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Transition from flooding to sprinkler irrigation in Mediterranean rice growing ecosystems: Effect on behaviour of bispyribac sodium

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Abstract

Aerobic rice has been proposed as an efficient management practice to save water and improve the sustainability of rice as a crop. However, these techniques strongly influence soil properties and can therefore modify the behaviour of pesticides. Bispyribac-sodium (BS) is a post-emergent herbicide frequently used in rice agroecosystems, but which is considered very toxic to aquatic organisms and hazardous for the environment. In order to evaluate the effects of the transition from flooding to sprinkler irrigation on the sorption-desorption, dissipation, and leaching of BS on Mediterranean rice growing ecosystems, field experiments were conducted over three consecutive years in SW Spain using four different management regimes: anaerobic with conventional tillage and flooding (CTF), aerobic with conventional tillage and sprinkler irrigation (CTS), aerobic with no-tillage and sprinkler irrigation (NTS), and long-term aerobic with no-tillage and sprinkler irrigation (NTS7). The management regimes significantly influenced BS sorption, although their effects were dependent on the time of implementation. After three years, the K_f values in NTS7 were 1.7, 4.2, and 1.3 times significantly higher than in NTS, CTS, and CTF, respectively. Sorption was negatively correlated with soil pH and positively correlated with total organic carbon (TOC), with the two variables accounting for 93% of the variation in BS sorption. In all management regimes, laboratory trials showed BS to be more persistent under anaerobic ($t_{1/2} = 45.4$-131 d) than aerobic conditions ($t_{1/2} = 30$-51 d), with the $t_{1/2}$ values being significantly greater for CTS under both conditions. Although soil pH was the main factor affecting the dissipation of BS, this property together with TOC accounted for 96% and 86% of the variation of the $t_{1/2}$ values under aerobic and anaerobic conditions, respectively. Leaching studies indicated that the greatest amount of BS leached occurred in CTS. Leaching losses of BS were reduced from 52% in CTS to 29%, 30%, and 19% in CTF, NTS, and NTS7, respectively. Thus, sprinkler irrigation under conventional tillage may increase water contamination by BS in Mediterranean paddy fields, but it may greatly reduce it under no-tillage practices, especially after long-term implementation of this alternative management strategy.

Keywords: Bispyribac-sodium; Leaching; Persistence; Rice; Sorption; Water and tillage management.

1. Introduction

Rice (Oryza sativa L.) is traditionally cultivated by conventional agricultural practices and flooding management, which implies high water consumption, large emissions of methane, and high global energy costs. Moreover, rice cropping conducted under flooded conditions is pointed to as being an activity of high polluting potential due to the usual proximity of the fields to surface water bodies (Machado et al., 2006). In addition, this management system affects soil properties, with a subsequent negative impact on the following non-rice upland crop in the rotation system (Hobbs & Gupta, 2003; Tripathi et al., 2005).

Although 90% of global rice production is in Asia, the crop is also widely cultivated in Africa and America, and both widely and intensively in some zones of Southern Europe, mainly in Mediterranean countries (FAO, 2009). Spain is one of the largest rice producers in the European Union, with 20% of the total of European farmland under rice cultivation. Within Spain, Extremadura, with an average output of 7300 kg ha^{-1}, has become consolidated as one of the largest rice producing regions, with the most productive areas located in the River Guadiana lowlands. However, this high productivity is also associated with intensive and expensive cultural practices that include soil tillage, intensive use of irrigation by flooding, and a high intensity of pesticide application directly to the water. These practices can contribute to an enhanced risk of surface and groundwater pollution, making it necessary to implement preventive measures (Barceló & Hennion, 1997; Bouman et al., 2002; Clayton, 2011).

With predictions suggesting that many countries will have severe water problems by 2025 (Rosegrant et al., 2002), the continuation of flooded irrigation in rice-growing ecosystems is highly endangered due to its lack of sustainability. Consequently, alternatives are being sought that will allow greater efficiency of water use (Feng et al., 2007 and Qu et al., 2008). This is especially urgent in the Mediterranean region where the problem of water scarcity is steadily worsening (Chenini, 2010). Therefore, there is a need to develop appropriate management regimes to cope with these problems, regimes that will be economically feasible and environmentally sustainable (Kumar & Ladha, 2011). In this sense, aerobic rice production (non-flooding, also termed intermittent irrigation) has been proposed as being an efficient management practice in the sense of reducing water use and the need for agricultural procedures without any notable decrease in rice grain yield (Bhushan et al. 2007; Mahajan et al. 2009; Sarkar et al., 2012). In Extremadura, aerobic rice using conservation agriculture techniques (no-tillage) and direct seeding with sprinkler irrigation has recently been implemented to change from the traditional cultivation of this crop. The purpose is to reduce the environmental impact of the crop and improve its sustainability in this region. This technique has undergone a very large expansion in recent decades in many parts of the world. It has also given promising results in preliminary studies aimed at maintaining optimal yields under Mediterranean conditions (Moreno-Jimenez et al., 2014).

However, these techniques strongly influence the properties of the soil, and in particular can modify the behaviour of pesticides in this agricultural ecosystem, affecting such processes as their adsorption, leaching, and persistence, this last being strongly dependent on microbial activity which in turn is dependent on whether the conditions are aerobic or anaerobic (Liesack et al., 2000; Vasquez et al., 2011). Also, the adoption of conservation agriculture techniques such as a no-tillage system generally increases the total organic carbon of the soil (TOC) and decreases its pH (Álvaro-Fuentes et al., 2012; Arshad et al., 1999; Muñoz et al., 2007; López-Piñeiro et al., 2013), and may therefore also influence the behaviour and environmental fate of soil-applied pesticides (Alletto et al., 2013; Novak et al., 1996). Usually, with the increase in TOC and decrease in pH, the sorption of herbicides onto soil particles also increases, and thus their mobility down the soil profile may be reduced (Si et al., 2011; López-Piñeiro et al., 2013), although measurements of these trends have frequently been contradictory (Alletto et al., 2013; Elliott et al., 2000; Sadeghi et al., 1998; Larsbo et al., 2009). In addition, although the surface soil microbial community and activity may increase under no-tillage management (Soon & Arshad, 2005; Muñoz et al., 2007; López-Piñeiro et al., 2013), this does not always imply that the specific microbial populations involved in the degradation of a compound will be more abundant and therefore that this degradation will be faster (Gaston & Locke, 2000). Indeed, compared with conventional tillage, slower pesticide dissipation rates have been reported under no-tillage or reduced tillage regimes (Gaston et al., 1996; Zablotowicz et al., 1998).

Despite aerobic rice cultivation being an attractive alternative to lowland rice in areas where water is the limiting factor, one disadvantage of this management system is the greater amount of weeds (Singh, 2008). Nonetheless, the availability of new herbicides for weed control have essentially made this shift technically viable (Mortimer et al., 2008;). Bispyribac-sodium (BS) – sodium 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxy]benzoate – is a pyrimidinyloxybenzoic herbicide intensively used on rice fields across the world. It is steadily gaining in popularity due to its effectiveness in controlling annual broadleaf and gramineous weeds. It is a systemic, selective, post-emergent herbicide which is considered highly mobile and very toxic to aquatic organisms and hazardous for the environment (EFSA, 2010). Furthermore, although BS is usually applied at low rates, to control weeds in more advanced stages of development, increasing dosages are needed. This has stimulated some rice producers to abuse the dosage, leading to increased risk of contamination of soils and water resources by this pesticide. Very few research studies have been published, however, on the environmental behaviour of BS. Moreover, we could find no work evaluating the impact of different rice management regimes on the behaviour of the herbicide, although such information would be useful for its management agriculturally and environmentally.

