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Optical properties of soil water-extractable organic matter respond to changes in irrigation water quality

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ABSTRACT

Treated wastewater (TWW) irrigation may harm soil and agricultural production. Adverse effects of TWW irrigation may be mitigated by changing irrigation water quality, *e.g.*, use of fresh water (FW), or management, *e.g.*, lower-frequency irrigation (LFI) with TWW. The influence of mitigation treatments on soil organic matter and water-extractable organic matter is unknown. To examine this influence, a study was conducted in an avocado orchard irrigated from 2009 with secondary TWW. Four parallel treatments were applied for six years (2016–2021), involving irrigation with FW, a 1:1 FW-TWW mixture, TWW at LFI (twice a week), and TWW irrigation three times a week as control. Soil samples from three depths were characterized for total organic and inorganic carbon and nitrogen and using Fourier-transform infrared spectra that were decomposed into components by nonnegative matrix factorization. Aqueous extracts of soil samples were characterized for dissolved organic carbon (DOC), inorganic carbon, and nitrogen concentrations, absorbance at 254 nm (Abs_{254}), and excitation-emission matrices of fluorescence that were decomposed into components by parallel factor analysis. The Abs_{254} and fluorescence of humic-like components in the soil extracts were the attributes most consistently responding to irrigation water quality. Irrigation with FW and a 1:1 FW-TWW mixture led to decreases in the concentrations of aromatic and humic-like constituents in the soil extracts compared with the control TWW irrigation. Changing soil irrigation management had no or little impact on those attributes compared with the control TWW irrigation. Results of the study support the use of optical properties related to the concentrations of ultraviolet-absorbing and light-emitting constituents in soil extracts, rather than the whole DOC concentration, as sensitive descriptors suitable for evaluating soil response in different agricultural scenarios.

Key Words: fluorescence, Fourier-transform infrared spectroscopy, humic-like substances, nonnegative matrix factorization, parallel factor analysis, specific ultraviolet absorbance, treated wastewater

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INTRODUCTION

Irrigation with treated wastewater (TWW) became widely used in areas with limited access to potable water. Yet, indications have been accumulating, showing that TWW irrigation may lead to detrimental effects on soil properties, including increased salinity and sodicity (Assouline *et al.*, 2016; Paudel *et al.*, 2016), damaged soil structure, reduced infiltration rate and soil permeability (Lado and Ben-Hur, 2010; Assouline and Narkis, 2011, 2013; Mavi *et al.*, 2012; Schacht and Marschner, 2015; Bardhan *et al.*, 2016), water repellence (Wallach *et al.*, 2005; Tarchitzky *et al.*, 2007; Rahav *et al.*, 2017), and reduced aeration (Assouline and Narkis, 2013; Yalin *et al.*, 2017). These changes in soils under TWW irrigation may also lead to loss of agricultural yield (Assouline and Narkis, 2013; Nicolás *et al.*, 2016; Yalin *et al.*, 2017; Paudel *et al.*, 2018). Furthermore, TWW irrigation may lead to soil contamination by residual inorganic and organic pollutants, the products of their transformation, disinfection byproducts, nanoparticles, microplastics, and antibiotic-resistant genes and bacteria (Fatta-Kassinos *et al.*, 2011; Helmecke *et al.*, 2020; Ofori *et al.*, 2021; Ben Mordechay *et al.*, 2022).

Practical solutions are needed to mitigate the negative consequences of TWW irrigation on soil properties and crop production (Nicolás *et al.*, 2016; Erel *et al.*, 2019; Nemera *et al.*, 2020). For example, mitigation approaches may involve i) improving irrigation water quality, *e.g.*, use of fresh water (FW) or mixing TWW with water of better quality (Oster *et al.*, 2007; Morugán-Coronado *et al.*, 2011; Russo *et al.*, 2015, 2020; Assouline *et al.*, 2020; Nemera *et al.*, 2020), ii) improving aeration at the root zone, *e.g.*, applying the irrigation water over a larger space and time intervals (Yalin *et al.*, 2017; Assouline *et al.*, 2020), or iii) repeated on-surface surfactant application (Ogunmokun and Wallach, 2021).

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Soil organic matter (SOM) has a significant impact on soil functioning, and SOM characterization is included in the evaluation of soil health (Gregorich *et al*., 1994; Reeves, 1997; Loveland and Webb, 2003; Magdoff and Weil, 2004; Lal, 2009; Garrigues *et al*., 2012; Cotrufo and Lavallee, 2022; Weng *et al*., 2022). The chemical composition and content of SOM could be affected by the type of irrigation water. Effects of TWW irrigation on SOM content, soil accumulation of aliphatic and aromatic substances, hydrophobic and hydrophilic SOM components, and concentration and composition of water-extractable SOM fraction were reported in the literature (Jueschke *et al*., 2008; Chen *et al*., 2010; Borisover *et al*., 2012; Bernier *et al*., 2013; Sánchez-González *et al*., 2017). However, there is little knowledge, if at all, on the way the content of SOM and its fractions respond to changes in irrigation practices aimed to diminish the ill-effects of previous long-term irrigation with TWW.

Dissolved organic matter (DOM) is considered the labile fraction of SOM that is linked to various soil biogeochemical processes (Kalbitz *et al*., 2000; Chantigny, 2003; Bolan *et al*., 2011; Gmach *et al*., 2020). Soil water-extractable organic matter (WEOM) obtained under laboratory conditions includes soil DOM but represents generally larger amounts of water-soluble soil organic carbon (C) (Zsolnay, 1996; Chantigny, 2003). It has been suggested to include WEOM in the minimum data set for assessing soil quality (Gregorich *et al*., 1994). Furthermore, WEOM (as well as permanganate-oxidizable C) was recommended for early detection of changes in SOM under different tillage practices, adjusting management and improving soil health (Awale *et al*., 2017). Fluorescent WEOM components were proposed as having the potential to serve as robust indicators for elucidating long-term land-use effects and changes in soil health caused by anthropogenic activities (Rinot *et al*., 2021).

Considering the significance of both SOM and WEOM as attributes in the evaluation of soil functioning, the goal of this research was to examine the response of the aforementioned attributes to either changes in irrigation water quality or management, both aiming at mitigating the adverse effects of long-term TWW irrigation. Our hypothesis was that soil WEOM, because of its labile nature, rather than the whole SOM, would be sensitive to the replacement of regular TWW irrigation with selected alternative irrigation practices. It is generally unknown how irrigation by different types of water or changes in its management affect SOM and WEOM in soils after long-term TWW irrigation. Therefore, the results of this study would be a novel contribution to a better understanding of SOM and WEOM sensitivity to different anthropogenic activities in cultivated lands.

MATERIALS AND METHODS

Study site, experimental design, and soil sampling

The study was conducted in an avocado orchard planted in 2009 in the Western Galilee (Kibbutz Yasour), Israel. The soil in the orchard is a Typic Haploxerert soil composed of 58% clay, 19% silt, and 23% sand with a cation exchange capacity of 30–35 $\text{cmol}_\text{c}\ \text{kg}^{-1}$, calcium carbonate content of 100–240 g kg^{-1}, and pH of 7.3–7.7 (Nemera *et al*., 2020, 2021, 2023). The description of site, crop, irrigation history, climatic data, and the implemented mitigating approaches were provided in detail by Nemera *et al*. (2020, 2023). In brief, the orchard was irrigated from 2009 to 2016 with local secondary TWW (from the nearby city of Karmiel, Israel). Three irrigation schemes implemented in 2016 and intended to mitigate the negative consequences of regular TWW irrigation were examined in this study, including i) irrigation three times a week with FW pumped from the local aquifer, ii) irrigation three times a week with a 1:1 FW and TWW mixture (FW-TWW), and iii) lower-frequency (twice a week) irrigation (LFI) with TWW, but at the same weekly volume as used in the other treatments with a control involving irrigation three times a week with TWW. Each treatment comprised six replicates from randomly distributed plots. The properties of the FW and TWW used were provided in Nemera *et al*. (2023).

In Autumn 2021, after six years of applying the aforementioned treatments, soil samples were taken from three depths, 0–30, 30–60, and 60–90 cm, under the dripper in all plots. Thus, changes in soil properties, if any, were affected by cumulative effects of long-term mitigation treatments. Altogether, there were 4 treatments × 6 replications × 3 depths (72 samples). The samples were brought to the laboratory, air-dried at ambient temperature, sieved (2.0 mm), and stored in closed boxes at room temperature. In two cases (the 0–30 cm depth of the FW-TWW treatment and the 60–90 cm depth of the LFI treatment), only samples from 5 replicated plots were available, such that finally 70 soil samples were used in this study. The residual moisture contents of the air-dried samples were determined by oven-drying at 105 °C for 24 h. The average moisture content of the soil samples was 49 g kg^{-1}, with a standard deviation of 13 g kg^{-1}.

Soil total organic C (TOC), inorganic C (TIC), and nitrogen (TN) determination

Soil TOC, TIC, and TN contents were measured using a Soli TOC Cube system (Elementar, Germany). Soil TOC was obtained by summing the organic C contents determined by oxidation at 400 and 600 °C, and TIC was measured by further heating from 600 to 900 °C. The TOC, TIC, and TN contents were reported on a dry soil basis.

