a slower dissipation rate of the remaining glyphosate from the adsorbed phase (Eberbach 1998; Gimsing et al. 2004b; Simonsen et al. 2008; Bento et al. 2016; Okada et al. 2019). A possible explanation for the observed bi-phasic pattern of glyphosate degradation in both the tested soils could be the fact that only a fraction of the herbicide in soil solution was available for degradation (Linn and Scow 1993). Non-linear sorption with a Freundlich exponent below 1, as occurred in this case and as often occurs for glyphosate (Glass 1987; Okada et al. 2016; Cederlund et al. 2016; Garba et al. 2018), results in decreasing availability of the herbicide in soil solution with decreasing concentration (Proctor and Toro-Vazquez 2009). This may have decreased its degradation rate at later stages of the experiment.

The DT50 of glyphosate in NT soil at 0–5 cm was not significantly different from that in CT soil at the same depth (9.1 ± 1.52 and 8.8 ± 0.66 days, for NT and CT, respectively), whereas a significantly higher DT50 was observed in the NT soil than in the CT soil at 5–20 cm (17.7 ± 2.24 and 8.3 ± 1.19 days, for NT and CT respectively). In the CT soil, no significant difference between the two depths was observed in terms of DT50, whereas in the NT soil, glyphosate dissipated faster at 0–5 than at 5–20 cm. The DT50 values found in this study, although being within the typical values from 5.7 to 40.9 days for field studies (European Food Safety Authority EFSA 2015), were generally low. Overall, the DT50 values found are in agreement with those reported by Stenrød et al. (2006), Al-Rajab and
Hakami (2014), Eberbach (1998), Simonsen et al. (2008) in conventionally tilled soils in the laboratory, by Zhang et al. (2015) in conventionally tilled soil in a field study, by Okada et al. (2019) in conventional and non-tilled soils in the laboratory, and by Bento et al. (2019) in non-tilled soils in a field study.

Although a higher DT50 was observed for NT than CT soil in the deeper layer, the DT50 values alone do not allow us to delineate a clear effect of conservation agriculture on glyphosate kinetics. Similarly, Okada et al. (2019) and Zablotowicz et al. (2009), measuring the dissipation of glyphosate in tilled and non-tilled soil in laboratory studies under controlled conditions, did not observe any significant variation in the DT50 of glyphosate in response to the different soil management systems. They also observed no significant alteration of the soil’s chemical, physical and biological properties in relation to the different tillage management, except for a higher OC content in the 0–2 cm of non-tilled soil compared to conventional soil observed by Zablotowicz et al. (2009). Regarding the present study, the differences in DT50 for the 5–20-cm layer could be probably related largely to the different intrinsic characteristics of NT and CT soil, mainly clay content and Feo and Alo content, which were significantly higher in NT than in CT soil at 5–20 cm. As observed in “Adsorption Of Glyphosate In Tilled And Non-Tilled Soil”, the $K_f$ of glyphosate was positively correlated with clay and Alo content. Thus, we hypothesise that adsorption processes may have played a key role in determining the observed difference in the DT50 of glyphosate between NT and CT at 5–20 cm. Glyphosate DT50 was higher in the NT soil at 5–20 cm, where adsorption was the highest, compared to the CT soil at 5–20 cm, where adsorption was weaker. The high adsorption observed in the NT soil at 5–20 cm supports the hypothesis of low bioavailability, thus limiting dissipation. Despite hindered dissipation, high glyphosate adsorption in surface NT soil may minimise leaching to lower soil depths. Despite a significantly higher content of clay, Feo, and Alo and a significantly higher adsorption observed in NT than CT soil also at 0–5 cm, no significant difference in the DT50 was observed between the surface layers of the NT and CT soils. However, it has to be noted that the extent of the difference in the clay, Feo, and Alo content and in glyphosate adsorption between NT and CT soil is substantially lower at 0–5 cm than 5–20 cm, and it could be not enough to determine a significant effect on DT50.

