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Impacts of fresh and aged holm-oak biochar on clomazone behaviour in rice cropping soils after transition to sprinkler irrigation

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ABSTRACT

Although alternative practices to traditional flooding rice cultivation urgently need to be implemented in water-stressed regions, these can modify soil properties, thereby affecting the environmental behaviour of pesticides. One of the most extensively used herbicides in rice cropping is clomazone. A field experiment covering two years was conducted to evaluate how fresh and aged holm oak biochar (BH) influenced clomazone's behaviour in rice cropping after transition from flooding to sprinkler irrigation with different tillage systems. The experiment involved traditional flooding irrigation and tillage either without (FT) or with (FTBH) first-year BH addition, and four treatments more where sprinkler irrigation had been in use for 3 years – sprinkler irrigation and tillage without (ST) or with (STBH) first-year BH addition, sprinkler irrigation and no-tillage without (SNT) or with (SNTBH) first-year BH addition. The measurements done in the first and second years after BH application were taken to constitute the temporal variability (i.e., "fresh" and "aged" effects, respectively). Adsorption-desorption, dissipation, and leaching studies were carried out under laboratory conditions using soils from the field experiment. The K_d (partition coefficient) values were 1.2, 1.1, and 1.1 and 1.5, 1.2, and 1.2 times greater in SNTBH, STBH, and FTBH than in the corresponding unamended soils for the fresh and aged years, respectively. The clomazone persistence was only significantly affected by BH addition in the treatments under sprinkler irrigation. Under anaerobic incubation conditions the application of BH led to an increase in the $t_{½}$ (half-live) values from 19 and 26 d and from 22 and 21 d in SNT and ST, to 36 and 35 d, and to 25 and 31 d in the corresponding amended soils for the fresh and aged years, respectively. However, under aerobic conditions, while for the fresh year $t_{½}$ values increased from 37 and 41 d in SNT and ST to 40 and 52 d in the corresponding amended soils, for the aged year these values were not significantly affected. The management regimes significantly influenced clomazone leaching, with the total leached values showing the following trend: ST = SNT > FT = STBH = SNTBH > FTBH. Therefore, the use of BH as organic amendment may be an effective tool to greatly reduce water contamination by clomazone in rice fields under conventional tillage and flooding irrigation, but also under sprinkler irrigation, particularly after BH aging under no-tillage practices.

1. Introduction

Rice (*Oryza sativa* L.) is a crucial crop for global food security. In the European Union (EU), its production extends over an area greater than 440 000 ha. After Italy, Spain is the second rice producer in the EU accounting for 30% of its total production. The traditional rice production system under flooding and conventional tillage is threatened due to its lack of sustainability, especially in Mediterranean countries where water scarcity is worsening due to the effects of climate change and its supply not always guaranteed for this crop. This fact leads to farmer's great uncertainty, and consequently a continuous decline in the area under rice cultivation in countries like Spain (MAPA, 2019), one of the European countries with the greatest water stress. Furthermore, the water footprint for rice cultivation in Mediterranean countries (2000–2500 m^3 t^{-1}; Sánchez-Llerena et al., 2016) is 2.3 times greater than that registered for Asian countries (1051–1088 m^3 t^{-1}; Arunrat et al., 2020). Therefore, to ensure the sustainability of rice production in water stressed regions, it is urgently necessary to implement alternatives to its

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traditional cultivation practices so as to adapt it to climate change by improving its water use efficiency.

The production of rice under sprinkler irrigation, with or without conventional tillage, has been recognized as an efficient management practice to save water and agricultural inputs, and can be considered as an interesting alternative for Mediterranean environments (Facchi et al., 2013; Sánchez-Llerena et al., 2016; Mukherjee et al., 2017), with a positive impact on the livelihoods of rice farmers who frequently lack viable alternatives to this crop. However, previous studies have found great variability and lower yields under sprinkler irrigation irrespective of the tillage system applied (Sánchez-Llerena et al., 2016; Girsang et al., 2019). Thus, although Sánchez-Llerena et al. (2016) reported that rice production under non-flooding irrigation in south-western Spain led to water savings greater than 70%, this also led to up to 1.9 times reductions in yields compared with those under flooding irrigation. These yield losses due to water-deficit stress were not observed under sprinkler irrigation in rice soils with total organic carbon (TOC) values greater than 15.0 g kg^{-1}, values which are unusual for Mediterranean agricultural soils (Muñoz et al., 2007; López-Garrido et al., 2012). For this reason, the use of organic amendments could enhance rice productivity, ensuring therefore its sustainability under non-flooding production systems which have also the greatest water use efficiency, particularly in regions whose soils are poor in organic matter.

Biochar is frequently being used as an organic amendment due to its potential for carbon sequestration (Li et al., 2021). Its application may also have beneficial effects on the soils' physicochemical and biological properties (Paz-Ferreiro et al., 2012; Méndez et al., 2013; Oleszczuk et al., 2014), water retention capacity (Głąb et al., 2016), and retention and availability of nutrients, which in some cases entails an increase in productivity (Marris, 2006; Alburquerque et al., 2013; Ding et al., 2016), including in rice cultivation (Thammasom et al., 2016). Unlike other types of organic amendment, biochar is highly stable against microbial decomposition, so its beneficial effect on the soils where it is added could potentially be prolonged for far greater periods of time than other soil organic amendments. However, for practical and viable use as organic amendment, the biochar should be easy to get hold of, reasonably priced, and be capable of being produced in large quantities. In this sense, extensive areas in the south-western of Mediterranean countries such as Spain and Portugal have an important socio-economic agroforestry system (the dehesa), where grassland is mainly combined with holm oak (*Quercus ilex* L.). However, the value of holm oak pruning residues has been declining lately (Teutscherova et al., 2018), so their conversion to commercial biochar and its use as organic amendment may help to optimize use of the system's resources by appropriate recycling. Moreover, although a great variety of raw materials have been used for biochar production, that obtained from holm oak pruning (BH) is characterized by its high TOC content and its greater capacity to adsorb water and possible pollutants relative to those obtained from other raw materials (Takaya et al., 2016). In the particular case of contaminated rice paddy soils and waters, studies have suggested that the use of biochar as organic amendments could be considered a useful remediation strategy (Qiao et al., 2018; Liu et al., 2020). In addition, rice production is very much constrained by weed infestation not only under sprinkler irrigation but also under flooding cropping conditions when weeds are not suitably controlled (Singh et al., 2018). Therefore, the use of pesticides is widely required for greater rice yields. In this sense, one of the most extensively used herbicides in rice cropping is -[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone (clomazone). This herbicide shows high effectiveness for pre- and post-emergent control of grasses and broadleaf weeds. However, because of its great water solubility (1102 mg L^{-1}), this compound has frequently been detected polluting surface and ground waters in rice-growing areas, at concentrations greater than 3.5 μg L^{-1} (Marchesan et al., 2007; Mattice et al., 2010). Furthermore, due to its long soil persistence (28–135 days), clomazone has a great potential to negatively impact both non-target living organisms such as invertebrates (Stenert et al., 2018) and nitrogen-fixing bacteria (Du et al., 2018) and cultivated plants after potential crop rotation (Andres et al., 2013), especially when it is successively applied year after year.