Soil characterization using Fourier-transform infrared (FTIR) absorption spectra

Use of FTIR spectroscopy of the whole soil samples was motivated by earlier studies (Bernier *et al.*, 2013; Sharma *et al.*, 2017) showing that, although both minerals and SOM contribute to soil FTIR spectra, changes in the spectra for a given mineralogical composition could be informative for SOM changes caused by an external organic matter input or changes in soil management. The FTIR absorption spectra of soil samples were obtained in KBr pellets using a Bruker Tensor 27 FTIR spectrometer (Bruker, Israel). The procedure used was described in detail in Nasonova *et al.* (2022). In brief, KBr of FTIR spectroscopic quality was pre-dried overnight at 150 °C. Then, 3 mg of each soil sample and 300 mg of KBr were homogenized carefully with an agate mortar and pestle. Transparent soil-containing KBr pellets were prepared using a PIKE Auto-Crush IR hydraulic apparatus (Bruker, Israel). For that, a fixed force of 8.2 t was applied for at least 7 min. The absorbance spectra were obtained in the 400–4 000 cm^{-1} range, at a resolution of 4 cm^{-1}, by performing 16 scans for a sample and a background. Before further analysis, the FTIR spectra were normalized using the OPUS software by assigning values of 0 and 2 to minimal and maximal absorbances, respectively.

Soil extracts and their characterization

Soil extracts were obtained by mixing pre-weighed soil samples (about 2.00 g) with 20.0 mL ultrapure water (Millipore, Germany) in 30-mL glass centrifugation vials at 25 °C. A 2-h mixing was performed in a Lab Companion SI-300R shaking incubator (Labotal Scientific Equipment Ltd., Israel) at a frequency of 120 strokes min^{-1} in the dark. The selection of extraction medium (water), water-to-soil ratio, and extraction time followed the procedure described by Maxin and Kögel-Knabner (1995). Then, the vials were centrifuged in a Hsiang Tai machine (MRC Laboratory Equipment, Israel) for 30 min at 2 500 r min^{-1}. The supernatants were filtered with prewashed polytetrafluoroethylene 0.45-μm syringe filters. Additionally, ultrapure water was passed through the prewashed syringes to verify the absence of water-soluble material leaching from polytetrafluoroethylene. The pH and electric conductivity (EC) of the filtered supernatant were measured using a pH meter (SL Analytics LAB 845, El Hamma Instruments, Israel) and an EC meter (Eutech instruments CON-700, Labotal Scientific Equipment Ltd., Israel), respectively. The pH of the filtered extracts varied, among all samples, in the 6.40–7.60 range, with an average of 7.24. The EC values varied between 0.052 and 0.304 dS m^{-1}, with an average of 0.151 dS m^{-1}. Concentrations of dissolved organic C (DOC), inorganic C (DIC), and nitrogen (DN) in the filtered extracts were measured using a TOC-L/TNM-L Shimadzu analyzer (Agentek, Israel).

The ultraviolet (UV)-visible spectra of the soil extracts, placed in a 1-cm quartz cuvette, were measured in the 190–600 nm range using a Genesys 10S UV-Vis spectrophotometer (Thermo Scientific, Bargal Analytical Instruments Ltd., Israel). Absorbance at 254 nm (Abs_{254}) and DOC concentration (mg L^{-1}) were employed to calculate the specific UV absorbance at 254 nm (SUVA_{254}, L mg^{-1} DOC m^{-1}):

$$\text{SUVA}_{254} = 100 \times \frac{\text{Abs}_{254}}{\text{DOC} \times d} \tag{1}$$

where d is the optical path length (*i.e.*, 1 cm in this case).

Fluorescence excitation-emission matrices (EEMs) of the soil extracts were measured in a 1-cm quartz cuvette using a FL-8500 spectrofluorometer (Perkin-Elmer, Israel). The excitation wavelength (λ_{ex}) varied in the 250–500 nm range, with a 5-nm step. The emission wavelength (λ_{em}) range was 250–600 nm, with a 0.1-nm step (permanently fixed for a given instrument/software). The excitation and emission slits were 10 nm, and the selected emission scan speed was 12 000 nm min^{-1}. A 400-V photomultiplier tube voltage and a 20-nm response width were used. Excitation and emission corrections were performed automatically using data provided by Perkin-Elmer. In order to minimize inner filter effects associated with absorption of exciting and emitted photons passing through the solution, prior to fluorescence measurements, the extracts were diluted with ultrapure water until their absorbance at 250 nm did not exceed 0.05 (Lakowicz, 1999). Ultrapure water blanks were routinely recorded during fluorescence measurements.

Decomposition of multivariate spectral data

Nonnegative matrix factorization (NMF) and parallel factor (PARAFAC) analysis are techniques capable of decomposing spectral data, *i.e.*, FTIR spectra of soil samples and EEMs of fluorescence of soil extracts, respectively, into the contributions of certain components that are expected to be of chemical meaning.

NMF of FTIR spectra. The NMF technique is a dimensionality reduction method that decomposes a matrix A (in our case, the measured FTIR spectra of a series of samples) into a product of two low-rank matrices in the form $A \approx W \times H$, where the matrix H represents the set of FTIR spectral loadings of NMF-identified components, common for all the samples. The matrix W represents the concentration scores of these components, and these scores vary among the samples. The advantage of NMF over other dimensionality reduction methods sometimes used to decompose spectral signatures, like principal component analysis, is that NMF introduces positive constraints in both W and H (Lee and Seung, 1999). Therefore, the interpretation of matrices of spectral loading and concentration scores is more straightforward. In the present study, a geometric approximation called volume regularization NMF (Ang and Gillis, 2019; Fu *et al*., 2019) was used, since it has been shown to outperform other NMF algorithms when dealing with complex mixtures (Ang and Gillis, 2019). The NMF decomposition was conducted in the RStudio environment (R Core Team, 2021) using the R package vrnmf (Soldatov *et al*., 2021). The optimal rank or number of components of the model was selected using cross-validation (Bro *et al*., 2008), employing the capability of NMF to account for missing values as described in Lado *et al*. (2023). One-third of all measured spectra were randomly selected and separated to form a held-out set. The remaining spectra were used to fit the NMF models with a different number of components. Then, each spectrum of the held-out set was divided into 5 folds, and the components obtained from NMF were fitted to 4 folds and used to predict the data in the 5th one. The procedure was repeated for each fold in the spectrum to ensure all data were used for validation. Errors were calculated as the difference between predicted and measured values. Coefficients of determination (R^2) of the regression of predicted *vs*. observed values and predicted error sum of squares (PRESS) were calculated to define the optimal number of components. The procedure was repeated 30 times with different random fold divisions. Final R^2 and PRESS values were computed as the average of their values obtained for each FTIR spectrum and each of the 30 iterations. Model rank was selected as the one that provided the minimum and maximum values of PRESS and R^2, respectively. It is worth noting that the NMF components extracted from FTIR spectra are not necessarily related to individual substances. Rather, a component intends to depict a set of chemical constituents whose contributions vary similarly in a series of different samples. Thus, the component behaves as "an associate" between chemically different constituents, which appear, in a stable proportion, among all the studied soils. The FTIR spectra of these components (*i.e*., the abovementioned matrix H) combined in accordance with the specific component's contributions (scores, the matrix W) reproduce the matrix A of FTIR spectra of all soils. The absolute values of concentration scores of the components cannot be compared between different samples because the actual amount of soil in a KBr pellet cannot be strictly controlled, *e.g*., due to soil losses during pellet preparation. Hence, only ratios of concentration scores between different components, in analogy to the ratios of absorption band heights or areas, can be examined in a series of samples. Changes in these ratios characterize quantitatively the changes in the composition of the studied soil samples.