The glyphosate concentration detected at the end of the study (182 days) at 0–5 cm in the NT soil (0.43 µmol/kg, corresponding to 73 µg/kg) was almost twice that in the CT soil (0.22 µmol/kg, corresponding to 38 µg/kg), even though the initial concentration was more than three times higher in the CT than in the NT soil. At the end of the study, at 5–20 cm, a concentration of 0.12 µmol/kg (corresponding to 21 µg/kg) was detected in the NT soil, whereas no glyphosate was detectable in CT, but in this case, the initial concentrations were comparable in the two soils. The higher glyphosate adsorption observed in NT than in CT soil is probably the key factor determining the higher final concentrations of glyphosate observed in NT than CT soil within the same depth, but we hypothesize that also the different management practices could have played a role. Non-tilled soils tend to be prone to compaction during the first years after switching from conventional tillage to no-till, due to the absence of tillage operations and the high traffic load, whereas the tillage should decrease the degree of soil compaction and increase soil porosity (Derpsh 2008; Piccoli et al. 2016, 2017). According to Penghamkeerati et al. (2011), severe soil compaction can induce changes in soil physical properties, especially pore size distribution. These changes cause an alteration of the soil microhabitat with a negative influence on the distribution, activity, and diversity of soil microorganisms (Grigal 2000). The degree of the observed effect is dependent on the severity of soil compaction and, generally, negative effects on C-mineralisation and microbial biomass are observed after a certain degree of compaction (Beylich et al. 2010). In the sight of this, we hypothesize that the higher degree of soil compaction occurring in the NT soil may have reduced the capacity of soil microorganisms to degrade glyphosate when its concentration is becoming low. To explore this possibility, further specific studies would be needed to verify this hypothesis. A possible increase in glyphosate persistence due to the soil compaction under no-till could be of concern for the environment because, in the first years of conservation agriculture, an intensified glyphosate use is often required to compensate for the lack of mechanical weed control and the higher abundance and density of weeds (Knowler and Bradshaw 2007; Armengot et al. 2015).

When interpreting these data, it is important to take into account not only the soil properties, but also the interference of weeds on the NT seedbed. Glyphosate is absorbed by the plant leaves and rapidly translocated to developing api-cal and roots meristems (Grangeot et al. 2006). Glyphosate can return to the soil by exudation (Coupland and Caseley 1979) and by the residues present in the biomass of weeds during biomass turnover in soil (Laitinen et al. 2007), thus providing a delayed contribution of this substance to the soil and an additional risk of environmental contamination. The amount of pesticide that returns to the soil with plants can be significant (Laitinen et al. 2007; Doubelt et al. 2009). To test these two alternatives exceeds the objectives of this work, but Doubelt et al. (2009) observed that the absorption of glyphosate in plants delays its subsequent soil degradation, increasing herbicide persistence in soil from two to six times. This interference could contribute to explain the persistence and accumulation of glyphosate in the NT soil profile (Fig. 4). A similar hypothesis was also advanced by Kremer (2017) and Soracco et al. (2018). The higher
persistence and the accumulation of glyphosate in the lower layer of NT soil is not only an environmental problem but it could also represent a productivity issue because it could increase the time during which residues of glyphosate are available for reabsorption by the crops back through the roots, with possible damage and growth inhibition (Pline et al. 2002; Wagner et al. 2003; Petersen et al. 2007).

**AMPA Formation/Dissipation in Tilled and Non-tilled Soil**

In the NT soil samples, the AMPA concentration measured 1 day before the treatment was 94 µg/kg at 0–5 cm depth and 15 µg/kg (<LOQ) at 5–20 cm depth. In the CT soil samples, the AMPA concentrations measured 1 day before the treatment were < LOD for both sampling depths. It must be noted that the CT soil was treated with glyphosate 14 months before the soil sampling, whereas the NT soil was treated only 6 months before the sampling; therefore, the AMPA concentration is expected to be lower in the CT soil than in the NT soil.

The formation and dissipation of AMPA in the NT and CT soils at 0–5 and 5–20 cm depths are represented in Fig. 4. AMPA began to form in the early stages after treatment in all the soils and depths. The fact that AMPA could already be detected 6 h after glyphosate application underlines the quick glyphosate degradation in soil, as reported by Mamy et al. (2005) and Todorovic et al. (2013). The fast decrease of glyphosate concentration at the beginning of the dissipation study was reflected by an increase in AMPA concentration. A different behaviour was observed by Okada et al. (2019), who did not observe any significant increase of AMPA concentration in response to the fast decrease of glyphosate concentration at the beginning of the study, suggesting that the preferred glyphosate degradation pathway in soils studied by them could have been via sarcosine. Like glyphosate, the AMPA concentrations in the present study were lower in the deeper soil layer. Although the vertical mobility of AMPA is higher than that of glyphosate, AMPA is as strongly adsorbed by the soil compounds as glyphosate is, and, like for glyphosate, most of this molecule tends to remain in the first centimetres of soil (Mamy et al. 2005).