We hypothesized that sprinkler irrigation under no-tillage practices would be an attractive strategy both to save water and to reduce the risk of water contamination by BS in Mediterranean paddy fields. The objective of this study was therefore to analyse how the transition from flooding to sprinkler irrigation affects the sorption-desorption, dissipation, and leaching of the herbicide BS in Mediterranean rice-growing ecosystems. Since herbicide persistence is directly dependent on microbial degradation, soil dehydrogenase activity was also monitored to assess the effect of the management regimes on the microbial activity of the soil.

2. Materials and Methods

2.1. Herbicide

Bispyribac-sodium (BS) – sodium 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxy]benzoate – of purity 98.3% was purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). It was used to prepare herbicide solutions for laboratory tests. BS assays were performed by high performance liquid chromatography (HPLC) using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector. The conditions used were the following: Nova-Pack C18 column (150 mm length × 4.6 mm i.d.), mobile phase of acetonitrile/water (55:45, v/v) containing 0.1% phosphoric acid at a flow rate of 1 mL min^{-1}, column temperature 30°C, 25 µL injection volume, and UV detection at 248 nm. External calibration curves with standard bispyribac-sodium solutions between 0.05 µM and 10 µM were used in the calculations. The detection and quantification limits under these conditions were 0.0068 µM and 0.0223 µM, respectively.

2.2. Rice cultivation

A field experiment was carried out from 2011 to 2013 on a Hydragric Anthrosol (FAO, 2006) with 17% clay, 35.9% silt, 47.1% sand, organic C 7.5 g kg^{-1}, total N 0.817 g kg^{-1}, and pH 5.5. The experimental field site is located in Extremadura, southwestern Spain (39° 06' N; 5° 40' W), where the climate is Mediterranean with mean annual precipitation of 480 mm, and very hot and dry summers. This region has serious limitations in developing sustainable agriculture as it has an aridity index of 0.49 (UNESCO, 1977).

Prior to beginning the study, the experimental area (2400 m²) was cropped with rice (*Oryza sativa* L.)

using the management practices traditional in the region (deep ploughing and waterlogging). A part of the field had already been devoted to direct seeding and sprinkler irrigated rice in the 7 years preceding the experiment. After the rice harvest in November 2010, the field was divided into twelve plots of 200 m² (20 × 10 m) each, that were subjected to the following four management regimes: (CTF) applying the techniques that are conventional in the region, i.e., tillage to 25 cm and flooding with continuous water flow; (CTS) conventional tillage and sprinkler irrigation; (NTS) conservation agriculture techniques (no-tillage and seeding by direct drilling) and sprinkler irrigation; and (NTS7) the same conservation agriculture techniques (no-tillage and direct drilling) and sprinkler irrigation but where this management regime had already been in use for 7 years, the purpose being to observe possible long-term effects. Three replicates of each treatment were performed in a completely randomized design. Different plots were separated with ridges 35 cm high with a 4-m wide protective buffer zone set up between adjacent plots. They were cropped with *Oryza sativa* L. var. Gladio, a traditional genotype in Extremadura. Water supply came from a surface catchment. The water use in different treatments was monitored with a water flow meter. Water consumption in sprinkler irrigated treatments (7010 m^3 ha^{-1}) was around one-third of that used for the flooded systems (24 000 m^3 ha^{-1}) (Moreno-Jiménez et al., 2014). Each year the plots were left uncultivated after harvest.

2.3. Sampling and physicochemical analysis of the soils

Soil samples from the plots were collected after the harvest in November 2011, 2012, and 2013 for the sorption-desorption study and in November 2013 for the leaching and dissipation studies. Four soil subsamples from each plot were taken randomly at a 20-cm depth. Samples were air dried, and the fraction that passed through a 2-mm sieve was stored at 4°C until use. TOC was determined by dichromate oxidation (Nelson & Sommers, 1996). Water-soluble organic carbon (WSOC) was extracted with de-ionized water at a 3:1 (water to soil) ratio. Humic and fulvic acids (HA and FA, respectively) were extracted by a solution of 0.1 M $Na_4P_2O_7$ using a ratio of extractant to sample of 10:1, and the humic acid was precipitated by acidifying the supernatant to pH 2 with H_2SO_4. Then WSOC, HA, and FA were determined by dichromate oxidation and measurement of the absorbance at 590 nm (Sims & Haby, 1971). The humification index (HI) was calculated as (HA/TOC) × 100 (Peña et al., 2015). The pH was measured in a 1:1 (w/v) soil/water suspension using a combination electrode. Electrical conductivity (EC) was measured in a saturation extract (US Salinity Laboratory Staff, 1954).

2.4. Adsorption-desorption experiment

The isotherms were determined using a batch equilibration method. Triplicate soil samples (5 g) were equilibrated with 10 ml of initial BS solutions (0.5 to 20 µM in 0.01 M $CaCl_2$) by shaking mechanically at 20 ± 2°C for 24 h. Equilibrium concentrations in the supernatants were determined by HPLC. The amount of BS sorbed (Cs) was calculated as the difference between the initial (Ci) and the equilibrium (Ce) solution concentrations.

Desorption was measured immediately after sorption by successive dilution from the 20 µM initial concentration points. The 5 mL of supernatant removed for the sorption analysis was replaced with 5 mL of 0.01 M $CaCl_2$. The samples were resuspended, shaken for another 24 hours, centrifuged, and the equilibrium concentration in the supernatant was determined. This desorption procedure was repeated thrice. The herbicide sorption and desorption experiments were fitted to the empirical Freundlich equation, $Cs = K_f Ce \exp(1/n_f)$, where Cs ($\mu M\ kg^{-1}$) is the amount of herbicide sorbed at the equilibrium concentration Ce ($\mu M\ L^{-1}$), and K_f and n_f are constants that characterize the relative sorption capacity. Hysteresis coefficients, H, for the sorption-desorption isotherms were calculated as $H = n_a/n_d$, where n_a and n_d are the Freundlich constants obtained from the sorption and desorption isotherms, respectively.

2.5. Dissipation studies and dehydrogenase activity

For each treatment, sextuplicate soil samples (5 g) were weighed into 50 mL glass tubes (three tubes were used for the dissipation experiment, and three for the dehydrogenase activity determination). Soils were supplemented with distilled water to obtain aerobic non-flooded (80% field capacity) and anaerobic flooded (soil-to-water ratio 1:1.25, w/v) moisture conditions. Bispyribac-sodium was added to the soils to give an application dose that was equivalent to 0.5 kg ha^{-1}. Prior to the addition of BS, soils were pre-incubated for 7 days in the dark at 20 ± 2°C to allow the soil microorganisms to adapt to the incubation conditions, and also to allow the development of reducing conditions in the flooded soils. The tubes were then incubated in the dark at 20 ± 2°C for 49 days. The moisture content was maintained at a constant level throughout the experiment by adding distilled water as necessary (checking by weight). Three replicate tubes from each treatment were removed periodically (at 2 hours and at 2 days after herbicide application, and then at 7-day intervals for 49 days) to measure the herbicide concentration. For the soils, 5 g aliquots of soil were extracted with 10 mL of a 60:40 (v/v) mixture of distilled water/methanol by shaking mechanically on an end-over-end shaker at 20 ± 2°C for 24 h followed by centrifugation, and the BS concentration in the extracts was determined by HPLC. Herbicide residues from water samples were also determined by HPLC. The BS dissipation curves in soils and water were fitted to first-order kinetics, and the half-lives ($t_{1/2}$) were calculated.

To determine the dehydrogenase activity (DHA), another three replicate tubes from each treatment were removed periodically at the same times as for the dissipation experiment. The DHA was determined by the method described in García et al. (1993). The tubes were incubated for 20 h at 20°C in the dark with 1 ml of 0.4% 2-p-iodophenyl-3p-nitrophenyl-5 tetrazolium chloride (INT) as substrate. At the end of the incubation, the iodonitrotetrazolium formazan (INTF) produced was extracted with methanol, and the absorbance was measured at 490 nm.