PARAFAC analysis of EEMs. The PARAFAC analysis decomposes three-dimensional EEMs of fluorescence into a set of EEMs of major identified fluorescent components and their contributions to the whole sample EEMs (Andersen and Bro, 2003; Murphy *et al*., 2013). The PARAFAC analysis was performed using the drEEM toolbox (Murphy *et al*., 2013) within Matlab R2021a. Preprocessing of the data generally followed the protocols published earlier (Borisover *et al*., 2009; Rinot *et al*., 2021). It included: i) converting both negative values in the EEMs of sample data and those of the blanks into not-a-number (NaN) values, ii) subtracting EEMs of water blanks from the EEMs of samples (and again converting negative values to NaN values), and iii) normalizing all the emission intensities in each EEM by the intensity of water Raman scatter. The latter was obtained in this study by integrating a spectrum of ultrapure water recorded in the 390–410 nm emission wavelength range upon excitation at 350 nm (similarly to Lawaetz and Stedmon, 2009). Then, the integrated area was divided by the emission wavelength interval (*i.e*., 20 nm). To minimize the impact of noisy areas with weak (if at all) light emission signals, the parts of EEMs with $\lambda_{\mathrm{ex}} > 450$ nm and/or $\lambda_{\mathrm{em}} > 500$ nm were further removed. The EEMs data smoothing was performed using the drEEM toolbox as follows: i) to treat the 1st and 2nd orders of elastic Rayleigh light scatter, signals observed within the wavelength corridors $\lambda_{\mathrm{ex}} - 30 \leqslant \lambda_{\mathrm{em}} \leqslant \lambda_{\mathrm{ex}} + 30$ and $2\lambda_{\mathrm{ex}} - 30 \leqslant \lambda_{\mathrm{em}} \leqslant 2\lambda_{\mathrm{ex}} + 30$ were defined as missing values; ii) similarly, to treat the 1st and 2nd orders of inelastic Raman light scatter, signals positioned 15 nm above and below Raman scatter were also defined as missing values; and iii) all those missing values in scatter corridors were interpolated (Murphy *et al*., 2013). The specific widths of the scatter corridors were selected to avoid the appearance of physically impossible results during PARAFAC analysis, *e.g*., when the wavelength of emission maximum is less than the wavelength of excitation maximum. Zeroes were assigned to the intensities at $\lambda_{\mathrm{em}} \leqslant \lambda_{\mathrm{ex}} - 30$. The PARAFAC modeling was performed by applying nonnegative constraints to excitation and emission spectra of fluorescent components and a 10^{-6} convergence criterion (Andersen and Bro, 2003). A randomly initialized f (number of components) model was fit 40 times to the experimental data, where f varied from 2 to 4. No samples or emission intensities at particular excitation or emission wavelengths were considered outliers. The number of identified components was selected by performing the split validation test. The latter was performed by applying an alternating split of the whole dataset and producing four different EEM subsets (Murphy *et al*., 2013). Following that, the newly produced subsets were PARAFAC-analyzed, and the excitation and emission spectra of each component were compared pairwise between the subsets, thus yielding 6 comparisons, and with the spectra obtained from the PARAFAC analysis of the whole dataset. A Tucker correlation coefficient > 0.95 indicated that the test was passed. Based on this test, a two-component model explaining 98.5% of the fluorescence data variability was selected. A three-component model did not pass the split validation test. Finally, the PARAFAC analysis of the EEMs of fluorescence provided the excitation and emission spectra of both fluorescent components and their fluorescence intensities at excitation and emission wavelengths of maximal emission for each sample. These fluorescence intensities were multiplied by a dilution factor specific to a given sample, thus producing emission intensities expected for a given component in a soil extract before any dilution step. Such dilution factor-corrected fluorescence intensities are considered to represent (be proportional to) the concentrations of fluorescent components in a given soil extract.

Statistical analysis

The variability of the properties studied in this study was attributed to the heterogeneity of the field-collected soil samples (soil spatial variability), the extraction procedure (when applied), and the analytical measurements. The primary interest was to identify the effects of a certain mitigation treatment as compared with the control (*i.e.*, continued TWW irrigation), *i.e.*, to compare the means associated with a treatment and the TWW control. No comparison between different mitigating treatments was of interest in this study. Hence, the statistical significance of differences between the means was examined using t-test with Statistica 7.0 (Statsoft). The absence of statistically significant differences was claimed for a probability level (P) exceeding 0.05. In addition, an analysis of variance (ANOVA) with the *post-hoc* Tukey test was used to identify differences between the control (continued TWW irrigation), the irrigation with improved irrigation water quality (the combined group of FW and FW-TWW data), and the changed management (the LFI data), with the same critical probability level. Outliers in the experimental data were identified using the Grubbs test (NIST, 2012).

RESULTS

DOC, DIC, and DN in the soil extracts

Neither improving water quality using FW or FW-TWW, nor improving aeration in the root zone using LFI with TWW, as well as soil depth, had statistically significant effects on DOC concentration in the soil extracts, compared with the control TWW irrigation (Fig. 1). Similarly, the DIC and DN concentrations in the soil extracts did not show statistically significant differences due to irrigation water quality, irrigation frequency, or soil depth (data not shown). Depending on treatment/depth, the DIC concentration varied from a minimal value of 14.6 ± 10.7 mg L^{-1} to a maximal value of 37.3 ± 23.4 mg L^{-1}. The DN concentration was in the range of 2.8 ± 2.0 to 4.0 ± 1.1 mg L^{-1}.

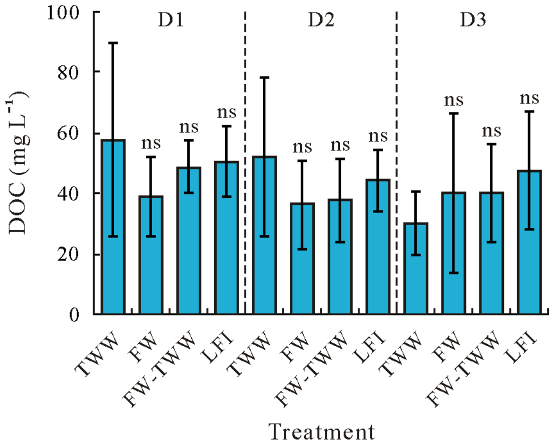

Fig. 1 Dissolved organic C (DOC) concentrations of the water extracts (1:10) of soils sampled in 2021 from the 0–30 (D1), 30–60 (D2), and 60–90 (D3) cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. TWW = irrigation three times a week with treated wastewater as a control; FW = irrigation three times a week with fresh water; FW-TWW = irrigation three times a week with 1:1 fresh water-treated wastewater mixture; LFI = lower frequency (twice a week) but the same weekly volume of irrigation with treated wastewater. Error bars are standard deviations of the means (n = 5 for D1 of FW-TWW and D3 of LFI, and n = 6 for the others). Within a given depth, ns indicates no significant difference between the treatment and the control (TWW) according to t-test at $P < 0.05$.

UV absorbance of WEOM

In contrast to the DOC and DN concentrations, the Abs_{254} values of the extracts showed statistically significant changes compared with the control TWW irrigation (Fig. 2). When irrigation was carried out with FW or FW-TWW, Abs_{254} decreased significantly for the soil samples taken from the 0–30 and 30–60 cm depths. For extracts of the 60–90 cm soil samples, such a statistically significant decrease in Abs_{254} was noted for the FW-TWW irrigation only. Comparing LFI and the control TWW irrigation, no statistically significant difference was found regarding Abs_{254}. When applying an ANOVA test considering three groups of the data, *i.e.*, control TWW, improved water quality (FW and FW-TWW), and modified management (LFI), indeed a significant difference (a decrease) in Abs_{254} was observed in the improved water quality group as compared with the control TWW in the samples from depths 0–30 and 30–60 cm, while no significant difference was found in the 60–90 cm samples.

The UV absorbances of the extracts signified the presence (and concentrations) of a variety of light-absorbing species, and the SUVA_{254} values were considered compositional characteristics of WEOM in the soil extracts (Fig. 2). Irrigation with FW and FW-TWW led to statistically significant reduction in SUVA_{254} value as compared with the control TWW irrigation for soil extracts from the 0–30 cm depth. In the soil extracts from the 30–60 cm depth, SUVA_{254}

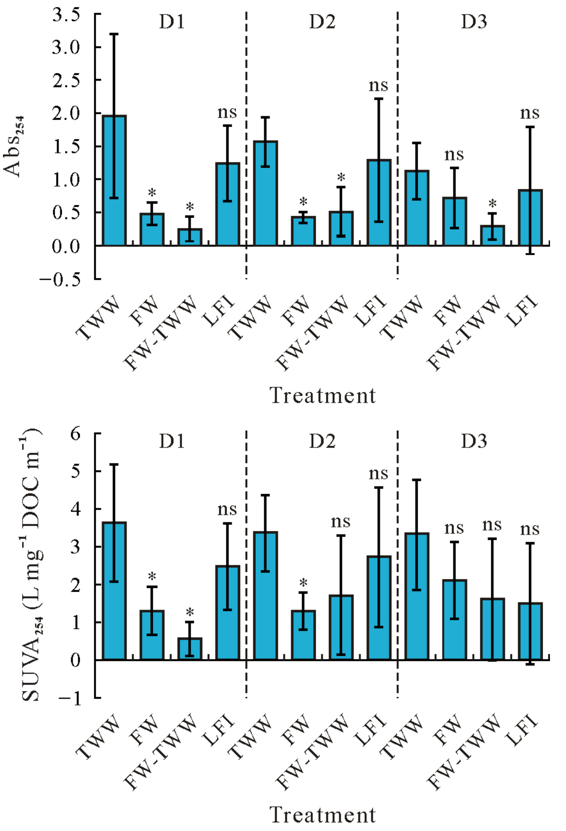

Fig. 2 Ultraviolet (UV) absorbance at 254 nm (Abs_{254}) and specific UV absorbance at 254 nm (SUVA_{254}) of the water extracts (1:10) of soils sampled in 2021 from the 0–30 (D1), 30–60 (D2), and 60–90 (D3) cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. TWW = irrigation three times a week with treated wastewater as a control ; FW = irrigation three times a week with fresh water; FW-TWW = irrigation three times a week with 1:1 fresh water-treated wastewater mixture; LFI = lower frequency (twice a week) but the same weekly volume of irrigation with treated wastewater. Error bars are standard deviations of the means ($n = 5$ for D1 of FW-TWW and D3 of LFI, and $n = 6$ for the others). Within a given depth, the asterisk (*) indicates significant difference between the treatment and the control (TWW), and ns indicates no significant difference according to t-test at $P < 0.05$. DOC = dissolved organic C.

exhibited a significant reduction in the FW irrigation. For the samples from these two depths, the ANOVA test and *post-hoc* examination confirmed that the improvement in irrigation water quality led to a significant decrease in SUVA_{254} value. No statistically significant difference regarding SUVA_{254} was noted between the soil extracts from the 60–90 cm depth samples. When comparing LFI and the control TWW irrigation, no statistically significant difference was found in SUVA_{254}.

