Effect of irrigation water quality on soil properties and infrared spectroscopic signatures

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Abstract

Aim of study: To study the effect of irrigation with medium-to-low-quality water on an olive farm that seems to be causing salinity and/or sodicity problems in soils, and the ability of infrared spectroscopy to detect this problem.

Area of study: The study was conducted in an olive (Olea europaea L.) grove located in Guarromán (Jaen, Spain), on the boundary of the Sierra Morena Mountains and the Guadalquivir Depression.

Material and methods: The olive farm is cultivated over two soil typologies, a calcareous area (carbonated) dominated by Regosols and a siliceous area with Leptosols. Typical soil physical and chemical parameters were determined, as well as near and mid infrared spectra were collected for analysis.

Main results: Soil physical properties were affected by irrigation, with low infiltration rates and symptoms of structural degradation. Chemical properties were also altered, showing high pH, low amounts of organic carbon and N, and high sodium concentrations. These effects were stronger in the samples directly affected by the irrigation bulb, with the siliceous soils more affected than carbonated, probably due to the positive effect of the higher amounts of calcium in the latter. Using infrared spectroscopy, it was possible to discriminate the samples of this farm affected by sodicity from similar soil samples in Jaen province not affected.

Research highlights: the use of medium-to-low quality irrigation water affected soil physical and chemical properties. Infrared spectroscopy could be useful for quick assessment of soil quality and soil degradation from salinity and sodicity.

Additional keywords: Olea europaea L.; soil degradation; fertility; olive groves; irrigation; sodicity.

Abbreviations used: CEC (cation exchange capacity); EC (electrical conductivity); ESP (exchangeable sodium percentage); FTIR (Fourier-transform mid-infrared); IR (infrared); NIR (near infrared); OC (organic carbon); OM (organic matter); PCA (principal component analysis); RSC (residual sodium carbonate); SAR (sodium adsorption ratio).

Authors’ contributions: Conceived, designed and performed the experiments: VA, AD. Acquisition of the data: AD, FC. Analyzed the data: FC, VA, MJAC, ADV. Contributed reagents/materials/analysis tools: AD, VA, MJAC, ADV. Wrote the paper: FC, VA, MJAC, ADV. All authors read and approved the final manuscript.

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Introduction

Soil salinity and sodicity are growing problems affecting soil worldwide, and are considered one of the major soil degradation threats in Europe (Dalia-kopoulos et al., 2016). Saline and sodic soils cover 932.2 Mha worldwide, and about 31 Mha in Europe alone (Rengasamy, 2006). Soil salinity generates an imbalance in nutrient amounts, usually a deficit (Gra-ttan & Grieve, 1998), as well as a decrease in biological activity and unbalanced biogeochemical cycles (Rietz & Haynes, 2003; Zeng et al., 2013). Soil salinity reduces the osmotic potential of the soil, water potential reducing its gradient between soil solution and the root interior, and, consequently, the plant water uptake which ends up affecting vegetative growth (Shannon
& Grieve, 1998; Setia et al., 2013) and even causing the plant death (Aragüés et al., 2005). Furthermore, high concentrations of some ions, such as sodium, chloride or boron, can cause toxicity and reduce uptake of nutrients (Hardie & Doyle, 2012). High sodium concentration in the soil solution generate other problems, such as dispersion of clays (Sumner, 1993), rapid decomposition of organic matters in the soil (Nelson & Oades, 1998) and soil structure degradation, crusting and sealing, limiting water infiltration (Amekzeta et al., 2003).

The Mediterranean basin is a semi-arid area whose most important crop is the olive (Olea europaea L.) tree. This climate zone is characterized by a long dry and hot season and a rainy season with scarce and highly irregular events. Water is the main limiting factor of production in olive groves (Garcia-Tejero et al., 2017). Therefore, olive trees respond very well to an additional water supply, such as deficit irrigation (Ruiz-Sanchez et al., 2010). However, it is important to characterize the water used for irrigation so its effects on the crop are known (Melgar et al., 2009), since the use of poor-quality irrigation water with a high concentration of salts, particularly sodium, could cause salinization and/or sodification of soils (Qadir & Oster, 2004; Jalali et al., 2008). This problem is accentuated in arid and semi-arid climates, where the leaching and transport of soluble salts is not as efficient as in humid regions (Gorji et al., 2015). It also becomes a serious economic problem when previously non-saline soils become saline as a result of irrigation, affecting their fertility (Singh, 2015).