It is widely recognized that the use of biochar as organic amendment could not only improve the soil's properties but also enhance the sorption of pesticides and hence influence the bioavailability and environmental fate of these compounds (Cabrera et al., 2011; Khorram et al., 2016a), although different trends have been reported mainly caused by the properties of the soils, biochars, and pesticides (Siedt et al., 2021). For instance, while the sorption of carbaryl in a soil amended with biochar obtained from pig manure was increased by a factor of 2.1, that of atrazine was only by a factor of 1.4 (Khorram et al., 2016a). Cabrera et al. (2014) found that while in a soil amended with biochar from wood chip pellets aminocyclopyrachlor sorption increased on average by a factor of 25 compared to the unamended soil, in the same soil amended with biochar from macadamia nut shells it decreased by a factor of 1.8. Yu et al. (2011) found that acetamiprid sorption increased in different soils under red gum wood biochar amendment, although the degree of enhancement was greater in soils with the lowest values of pH and organic matter. Tatarková et al. (2013) observed that MCPA leaching was 35% lower in a wheat straw biochar amended soil. However, Cabrera et al. (2011) reported that the amount of this compound leached was 15% greater in a soil amended with macadamia nut shell biochar than in the unamended soil. Furthermore, after biochar incorporation into soil, aging has been shown to change its physicochemical properties, which could modify its capacity to sorb pesticides, thus influencing their environmental fate (e.g., Trigo et al., 2016; Gámiz et al., 2019). Further research studies are therefore required in which the effects of aging the char should also be considered, preferably under natural field conditions (Bakshi et al., 2016).

Despite biochars frequently being used in farmlands as soil organic amendments (Siedt et al., 2021), including rice agroecosystems (e.g. Farhangi-Abriz et al., 2021), and clomazone being regarded as a potential pollutant for water resources, only very few works have focused on how biochar amendment affects its behaviour, all of them in laboratory experiments in which aging effects were not measured. Furthermore, we found no work analysing how biochar amendment impacts clomazone's fate when it is applied to soils subjected to different irrigation and tillage management regimes. Therefore, the aim of the present study was to evaluate how amendment with fresh BH influences the sorption–desorption, leaching and persistence of clomazone in rice cropping soils after transition from traditional flooding to an alternative strategy based on sprinkler irrigation with and without tillage practices. Because the physicochemical properties of BH may be altered by aging and weathering processes, field-aged effects under different tillage and irrigation regimes were also evaluated in the second year after its application.

2. Material and methods

2.1. Herbicide

The clomazone (99.8% purity) herbicide was supplied by Dr Ehrenstorfer, GmbH (Germany). Its concentrations were determined by high-performance liquid chromatography (HPLC) as detailed in Text S1 of supporting information (SI).

2.2. Biochar

The commercial biochar (BH) used in the field experiment was produced from slow pyrolysis (550 °C) for 48 h of holm oak prunings by Carylevere Co., Ltd (Zahinos, Spain). Before analysis and incorporation to soil, the BH was ground to pass through a sieve of 2 mm. Total C (TC), H (TH), and N (TN) contents were determined by combustion (950 °C) using a CHNS628 analyser (LECO, United States). The ash content was measured by BH combustion in a muffle furnace at 750 °C for 6 h.

Oxygen content was calculated through mass difference based on total C, H, and N determinations. The water-soluble organic carbon (WSOC) content was extracted with 0.01 M $CaCl_2$ de-ionized water at a 20:1 ($CaCl_2$ to BH) ratio and determined by analysis with a TOC-V analyser (Shimazdu, Japan). The BET (Brunauer-Emmett-Teller) specific surface area (SSA) was measured by N_2 adsorption at 77 K using a Quadrasorb Evo analyser (Quantachrome Instruments, United States). The BH porosity and pore size distribution (from 1×10^5 to 1 nm) were determined using a Poremaster 33GT mercury intrusion porosimeter (Quantachrome Instruments, United States). The surface functional groups of biochar samples were analysed by Fourier transform infrared (FTIR) spectroscopy (Nicolet IS10, Thermo Scientific). Electrical conductivity and pH were measured in a 1:5 (w/v) biochar/water suspension using a conductivity meter and a pH-meter, respectively. Heavy metals (Cr, Ni, As, Cd, Hg, and Pb) and polycyclic aromatic hydrocarbons (the 16 priority PAHs monitored by the US-EPA) were extracted according to the European Biochar Certificate (EBC, 2021). After extraction, heavy metal contents were assayed using inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7900), and PAHs were assayed by gas chromatography mass spectrometry (GC–MS). For analysis of aged BH, in the second year after harvest, soil samples (0–20 cm) were collected from the treatments FTBH, STBH, and SNTBH, and the BH particles were then separated. These BH samples were suspended in distilled water (1:10 w/v) followed by shaking to remove soil particles. The BH was rinsed four times with distilled water prior to analysis. Its main properties fresh (before incorporation to soil) and aged (18 months of aging under natural field conditions with different management systems) are listed in Table 1 and briefly discussed in text S2 of SI. The BH characteristics complied with the standards of the European Biochar Certificate (Version 9.5E of 1st August 2021 of EBC) (Table S1).

2.3. *Experimental design, soil sampling, and analysis*

The field experiment covering two years (2018 and 2019) was conducted in a paddy field at Gévora village, Badajoz province, southwestern Spain (38°55′N; 6°57′W), under a semi-arid Mediterranean climate with mean annual temperature and rainfall of 15.7 °Cand 439 mm, respectively, during the experiment. This experimental area had been under conventional rice (*O. sativa* L.) cropping (tillage and flooding) for 14 years, but a part of the field had already been under sprinkler irrigation in the 3 years preceding the experiment. The soil is loam textured, with a particle size distribution (0–20 cm) of 20.8% clay, 28.9% silt, and 50.3% sand. The experiment involved six treatments in triplicate, with a total of 18 plots (18 m in length × 10 m in width). The treatments were: traditional flooding irrigation and tillage without (FT) or with (FTBH) first-year BH addition, sprinkler irrigation and tillage without (ST) or with (STBH) first-year BH addition, sprinkler irrigation and no-tillage without (SNT) or with (SNTBH) first-year BH addition. The BH addition dosage in the FTBH, STBH, and SNTBH treatments was 28 Mg ha^{-1}. BH was spread on the soil surface only once (April 2018) and incorporated to a depth of 15 to 20 cm approximately, using a rotatory hoe. After harvest (October) in 2018 and 2019 (170 d and 542 d after the biochar application), four subsamples of soil were taken from each of the plots to a 0–20 cm depth for sorption–desorption, leaching, and dissipation determinations. These were carried out under laboratory conditions with soils from the field experiment. The measurements done in the first and second years after BH application were taken to constitute the “fresh” and “aged” effects, respectively. Weed management was by pesticide application in all treatments, with glyphosate (1.5 L ha^{-1}) in pre-seeding and imazamox (1.75 L ha^{-1}) in post-emergence. In both years, in order to get maximum grain yield, 9–18-27 composite fertilizer (550 kg ha^{-1}) was applied (April) as basal in all treatments, and N (urea) was applied in two splits of 200 kg ha^{-1} at tillering (July) and 150 kg ha^{-1} at the panicle initiation stage (August). Measurements were also made of the soil TC, TN, and WSOC contents, pH, and EC. The TC, TN, and WSOC contents were determined as in the BH samples. The pH was also determined as in the BH samples but in a 1:1 (w/v) soil/ water mixture. EC was measured in a saturation extract (US Salinity Laboratory Staff, 1954). Selected properties of the unamended and BH-amended soils for fresh and aged years are listed in Table 2.

2.4. *Adsorption-desorption experiments*

The clomazone adsorption isotherms in unamended and BH-amended soils were determined using the batch equilibration technique as previously has been described in López-Piñeiro et al. (2011). Briefly, soil samples (5 g) were treated by mechanical shaking for 24 h (20 ± 1 °C) with 10 mL of solutions of clomazone in 0.01 M $CaCl_2$ at initial concentrations (C_i) of 5, 10, 20, 40, and 50 μM. Equilibrium concentrations in the supernatants were determined by HPLC, and the adsorption–desorption data were fitted to the linear form of the Freundlich equation. Detailed information is given in Text S3 of SI.