Fluorescence emission of WEOM

The two fluorescent WEOM components identified in the soil extracts are elucidated by their EEMs in Fig. 3. The first component (C1) was characterized by an emission wavelength maximum at 450 nm and maximal excitation below 250 nm. It represented humic-like substances, widely reported in the literature (Ohno and Bro, 2006; Coble, 2007; Ishii and Boyer, 2012). Maximum fluorescence emission of the second component (C2) was located at excitation and emission wavelengths of 280 and 325 nm, respectively, which coincided essentially with tryptophan-like fluorescence. The latter is commonly linked to the presence of tryptophan-containing proteinaceous material (Ohno and Bro, 2006; Coble, 2007; Fellman *et al.*, 2008). Tryptophan, when part of protein macromolecules, is protected from exposure to a polar solvent (water) and, therefore, is characterized by emission at wavelengths that are essentially lower than that of free tryptophan (Vivian and Callis, 2001). Nevertheless, it should be noted that the excitation/emission maxima for this signal could be related to a broader list of substances, including, for example, lignin phenols, phenolic acids, and some aromatic hydrocarbons (Carstea *et al.*, 2016). Hence, although the C2 fluorescent component is believed to represent proteinaceous material, it is yet to be termed a tryptophan-like constituent.

The fluorescence intensities of components C1 and C2 at their excitation and emission maxima, *i.e.*, F1 and F2, respectively, in the extracts of the differently irrigated soils are shown in Fig. 4. In the soil extracts from all soil depths, statistically significant decreases in F1 and thus the concentration of humic-like substances were observed when using FW and the FW-TWW mixture in comparison with the TWW irrigation. A statistically significant effect of LFI regarding F1, compared with the TWW irrigation, was found in the soil extracts from the 60–90 cm depth. The ANOVA test showed that F1 value was significantly reduced in the improved water quality group as compared with the TWW control at all depths.

The tryptophan-like fluorescence (F2) and hence the expected presence of proteinaceous material (Fig. 4) showed less sensitivity to the tested treatments than the humic-like substances. Statistically significant decreases in tryptophan-like fluorescence were observed when using FW-TWW (in the 0–30 and 60–90 cm depths) and LFI (in the samples from the 60–90 cm depth) in comparison with the values obtained under TWW irrigation. The further ANOVA testing of the F2 values in the three groups (the control TWW, the improved water quality group, and the modified management) showed no statistical difference in the samples from the 0–30 and 30–60 cm depths. However, statistically significant reductions in proteinaceous material in the samples from the 60–90 cm depth were observed after the application of the two mitigation measures compared with the control.

In analogy to SUVA_{254}, the ratios between the emission intensity of each component and DOC concentration, *i.e.*, F1/DOC and F2/DOC, were also examined in the soil extracts. These ratios are supposed to reflect (*i.e.*, be proportional to) the fraction of a given fluorescent component in the

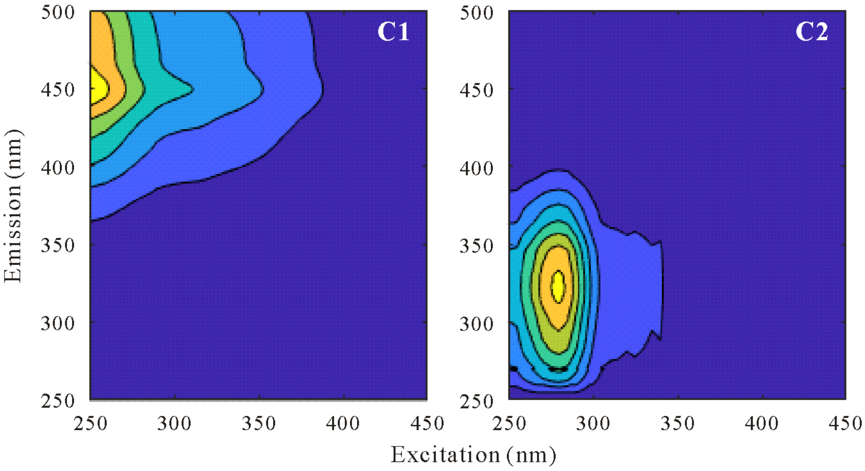

Fig. 3 Representative excitation-emission matrices of the two fluorescent water-extractable organic matter components (C1 and C2) in the water extracts (1:10) of soils sampled in 2021 from the 0–30, 30–60, and 60–90 cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. Emission intensity increases according to the color changes from blue to green, orange, and yellow.

entire WEOM. The ratio between the emission intensities of the two PARAFAC-identified components (F2/F1 ratio) is proportional to the ratio of the fractions of these components, and thus it describes the composition of the fluorescent organic matter. Both the DOC-normalized emission intensities of the components (F1/DOC and F2/DOC) and their ratios of fluorescence emissions are presented in Fig. 5.

Only a limited number of statistically significant effects on F1/DOC, F2/DOC, and F2/F1 ratio were noted (Fig. 5). Namely, compared with the control TWW irrigation, the FW-TWW irrigation led to lower values of F1/DOC in the 0–30 and 30-60 cm depths, F2/DOC in the 0–30 and 60–90 cm depths, and F2/F1 ratio in the 0–30 cm depth. The LFI treatment, in only two cases, led to significant decreases in F2/DOC and F2/F1 values in the extracts from the 60–90 cm depth. The ANOVA test of differences within the three groups of data showed that the fraction of humic-like substances in the whole DOC (*i.e.*, F1/DOC) was significantly reduced in the samples from the 0–30 and 60–90 cm depths compared with the TWW irrigation when improved quality water was applied. In this comparison, the LFI management led to significant decreases of the fractions of humic-like and proteinaceous components in samples from the 60–90 cm depth.

TOC, TIC, and TN contents of soil samples

Soil TOC content was generally indifferent to changing irrigation water quality or management (Fig. 6). Only in the case of FW-TWW irrigation, TOC decreased significantly in the samples from the 60–90 cm depth. Compared with the control TWW irrigation, the TN content in LFI decreased significantly in the samples from both the 0–30 and 60–90 cm depths. Yet, under change in water quality, TN content decreased significantly compared with that in the control TWW irrigation only in the samples from the 60–90 cm depth. No effect of the treatments was found in TIC content (data not shown), which varied, depending on treatment and depth, between 16.4 ± 8.5 and 21.3 ± 5.7 g kg^{-1}. The ANOVA examination of the differences between the control TWW irrigation, the improved water quality group, and the modified management (LFI) showed no difference in TOC content in all three depths. The only statistically significant difference was found in TN content for the improved water quality group compared with the control TWW irrigation in the samples from the 60–90 cm depth and LFI in the samples from the 60–90 cm depth.

FTIR spectrum decomposition

Decomposition of soil FTIR spectra yielded four components, *i.e.*, K1–K4. The FTIR spectra, representing the loading (absorbance in arbitrary unit) against wavenumber, for each of the four components are presented in Fig. 7. The K1 component included calcium carbonate with characteristic peaks at 2 515, 1 431, 876, and 716 cm^{-1} (Reeves III, 2010; Bruckman and Wriessnig, 2013). This component included also the fingerprints of O–H stretching (3 429 cm^{-1}) in water and carboxyl and hydroxyl groups (Ouatmane *et al*., 2000; Ellerbrock and Gerke, 2004; Simkovic *et al*., 2008), C–H stretching (2 875 cm^{-1}) of CH_3 and CH_2 groups (Ellerbrock and Gerke, 2004; Simkovic *et al*., 2008), and absorbance at 1 026 cm^{-1} that may be related to Si–O stretching (Nguyen *et al*., 1991; Ravisankar *et al*., 2011) and various organic functionalities, such as in-plane bending of the aromatic ring C–H bonds, the C–O stretching in alcohols, ethers, phenols, carboxylic acids, esters, and polysaccharides, and C–N stretching in amines (Silverstein and Webster, 1998;