2.6. Leaching studies

Leaching studies were carried out using PVC disturbed soil columns of 30-cm length × 5-cm i.d. To minimize losses of soil during the experiment, the top 5 cm of the columns was filled with sea sand and the bottom 5 cm with sea sand plus glass wool. The remaining 20 cm was hand-packed with air-dried soil. Each treatment was performed in triplicate. The soil columns were saturated with 0.01 M $CaCl_2$ and allowed to drain for 24 h, and then the amount of BS corresponding to an application rate of 0.5 kg ha^{-1} dissolved in water was applied dropwise to the top of the columns so as to cover the entire column surface. Each day, the columns were leached with 0.01 M $CaCl_2$ at a rate of 50 mL day^{-1} until no herbicide was detected in the leachates. Leachates containing the herbicide were collected daily, filtered, and assayed by HPLC. At the end of the monitoring period, the soil columns were sectioned into four depths (0-5 cm, 5-10 cm, 10-15 cm, and 15-20 cm), and BS extracted by shaking (24 h at 20°C) 5 g of soil with 10 mL of a mixture of 60:40 (v/v) distilled water/methanol. The suspensions were centrifuged, filtered, and assayed by HPLC in order to determine the residual amount of herbicide in the different depths of the soil column.

2.7. Statistical analyses

Statistical analyses were carried out using the SPSS package (22.0) for Windows. The data obtained were subjected to a one-way ANOVA. Pairwise multiple comparisons were performed using the Duncan test. A statistical significance level of $p<0.05$ was taken for results to be considered as significantly different.

3. Results and Discussion

3.1. Soil properties

The soils' physicochemical parameters at 0-20 cm depth for the years 2011, 2012, and 2013 are listed in Table 1. All the TOC values were low, as is usual for agricultural soils in Mediterranean environments (López-Garrido et al., 2014). The highest values were for NTS7 in all three years (15.6, 15.5, and 16.2 g kg^{-1}), reflecting a major effect of long-term no-tillage practices on this parameter. There were no significant variations of the TOC content in the NTS management regime over the three years studied (Table 1), indicating that the short-term effects of no-tillage practices on TOC are complex (Muñoz et al., 2007). But CTS and CTF showed significant declines (by 23.9% and 13.4%, respectively) in TOC content for 2013 compared to 2011. The irrigation method is an important factor that may help explain the differences in TOC losses between the CTS and CTF management regimes. In this sense, the anaerobic conditions caused by the flooding in CTF may have resulted in a slower rate of organic matter decomposition than in CTS (Sahrawat, 2001). The greatest WSOC content throughout the trial corresponded to NTS7 (Table 1). Even this value, however, would be insufficient to promote an increase in the mobility and leaching of the herbicide.

The greatest HA content throughout the trial corresponded to NTS7. All the treatments presented significant decreases in 2012 relative to 2011 (Table 1), and reached their highest values in 2013. That this pattern is independent of the type of management and irrigation technique points to the strong influence of external factors. In particular, high rainfall was recorded in autumn 2012, with very wet months of September, October, and November (AEMET, 2012). There was some 40 mm of rainfall prior to the 2012 soil sampling, which may have slowed down organic matter humification in all the treatments. The more favourable weather conditions in 2013 could have led to the major rise in HA content due to the cumulative humification of both organic matter left over from 2012 and that of 2013. These results are consistent with studies which report that the mineralization and humification of soil organic matter depends on the climatic factors such as rainfall (Martin-Neto et al., 1998). The greatest FA content throughout the trial also corresponded to NTS7. There were no significant changes in this parameter between years for the NTS7 or CTF treatments (Table 1). It is important to recall that the management techniques applied in these two treatments did not differ from those applied prior to the experiment, reflecting a long-term stabilization. But the NTS and CTS management regimes showed contrasting trends: while the FA content in NTS had increased by 43.6% in 2013 relative to 2011 due to the annual input of organic matter, the FA content in CTS fell by 13.3% over the same period. This fact could be attributed to the differences in microbial numbers and diversity frequently observed between soils under conventional and no-tillage management (Borie et al., 2006; Muñoz et al., 2007).

In 2013, after three years of the trial, the lowest value of EC corresponded to CTS and the highest to NTS7 and NTS (Table 1). The TOC accumulation in the no-tillage management regimes and the organic matter depletion in CTS may help to explain these contrasting trends. The treatments greatly influenced the pH levels (Table 1). There was acidification of the NTS7 and NTS soils in 2013 relative to 2012. This was probably because of a build-up of organic residues on the surface, as was noted by Limousin & Tessier (2007) in studying topsoil acidification in no-tillage maize and wheat plots. The pH of the CTS soil rose from 5.63 in 2011 to 6.25 in 2013. The CTF soil showed a similar trend, but with a much smaller increase in pH (Table 1). This behaviour is coherent with the changes in TOC content discussed above.

3.2. Sorption-desorption studies

The adsorption isotherms of BS in all soils were satisfactorily described by the Freundlich model with $R^2 > 0.972$ (Table 2). Values of n_f were less than unity, indicating an L-type curve (Giles et al., 1960), and therefore a decrease in specific sorption sites as concentrations in solution increased. The BS K_f values ranged from 0.488 to 2.05 (Table 2). This is much lower than values reported by Chirukuri & Atmakuru (2015) of 5.6 and 4.8 for soils from the USA and Netherlands with 33 and 44 g kg^{-1} TOC content, respectively, but is of the same order as the data reported by those authors for soils from Italy, Spain, and the UK with K_f values of 0.5, 1.2, and 2.0, and 6.0, 13, and 18 g kg^{-1} TOC, respectively. The K_f values published by Singh & Singh (2015) for Indian soils very poor in organic matter content ranged from 0.37 to 0.87, values within our range. The management regimes significantly influenced the K_f values in the three years (Table 2). Their effects on K_f were different in the three years as determined by the significant treatment × year interaction ($p<0.001$; Table 2). While the K_f values were significantly greater for CTF for the first and second years – 1.4, 2.3, 1.5, and 1.4, 2.4, 2.1 times greater than NTS7, NTS, CTS in the first and second years, respectively – for the third year, the K_f values were significantly greater for NTS7 – 1.7, 4.2, and 1.3 times greater than NTS, CTS, and CTF, respectively. These results suggest that in rice cultivated with conventional tillage the use of sprinkler instead of flooding irrigation may reduce BS sorption. But, in the long term with conservation (no-tillage) cultivation techniques, sprinkler irrigation may increase BS sorption, and the movement of this chemical should be significantly lower than with traditional rice crop management (i.e., conventional tillage and flooding irrigation).

The order of BS sorption in the soils of each management regime was indicative of decreasing affinity for BS with both increasing soil pH and decreasing soil organic carbon content (Tables 1 and 2). Indeed, K_f was negatively and highly significantly correlated with soil pH (r = -0.524**) and positively with TOC (0.420*). This is consistent with previous studies which report greater adsorption of pesticides in soils under no-tillage than under conventional tillage due to an increase in organic matter (Reddy & Locke, 1998; Zablotowicz et al., 2000) and a decrease in pH (Levanon et al., 1994). In this sense, a decrease in pH can lead to increasing the proportion of neutral herbicide molecules which may be more easily adsorbed by the negatively charged surface of soil particles (Loux et al., 1989; Hyun et al., 2003). Because many soil properties are mutually correlated, it would be misleading to use only simple correlations to predict BS sorption. Of the various combinations tested, K_f was predicted best by combining TOC (X1) and pH (X2), as shown by the following regression equation:

$$K_f = 4.40 + 0.136\text{TOC} - 0.776\text{pH};\ R = 0.963^{***}$$

These two variables accounted for 93% of the variation in the BS sorption. Our findings agree with those of Chirukuri & Atmakuru (2015) who reported that, in 21 agricultural soils from different countries, the soil pH and TOC had negative and positive influences on BS sorption, respectively. Similar observations have frequently been reported for other ionic herbicides such as MCPA (e.g., López-Piñeiro et al., 2013) and 2,4-D (e.g., Singh et al., 2014). However, the present findings contrast with the report of Singh &

Singh (2015) in which the sorption of BS showed a positive correlation with soil pH and no correlation with TOC, although that study was of soils which were very poor in organic content, which had pH values much higher than those of the present study, and whose clay fraction was the major contributor to BS sorption.