2.5. *Herbicide dissipation studies*

To determine the clomazone dissipation, studies in unamended and

Table 1
Selected properties of the fresh and aged biochar.

	Fresh	Aged-SNTBH	Aged-STBH	Aged-FTBH
TC (%)	77.1c	74.1a	74.0a	75.2b
TH (%)	3.61c	3.22b	3.22b	3.18a
TN (%)	0.470a	0.690c	0.690c	0.520b
TO* (%)	18.8a	22.0c	22.1c	21.1b
Ash (%)	9.94a	10.9a	13.8b	15.7c
H/C (molar ratio)	0.562c	0.521b	0.522b	0.507a
O/C (molar ratio)	0.183a	0.223c	0.224c	0.210b
pH	9.08d	6.78c	6.21a	6.38b
EC (dS m^{-1})	3.54d	0.603c	0.373a	0.457b
WSOC (mg kg^{-1})	368c	273b	261ab	258a
SSA (m^2 g^{-1})	17.4a	20.0b	52.7c	67.1d

The data for total carbon (TC), total hydrogen (TH), total nitrogen (TN), total oxygen (TO), electrical conductivity (EC), and water-soluble organic carbon (WSOC) are mean values. *TO calculated assuming < 1% of S without ash content. Values with the same letter within a row are not significantly different at the p < 0.05 level of probability.

Table 2
Selected soil properties.

	TC (g kg^{-1})	WSOC (mg kg^{-1})	EC (dS m^{-1})	pH	TN (g kg^{-1})
2018					
SNT	9.30aA	101bcA	1.45aA	6.73 dB	1.16abA
SNTBH	15.8cA	107cA	1.99cA	7.10eB	1.16abA
ST	10.0bA	94.6bcA	1.87bcA	6.27bA	1.10abA
STBH	17.5dA	81.7abA	1.72bA	7.09eA	1.02aA
FT	10.2bA	63.3aA	1.93bcA	5.53aA	1.23abA
FTBH	22.2eA	69.5aA	2.70dA	6.40cA	1.32bB
2019					
SNT	9.70aA	105bA	5.98 dB	6.46cA	1.36aB
SNTBH	17.0dA	126cA	3.44cB	7.03dA	1.28aB
ST	10.7cA	83.5aA	2.12aB	6.29bA	1.32aA
STBH	17.9eA	83.0aA	1.88aB	7.15 dB	1.35aA
FT	10.1bA	74.0aB	2.74bB	5.65aB	1.35aA
FTBH	20.4fA	73.5aA	2.77bA	6.50cB	1.22aA
Y	*	*	***	*	**
M	***	***	***	***	NS
Y × M	***	NS	***	***	NS

The data for total carbon (TC), water-soluble organic carbon (WSOC), electrical conductivity (EC), pH, and total nitrogen (TN) are mean values. ANOVA factors are: Y, year; M, management regime; Y × M, interaction year × management regime; significant at *$p < 0.05$, **$p < 0.01$, and ***$p < 0.001$, 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).

BH-amended soils were performed under both non-flooded (80% field capacity) and flooded incubation conditions (soil-to-water ratio 1:1.25, w/v). Clomazone dissolved in distilled water was applied to produce an initial soil concentration of 3.3 μg g^{-1} which is equivalent to the recommended field dosage (1 kg ha^{-1}). Three replicate tubes were removed (at 2 h and at 2 and 5 days after herbicide application, and then at 7-day intervals for 49 days) from each treatment to measure the herbicide concentrations. For the assay, the soils (5 g) were extracted with methanol (10 mL) by shaking mechanically on an end-over-end shaker at 20 ± 1 °C for 24 h followed by centrifugation, and the residues of the herbicide in the extracts were determined by HPLC. Recoveries were greater than 95% of the herbicide applied to the soil. Clomazone residues from water samples were also determined by HPLC. Dissipation data were fitted to a first-order kinetics equation, followed by the respective half-life ($t_{1/2}$) calculation. Measurements were also made of the dehydrogenase activity (DHA) under both incubation conditions using INT as substrate (García et al. (1993). Further information about dissipation studies and DHA determination can be found in SI (Text S4).

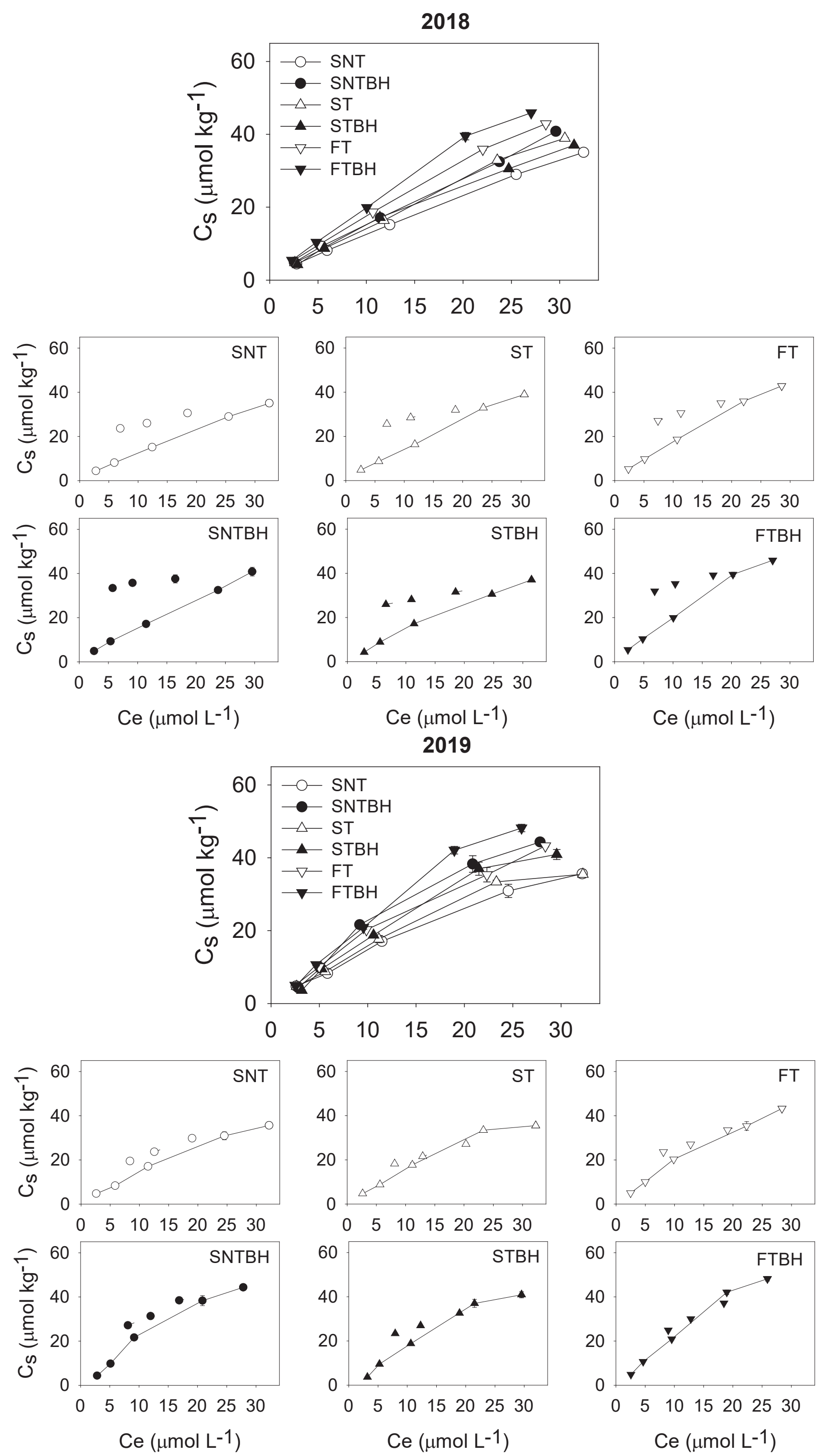

Fig. 1. Clomazone sorption and desorption isotherms. Vertical bars representing one standard error of the mean were smaller than the symbols in all cases. Ce: equilibrium clomazone concentration; Cs: amount of clomazone sorbed. Treatments are: sprinkler irrigation and no-tillage without (SNT) or with biochar application (SNTBH); sprinkler irrigation and conventional tillage without (ST) or with biochar application (STBH); traditional flooding irrigation and tillage without (FT) or with biochar application (FTBH).