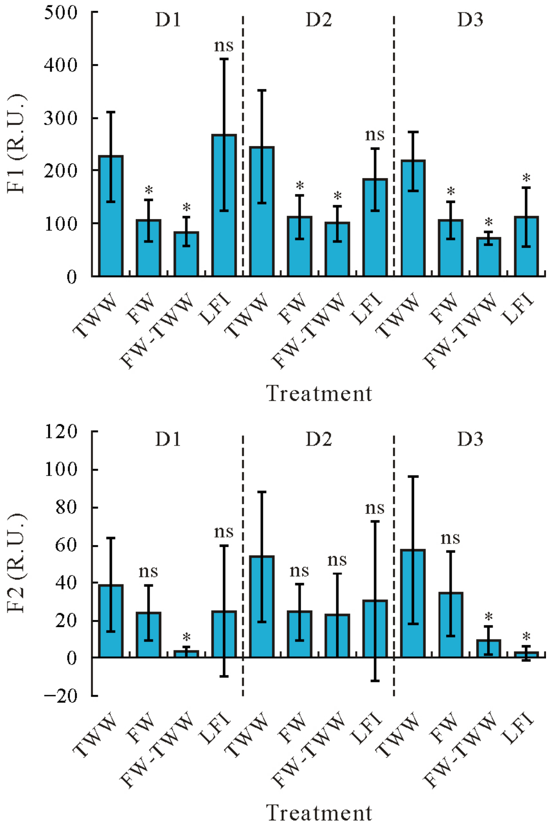

Fig. 4 Fluorescence intensities of humic-like (F1) and tryptophan-like (F2) components at their excitation and emission maxima in the water extracts (1:10) of soils sampled in 2021 from the 0–30 (D1), 30–60 (D2), and 60–90 (D3) cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. TWW = irrigation three times a week with treated wastewater as a control; FW = irrigation three times a week with fresh water; FW-TWW = irrigation three times a week with 1:1 fresh water-treated wastewater mixture; LFI = lower frequency (twice a week) but the same weekly volume of irrigation with treated wastewater. Error bars are standard deviations of the means (n = 5 for D1 of FW-TWW and D3 of LFI, and n = 6 for the others). Within a given depth, the asterisk (*) indicates significant difference between the treatment and the control TWW treatment, and ns indicates no significant difference according to t-test at $P < 0.05$. R.U. = Raman unit.

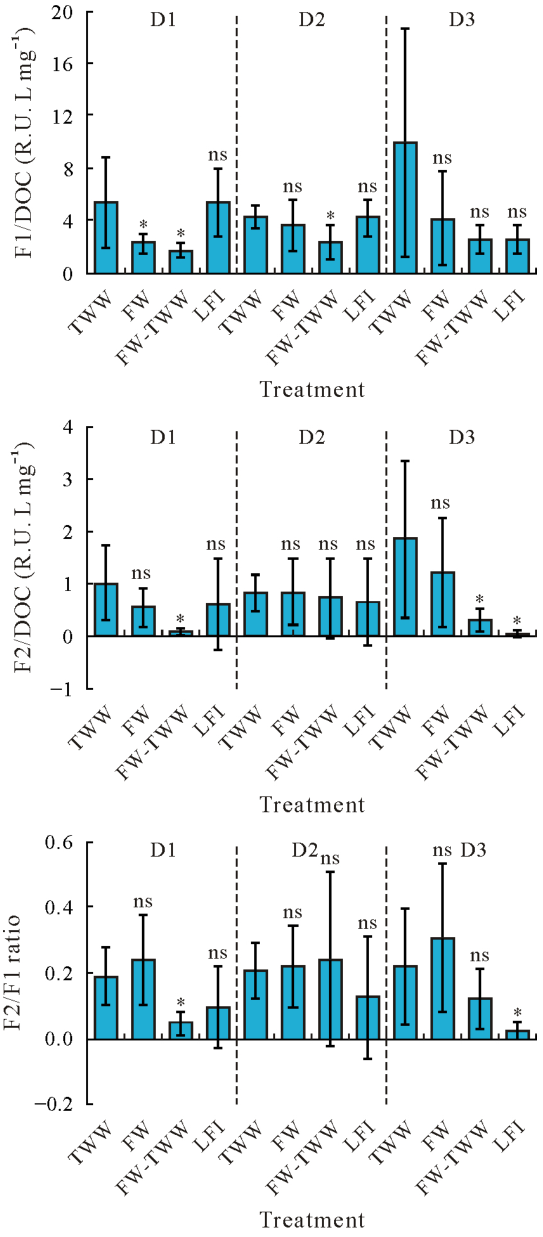

Fig. 5 Dissolved organic C (DOC)-normalized fluorescence intensities of the humic-like (F1/DOC) and tryptophan-like (F2/DOC) components at their excitation and emission maxima and the fluorescent intensity ratio (F2/F1) of these two components in the water extracts (1:10) of soils sampled in 2021 from the 0–30 (D1), 30–60 (D2), and 60–90 cm (D3) depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. TWW = irrigation three times a week with treated wastewater as a control; FW = irrigation three times a week with fresh water; FW-TWW = irrigation three times a week with 1:1 fresh water-treated wastewater mixture; LFI = lower frequency (twice a week) but the same weekly volume of irrigation with treated wastewater. Error bars are standard deviations of the means (n = 5 for D1 of FW-TWW and D3 of LFI, and n = 6 for the others). Within a given depth, the asterisk (*) indicates significant difference between the treatment and the control (TWW), and ns indicates no significant difference according to t-test at $P < 0.05$. R.U. = Raman unit.

Tarchitzky *et al*., 2007). The K2 component demonstrated absorbance at 3 445 cm^{-1}, representing water and hydroxyls and a band with the maximum at 1 640 cm^{-1} characteristic of C=O stretching vibrations in amides (amide I band), asymmetric stretching vibrations of COO$^-$, bending of hydration water of soil phyllosilicates, hydrogen (H)-bonded C=O of carbonyl, and stretching of C=C conjugated with other non-saturated groups (Silverstein and Webster, 1998; Spaccini *et al*., 2001; Ellerbrock and Gerke, 2004; Ellerbrock and Kaiser, 2005; Hay and Myneni, 2007; Simkovic *et al*., 2008).

The K3 component represented a mixture of both inorganic (mainly clay) and organic constituents. Clay signatures, particularly 1:1 clays, were noticeable by peaks at 3 696 cm^{-1} (attributed to octahedral OH groups forming H bonds with O in tetrahedral layers), 3 622 cm^{-1} (OH between octahedral and tetrahedral layers), 1 107 cm^{-1} and

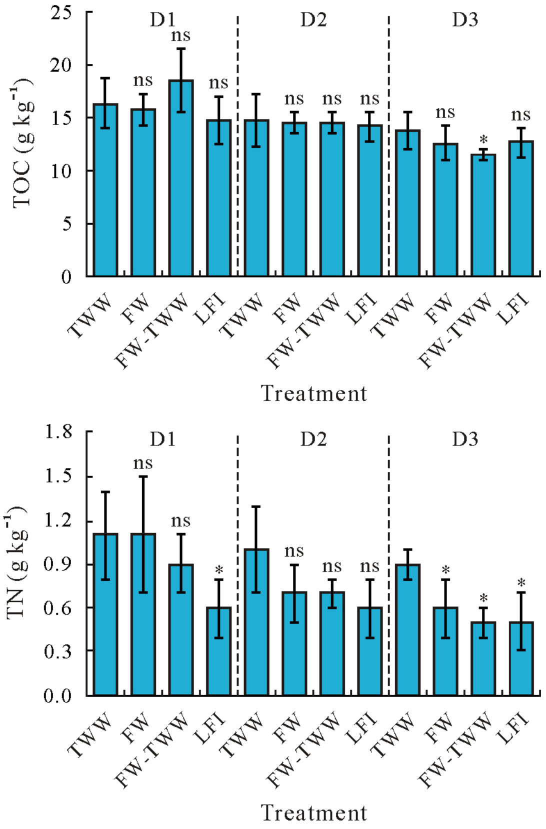

Fig. 6 Soil total organic C (TOC) and N (TN) contents at 2021 at the 0–30 (D1), 30–60 (D2), and 60–90 (D3) cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. TWW = irrigation three times a week with treated wastewater as a control; FW = irrigation three times a week with fresh water; FW-TWW = irrigation three times a week with 1:1 fresh water-treated wastewater mixture; LFI = lower frequency (twice a week) but the same weekly volume of irrigation with treated wastewater. Error bars are standard deviations of the means (n = 5 for D1 of FW-TWW and D3 of LFI, and n = 6 for the others). Within a given depth, the asterisk (*) indicates significant difference between the treatment and the control (TWW) , and ns indicates no significant difference according to t-test at $P < 0.05$.

991 cm^{-1} (SiO groups of kaolinite), and 891, 777, 692, 570, and 433 cm^{-1} (Madejová, 2003), with quartz appearance at 777 cm^{-1} (Hanna, 1965; Bosch Reig *et al.*, 2002; Ravisankar *et al.*, 2011) and overtones and combination bands of quartz and silicates at 1 869 cm^{-1} (Nguyen *et al.*, 1991; Calderón *et al.*, 2011). Organic signatures were found at 3 014 cm^{-1} (aliphatic C–H stretches), 1 618 cm^{-1} (carbonyl and carboxyl groups, C=C stretch, *i.e.*, similar to those abovementioned at 1 640 cm^{-1} in component K2), and 991 and 1 107 cm^{-1} of in-plane aromatic C–H bending and C–O stretching, respectively (Silverstein and Webster, 1998; Ellerbrock and Gerke, 2004; Simkovic *et al.*, 2008; Parikh *et al.*, 2014). Component K4 was related to the presence of clay minerals, with a peak at 1 031 cm^{-1} indicating the stretching of Si–O bonds in 2:1 clays (Parikh *et al.*, 2014), probably smectites. The peaks at 534 and 467 cm^{-1} were related to Si–O–Al and Si–O–Si bending vibrations, respectively (Madejová, 2003). The concentration score ratios between different combinations of components were examined and compared between the different treatments (Fig. 8). Virtually in all the comparisons, the concentration score ratios were insensitive to changes in water quality (*i.e.*, FW and FW-TWW irrigation) and management (LFI).