Before presenting the result of the dissipation kinetics of AMPA, a remark must be made about the cases of NT soil at 0–5 cm and CT soil at 5–20 cm. In these cases, it was not possible to obtain a satisfactory fit for AMPA by applying the model described by Eq. (4) (“Data Analysis”). The $ff$ should not be constrained to $0 \leq ff \leq 1$ to obtain a good fit. However, without constraining this parameter, $ff$ values higher than 1 would be obtained (1.096 and 2.43 for NT at 0–5 cm and CT at 5–20 cm, respectively), and this is not realistic (FOCUS 2006). When the analysis was repeated by constraining the $ff$ parameter to $0 \leq ff \leq 1$, the fitting was unsatisfactory and large standard errors associated with the DT50 of AMPA in the NT soil at 0–5 cm and in the CT soil at 5–20 cm were obtained, making the parameters estimates not reliable. Modifying the fitting routine and adopting a stepwise approach, firstly determining the glyphosate parameters and then determining the AMPA parameters, did not substantially improve the results. Therefore, in these cases, the dissipation rate and DT50 for AMPA were estimated separately by fitting the decline phase with SFO, using as a starting point the peaked AMPA concentration observed, as FOCUS (2006) suggested. This approach provides conservative estimates of the DT50 values. The results from the $t$ test for the SFO parameters and the $\chi^2$ error were satisfactory. However, in CT soil at 5–20 cm, the visual inspection of fitted and observed data versus time and the residuals plot suggests a non-so accurate correspondence with the SFO kinetics. Extrapolation beyond the study period was necessary to estimate the DT50 of AMPA in NT soil at 0–5 cm; therefore, this value should be interpreted with caution and considered only as indicative value.

The observed maximum concentration of AMPA was 3.82 µmol/kg soil d.w. (corresponding to 424 µg/kg soil d.w. and to 29.8% of applied glyphosate, using molar conversion) in NT at 0–5 cm (50 DAT), 0.46 µmol/kg soil d.w. (corresponding to 52 µg/kg soil d.w. and to 10.9% of applied glyphosate) in NT at 5–20 cm (50 DAT), 5.42 µmol/kg soil d.w. (corresponding to 602 µg/kg soil d.w. and to 42.3% of applied glyphosate) in CT at 0–5 cm (29 DAT), and 0.60 µmol/kg soil d.w. (corresponding to 66 µg/kg soil d.w. and to 13.9% of applied glyphosate) in CT at 5–20 cm (50 DAT). When expressed in % of applied glyphosate, the observed maximum AMPA concentrations in the 0–5 cm of both NT and CT soils are comparable with the maximum concentrations observed by Bento et al. (2016) in a laboratory study and observed by Bento et al. (2019) in non-tilled soybean and maize fields. However, the time of maximum AMPA concentration observed in the present study was longer compared to what has been observed by Bento et al. (2016) and Bento et al. (2019). The maximum AMPA concentrations observed in NT soil at 0–5 cm and CT soil at 5–20 cm were 45.3 and 14.7% higher than the glyphosate concentration at 0 DAT, respectively. Moreover, in the case of CT soil at 5–20 cm, the AMPA concentration after the plateau decreased in an unexpected way, declining slower in the first stages and then faster by the last sampling dates. As mentioned above, these factors contributed to a poor model fit and an $ff$ higher than 1 when the model described by Eq. (4) was applied by constraining the parameter $ff$ to $0 \leq ff \leq 1$. In the case of NT soil at 0–5 cm, we hypothesize that a possible factor contributing to the observed situation could be the delayed inputs of glyphosate to soil via the wash-off from crop residues during rainfall events combined with the gradual release of glyphosate via weed biomass turnover in
the soil, followed by the rapid degradation of glyphosate to AMPA. Indeed, as described in “Glyphosate Dissipation in Tilled and Non-tilled Soil”, the glyphosate concentration detected in NT soil at 0–5 cm at 0 DAT was much lower than the dose applied, and this was attributed to the interception of a fraction of the applied glyphosate by weeds and crop residues during the application. Regarding the CT soil, since neither crop residues nor weeds were present on the soil at the moment of glyphosate application, the reason for the observed behaviour should be searched elsewhere. Glyphosate adsorption was the lowest in the 0–5-cm layer of CT soil compared to the other soils and depths; therefore, we hypothesize a delayed arrival of glyphosate (and its further degradation to AMPA) and AMPA to the 5–20-cm layer of CT soil via leaching from the 0–5-cm layer of CT soil, facilitated by some intense storms and rainfall occurring between the end of October and the beginning of November 2018.