2.6. Leaching studies

To measure clomazone leaching, unamended and BH-amended soils were packed in PVC columns of 5 cm (inner diameter) × 30 cm (length) in triplicate. The columns were oversaturated with 0.01 M $CaCl_2$, and then allowed to drain for 24 h. A solution of clomazone in methanol was then added at a rate of 1 kg ha^{-1}. The columns were eluted daily with 50 mL of 0.01 M $CaCl_2$ and the collected leachates analysed by HPLC. When the monitoring period had concluded, each column was sectioned into four (5 cm depth) to determine the amount of clomazone residue. The herbicide was extracted as was described above in the dissipation studies. Detailed information about the leaching studies is given in SI (Text S5).

2.7. Statistical analyses

Statistical analyses were performed using the SPSS (version 22) software. After having verified the normality distribution and homoscedasticity of the data, selected soil properties and sorption–desorption, dissipation and leaching parameters were subjected to a two-way ANOVA with repeated measures on the factor "year". A one-way ANOVA was use to analyse biochar properties. All pairwise multiple comparisons were performed using the Duncan test. The Pearson correlation coefficient (r) was used to study possible correlations between different parameters. Differences at *p* greater than 0.05 were regarded as statistically not significant

3. Results and discussion

3.1. Sorption-desorption studies

Fig. 1 illustrates sorption–desorption isotherms of clomazone for fresh and aged years. For all treatments in both years the sorption isotherms were appropriately fitted by the Freundlich model (R^2 greater than 0.960; Table 3). For the unamended soils, the clomazone sorption was concentration-dependent (n_f values < 1). The values of K_d were significantly affected by the treatments, with differences between the fresh and aged years as indicated by the significant ($p < 0.05$) treatment × year interaction (Table 3). The clomazone K_d values ranged from 1.16 to 1.66 (Table 3) which were slightly greater than those obtained by Xu et al. (2008) and Gámiz et al. (2017) who, in soils from China and Spain, reported K_d values of 1.11 and 1.14, respectively, also in original soils with very low (5.8 g kg^{-1}) and low (13 g kg^{-1}) TOC contents, respectively. However, our K_d values were in a narrower range than those reported by Gunasekara et al. (2009) who found K_d values of 2.3–11 for soils from the USA with TOC contents of 21–45 g kg^{-1} and pH values of 4.7–6.4. Also, clomazone was adsorbed to a much lesser extent in our soils than in Brazilian soils studied by Pereira et al. (2018) who reported K_f values of 1.48–22.11 for soils with TOC contents of 12.1–117 g kg^{-1} and pH values of 5.1–6.5, indicating a greater potential risk of water pollution by this non-ionic herbicide after its application in our typical Mediterranean soils characterized by very low TOC content than that to be expected in other types of soils. After five years of transition from flooding to sprinkler irrigation, the K_d values in FT were 1.3 and 1.2 times greater than in SNT and ST, respectively (Table 3). These results agree with those of our previous study (Fernández et al., 2020) in which, despite the fact that one year after transition to sprinkler irrigation the clomazone K_d values were 1.2 times lower in ST than in FT and SNT, after three years these values were 1.4 and 1.2 times greater in FT than in SNT and ST, respectively, corroborating the influence not only of different tillage and water management regimes on clomazone's sorption behaviour, but also of the implementation's timing. The observed decrease in clomazone sorption may be attributable to the increase in soil pH as a consequence of the transition to sprinkler irrigation, especially under no-tillage management (Tables 2 and 3). Thus, while the lowest K_d value was obtained in the soil with the highest pH (SNT), the greatest K_d value was in the soil with the lowest pH (FT). Furthermore, in a correlation analysis in which only unamended soils were included, K_d was correlated significantly and negatively with pH (r = –0.895, p < 0.01). This trend agrees with Liu et al. (2010) who, also for a non-ionic herbicide (diuron), found a decrease in sorption values with increasing pH. According to Chagas et al. (2019) and Chagas et al. (2020), these results seem to indicate that, at pH values observed in FT management (<5.7), the compound would be capable of accepting protons, thereby increasing its sorption on negatively charged soil surfaces.

The addition of BH to soil influenced the sorption parameters (Table 3). While for the fresh year there were no differences (*p* greater than 0.05) between the n_f values of unamended and BH-amended soils, for the aged year these values increased significantly from 0.827, 0.846, and 0.877 in SNT, ST, and FT, respectively, to 1.01, 1.06, and 0.999 in the corresponding amended soils (Table 3), indicating that changes in the intensity of clomazone sorption were greater in the aged than in the fresh year. Furthermore, the greater than unity slope of the isotherm (SNTBH, and STBH and FTBH) indicates a lack of any dependence of sorption on initial solution concentration. For all treatments, the BH field application significantly (p < 0.05) and positively influenced clomazone sorption with K_d values in the BH-amended soils ranging from 1.42 to 2.08 (i.e., increases by factors of 1.1 to 1.5 compared to unamended soils). Gámiz et al. (2017) reported a slightly greater (by factors of 1.4 and 1.7) increase in clomazone sorption in a Mediterranean agricultural soil amended with two hardwood biochars prepared at a similar temperature (500 °C) to that used in the present work, although in a laboratory study where the biochar addition dosages were approximately twice as large and in which only fresh effects were measured. The greater sorption capacity observed in biochar amended soils has been extensively ascribed to its great SSA (Table 1), which can provide additional sorption sites (e.g., Gámiz et al., 2017; Khorram et al., 2018; Khalid et al., 2020). Likewise, it might be also explained by the high carbon content in the soil as result of BH addition (Spokas et al., 2009; Si et al., 2011). Indeed, K_d values had a positive and significant correlation with TC (r = 0.691**), corroborating its key role in the sorption of clomazone (e.g., Fernández et al., 2020).