DISCUSSION

Effects of irrigation water quality

There are multiple studies in which the reported effects of TWW irrigation on soil TOC content were inconsistent. In some studies, TWW containing organic matter resulted in a certain increase in soil TOC content (Jueschke *et al.*, 2008; Chen *et al.*, 2010; Morugán-Coronado *et al.*, 2011; Borisover *et al.*, 2012; Bernier *et al.*, 2013; Sánchez-González *et al.*, 2017; Lyu *et al.*, 2022), whereas in others, a decrease in TOC content was noted and ascribed to a "priming effect" (Jueschke *et al.*, 2008; Ganjegunte *et al.*, 2019; Chaganti *et al.*, 2021). The specific impact of TWW irrigation on soil TOC content is expected to depend on the type of TWW and its organic matter load, duration of irrigation, soil type, climate zone, land use, and other factors.

Introducing FW leads to reduced input of organic matter to the soil compared with the control TWW irrigation. Hence, the lack of significant changes in soil TOC content after switching from TWW to irrigation water containing FW (Fig. 6) is understood as an indication that either the overall input of organic matter by TWW was minor or a steady state was reached such that leaching and biological consumption of organic matter balanced its addition by TWW irrigation, and, hence, introducing FW for irrigation did not change this balance. Since changes in water quality also had no effect on DOC concentration in the extracts of the soils from all three depths (Fig. 1), it appears that leaching could not be a mechanism responsible for maintaining such a steady state and the absence of TOC sensitivity to irrigation water quality.

A distinct effect was that UV-absorbance characterized by Abs$_{254}$ value was significantly lower in the presence of FW (both in the FW and FW-TWW irrigation), in five out of the six combinations of irrigation water quality and depth studied relative to that in the TWW irrigation (Fig. 2). The improved quality of irrigation water (FW and FW-TWW), compared with TWW, led to the decrease in Abs$_{254}$ value at the 0–30 and 30–60 cm depths. The same was correct regarding SUVA$_{254}$ albeit, in paired comparisons, SUVA$_{254}$ decreased in the presence of FW in a fewer number of water quality-depth combinations.

Commonly, SUVA$_{254}$ is linked to the aromaticity of organic matter (Zhang *et al.*, 2011; Nkhili *et al.*, 2012; Guigue

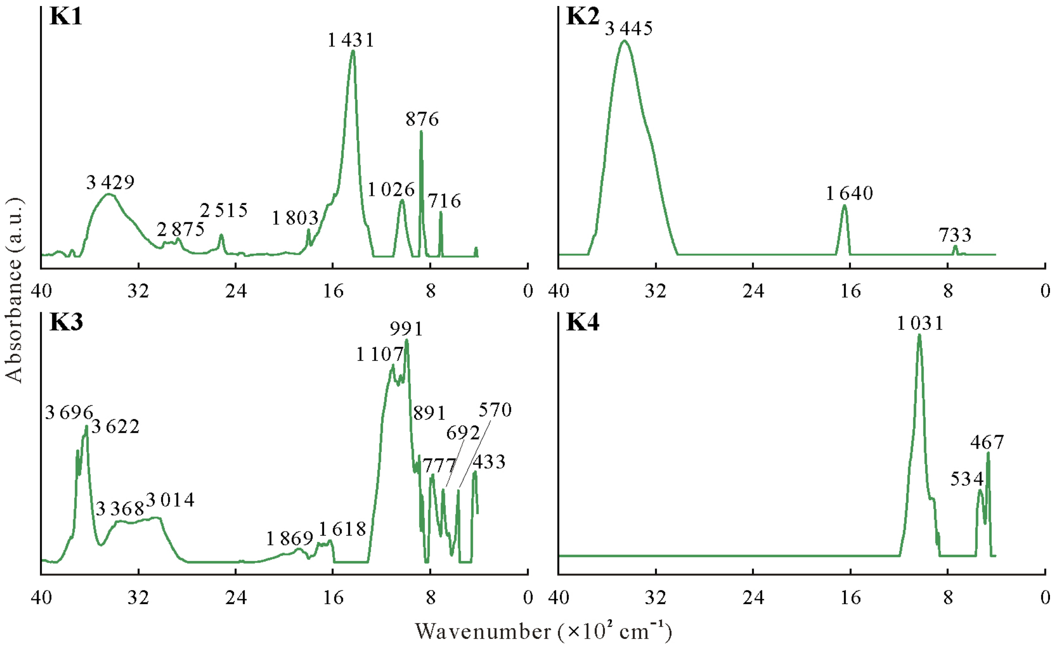

Fig. 7 Representative Fourier-transform infrared (FTIR) spectra of the four nonnegative matrix factorization components (K1, K2, K3, and K4) extracted from the FTIR spectra of the soils sampled in 2021 from the 0–30, 30–60, and 60–90 cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. a.u. = arbitrary unit.

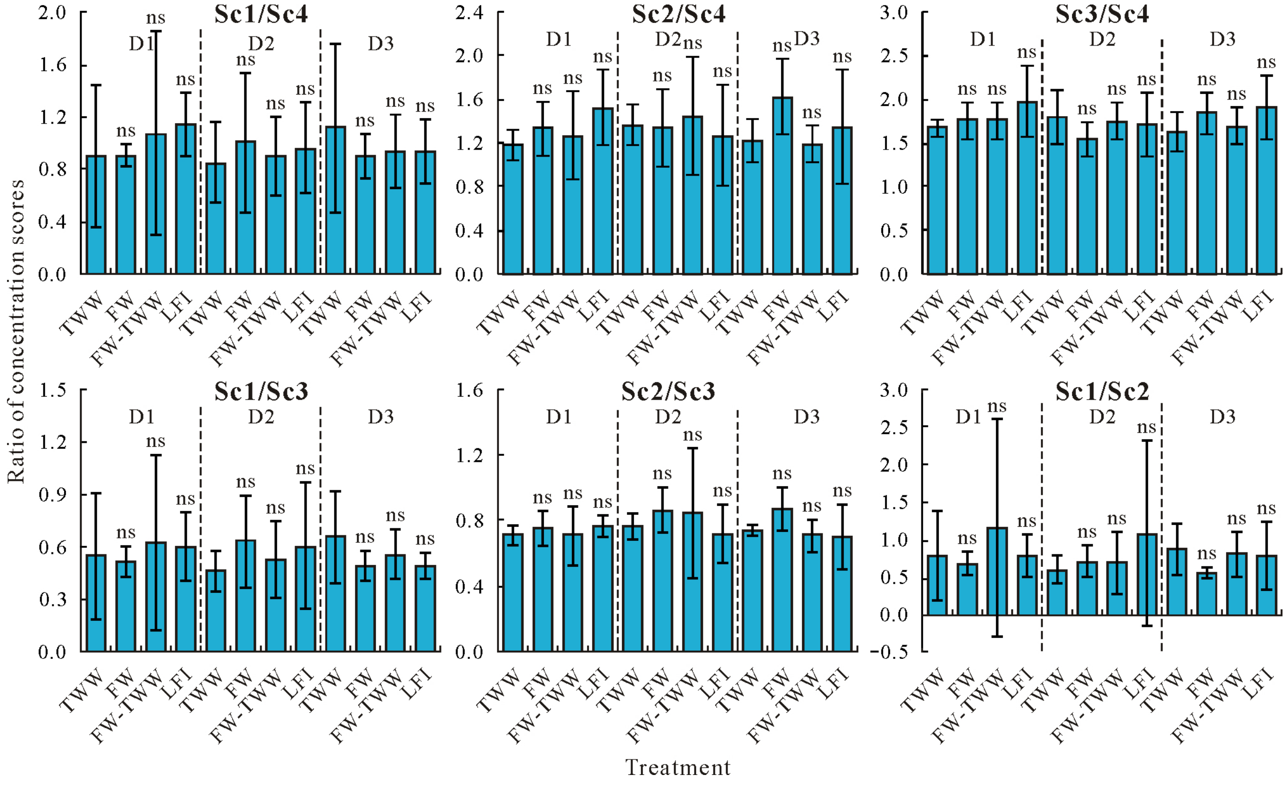

Fig. 8 Ratios of concentration scores (Sc1, Sc2, Sc3, and Sc4) of the nonnegative matrix factorization components (K1, K2, K3, and K4, respectively) identified from the Fourier-transform infrared spectra of soils sampled in 2021 from the 0–30 (D1), 30–60 (D2), and 60–90 (D3) cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. TWW = irrigation three times a week with treated wastewater as a control; FW = irrigation three times a week with fresh water; FW-TWW = irrigation three times a week with 1:1 fresh water-treated wastewater mixture; LFI = lower frequency (twice a week) but the same weekly volume of irrigation with treated wastewater. Error bars are standard deviations of the means ($n = 5$ for D1 of FW-TWW and D3 of LFI, and $n = 6$ for the others). Within a given depth, ns indicates no statistically significant difference between the treatment and the control (TWW) according to t-test at $P < 0.05$.

et al., 2014). For example, this association is reflected in a strong correlation of SUVA$_{254}$ with the ^{13}C nuclear magnetic resonance (NMR)-detected percentage of C involved in the aromatic structures (and non-saturated bonds with other C atoms) in humic substances (Weishaar *et al.*, 2003). In addition, SUVA$_{254}$ correlated with the ^{1}H NMR-quantified fraction of H atoms linked to the aromatic C in soil-extracted organic matter (Fernández-Romero *et al.*, 2016). Hence, Abs$_{254}$ represents (is proportional to) the concentration of aromatic substances (*e.g.*, expressed as "aromatic" C) in solution.