The BS desorption data were satisfactorily described by the Freundlich model with $R^2 > 0.955$ (Table 2). Desorption was hysteretic for BS in all treatments (n_f desorption > n_f adsorption). According to Koskinen et al. (2006), this implies that it is difficult to desorb the previously adsorbed pesticide, and desorption cannot be predicted accurately on the basis of adsorption isotherms. The tillage and irrigation systems significantly influenced the H values in the three years (Table 2). The effect of the different treatments on H was similar in the three years (the treatment × year interaction was non-significant, Table 2). The H coefficients were greater (i.e., lower reversibility) under no-tillage and sprinkler irrigation (NTS7 and NTS) than under conventional tillage and sprinkler or flooding irrigation (CTS and CTF). This means that sorbed BS molecules in the NTS7 and NTS soils are more difficult to desorb than in the CTS and CTF soils despite the greater WSOC content in the former (Table 1). The order of the H coefficients reflects a direct relationship with soil organic matter content (Tables 1 and 2). Indeed, a significant correlation was observed of H with TOC ($r = 0.665^{**}$) and WSOC ($r = 0.706^{**}$), but not with HI ($r = 0.215$, $p > 0.05$), indicating that the transformed soil organic matter does not necessarily provide more active sites than does the fresh soil organic matter. The lowest desorption rates were observed with the NTS7 and NTS treatments (Table 2), confirming that the adsorbed BS was more easily desorbed in the rice soils under tillage, independently of the type of irrigation applied. This can be attributed to the greater soil organic matter content observed in the no-tillage soils than in those under tillage (Table 1). Indeed, BS desorption was significantly and negatively correlated with TOC ($r = -0.662^{**}$) and WSOC ($r = -0.553^{**}$), confirming that an increase in the soluble organic matter does not necessarily imply an increase in its capacity to desorb BS. This contrasts with reports that the WSOC content might enhance sorption reversibility of such pesticides as diuron and terbuthylazine (Cabrera et al., 2007), and metribuzine (López-Piñeiro et al., 2013). However, our findings are consistent with those described in López-Piñeiro et al. (2014) of lower reversibility of MCPA in soils with high WSOC content, indicating that its effect on the herbicide desorption of a soil also depends on the properties of the herbicide.

3.3. Dissipation studies

The time dependence of the BS dissipation rates and of the dehydrogenase activity (DHA) for each treatment (under aerobic and anaerobic conditions) is shown in Fig. S1 of the supporting information. The experimental data for all treatments fit first-order kinetics with $R^2 > 0.905$ (Table 3). Under aerobic conditions the BS $t_{1/2}$ values ranged between 30 d for CTF and 51 d for CTS. As far as we know, only one study has investigated the dissipation of BS in soils under aerobic conditions (Chirukuri & Atmakuru, 2015), and the present half-life values are greater than those reported in that work which ranged between 5.3 d and 16.2 d in different soil types. In that study, however, the moisture content was adjusted to 33% field capacity, whereas in the present study the samples were adjusted to 80% field capacity. The management regimes significantly influenced the $t_{1/2}$ values (Table 3). Those values showed the trend in BS dissipation rates to be CTS < NTS= NTS7= CTF. Thus, while in CTS less than 49% of the applied BS had been dissipated by the end of the experiment, the figures were 66%, 65%, and 63% for CTF, NTS, and NTS7, respectively (Fig. S1). Interestingly, although CTS presented the lowest K_f values (Table 2), its BS half-life was significantly longer than those of the rest of the treatments (Table 3). Although significant correlations between DHA and dissipation of several herbicides have been found for different soils (e.g., Paszko 2009; López-Piñeiro et al., 2014), in the present study the differences in the dissipation rates of BS could not be due to the differences in their DHA values, since the highest value corresponded to CTS and the lowest to CTF, both being in the soils treated with the pesticide at the start of the experiment (Table 3) (see Supplementary Material, Text S1). The order of the $t_{1/2}$ values reflects a direct relationship with soil pH (Tables 1 and 3). Indeed, $t_{1/2}$ was positively and highly significantly correlated with soil pH ($r = 0.787^{**}$), suggesting that BS was more stable and less available for dissipation with increasing pH. This is consistent with Hultgren et al. (2002) who reported that a decrease in soil pH increased the dissipation rates of weak acid herbicides due to enhanced hydrolysis of these compounds at the lower pH values. Although simple correlation analyses found no significant relationship between $t_{1/2}$ values and TOC, the $t_{1/2}$ values were predicted best when pH (X1) and TOC (X2) were included in a multiple regression analysis, as shown by the following equation

$$t_{1/2} = -56.3 + 18.8\text{pH} - 1.40\text{TOC}; R = 0.977^{***}$$

The two variables accounted for 96% of the variation in the $t_{1/2}$ values. The results suggest that the half-life of BS could be estimated accurately by using only pH and TOC in the multiple regression equation, with the dissipation of this herbicide being faster in soils with acidic pH and higher organic carbon content. Our findings are consistent with those of Chirukuri & Atmakuru (2015) who reported that the availability of organic carbon and the acidity of the soils influenced the degradation of BS, with the herbicide being less stable in acidic soils.

In all managements, BS was less persistent under aerobic conditions ($t_{1/2} = 30\text{-}51$ d) than under anaerobic conditions ($t_{1/2} = 45.4\text{-}131$ d) (Table 3) (see Supplementary Material, Text S2). Although also under anaerobic conditions the management regimes significantly influenced the BS $t_{1/2}$ values (Table 2), with the trend of BS dissipation rates being CTS < NTS7= NTS < CTF, the effects of management regime on BS dissipation differed between anaerobic and aerobic conditions, with the management × incubation condition interaction being significant ($p<0.01$). Thus, while the $t_{1/2}$ values were significantly greater for CTS in both incubation studies, for aerobic conditions the value was 1.6, 1.6, and 1.7 times greater, and for anaerobic conditions it was 1.8, 1.8, and 2.9 times greater than for NTS7, NTS, and CTF, respectively. Similar to aerobic conditions, $t_{1/2}$ was positively and highly significantly correlated with soil pH ($r = 0.835^{**}$), indicating that the differences in this property may well explain the dissipation rates of BS under anaerobic conditions also. These results suggest that chemical hydrolysis, which is generally favoured under acidic conditions, might be the dominant process of BS degradation under both aerobic and anaerobic conditions (Sarmah & Sabadie, 2002).

Neither under anaerobic conditions was the correlation between the $t_{1/2}$ values and TOC significant ($p>0.05$). Again however, $t_{1/2}$ was best predicted when the two soil properties, pH (X1) and TOC (X2), were included in a multiple regression analysis, as shown by the following regression equation

$$t_{1/2} = -275 + 68.8\text{pH} - 3.42\text{TOC};\ R = 0.925^{***}$$

Although the equation obtained for aerobic conditions was a better predictor of $t_{1/2}$ than the above equation for anaerobic conditions, the two variables still accounted for 86% of the variation in the $t_{1/2}$ values, indicating that the half-life of BS under anaerobic conditions could also be estimated well using just soil pH and TOC in the multiple regression equation. Again, the dissipation of this herbicide was faster in the soils with acidic pH and higher organic carbon content as also had been observed under aerobic conditions. For both conditions, the coefficients obtained for each variable confirm the major role of pH in BS dissipation. This fact suggests that BS dissipation increases with soil adsorption, confirming the hydrolysis process discussed above. In this sense, several studies found that the strong adsorption onto soil particles could enhance the hydrolytic cleavage of some molecular bonds (e.g., Armstrong & Chesters, 1968; Kah & Brown, 2006).