As would be expected according to the greater SSA of the BH in the aged than in the fresh year (Table 1), with aging this amendment better improved the soils' capacity to sorb clomazone, indicating that the

Table 3
Clomazone sorption–desorption parameters.

	n_f	R^2 sorption	K_d	% D[†]	R^2 desorption
2018					
SNT	0.852aA	0.999	1.16aA	32.7bcA	0.973
SNTBH	0.858aA	0.998	1.42bcA	17.8aA	0.978
ST	0.871aA	0.997	1.35bA	34.4bcA	0.999
STBH	0.892aA	0.993	1.50cdA	20.0aA	0.992
FT	0.854aA	0.999	1.60dA	36.8cA	1.00
FTBH	0.886aA	0.997	1.84eA	30.4bA	0.998
2019					
SNT	0.827aA	0.991	1.26aA	45.4bcB	0.997
SNTBH	1.01bB	0.963	1.84bcB	38.9aB	0.946
ST	0.846aA	0.983	1.33aA	48.6cB	0.988
STBH	1.06bB	0.960	1.61bA	42.8abB	0.976
FT	0.877aA	0.988	1.66bA	45.4bcB	0.967
FTBH	0.999bB	0.990	2.08cA	48.3cB	0.997
Y	***		***	***	
M	**		***	***	
Y × M	***		*	***	

The data for nf, Kd, and desorption (D) are mean values. ANOVA factors are: Y, year; M, management regime; Y × M, interaction year × management regime; significant at *p < 0.05, **p < 0.01, and ***p < 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). R^2 is the coefficient of determination.

[†] The percentage of D was calculated after three cycles of desorption.

impact of BH amendment on the herbicide's sorption was not only treatment but also timing dependent. Thus, while for the fresh year the application of BH led to more clomazone sorption in SNTBH, STBH, and FTBH than in the corresponding unamended soils by factors of 1.2, 1.1, and 1.1, for the aged year these increases were by factors of 1.5, 1.2, and 1.2, respectively (Table 3). The SSA of BH increased with aging in the soils from 17.4 $m^2 g^{-1}$ for the fresh BH to 20.0, 52.7, and 67.1 $m^2 g^{-1}$ for aged BH under SNTBH, STBH, and FTBH treatments, respectively (Table 1). However, the greater observed increase in the K_d values under no-tillage (SNTBH) than under tillage management system (STBH and FTBH) in the aged year are not attributable to differences in SSA values of the BH, since the lowest values corresponded to SNTBH while the greatest to STBH and FTBH (Table 1). These results may be explained by the greater salts content observed in the SNTBH than in STBH and FTBH, as was indicated by the values of EC which in SNTBH was 1.8 and 1.2 times greater than in STBH and FTBH, respectively (Table 2). This agrees with Redman and Tjeerdema (2018) who, also in rice soils but from California, observed sorption enhancement of chlorantraniliprole as a result of a reduction in its solubility as salinity increased (salting-out effect). Furthermore, besides the significantly greater WSOC observed in SNTBH than in STBH and FTBH (Table 2) which could provide additional sites for clomazone sorption, its greater salts concentration could have altered the configuration of water soluble soil organic matter, leading also to enhancement sorption of this pesticide (Li et al., 2006).

In a previous study, Fernández et al. (2020) reported in the same rice soils a slightly greater increase in clomazone sorption (1.4- to 1.7-fold increase) in unamended soils when olive mill waste compost (W) was used as organic amendment than the increases obtained in the present study using BH amendment (1.1 to 1.5-fold), although with an addition dosage 2.5 times greater in the case of W than in the BH-amended soils. This indicates a greater affinity of the herbicide for BH than for W. In agreement with Cabrera et al. (2011), the greater WSOC content in the W that in the BH amendment could have contributed to a potentially greater sorption of clomazone in the BH-amended soils.

As one observes in Table 3, for soils without BH amendment the desorption values (*D*) were not significantly affected by the different treatments. With the exception of flooding treatment in the aged year, the BH field application influenced negatively and significantly ($p < 0.05$) the *D* values in the fresh and aged years, for which the lowest and greatest *D* values corresponded to the SNTBH and FTBH treatments, respectively in both years (Table 3), suggesting a lower reversibility of clomazone in BH-amended soils under non-flooding irrigation, especially with no-tillage management. Several researchers have also demonstrated lower reversibility of pesticides after biochar addition to soil, including clomazone (Gámiz et al., 2017) and other non-ionic compounds such as diuron (Yu et al., 2006), results which were mainly attributed to partitioning into condensed structures or entrapment in micropores (e.g., Khorram et al., 2016a). Similar to the case of sorption, our findings indicate temporal variability of BH desorption capacities with field-aging. Thus, while for the fresh year BH application led to lower values of *D* in SNTBH, STBH, and FTBH than in the corresponding unamended soils by factors of 1.8, 1.7, and 1.2, for the aged year these decreases were by factors of 1.2, 1.1, and 1.1, respectively (Table 3). According to Khorram et al. (2018), the increase in sorption reversibility detected with the aging effect may be attributable to the significantly greater micro-pore volume/total pore volume ratios observed in the aged than in the fresh BH, with values for this ratio of 0.743 in the fresh BH and 0.767, 0.790, and 0.861 for aged BH in the SNTBH, STBH, and FTBH treatments, respectively (Table S2). These findings suggest that, although BH addition may increase clomazone sorption and thereby reduce the risk of water contamination by this compound in rice-growing areas, it also could impede its subsequent release for the optimal efficacy of the herbicide, particularly if BH were applied to rice cropping soils under sprinkler irrigation without prior aging of the biochar (Table 3).

3.2. Dissipation studies

The clomazone dissipation curves and DHA are shown in Fig. 2. The data fit first-order kinetics for both years and both experimental conditions (R^2 greater than 0.850; Table 4). For both years, the values of DHA determined considering the total incubation period (DHAT) were up to 2.9 (fresh year) and 4.4 (aged year) times less under non-flooded incubation conditions (Table 5). This is consistent with Fernández el al. (2020) and Gómez et al. (2020) who also reported lower DHAT values under non-flooded than flooded incubation conditions, but using W instead of BH as the organic amendment in rice soils after clomazone and MCPA application, respectively.

The clomazone persistence was significantly influenced by the treatments, with differences between the fresh and aged years as indicated by the significant ($p < 0.001$) treatment × year interaction (Table 4). For unamended soils, the dissipation rates of clomazone were greater under flooded than non-flooded incubation conditions, with half-lives ($t_{1/2}$) ranging from 12.9 to 25.7 d and 37.0 to 53.2 d for flooded and non-flooded incubation conditions, respectively. (Table 4). This is consistent with Tomco et al. (2010) who attributed a faster dissipation under flooded conditions to the lower values of soil redox potential, which could lead to a rapid biotransformation to the open-ring form due to hydroxylation in different positions of the aromatic ring (Cao et al., 2013). Under non-flooded conditions, similar persistence was found by Fernández et al. (2020) who reported $t_{1/2}$ values of 33 to 62 d, but slightly greater than that of 29 d reported by Gámiz et al. (2017), although in a non-rice soil with lower sorption than that of the present study. Under flooded conditions, our $t_{1/2}$ values were slightly greater than those reported by Fernández et al. (2020) of 3 to 20 d, but greater than the value (8 d) reported by Tomco et al. (2010) also in a rice soil, although with a TC much lower (4.1 g kg^{-1}) than in the present work. Under flooded conditions, FT showed faster dissipation rates with $t_{1/2}$ values in this treatment 1.5 and 2.0 and 1.4 and 1.3 times lower than in SNT and ST for the first and second years, respectively (Table 4). In agreement with the DHAT values, the expected increase in clomazone persistence was attributable to the observed decrease in microbial activity when soils under sprinkler irrigation for more than 4 years were subjected to flooded incubation conditions. Indeed, the DHAT values in FT were 1.4 and 2.3 and 1.4 and 1.3 times greater in FT than in SNT and ST for the first and second years, respectively (Table 4). Under non-flooded conditions, significant ($p < 0.05$) differences between unamended treatments were only found in the first year of the study. As occurred under flooded incubation conditions, the lowest persistence value was obtained in the treatment with the greatest DHAT, but in this case it corresponded to the SNT treatment (Table 4). Besides corroborating that clomazone was preferably degraded by biological processes, these results also indicate a better adaptation of soil microbial communities to aerobic or anaerobic conditions after years under sprinkler or flooding irrigation, respectively.