It cannot be assumed that Abs$_{254}$ could be contributed by nitrate in the solution. Even if all the determined DN that reached the upper concentration level of 4.0 ± 1.1 mg L^{-1} in the extracts would represent nitrate, the latter would contribute to the absorbance at 254 nm by a value less than 4×10^{-4} (Weishaar *et al.*, 2003).

The differences in the sensitivities of DOC concentration and Abs$_{254}$ to changes in water quality could hardly be explained by the variability among the field replications. Figure 9 depicts the coefficient of variation (CV), standard deviation normalized by mean, of DOC concentration plotted against that of Abs$_{254}$ for each combination of treatment and depth. It can be seen that in all cases but two (Points A and B in Fig. 9), the DOC variability (expressed as CV) was similar to or lower than that of Abs$_{254}$. Notably, the two cases in which the variability of DOC exceeded that of Abs$_{254}$ represented the samples from the 30–60 cm depth irrigated with FW and TWW (*i.e.*, the control treatment). It appeared that UV-absorbing substances did not dominate the WEOM, and the changes in their concentrations were masked in the DOC measurements by the variabilities in the concentrations of other WEOM components (in particular, those not absorbing at 254 nm).

The response of humic-like fluorescence in the soil extracts, *i.e.*, the concentration of humic-like substances (Fig. 4), to the changes in irrigation water quality resembled that of UV-absorbance (Fig. 2). The similarity in responses between Abs$_{254}$ and F1 may not be surprising considering that the excitation maximum of aromatic humic-like substances was situated in the UV range (Fig. 3). For example, the correlations between fluorescence emission of humic-like substances and absorbance of DOM were reported for different systems in the past (Luek *et al.*, 2017; Sharma *et al.*, 2017; Sgroi *et al.*, 2020). Also, in an earlier study of ours, examining the effect of TWW *versus* FW irrigation on soil WEOM composition in a series of soils (Borisover *et al.*, 2012), it was found that the direction of changes, *i.e.*, the increase or decrease in the fluorescence emission of humic-like substances and UV absorbance of soil extracts, depended on whether the soils were coarse- or fine-textured. However, regardless of soil texture, the changes in fluorescence intensity and absorbance occurred in parallel. Indeed, when testing the relation between the F1 and Abs$_{254}$ averages of all the soil extracts studied in our study, differing only by irrigation water quality, a statistically significant correlation was found with $r^2 = 0.87$ ($P < 0.001$). The similar response of the concentrations of humic-like substances in the soil extracts and those absorbing light in the UV range to the improved water quality is also clearly demonstrated in Fig. 10, where the means of the F1 values are plotted against those of the Abs$_{254}$ values, resulting in a correlation with $r^2 = 0.87$ ($P = 0.000\,3$). There is a distinct separation between the data of the control samples (the TWW irrigation) and those of the improved water quality group. Improvement in the irrigation water quality reduced both the F1 and Abs$_{254}$ values.

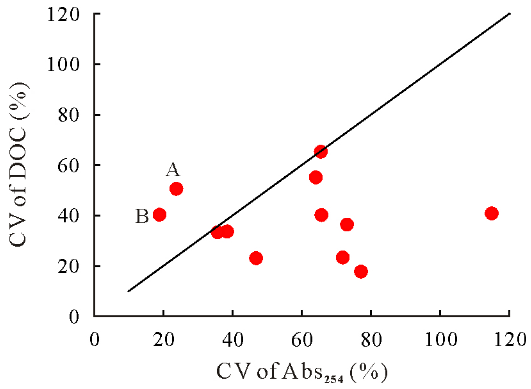

Fig. 9 Coefficients of variation (CVs) of dissolved organic C (DOC) concentrations *versus* CVs of ultraviolet absorbances at 254 nm (Abs$_{254}$) of the water extracts (1:10) of soils sampled in 2021 from the 0–30, 30–60, and 60–90 cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. The line represents a 1:1 relation. Point A represents the samples from the 30–60 cm depth in the treatment of irrigation three times a week with treated wastewater, and point B represents the samples from the 30–60 cm depth in the treatment of irrigation three times a week with fresh water.

The decreases in the concentrations of water-extractable UV-absorbing and humic-like light-emitting constituents in the extracts from soils irrigated by FW or FW-TWW, as compared with the TWW irrigation, cannot be related to the differences in SOM dissolution/desorption caused by changes in solution pH. The pH values of the extracts are reported in Fig. S1a (see Supplementary Material for Fig. S1). The data showed no statistically significant difference in the extract-derived pH values across treatments/depths, in agreement with similar observations for soil extracts from earlier samplings (2017–2018) in the same field experiment (Nemera *et al.*, 2023). The variability among field replicates exceeded the differences between the pH means in the treatments, where for each soil depth, the range of pH means did not exceed 0.2. Figure S1b reports the data on the EC values of the extracts. Relative to the EC values of the extracts from

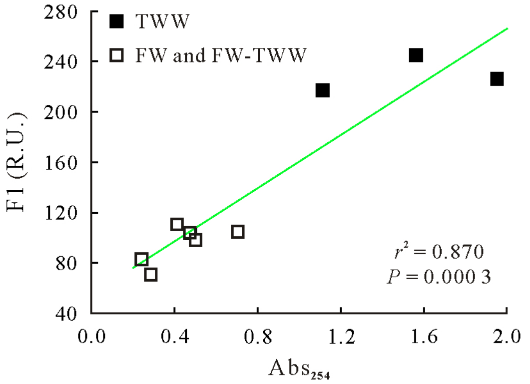

Fig. 10 Correlation between the means of fluorescence intensities of humic-like substances (F1) and the means of ultraviolet absorbances at 254 nm (Abs_{254}) of the water extracts (1:10) of soils sampled in 2021 from the 0–30, 30–60, and 60–90 cm depths of the different irrigation treatments of a six-year (2016–2021) field experiment conducted in an avocado orchard in the Western Galilee (Kibbutz Yasour), Israel with a history of secondary treated wastewater irrigation since 2009. TWW = the control treatment of irrigation three times a week with treated wastewater; FW = irrigation three times a week with fresh water; FW-TWW = irrigation three times a week with 1:1 fresh water-treated wastewater mixture. R.U. = Raman unit.

the TWW-irrigated soils, there was a slight decrease in the EC values of the extracts from the FW-irrigated soils taken at the 30–60 cm depth. However, in general, no detectable difference was found between the EC values, and no consistent effects that could link the EC data to the changes in Abs_{254} and F1 could be detected. Hence, it is unlikely that the differences in ionic strength of the extracts could lead to the differences in WEOM composition responsible for the studied optical properties between the TWW control and FW-containing treatments. The decreases in Abs_{254} and F1 values in soil extracts, following irrigation with FW or FW-TWW, could indicate a retarded formation of water-soluble aromatic and humic-like matter, compared with the TWW irrigation. An alternative explanation could be that when irrigating with FW or FW-TWW, water-soluble aromatic and humic-like constituents contributing to UV absorbance and fluorescence undergo an intensive degradation, thus reducing their presence in water extracts. This latter explanation is supported by suggestions in the literature that decrease in the UV absorbance of extracts from various manure samples is linked to decomposition of aromatic and phenolic compounds with C=C and C=O double bonds (Waldrip *et al.*, 2014) and the decrease in fluorescence of humic-like substances in paddy soil extracts is caused by decomposition of recalcitrant SOM (Su *et al.*, 2023). Future work may help in better understanding whether change from TWW irrigation to irrigation with improved water quality could lead to enhanced degradation of water-soluble aromatic and humic-like constituents contributing to UV absorbance and fluorescence.

Tryptophan-like fluorescence expressed as F2 did not show a systematic and consistent response to the presence of FW in the irrigation water (Fig. 4). When irrigation was performed using FW-TWW mixture, there was a decrease in the concentration of tryptophan-like light-emitting species in the extracts from two depths out of three, as compared with the control samples. However, no effect was found when FW irrigation was applied. It is difficult to explain the generally non-consistent response of tryptophan-like fluorescence to the presence of FW in irrigation water. One might hypothesize that the combined use of FW and TWW could affect soil microbial activity, as compared with TWW irrigation, and influence the interplay between the formation of water-soluble enzymatic matter containing tryptophan and its further degradation.