3.4 Leaching studies

Figure 1 shows the relative and cumulative BS breakthrough curves for each management regime. The total BS leached and the percentage extracted from the soil columns are presented in Table 4. The breakthrough of BS in all managements occurred after the passage of less than one pore volume of water (Fig. 1), which is typical of highly mobile compounds (Beck et al., 1993). The total BS leached ranged between 18.7% and 51.7% of the amount initially applied (Table 4; Fig. 1). Much greater leaching losses of BS were found by Singh & Singh (2015) who reported recovering 100% of the initially applied BS from a leachate, although this was in an alkaline soil with very low organic matter content. The management regimes influenced the downward movement of BS in the columns, and significantly affected both the breakthrough and the maximum concentration of BS in the leachate (Table 4; Fig. 1). Thus, while in CTF the BS breakthrough occurred after 0.30 pore volumes of water, it was after 0.66, 0.66, and 0.97 pore volumes in CTS, NTS, and NTS7, respectively, despite the WSOC content of the CTF soil being about 3.4 times less than that in CTS, NTS, and NTS7. This suggests that BS was mainly bound to the solid-phase organic matter, so that an increase in the soluble organic matter did not necessarily imply any faster movement of the BS. A mass balance calculation indicated that the greatest amount of BS leached occurred in the CTS treatment. The cumulative breakthrough curves show that leaching losses of BS were significantly ($p<0.05$) reduced for the CTF, the NTS, and especially the NTS7 managements. Thus, while 51.7% of the initially applied BS was recovered from the leachate of CTS, the amounts of BS leaching out of the CTF, NTS, and NTS7 soils were 28.6%, 29.6%, and 18.7%, respectively (Fig. 1). Moreover, the average maximum concentration of BS in the leachate from CTS reached 1.27 µM, whereas its maximum concentrations in CTF, NTS, and NTS7 were 0.518, 0.409, and 0.118 µM. The decrease in sorption may explain the greater increase of this herbicide in the leachate of the CTS management (Tables 2 and 4). Indeed, the amount of BS leached was significantly ($p<0.01$) negatively correlated with K_f ($r = -0.618$) and HA ($r = -0.614$), indicating that BS leaching also depends, at least partially, on the degree of polymerization of the of the soil. These results suggest that the transition from flooding to sprinkler irrigation under conventional tillage may increase water contamination by BS in Mediterranean environments, but may greatly reduce it under no-tillage practices.

The BS leached down to 20 cm depth in all soil columns. However, the CTS management decreased the retention of BS by the soil, so that it was not surprising that lower amounts of this herbicide were recovered in the CTS (11%) than in the CTF, NTS7, and NTS management systems (17%, 20%, and 25%, respectively), although the differences were not significant. Furthermore, while the amount of BS recovered decreased with depth in CTS, the herbicide presented uniform concentration profiles for the other treatments (data not shown). The total amounts recovered (leached + extracted) from the CTS soil columns were greater than the amounts recovered for the rest of the treatments (Table 4). In particular, compared to CTS, the amounts of herbicide recovered were lower by factors of 1.6, 1.2, and 1.4 in NTS7, NTS, and CTF, respectively. These results are coherent with those described above for the sorption and persistence experiments (Tables 2 and 3).

4. Conclusions

Aerobic rice production may induce important transformations in soil properties, leading to changes in the sorption-desorption, dissipation, and leaching of the herbicide bispyribac-sodium (BS). Soil organic carbon and pH were found to be the major factors contributing to the behaviour of BS in rice agroecosystems under different management regimes. Since the persistence of BS was significantly greater under anaerobic than aerobic incubation conditions for all management regimes of this study, rice production under sprinkler irrigation would contribute to disappearance of BS from the environment, but it could also potentially reduce the herbicide's activity. The implementation of sprinkler irrigation under tillage led to a decrease in the BS sorption capacity of the soil and enhanced the amount of herbicide leached, but under no-tillage practices it led to an increase in the BS sorption capacity and a decrease in the leaching losses of the herbicide. Therefore, sprinkler irrigation under conventional tillage may increase the risk of water contamination by BS in Mediterranean rice-growing ecosystems, but may greatly reduce it under no-tillage practices, especially after long-term implementation of this alternative management system.

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References

AEMET [Agencia Estatal de Meteorología], 2012. Informe meteorológico y agrofenológico de otoño de 2012. Madrid. http://www.aemet.es (retrieved 26.11.15).

Álvaro-Fuentes, J., Easter, M., Paustian, K., 2012. Climate change effects on organic carbon storage in agricultural soils of northeastern Spain. Agric. Ecosyst. Environ. 155, 87-94.

Alletto, L., Benoit, P., Bolognési, B., Couffignal, M., Bergheaud, V., Dumény, V., Longueval, C., Barriuso, E., 2013. Sorption and mineralisation of S-metolachlor in soils from fields cultivated with different conservation tillage systems. Soil Till. Res. 128, 97-103.

Armstrong, D.E., Chesters, G., 1968. Adsorption catalyzed chemical hydrolysis of atrazine. Env. Sci. Tec. 2, 683-689.

Arshad, M.A., Franzluebbers, A.J., Azooz, R.H., 1999. Components of surface soil structure under conventional and no-tillage in northwestern Canada. Soil Till. Res. 53, 41-47.

Barceló, D., Hennion, M.C., 1997. Trace determination of pesticides and their degradation products in water, ed. Elsevier, Amsterdam.

Beck, A.J., Johnston, A.E.J., Jones, K.C., 1993. Movement of nonionic organic chemicals in agricultural soils. Crit. Rev. Env. Sci. Tec. 23, 219-248.

Bhushan, L., Ladha, J.K., Gupta, R.K., Singh, S., Padre, A.T., Saharawat, Y.S., Gathala, M., Pathak, H., 2007. Saving of water and labour in a rice–wheat system with no tillage and direct seeding technologies. Agron. J. 99, 1288-96.

Borie, F., Rubio, R., Rouanet, J.L., Morales, A., Borie, G., Rojas, C., 2006. Effects of tillage systems on soil characteristics, glomalin and mycorrhizal propagules in a Chilean Ultisol. Soil Till. Res. 88, 253-261.

Bouman, B.A.M., Castañeda, A.R., Bhuiyan, S.I., 2002. Nitrate and pesticide contamination of groundwater under rice-based cropping systems: Past and current evidence from the Philippines . Agric. Ecosyst. Environ. 92, 185-199.

Cabrera, A., Cox, L., Velarde, P., Koskinen, W.C., Cornejo, J., 2007. Fate of diuron and terbuthylazine in soils amended with two-phase olive oil mill waste. J. Agr. Food Chem. 55, 4828-4834.

Chenini, F., 2010. Effects of hydrologic alterations on the ecological quality of river ecosystems. in: Sabater, S., Barceló. D. (Eds.), Water scarcity in the Mediterranean perspectives under global change. Springer, New York, pp. 162-172.

Chirukuri, R., Atmakuru, R., 2015. Sorption characteristics and persistence of herbicide bispyribac sodium in different global soils. Chemosphere 138, 932-939.

Clayton, M. 2011. Memorandum to L. Ross: Selection of pesticide active ingredients for future analytical method development and ground water monitoring. Available at: (verified January 31, 2013). California Department of Pesticide Regulation, Sacramento, California.

EFSA. European Food Safety Authority, 2010. Conclusion on the pear review of the pesticide risk assessment of the active substance bispyribac. EFSA J. 8, 1692.

Elliot, J.A., Cessna, A.J., Nicholaichuk, W., Tollefson, L.C., 2000. Leaching rates and preferential flow of selected herbicides through tilled and untilled soil. J. Environ. Qual. 29, 1650-1656.