The maximum concentrations of AMPA estimated with the model described by Eq. (4) were 0.45 ± 0.006 µmol/kg soil d.w. (corresponding to 50 µg/kg soil d.w.) in NT at 5–20 cm and 4.92 ± 0.113 µmol/kg soil d.w. (corresponding to 546 µg/kg soil d.w.) in CT at 0–5. The time of maximum AMPA concentration was estimated to be 21 days in the NT soil at 5–20 cm and 27 days in the CT soil at 0–5 cm. For the NT soil at 0–5 cm and CT soil at 5–20 cm, where the model fitting was poor, the estimated maximum concentrations of AMPA were 22 and 28% lower than the observed maximum concentrations for NT soil at 0–5 cm and CT soil at 5–20 cm, respectively, highlighting the wrong results obtained with this approach (data not shown). In the cases of NT soil at 5–20 cm and CT soil at 0–5 cm, the estimated and observed maximum concentrations of AMPA were comparable.

The dissipation of AMPA was substantially slower than that of glyphosate, resulting in longer DT50 for both soils and depths compared to glyphosate. In the surface layer, AMPA DT50 was significantly higher in the NT soil than in the CT soil (249.9 ± 27.37 and 110.0 ± 6.61 days for NT and CT, respectively). Similarly, in the deeper layer, a significantly higher DT50 was observed in the NT soil than in the CT soil (145.7 ± 6.45 and 99.3 ± 11.69 days for the NT and CT soils, respectively). In NT soil, a significant difference in the DT50 was observed between the 0–5 and 5–20 cm layer, whereas in the CT soil, the difference between the two depths was not statistically significant. The DT50 of AMPA in NT soil at 5–20 cm and in CT soil at both depths was in line with the value reported by Bergström et al. (2011) for subsoil samples of sandy and clay soil. The AMPA DT50 values found in the present study were generally longer than those reported by Simonsen et al. (2008), Bento et al. (2016), and Bento et al. (2019), but shorter than the DT50 values reported by European Food Safety Authority EFSA (2015).