Salinity is not an unfamiliar problem for olive tree cultivation, since its productivity is affected by the quality of the soil, despite its excellent adaptability to the environment. Soil salinity has been demonstrated to cause a decrease in the quality of the olive fruit (Zeleke et al., 2012), as well as vegetative growth problems (Rahemi et al., 2017), leading in extreme cases to the death of young plants (Benloch et al., 1991; Aragüés et al., 2005). Luckily, the presence of sodic soils in Andalusian olive groves (the world’s largest olive growing region) is scarce, and almost non-existent in rain-fed olive groves, but starting to show up in areas with high-water irrigation. Thus, Mediterranean semi-arid zones are quite susceptible to secondary salinization and sodification due to inadequate irrigation (Calero et al., 2013).

Considering the enormous agro-environmental and economic importance of salinization and sodification in agricultural soils, it would be of interest to develop tools for early diagnosis, to maintain agriculture and environment sustainable (Herrero & Snyder, 1997). One possibility is the use of infrared (IR) spectroscopy, a fast and robust analytical technology, typically used for assessing soil properties like carbon and nitrogen content, as well as other parameters (Soriano-Disla et al., 2014; Vohland et al., 2014), including some biochemical properties (Reeves et al., 2000; Comino et al., 2018). Infrared spectroscopy has been shown to be able to classify soils according to type or management (Aranda et al., 2014). Some studies on the prediction of salinity and sodicity have used mapping techniques and satellite data (Castignanò et al., 2008; El Harti et al., 2016), but few have used laboratory IR spectroscopy to determine salinity and sodicity-related parameters in soil.

Thus, the objective of this work was double: First, to study the mid-term effects of irrigation water with a relative risk of sodicity and salinity on soil quality. Second, to study the feasibility of IR spectroscopy for detecting salinity and sodicity in different types of soil.

**Materials and methods**

**Study site and soil sampling**

The study was conducted in an olive grove located near Guarromán (Jaén), 38°12’48’’N, 3°39’47’’W. Guarromán is geologically located on the boundary of two major morphological domains, the Sierra Morena Mountains and the Guadalquivir Depression, which in these latitudes manifests as a narrow depression known as the Bailén-La Carolina tectonic pit. In the hillside areas most exposed to erosion, and where the farm is located, the formation of Leptosols on sandstones and calcareous Regosols on medium-textured colluvial materials are facilitated. The lithology of this area includes conglomerates, sands and silts from the Pleistocene, and marl-sandstones and limestone sandstones from the Tertiary (Junta de Andalucía, 2005). The predominant landscape is the dehesa, a savanna type with grass and holm oaks, and forest repopulation species. The climate is characterized by its mild winters, with minimums of a few degrees below zero, and hot, dry summers, with maximums above 40°C. The average annual rainfall is about 560 mm.

The farm has 14.5 ha of thirty years old picual olive groves spaced 10 × 10 m on average slopes ranging from 8% near the top to 5% lower down. Management consists of non-tillage of bare soil, with the application of a residual herbicide in autumn (usually October 1st) and post-emergence herbicide in spring (usually last few days in March), to avoid competition for nutrients and water by eliminating weeds. Mineral fertilizers are applied: nitrogenous compounds are added to the soil through the irrigation water (fertigation
system) in several applications in spring, and foliar fertilization, mainly phosphorus and potassium along with micronutrients, twice in autumn (October) and spring (April-May), respectively, coinciding with phytosanitary treatments. These plots are located in private farms. Productivity after irrigating started increased considerably to 7.2 Mg ha\(^{-1}\) olives with oil content of 19.5-20.8%, but after 15 years of irrigation, the productivity decreased down to 2.1 Mg ha\(^{-1}\) of olives with an oil content of 16.5-19% (unpublished data).

Two soil types are found in the study site. A calcareous area (carbonated) dominated by Regosol soil type and a siliceous area with Leptosol soil type (FAO, 2006). Ten locations were randomly selected, according to the different soil types found, five corresponding to the calcareous soils and five to the siliceous soils. In each sampling location, two different samples were taken (30 cm depth), one corresponding to the soil directly affected by the irrigation bulb and the other corresponding to the intercanopy soil, without direct influence of irrigation. Samples were always composed of four different random subsamples. The topsoil layers (0-30 cm) studied cover the essential depth for the root system of the olive tree and they represent the total thickness of the typical soils of the sampled farms, without distinction between horizons, due to agricultural management and the scarce evolution of soils (Regosol and Leptosol). For further comparison, we included 71 olive grove soil samples from Jaen province, with similar lithological material, but different management systems, and with no salinization or sodicity problems.