As was to be expected according to the DHAT values, faster dissipation of clomazone was also observed for BH-amended soils under flooded than non-flooded incubation conditions for both fresh and aged years, especially in FTBH in which the $t_{1/2}$ values were 3.5 (fresh year) and 3.1 (aged year) times lower under anoxic conditions (Table 4). Despite an increase in sorption capacity being detected in all BH-amended relative to unamended treatments, for both fresh and aged years significant persistence differences between unamended and BH-amended soils were only found in the treatments under sprinkler irrigation (Table 4). This suggests that the increase in sorption was not enough to alter clomazone dissipation in treatments under flooding irrigation, which is in agreement with the better adaptation of anaerobic microorganisms to degrade clomazone, including in soils receiving BH. Although the determinations in the fresh year showed that clomazone dissipation rates decreased significantly ($p < 0.05$) after BH application in SNT and ST treatments under both experimental incubation conditions, this was more evident under flooded incubation conditions in

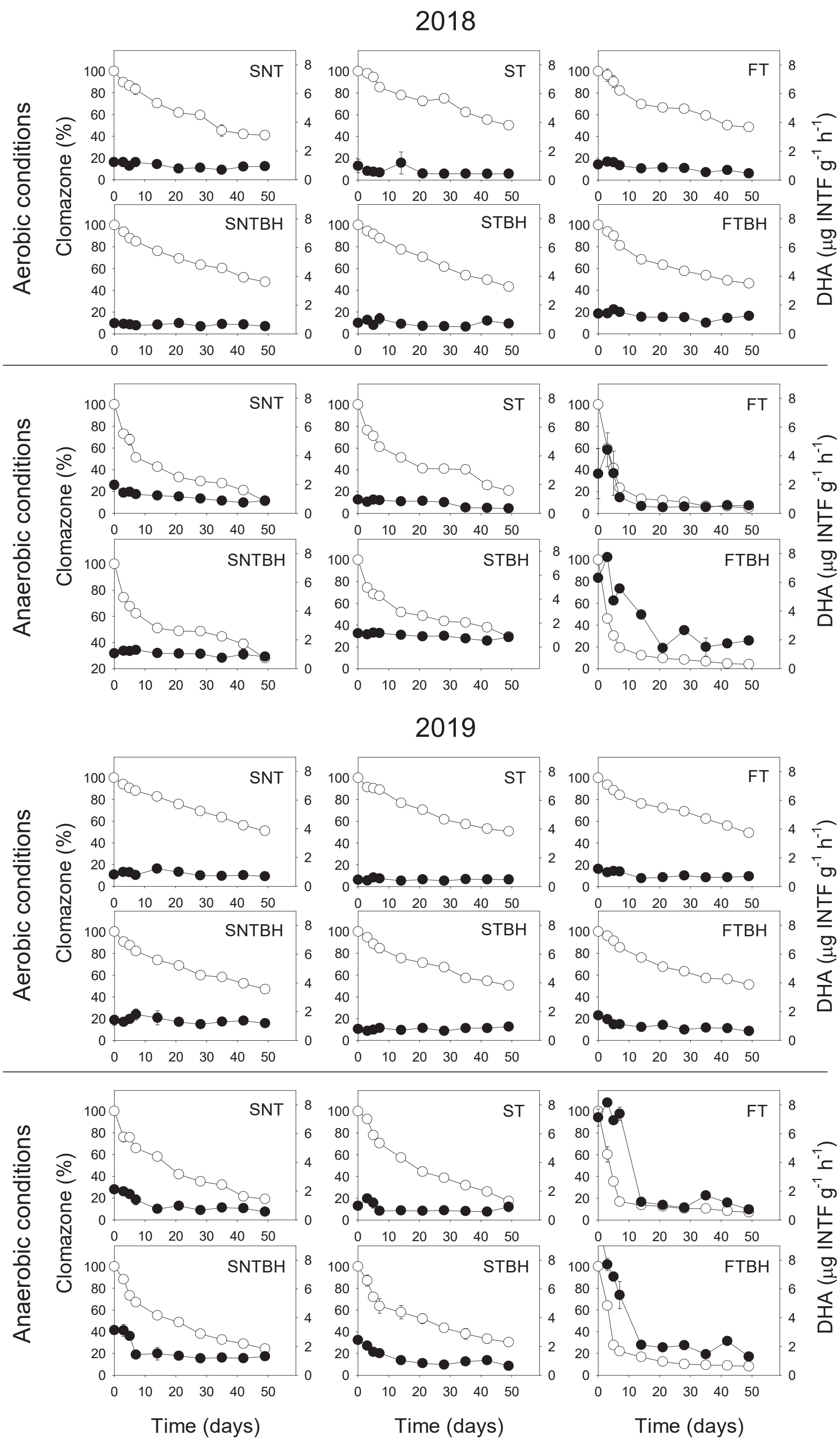

Fig. 2. Clomazone dissipation (○) and dehydrogenase activity (●). Vertical bars representing one standard error of the mean were smaller than the symbols in most cases. Treatments are: no-tillage and sprinkler irrigation without (SNT) or with biochar application (SNTW); conventional tillage and sprinkler irrigation without (ST) or with biochar application (STW); continuous flooding irrigation and tillage without (FT) or with biochar application (FTW).

which lower $t_{1/2}$ values were found, especially in the SNT treatment. Thus, while under flooded incubation conditions, $t_{1/2}$ values increased by factors of 1.9 and 1.4 in SNTBH and STBH compared to SNT and ST, these increases were by a factor of 1.3 when the experiment was conducted under non-flooded conditions. This contrasts with Manna and Singh (2019) who reported increased persistence of pyrazosulfuron-ethyl in rice biochar-amended soils, but with an effect more pronounced under non-flooded experimental conditions, although in an alkaline soil (pH = 8.1) and with a much lower TC (4.6 g kg^{-1}) than in this work. The observed increase in clomazone persistence may be attributable to the increase in K_d values after BH addition (Tables 3 and 4), which may result in lower compound availability for biodegradation (Khorram et al., 2016a), especially under no-tillage management. Indeed, compared to SNT and ST respectively, while for SNTBH the

Table 4
Dehydrogenase activity and clomazone dissipation parameters.

	$t_{1/2\ 1:1.25}$ (days)	R^2 1:1.25	$t_{1/2\ 80\%}$ (days)	R^2 80%	$DHA_{T1:1.25}$ (µg INTF g^{-1}h^{-1})	$DHA_{T80\%}$ (µg INTF g^{-1}h^{-1})
2018						
SNT	19.1bA	0.936	37.0aA	0.970	12.1 bcA	9.75 dB
SNTBH	35.9 dB	0.877	48.4cdA	0.983	10.5 abA	6.44aA
ST	25.7cB	0.932	40.8abA	0.955	7.20 aA	6.01aB
STBH	34.8dA	0.909	51.5dA	0.993	9.43 abA	7.20bA
FT	12.9aA	0.850	48.1cdA	0.950	14.0 cA	8.73cA
FTBH	12.5aA	0.851	44.0bcA	0.948	37.4 dA	12.6eB
2019						
SNT	21.7bB	0.980	52.9aB	0.989	11.9bB	8.67cA
SNTBH	25.2cA	0.974	48.5aA	0.976	18.1cB	13.9eB
ST	20.9bA	0.979	48.9aA	0.979	8.31aB	4.85aA
STBH	30.8dA	0.946	51.4aB	0.971	12.8bB	7.89bA
FT	15.9aB	0.788	53.2aB	0.973	36.4 dB	8.29bcA
FTBH	16.0aB	0.777	50.5aB	0.968	42.1eB	10.5dA
Y	**		***		***	***
M	***		*		***	***
Y × M	***		***		***	***

Half-lives: $t_{1/2\ 1:1.25}$ in soils with 1:1.25 (w/v) (soil/water) moisture content; $t_{1/2\ 80\%}$ in soils at 80% field water capacity. DHAT, total dehydrogenase activity considering all the incubation times in soils conditioned to 1:1.25 (w/v) (soil/water) moisture content and 80% field capacity. The data are presented as mean values. ANOVA factors are: Y, year; M, management regime; Y × M, interaction year × management regime; significant at *$p < 0.05$, **$p < 0.01$, and *** $p < 0.001$, 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). R^2 is the coefficient of determination.