Feng, L.P., Bouman, B.A.M., Tuong, T.P., Cabangon, R.J., Li, Y.L., Lu, G.A., Feng, Y.H., 2007. Exploring options to grow rice under water-short conditions in northern China using a modeling approach. I: field experiments and model evaluation. Agr. Water Manage. 88, 1-13.

FAO, 2009. Agricultural data. Food and Agriculture Organization of the United Nations, Rome Online at http://faostat.fao.org/.

García, C., Hernández, T., Costa, C., Ceccanti, B., Masciandaro, G., Ciardi, C., 1993. A study of biochemical parameters of composted and fresh municipal wastes. Bioresour. Technol. 44, 17-23.

Gaston, L.A., Locke, M.A., 2000. Acifluorfen sorption, degradation, and mobility in a Mississippi delta soil. Soil Sc. Soc. Am. J. 64, 112-121.

Gaston, L.A., Locke, M.A., Zablotowicz, R.M., 1996. Sorption and degradation of bentazon in conventional- and no-till Dundee soil. J. Environ. Qual. 25, 120-126.

Giles, C.H., McEwan, J.H., Nakwa, S.N., Smith, D., 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem. Soc. 3, 3973-3993.

Hobbs, P. R., Gupta, R. K., 2003. Resource-conserving technologies for wheat in the rice–wheat system, in: Ladha, J.K., Hill, J.E., Duxbury, J. M., Gupta, R. K., Buresh, R. J. (Eds.), Improving the Productivity and Sustainability of Rice–Wheat Systems: Issues and Impacts. ASA Special Publication Number 65. ASA-CSSASSSA. Madison, Wisconsin, pp. 149-172.

Hultgren, R.P., Hudson, R.J.M., Sims, G.K., 2002. Effects of soil pH and soil water content on prosulfuron dissipation. J. Agr. Food Chem. 50, 3236-3243.

Hyun S, Lee L.S., Rao P.S.C., 2003. Significance of anion exchange in pentachlorophenol sorption by variable-charge soils. J. Environ. Qual. 32, 966–97.

Kah M, Brown C.D., 2006. Adsorption of ionisable pesticides in soils. Rev. Environ. Contam. Toxicol. 188, 149–217.

Koskinen, W.C., Calderón, M.J., Rice, P.J., Cornejo, J., 2006. Sorption-desorption of flucarbazone and propoxycarbazone and their benzenesulfonamide and triazolinone metabolites in two soils. Pest Manag. Sci. 62, 598-602.

Kumar, V., Ladha, J.K., 2011. Direct seeding of rice: recent developments and future research needs. Adv. Agron. 111, 297-396.

Larsbo, M., Stenström, J., Etana, A., Börjesson, E., Jarvis, N.J., 2009. Herbicide sorption, degradation, and leaching in three Swedish soils under long-term conventional and reduced tillage. Soil Till. Res. 105, 200-208.

Levanon, D., Meisinger, J.J., Codling, E.E., Starr, J.L., 1994. Impact of tillage on microbial activity and the fate of pesticides in the upper soil. Water Air Soil Poll. 72, 179-189.

Liesack, W., Schnell, S., Revsbech, N.P., 2000. Microbiology of flooded rice paddies. FEMS Microbiol. Rev. 24, 625-645.

Limousin, G., Tessier, D., 2007. Effects of no-tillage on chemical gradients and topsoil acidification. Soil Till. Res. 92, 167-174.

López-Garrido, R., Madejón, E., Moreno, F., Murillo, J.M., 2014. Conservation tillage influence on carbon dynamics under Mediterranean conditions. Pedosphere 24, 65-75.

López-Piñeiro, A., Peña, D., Albarrán, A., Sánchez-Llerena, J., Becerra, D., 2013. Behaviour of MCPA in four intensive cropping soils amended with fresh, composted, and aged olive mill waste. J. Contam. Hydrol. 152, 137-146.

López-Piñeiro, A., Peña, D., Albarrán, T., Sánchez-Llerena, J., Becerra, D., 2014. Long-term effects of olive mill waste amendment on the leaching of herbicides through undisturbed soil columns and mobility under field conditions. Soil Till. Res. 144, 195-204.

Loux, M.M., Liebl, R.A., Slife, F.W., 1989. Adsorption of imazaquin and imazethapyr on soils, sediments, and selected adsorbents. Weed Sci. 37, 712–718.

Machado, S.L.O., Marchezan, E., Righes, A.A., Carlesso, R., Villa, S.C.C., Camargo, E.R., 2006. Water use and nutrients and sediments losses on the initial water drainage on flooded rice. Ciência Rural 36, 65-71.

Mahajan, G., Chauhan, B.S., Johnson, D.E., 2009. Weed management in aerobic rice in northwestern Indo-Gangetic plains. J. Crop. Improv. 23, 366-82.

Martin-Neto, L., Rosell, R., Sposito, G., 1998. Correlation of spectroscopic indicators of humification with mean annual rainfall along a temperate grassland climosequence. Geoderma, 81,305-311.

Moreno-Jiménez, E., Meharg, A., Smolders, E., Manzano, R., Becerra, D., Sánchez-Llerena, J., Albarrán, A., López-Piñeiro, A., 2014. Sprinkler irrigation of rice fields reduces grain arsenic but enhaces cadmium. Sci. Total Environ. 485-486, 468-473.

Mortimer, A. M., Riches, C. R., Mazid, M., Pandey, S., and Johnson, D. E., 2008. Issues related to direct seeding of rice in rainfed cropping systems in northwest Bangladesh, in: Singh, Y., Singh, V.P., Chauhan, B., Orr, A., Mortimer, A.M., Johnson, D.E., Hardy, B. (Eds.), Direct seeding of rice and weed management in the irrigated rice-wheat cropping system of the Gangetic plains. International Rice Research Institute, and Pantnagar (India): Directorate of Experiment Station, G.B. Pant University of Agriculture and Technology. Philippines, pp. 23-30.

Muñoz, A., López-Piñeiro, A., Ramírez, M., 2007. Soil quality attributes of conservation management regimes in a semi-arid region of south western Spain. Soil Till. Res. 95, 255-265.

Nelson, D.W., Sommers, L.E., 1996. Total carbon, organic carbon, and organic matter, in: Sparks, D.L. (Ed.), Methods of Soil Analysis. Chemical Methods. American Society of Agronomy, Madison, Wisconsin, pp. 961-1010.

Novak, J.M., Watts, D.W., Hunt, P.G., 1996. Long-term tillage effects on atrazine and fluometuron sorption in Coastal Plain soils. Agric. Ecosyst. Environ. 60, 165-173.

Paszko, T., 2009. Degradation of MCPA in soil horizons of polish agricultural soils. Pol. J. Environ. Stud. 18, 1083-1091.

Peña, D., López-Piñeiro, A., Albarrán, A., Becerra, D., Sánchez-Llerena, J., 2015. Environmental fate of the herbicide MCPA in agricultural soils amended with fresh and aged de-oiled two-phase olive mill waste. Environ. Sci. Pollut. R. 22, 13915-13925.

Qu, Y., Ping, M., Hongliang, Z., Chen, Y., Gao, Y., Tian, Y., Wen, F., Li, Z., 2008. Mapping QTLs of root morphological traits at different growth stages in rice. Genetica 133, 187–200.

Rosegrant, M.W., Cai, X., Cline, S.A., 2002. World Water and Food to 2025: Dealing with Scarcity. International Food Policy Research Institute, Washington, D.C.

Reddy, K.N., Locke, M.A., 1998. Sulfentrazone sorption, desorption, and mineralization in soils from two tillage systems. Weed Sci. 46, 494-500.

Sadeghi, A.M., Isensee, A.R., Shelton, D.R., 1998. Effect of tillage age on herbicide dissipation: A side-by-side comparison using microplots. Soil Sci. 163, 883-890.