Contrasting variations of DT50 in different soils and depths were observed for glyphosate with respect to AMPA. In particular, in the NT soil, glyphosate DT50 was longer in the 5–20-cm layer compared to the 0–5-cm layer, whereas for AMPA, the opposite situation was observed, with longer DT50 in the upper layer of the NT soil compared to the lower layer. A higher glyphosate DT50 in NT soil compared to CT soil was observed only for the 5–20 cm depth, whereas a higher AMPA DT50 was observed in NT than CT soil for both soils and depths, but with a much more pronounced difference in the 0–5-cm layer. In the case of AMPA, the different soil characteristics that were observed to play a major role in glyphosate adsorption and dissipation (clay, Feo, and Al0 content) could only partly explain the observed behaviour. However, an effect of the different soil management systems on the dissipation of AMPA could also be hypothesized. AMPA was still detected in the soil on the last sampling date, 182 DAT, in all soils and depths. This is in agreement with what was observed by Many et al. (2005) in a field study with a lower glyphosate application rate. Although the initial parent molecule concentration and amount of AMPA formed were higher in the CT soil than in the NT soil at 0–5 cm depth, at the end of the experiment, the measured concentration of AMPA in the NT soil was twice that in the CT soil (2.56 and 1.23 µmol/kg for NT and CT, respectively, corresponding to 284 and 136 µg/kg for the NT and CT, respectively). In the deeper soil layer, the amount of AMPA formed and its concentration measured at the end of the experiment were comparable to each other and much lower than in the upper layer (0.17 and 0.17 µmol/kg for NT and CT, respectively, corresponding to 19 and 17 µg/kg for the NT and CT, respectively). This finding is in agreement with what has been observed by Napoli et al. (2016). One year after glyphosate application along the rows, Napoli et al. (2016) detected a significantly higher AMPA concentration in non-tilled soil with permanent grass cover compared to the harrowed soil, at 0–5 cm depth. The authors stated that the grass cover on non-tilled soil could have favoured the adsorption of AMPA, thus increasing its persistence in the soil. Although the adsorption of AMPA was not investigated in the present study, according to Báez et al. (2015) and Sidoli et al. (2016), AMPA is in the same high adsorption range as glyphosate, and they seem to be adsorbed to the same extent in the soil. Thus, it is possible that higher adsorption of AMPA in NT soil than in CT soil, as observed for glyphosate, may have reduced AMPA concentration in solution in NT soil, impeding the degradation and leading to an higher amount of AMPA at the end of the study period in the upper layer of the NT soil compared to CT soil. Moreover, as discussed for glyphosate in “Glyphosate Dissipation In Tilled And Non-Tilled Soil”, the no-till management could have played a role in determining the higher final concentration of AMPA in NT than in CT soil.
thanks to the effect of the soil compaction, which could have altered the soil microhabitat reducing the ability of microorganisms to degrade AMPA. Long-term dissipation studies under no-till and conventional tillage management activities are recommended to investigate if no-till could determine a higher risk of AMPA accumulation in the soil compared to conventional tillage, especially in the case of recurrent glyphosate application.

**Conclusions**

This study only partially answered the initial question, which aimed to investigate whether the no-tillage regime affected the dynamics of glyphosate and AMPA in the soil compared to the conventional tillage. Indeed, the glyphosate and AMPA dynamics in NT and CT soils were primarily influenced by the intrinsic characteristics of the two soils, which were different despite their proximity (higher clay content along the entire soil profile, higher amorphous and organically bound Fe and Al oxides content in the deeper layer, and higher OC content in the surface layer in NT soil compared to CT soil).

Nevertheless, this study highlighted some interesting results concerning the behaviour of glyphosate in NT soil. At the time of glyphosate application, the weeds and crop residues present on the NT soil surface intercepted a significant amount of glyphosate, determining an initial glyphosate concentration in the 0–5-cm layer of the NT soil considerably lower than the dose applied and lower than the initial concentration in CT soil at the same depth. Nevertheless, 6 months after treatment, glyphosate concentration in NT soil was higher than in CT soil in both the 0–5- and 5–20-cm layers; in particular, in the deeper layer of CT soil, glyphosate was not even detectable. Besides the influence of soil characteristics, the higher persistence of glyphosate observed in the 0–5 cm layer of NT soil compared to CT soil could also be due to the higher OC content of NT compared to CT soil and also to the higher soil compaction in non-tilled soil during the transition phase from conventional tillage, which could have reduced the ability of soil microorganisms to degrade glyphosate. These two characteristics are typical consequences of no-tillage soil management, and further specific studies are needed to confirm this hypothesised role of tillage management on glyphosate persistence. Moreover, glyphosate dynamic in NT soil resulting from its absorption by weeds, followed by a delayed return to the soil by root exudation or plant decomposition, was also hypothesised.

An increase in glyphosate persistence under no-tillage management might entail an increase in the risk of groundwater contamination due to the accumulation of glyphosate and AMPA in the soil, especially in the case of repeated applications of glyphosate, although greater observed adsorption can limit this eventuality. For this reason, glyphosate-based herbicides, still essential nowadays in no-till systems for effective weed management, must be used sparingly. The doses should be carefully calibrated based on the actual infestation (weed species, density, and development stage). It is recommendable to limit the glyphosate applications in no-till to not more than one time per year within an integrated strategy that could also include the use, every 4–5 years, of surface decompaction of the soil, to the benefit not only of crops but also of microorganisms that degrade glyphosate and AMPA. It is also crucial to implement agroecology principles for weed management and, in particular, to develop and evaluate the performances and the critical issues of roller-crimper technology to terminate the cover crops by flattening and crimping them.

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**Availability of Data and Material** The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

**Code Availability** Not applicable.

**Declarations**

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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