Table 5
Clomazone leaching parameters.

	Initial Pore volume[†]	Max. Concentration leached (µM)	Total leached (%)	Total extracted (%)	Not Recovered (%)
2018					
SNT	1.89cB	1.40bA	44.4cA	25.9aA	29.7abA
SNTBH	2.14 dB	0.748abA	36.6bB	46.7bB	16.7aA
ST	1.98cB	2.44cB	55.6 dB	25.3aA	19.1abA
STBH	1.20bB	0.810abA	31.8bA	48.3bA	19.9abA
FT	0.717aA	0.969abA	37.26bB	30.15aA	32.6bA
FTBH	3.04eB	0.478aA	12.3aA	23.2aA	64.5cB
2019					
SNT	1.70cA	1.39bA	46.9cA	25.1aA	28.0aA
SNTBH	1.69cA	0.818aA	29.0bA	37.6abA	33.4aA
ST	1.03bA	1.49bA	48.3cA	26.3aA	25.4aA
STBH	0.693aA	0.871aA	33.5bA	46.6bA	19.9aA
FT	0.996bB	0.633aA	31.9bA	33.4abA	34.7aA
FTBH	0.692aA	0.585aA	23.4aA	45.7bB	30.9aA
Y	***	*	*	*	*
M	***	***	***	*	**
Y × M	***	*	*	*	**

The data are presented as mean values. ANOVA factors are: Y, year; M, management regime; Y × M, interaction year × management regime; significant at *$p < 0.05$, **$p < 0.01$, and *** $p < 0.001$, 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).

[†] Pore volume for initiation of the herbicide's leaching.

sorption capacity increased by 22%, for STBH it increased by 11% (Table 3). Decreases in clomazone dissipation after addition of different fresh biochars were also reported by Gámiz et al. (2017), although in a study where its effects were tested in an agricultural soil only under non-flooded incubation conditions. Likewise, Tatarková et al. (2013), Khorram et al. (2016b), and You et al. (2020) found, after the addition of several different biochars, decreases in dissipation of MCPA, fomesafen, and thiamethoxam, respectively, although unlike our work in studies only under non-flooded conditions and in soils not subjected to different management systems. However, increases in dissipation of pesticides have been also reported due to the stimulation of soil microorganisms by biochar amendment (e.g., Yavari et al., 2019), highlighting the importance of the specific characteristics of the biochar (e.g., elemental composition, pH, surface area) as and pesticides when their environmental fates are evaluated in amended soils (Siedt et al. 2021).

With regard to the determinations in the aged year, significant ($p < 0.05$) differences were only found when the experiments were conducted under flooded conditions, with $t_{1/2}$ values increasing by factors of 1.2 and 1.5 in SNTBH and STBH over SNT and ST, respectively (Table 4). Compared with the unamended treatments, despite increases in the sorption capacity in BH-amended treatments being greater in the aged than in the fresh year (46% and 21% versus 22% and 11% for SNTBH and STBH, respectively), decreases in dissipation were lower in the aged than the fresh year, especially in SNT (Table 4). These differences may be explained by the greater reversibility of clomazone sorption in the aged than in the fresh year, as was indicated by the values of D which in SNTBH and STBH were 2.2 and 2.1 times greater in the aged than in the fresh year (Table 3), possibly increasing the amount of the compound ready to be biodegraded. This is supported by the fact that $t_{1/2}$ was significantly and negatively correlated with D ($r = -0.531$**).

3.3. Leaching studies

The breakthrough curves for clomazone are shown in Fig. 3. The percentages of the herbicide leached and extracted from the soil columns at the end of the leaching experiment are presented in Table 5. The total clomazone leached was significantly affected by the treatments, with there being differences between the fresh and aged years as indicated by the significant ($p < 0.05$) treatment × year interaction (Table 5). For unamended soils, after five years of transition from flooding to sprinkler irrigation, the total of clomazone leached was 1.5 times less in FT than in SNT and ST. Moreover, the maximum concentration of clomazone in the leachate was lower in FT than in SNT and ST by factors of 2.1 and 2.4, respectively. This may be explicable by the greater clomazone sorption capacity observed in FT than in SNT and ST, as was indicated by the values of K_d which in FT were 1.3 times greater than in both SNT and ST (Table 3). However, these results contrast with those previously reported by Fernández et al. (2020) in which, after three years of transition from flooding to sprinkler irrigation, the amount of clomazone leached was significantly lower in SNT than in ST and FT. The above findings suggest that, while the changes in soil properties promoted by a short-term transition from flooding to non-flooding irrigation, particularly under non-tillage management, could lead to reducing the leaching of clomazone, in the medium and long terms they might lead to enhancing it, regardless of the tillage system implemented.

After BH addition, a significant ($p < 0.001$) decline in the total amount of clomazone leached was detected for both fresh and aged years in all BH-amended compared with unamended treatments (Table 5; Fig. 3). This may be explained by the greater sorption capability observed in the BH-amended than in the unamended soils (Tables 3 and 5). Indeed, the percentage of clomazone leached had a negative and significant correlation with K_d values ($r = -0.825$**). Besides the greater sorption capacity, the greater decline in the amount of clomazone leached observed in the FTBH than in the SNTBH and STBH treatments, particularly in the fresh year (36.6%, 31.8%, and 12.3% for SNTBH, STBH, and FTBH, respectively), might also be explained by its lesser persistence (Tables 4 and 5). Compared with the unamended soils, limited leaching by biochar amendment due to its greater sorption capacity has been extensively reported (Si et al., 2011; Khorram et al., 2016a; Manna and Singh, 2019). Even a complete failure to detect any clomazone leaching was reported by Gámiz et al. (2017) in a soil amended with different biochars, although in this case the amendments were applied at a dose of 2%, twice that used in the present work. The