Sahrawat, K.L., 2001. Organic matter accumulation in submerged soils. Advances in Agronomy, 81, 169-201.

Sarkar, S., Basu, B., Kundu, C.K., Patra, P.K., 2012. Deficit irrigation: An option to mitigate arsenic load of rice grain in West Bengal, India. Agric. Ecosyst. Environ. 146, 147-152.

Sarmah, A.K., Sabadie, J., 2002. Hydrolysis of sulfonylurea herbicides in soils and aqueous solutions: A review. J. Agr. Food Chem. 50, 6253-6265.

Si, Y., Wang, M., Tian, C., Zhou, J., Zhou, D., 2011. Effect of charcoal amendment on adsorption, leaching and degradation of isoproturon in soils. J. Contam. Hydrol. 123, 75-81.

Sims, J.R., Haby, V.A., 1971. Simplified colorimetric determination of soil organic matter. Soil Sci. 112, 137-141.

Sims, J.R., Haby, V.A., 1971. Simplified colorimetric determination of soil organic matter. Soil Sci. 112, 137-141.

Singh, N., Singh, S.B., 2015. Adsorption and leaching behaviour of bispyribac-sodium in soils. B. Environ. Contam. Tox. 94, 125-128.

Singh, B., Farenhorst, A., Gaultier, J., Pennock, D., Degenhardt, D., McQueen, R., 2014. Soil characteristics and herbicide sorption coefficients in 140 soil profiles of two irregular undulating to hummocky terrains of western Canada. Geoderma 232-234, 107-116.

Singh, G., 2008. Integrated weed management in direct-seeded rice, in Singh, Y., Singh, V. P., Chauhan, B., Orr, A., Mortimer, A. M., Johnson, D. E., Hardy, B. (Eds.), Direct Seeding of Rice and Weed Management in the Irrigated Rice-Wheat Cropping System of the Indo Gangetic Plains. International Rice Research Institute, and Pantnagar (India): Directorate of Experiment Station, G.B. Pant University of Agriculture and Technology. Philippines, pp. 161-176.

Soon, Y.K., Arshad, M.A., 2005. Tillage and liming effects on crop and labile soil nitrogen in an acid soil. Soil Till. Res. 80, 23-33.

Tripathi, R. P., Sharma, P., Singh, S., 2005. Tillage index: An approach to optimize tillage in rice-wheat system. Soil Till. Res. 80, 125-137.

UNESCO, 1977. Map of the World Distribution of Arid Regions. MAB. UNESCO, Paris, Technical Notes 7.

United States Salinity Laboratory. Staff, 1954. Diagnosis and Improvement of Saline and Alkali Soil. Agric. Handbook No. 60, U.S. Dep. Agric., Washington D.C., 160 pp.

Vasquez, M.E., Holstege, D.M., Tjeerdema, R.S., 2011. Aerobic versus anaerobic microbial degradation of etofenprox in a California rice field soil. J. Agr. Food Chem. 59, 2486-2492.

Zablotowicz R.M., Locke M.A., Smeda R.J., 1998. Degradation of 2,4-D and fluometuron in cover crop residues. Chemosphere 37, 87–101.

Zablotowicz, R.M., Locke, M.A., Gaston, L.A., Bryson, C.T., 2000. Interactions of tillage and soil depth on fluometuron degradation in a Dundee silt loam soil. Soil Till. Res. 57, 61-68.

Table 1. Effect of different management regimes on the soil's physicochemical properties.

	TOC ($g\ kg^{-1}$)	**WSOC ($mg\ kg^{-1}$)**	**HA ($g\ kg^{-1}$)**	**FA ($g\ kg^{-1}$)**	**HI (%)**	**EC ($\mu S\ cm^{-1}$)**	**pH**
2011							
NTS7	15.6cA	219.6dA	1.60cB	1.03cA	10.2bB	1.51dC	5.84cA
NTS	7.93aA	133.1cC	0.833bB	0.532aA	10.5bB	0.906bB	5.91cB
CTS	9.23abC	96.1bB	0.604aB	0.676bB	6.55aA	0.698aA	5.63bA
CTF	9.92bB	74.4aB	0.627aB	0.634bA	6.32aA	1.26cB	5.15aA
2012							
NTS7	15.5cA	198.4cA	1.33bA	0.993cA	8.62cA	0.490aA	5.92dA
NTS	6.80aA	66.4aA	0.514aA	0.579aB	7.32bA	0.857bA	5.92cB
CTS	8.22bB	97.1bB	0.515aA	0.685bB	6.27aA	1.09cB	5.84bB
CTF	8.25bA	61.2aA	0.481aA	0.661bA	5.83aA	1.27dB	5.21aB
2013							
NTS7	16.2dA	213.9dA	1.76dC	0.998dA	10.8aB	1.26cB	5.84cA
NTS	7.67bA	112.4cB	1.13cC	0.764cC	14.8cC	1.38dC	5.22aA
CTS	7.03aA	80.5bA	0.908aC	0.586aA	12.9bB	0.753aA	6.24dC
CTF	8.60cA	64.9aA	0.984bC	0.639bA	11.4aB	1.08bA	5.33bC
Y	**	***	***	**	***	***	*
M	***	***	***	***	***	***	***
Y*M	***	***	***	***	***	***	***

TOC: total organic carbon; **WSOC**: water soluble organic carbon; **HA**: humic acid; **FA**: fulvic acid; **HI**: humic index; **EC**: electrical conductivity; **N**: total nitrogen; **P**: phosphorus. ANOVA factors are **Y**: year; **M**: management regime; **Y*M**: interaction year*management regime; *, **, and *** significant at α levels of 0.05, 0.01, and 0.001, respectively; **NS**: not significant. Different letters indicate significant differences (p<0.05) between management regimes in the same year (lower case letters) and between years within the same management regime (upper case letters).

Table 2. Effect of different management regimes on bispyribac-sodium sorption-desorption parameters

	n_f	K_f	R^2	H^a	D^b (%)
2011					
NTS7	0.840aA	0.872bA	0.993	4.94bB	29.4aA
NTS	0.932aB	0.526aA	0.986	2.62aA	52.4cC
CTS	0.894aA	0.805bB	0.994	2.75aA	45.1bcB
CTF	0.925aB	1.21cA	0.980	2.85aA	42.6bA
2012					
NTS7	0.832aA	1.09bB	0.979	2.97aA	37.4bB
NTS	0.834aA	0.635aB	0.975	4.40bB	36.6bA
CTS	0.827aA	0.726aB	0.972	5.52cB	24.4aA
CTF	0.764aA	1.55cB	0.992	2.44aA	41.2cA
2013					
NTS7	0.778aA	2.05dC	0.998	4.47bB	38.3aB
NTS	0.837bA	1.21bC	0.99	4.38bB	43.4abB
CTS	0.840bA	0.488aA	0.974	2.52aA	52.8cB
CTF	0.784aA	1.63cB	0.993	2.78aA	46.4bA
Y	***	***	-	*	***
M	*	***	-	***	**
Y*M	NS	***	-	***	***

[a]values of hysteresis; [b]values of percentage of bispyribac-sodium after three desorption steps. ANOVA factors are **Y**: year; **M**: management regime; **Y*M**: interaction year*management regime; *, ******, and ******* significant at α levels of 0.05, 0.01, and 0.001, respectively; **NS**: not significant. Different letters indicate significant differences ($p<0.05$) between management regimes in the same year (lower case letters) and between years within the same management regime (upper case letters).