No difference in the FTIR-active soil components was observed when varying irrigation water quality (Fig. 8). The ideal case would be that the different NMF components containing a mixture of FTIR spectral features of inorganic and organic constituents would appear in different proportions in the soil samples, depending on a specific irrigation treatment. These different proportions might appear due to changes in SOM affected by changes in irrigation water quality or soil management. There are multiple indications in the literature that TWW irrigation affects SOM composition. For example, hydrophobic organic matter may be accumulated in soils, thus inducing soil water repellence (Wallach *et al.*, 2005; Nadav *et al.*, 2013; Tolkin *et al.*, 2020). Chen *et al.* (2010) indicated that TWW irrigation enriched soil with humic acids characterized by high H/C atomic ratios and reduced contents of carboxylic and phenolic groups. Alternatively, Sánchez-González *et al.* (2017) suggested that SOM becomes more hydrophilic with wastewater irrigation. Hence, the lack of an effect of irrigation water quality on the ratios of concentration scores in Fig. 8 could be interpreted as an indication that mitigation attempts, *e.g.*, using water of improved quality, applied during the six years had no impact on the whole SOM composition. However, most probably, the components' FTIR absorbance spectra, decomposed by NMF analysis, were dominated by soil mineral components, which are not expected, for a single soil, to be considerably modified by the irrigation treatments or depth. Hence, the ratios of the component concentration scores in Fig. 8 were controlled mainly by the absorbance of mineral components and were independent of irrigation treatments and soil depth. Moreover, the lack of change in soil TOC content (Fig. 6) contributed to the lack of difference in component concentration score ratio between different irrigation treatment/soil depth combinations. Thus, potential variability in SOM composition remained hidden in the current examination using NMF decomposition of the FTIR spectra of soil samples.

Management effect

In the LFI treatment, the same water quality (TWW) and volume as in the TWW control were used on a weekly basis, but at a reduced frequency (*i.e.*, irrigation twice a week instead of three times a week). This was expected to impose on the wetted area a lower average moisture content and thus better aeration (Nemera *et al.*, 2023), and possibly result in a lower load of organic C at the 0–90 cm depth due to the greater leaching fraction. Yet, the LFI treatment demonstrated generally weak effects (if at all). Thus, compared with the control TWW irrigation, LFI generally showed no effects on the concentrations of DOC, which was in agreement with a similar observation (Nemera *et al.*, 2023), DIC, DN, Abs_{254}, and SUVA_{254} of the soil extracts, humic-like fluorescence except the samples from the 60–90 cm depth, TIC and TOC of the soil samples, and the concentration score ratios of components identified from the soil FTIR spectra (Figs. 2, 4, 6, and 8). A few noted effects of LFI included the decrease in tryptophan-like fluorescence as well as in DOC-normalized tryptophan-like fluorescence in the deepest 60–90 cm soil layer (Fig. 5). Only the decrease in soil TN content seemed to be larger with LFI compared with the control TWW irrigation (Fig. 6), which might suggest that nitrogen is a limiting factor in the microbial transformation of organic matter (Averill and Waring, 2018; Cui *et al.*, 2022), resulting in less degradation of SOM, when the frequency of TWW irrigation was reduced. It can be argued that the expected reduction in average moisture content did not result in a subsequent increase in aeration with LFI, and thus did not exert an effect on organic matter at a rate adequate to produce meaningful impacts over the six years of the study. Indeed, for the same field experiment, Nemera *et al.* (2023) showed even lower oxygen concentrations in the soil under LFI on the irrigation days as compared with the control, whereas no difference was observed between irrigation events. In addition, no effect was found for LFI on soil aggregate stability (Nemera *et al.*, 2023).

Some potential agricultural and environmental implications

In this study, we hypothesized that soil WEOM characteristics could be sensitive to replacing regular TWW irrigation with other irrigation water qualities and conditions favoring soil aeration. Indeed, when the new treatment involved the use of FW or FW-TWW mixture, such sensitivity was found for UV absorbance and some fluorescence emission characteristics of soil extracts, but not for DOC concentration. Notably, in a recent study (Rinot *et al.*, 2021) in which land use and climatic region effects on soil WEOM were examined, a similar pattern was noted, namely, DOC concentrations in soil extracts were not affected by land use, climatic region, or the interaction of these factors, whereas Abs_{254} (as well as SUVA_{254}) was found sensitive to climatic region and land use-climate region interaction. Light emission intensities of some PARAFAC-identified fluorescent components showed even greater sensitivity to land use, climatic region, and their interaction. Thus, the results of our study provide further support for the use of optical properties of WEOM, as distinct from DOC concentration in soil extracts, as indicators for changes in soil WEOM caused by anthropogenic activities. However, it should be borne in mind that this specific research was performed on a soil from one site characterized by a specific climate. Therefore, more data collected in experiments performed under different conditions would be helpful to further examine the optical properties of soil extracts in terms of their sensitivity to anthropogenic effects in comparison with the DOC concentration. In addition, our results clearly indicate that Abs_{254} could not be considered a proxy for DOC concentrations in the soil extracts studied.

The decrease in UV absorbance and humic-like fluorescence emission in soil extracts, observed in our study and associated with replacing TWW with FW or FW-TWW for irrigation, indicates changes in the concentrations of water-soluble aromatic compounds. Such a decrease in concentrations of aromatic constituents in the soil extracts may suggest important changes in the soil ecosystem, *e.g.*, increased biodegradation of organic matter in the soil solution (Marschner and Kalbitz, 2003; Toosi *et al.*, 2012), a reduction in the recognized ability of water-soluble organic matter to bind heavy metals (Amery *et al.*, 2007; Araújo *et al.*, 2019) and therefore diminished subsurface transport of metals, and changes in photosensitizing properties of organic matter (Nkhili *et al.*, 2014). Furthermore, a decrease in the aromaticity of WEOM in soil extracts correlates with the decrease in the aromaticity of soil particulate organic matter (Filep *et al.*, 2022). Chromophoric DOM can form complexes with calcium ions (Gao *et al.*, 2015; Liu *et al.*, 2021). Hence, the decrease in the concentration of UV- and fluorescence-active (*i.e.*, chromophoric) organic matter in soil extracts may indicate a lesser fraction of calcium complexed with organic matter and, therefore, a decreased exchange in clayey soils by soluble sodium. The latter would trigger a decrease in soil clay sensitivity to dispersion and the subsequent harm to soil structure, commonly resulting from sodium exchanging calcium in clay minerals (Assouline and Narkis, 2013; Bardhan *et al.*, 2016).

Changes in soil WEOM characteristics may hint at a lack of reversibility in the ability of SOM to release water-soluble organic matter, caused by a specific sequence of the use of irrigation water of different qualities. This may be illustrated by recalling an earlier study (Borisover *et al.*, 2012) in which soil WEOM was studied in an avocado plantation in the Western Galilee (Israel), near the one used in the present study, and in a similar soil type. In that orchard studied, irrigation by secondary TWW was performed for at least five years (following long-term irrigation with FW), and WEOM properties were compared with those from a soil taken from an adjacent plantation irrigated with FW. The irrigation with TWW led to a reduction in Abs_{254} and emission intensities of WEOM fluorescent components in a soil extract from the 0–20 cm depth, as compared with FW irrigation. This observation implies that, compared with FW irrigation, TWW irrigation resulted in a lower concentration of aromatic and fluorescent WEOM components in a clayey soil extract. Hence, switching to irrigation with FW (or FW-TWW) after a previous long-term TWW irrigation could be expected to reverse the changes in optical WEOM indicators and associated concentrations of WEOM constituents in soil extracts. Since such a reverse in optical WEOM indicators did not occur, one may, therefore, postulate that the order in which irrigation water of different qualities is used could lead to irreversible effects in the concentrations of SOM constituents in soil extracts.

CONCLUSIONS

Irrigation with FW and FW-TWW, or LFI with TWW of soil following a long-term history of secondary TWW irrigation had no significant impacts on soil TOC content, concentrations of DOC, DIC, and DN in soil extracts, and compositional soil characteristics determined using NMF decomposition of FTIR spectra, compared with the control TWW irrigation. The lack of influence was distinct virtually in all comparisons for soil samples and extracts from three different depths, *i.e.*, 0–30, 30–60, and 60–90 cm. Of all properties and indices studied, the most consistent and general responses to the irrigation water quality were obtained in UV absorbance (at 254 nm) and fluorescence emission intensities of humic-like components in the soil extracts. Accumulation of water-soluble aromatic and humic-like SOM components could be retarded when irrigation water of improved quality was used to mitigate the effects of long-term TWW irrigation. However, no marked response of UV absorbance (at 254 nm) and fluorescence emission intensity of humic-like components was found in soil extracts due to the change in irrigation management. Neither UV absorbance nor humic-like fluorescence can provide a proxy for DOC concentrations in the soil extracts studied, and *vice versa*. Tryptophan-like fluorescence (representing the concentration of proteinaceous matter in soil extracts), the relative composition of fluorescent WEOM and DOC-normalized fluorescence emission provided less distinct and systematic responses, compared with UV absorbance and humic-like fluorescence, to changes in irrigation water quality and management.

Our study provides further support for using optical properties of soil extracts, rather than DOC concentration, as sensitive descriptors useful for evaluating soil responses under different agricultural scenarios and, in particular, as indicators for changes induced by irrigation water quality when intending to mitigate TWW ill-effects. However, additional studies performed with other soils under different climatic conditions are needed to further support our observations.

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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SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version.

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