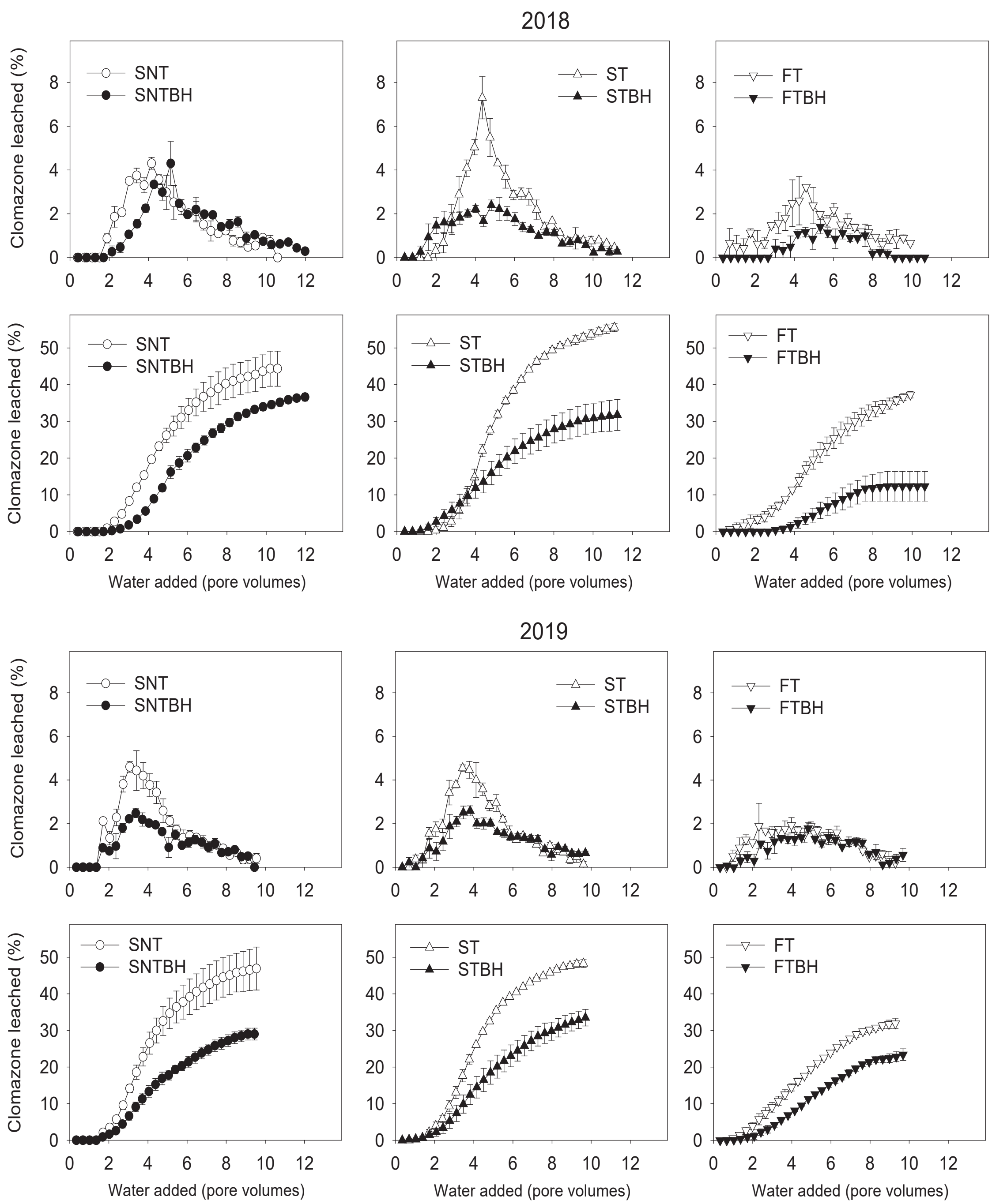

Fig. 3. Relative and cumulative breakthrough curves of clomazone. Vertical bars represent one standard error of the mean. Treatments are: no-tillage and sprinkler irrigation without (SNT) or with biochar application (SNTW); conventional tillage and sprinkler irrigation without (ST) or with biochar application (STW); continuous flooding irrigation and tillage without (FT) or with biochar application (FTW).

results given in Table 5 indicate that the effect of BH on clomazone leaching was both treatment and timing dependent. Thus, the amount of the compound leached was 1.2, 1.7, and 3.1 and 1.6, 1.4, and 1.4 times lower in SNTBH, STBH, and FTBH than in the corresponding unamended SNT, ST, and FT, for the fresh and aged years, respectively. This indicates that while aging of BH in no-tillage and sprinkler-irrigation soils might improve their capacity to reduce clomazone leaching, in those under conventional tillage this capacity could be reduced, especially under flooding irrigation (Table 5). These results may be explained by the observed differences in clomazone desorption in the aged relative to the fresh year, with *D* values increasing from 17.8%, 20.0%, and 30.4% to 38.9%, 42.8%, and 48.3% for SNTBH STBH, and FTBH in the fresh and aged years, respectively (Table 3). This agrees with Khorram et al. (2017) who also found greater leaching of fomesafen in biochar amended soils as a consequence of greater desorption in the aged treatment. Despite the significant increase in *D* observed in SNTBH for the aged over the fresh year, a significant reduction in clomazone leaching was detected in this treatment after BH aging, which could be attributable to the significant increases observed in K_d in the aged compared with the fresh year (Tables 3 and 5). In a previous study, Fernández et al. (2020) also reported decreased clomazone leaching in W-amended rice soils subjected to different tillage and irrigation systems. However, while in the present work after aging the capacity of BH to reduce clomazone leaching in the BH-amended soils decreased, especially in those under conventional tillage and flooding irrigation, Fernández et al. (2020) reported that in W-amended soils this effect was more pronounced under non-flooding irrigation irrespective of the tillage system implemented, again highlighting that the environmental fate of pesticides applied in amended soils under different management systems is strongly dependent on specific properties of each selected organic amendment.

After the leaching experiment, except for FTBH, a significant ($p < 0.05$) increase in the total amount of clomazone retained in the soil columns was observed for both fresh and aged years in BH-amended relative to the unamended treatments (Table 5). For each treatment, similar amounts of herbicide were recovered from the four sections of the soil columns (data not shown), indicating that the compound was homogeneously distributed through the unamended and BH-amended columns. In the BH-amended soils, although in the aged year no significant differences between amended treatments were observed, in the fresh year the percentage of clomazone recovered was on average 2.0 times lower in FTBH that in SNTBH and STBH, which contrasts with the smaller amounts of this compound leached in FTBH (12.3%) compared with SNTBH (36.6%) and STBH (31.8%) (Table 5). These findings agree with those found in the dissipation study. Indeed, the total amount of clomazone retained and not recovered were positively correlated with $t_{1/2}$ ($r = 0.483^{**}$ and 0.619^{**}, respectively) measured under flooded conditions, reflecting that in BH-amended soils under different tillage and irrigation regimes, the mobility of clomazone depends not just on the sorption but also on the dissipation process, except for FTBH in the aged year.

4. Conclusions

The addition of holm oak biochar (BH) as organic amendment in rice production had different impacts on the sorption–desorption, dissipation, and leaching processes of clomazone depending on both the treatment (tillage and irrigation regimes) and BH aging. The increased clomazone sorption in all BH-amended soils, which was enhanced after aging, and its reversibility is strongly dependent not only on the BH's properties such as SSA and pore size distribution, but also on the soils' TC and EC, particularly after BH field-aging under a sprinkler irrigation and no-tillage practice. Furthermore, fresh and aged BH increased clomazone persistence, only in soils subjected to sprinkler irrigation as result of the poor adaptation of aerobic microorganisms to degrade the herbicide. As a consequence of the changes in both BH and soil properties affecting sorption and dissipation process, the implementation of sprinkler irrigation led to more clomazone being leached from soils regardless of whether tillage was applied. Nonetheless, there was reduced leaching of the herbicide in all BH-amended soils, although to a greater extent in those with conventional tillage and flooding. BH field-aging improved the effectiveness in reducing clomazone leaching only when this process was carried out in soils under no-tillage and sprinkler irrigation. Therefore, although the risk of water contamination by clomazone applied to rice-growing soils in water stressed regions may be higher after transition to sprinkler irrigation, the use of BH can be an effective tool to greatly reduce this effect, particularly after aging the BH under no-tillage practices. Further research, including effectiveness studies, is required for a better understanding of how the environmental fate of pesticides with different characteristics is influenced by alternative management practices in rice agroecosystems with high water stress.

Declaration of Competing 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2022.115768.

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