Table 3. Effect of different management regimes on dehydrogenase activity and Bispyribac-Sodium dissipation parameters

	$t_{1/2\ 80\%}$ (days)	**$R^2_{80\%}$**	**$t_{1/2\ 1:1.25}$ (days)**	**$R^2_{1:1.25}$**	**$DHA_{B\ 80\%}$ (μg INTF g^{-1} h^{-1})**	**$DHA_{A\ 80\%}$ (μg INTF g^{-1} h^{-1})**	**$DHA_{B\ 1:1.25}$ (μg INTF g^{-1} h^{-1})**	**$DHA_{A\ 1:1.25}$ (μg INTF g^{-1} h^{-1})**
NTS7	31.0ab	0.976	73.2b	0.948	0.456b	0.590b	1.14c	1.08b
NTS	32.6b	0.974	71.8b	0.923	0.441b	0.403a	0.721b	0.549a
CTS	51.5c	0.957	131.8c	0.905	0.531c	0.646c	0.583a	0.619a
CTF	30.0a	0.96	45.4a	0.969	0.382a	0.380a	0.581a	0.602a
M	***	-	***	-	***	***	***	***

$t_{1/2\ 80\%}$: half-life from soils conditioned to 80% water holding capacity; **$t_{1/2\ 1:1.25}$**: half-life from soils conditioned to 1:1.25 (p/v) (soil/water) moisture content; **DHA**: dehydrogenase activity before (**B**) and after (**A**) two hours herbicide application from soils conditioned to 80% water holding capacity and 1:1.25 (p/v) (soil/water) moisture content. ANOVA factor is **M**: Management Regime; ******* significant at α levels of 0.001. Different letters show significant differences ($p<0.05$) between treatments.

Table 4. Effect of different management regimes on leaching of Bispyribac-Sodium

	Initial Pore Volume	**Max. Amount Leached (µg)**	**Total Leached (%)**	**Total Extracted (%)**
NTS7	0.970c	2.53a	18.7a	20.0bc
NTS	0.660b	8.81a	29.6b	25.3c
CTS	0.660b	28.8b	51.7c	10.7a
CTF	0.323a	11.7a	28.6b	16.5ab
M	*	**	***	*

ANOVA factor is **M**: Management Regime; *, and ******* significant at α levels of 0.05 and 0.001, respectively. Different letters show significant differences (p<0.05) between management regimes.

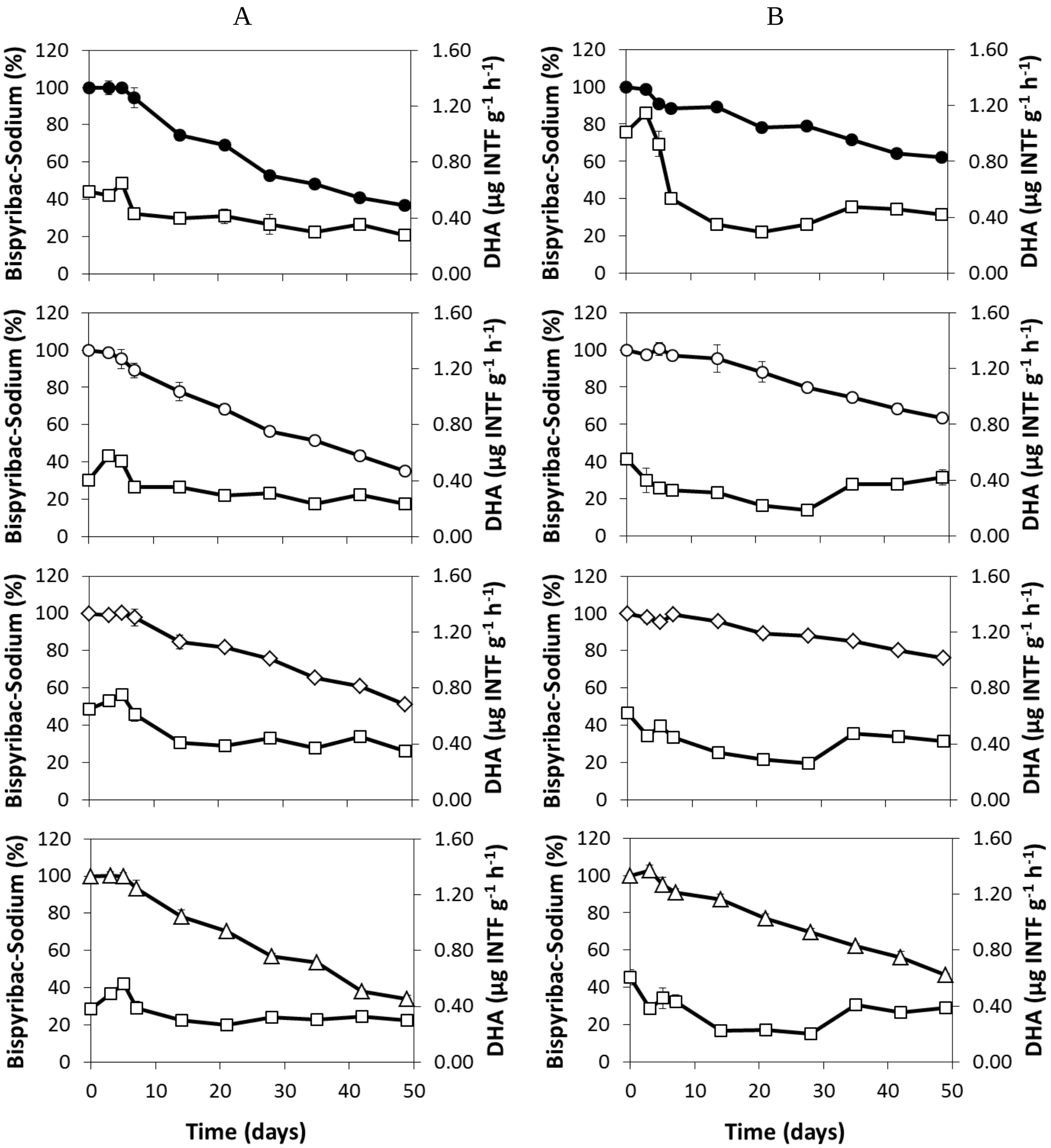

Figure 1. Effect of different management regimes on bispyribac-Sodium dissipation and dehydrogenase activity (□) on soils under aerobic (A) and anaerobic (B) conditions. NTS7 (●), NTS (○), CTS (◇) and CTF (△). Error bars represent one standard error of the mean.

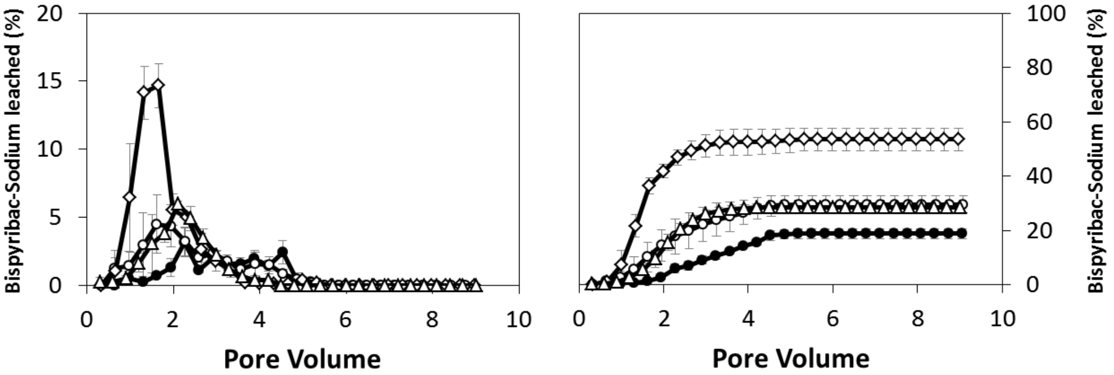

Figure 2. Effect of different management regimes on the relative (left) and cumulative (right) breakthrough curves of bispyribac-sodium. NTS7 (●), NTS (○), CTS (◇) and CTF (△). Error bars represent one standard error of the mean.