Irrigation and water analysis

A drip irrigation system was installed on the farm in 1995, using water from its own well. Each tree was irrigated by two 8 L h\(^{-1}\) self-compensating emitters located on both sides of the trunk. The trees were irrigated for 8 hours every 3 days, each tree receiving 128 L every day with irrigation, for a total of 102.4 m\(^3\) ha\(^{-1}\) month\(^{-1}\). Irrigation begins between March and May, depending on the rainfall, and continues until the middle or end of September. The chemical characteristics of the water used for irrigation and fertigation were measured in water sample taken directly from the well. Measurement of pH was realised using a CRISON micropH 2001 pH meter, electrical conductivity (EC) using a CRISON-522 conductometer. Chloride, carbonate and bicarbonate contents were determined by direct titrations with silver nitrate and sulfuric acid, respectively. To analyze sulphate concentration an indirect titration with EDTA was used. Nitrate and boron were determined by means of ionic chromatography and UV-vis spectroscopy, respectively. Cations (Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\) and Na\(^{+}\)) were analyzed by atomic absorption spectrometry (AAS). Various ratios were also calculated, that are sodium adsorption ratio (SAR), the residual sodium carbonate (RSC), exchangeable sodium percentage (ESP), total hardness, Langelier saturation index (LSI), and Ca\(^{2+}\)/Na\(^{+}\) and Ca\(^{2+}\)/Mg\(^{2+}\) ratios.

Soil analysis

Soil samples were air dried for 24 h and sieved at 2 mm. Soil analyses followed the official American Society of Agronomy and Soil Science Society of America methods (Page, 1982; Klute, 1986). The pH was determined by potentiometry in extract 1:2.5 soil:water. EC was measured with a CRISON-522 conductometer in saturated paste extract giving the values at 25°C. The procedure to determine cation exchange capacity (CEC) involves a saturation solution (0.4 N NaOAc – 0.1 N NaCl, pH 8.2) and an extracting solution (0.5 N MgNO\(_3\)); cations and anions were determined either in water, and in the saturation extract obtained by ammonium acetate (pH 7) or sodium chloride methods, respectively, and determined by atomic absorption spectrophotometry. Again, some ratios were calculated to characterize the soils.

Furthermore, the organic carbon (OC) and OM contents were obtained by the dichromate oxidation method. Total N was measured by the Kjeldhal method. Bernard calcimeter was used to calculate equivalent carbonate. Clay, silt and sand contents were determined by the Robinson pipette method after elimination of OM with H\(_2\)O\(_2\) and dispersion with sodium polyphosphate. Saturated hydraulic conductivity (Ks, cm h\(^{-1}\)) was measured by a constant-head permeameter (Eijkelkamp Agrisearch Equipment, Giesbeek, NL) in laboratory, using intact cylindrical cores of 98.2 cm\(^3\) that were taken from the pit faces, to a depth of 15 cm. Soil bulk density was measured using a cylindrical core of known volume. The soil aggregate stability index (ASI) was determined with the method described by Kemper & Rosenau (1986), using a wet sieving apparatus (Eijkelkamp Agrisearch Equipment, Giesbeek, NL).

Soil erodibility (USLE K factor) was calculated with the equation of Wischmeier & Smith (1978), that takes into account the texture, particle size, the percentage of OM, the soil structure and the permeability. The dispersion of clays induced by water and mechanical stirring were evaluated through the spontaneous dispersion test (SDC) and the mechanical dispersion test (MDC) respectively (Rengasamy et al., 1984).
Infrared spectroscopy

Soil samples were finely ground for IR measurements. Diffuse reflectance near infrared (NIR) spectra were registered in the range between 4000 and 12000 cm\(^{-1}\) using an Antaris FT-NIR analyzer (Thermo Nicolet Corporation) with gold integrating sphere with internal reference, 4 cm\(^{-1}\) resolution, and 128 accumulations. The sample cup filled with the sample was placed on top of the integrating sphere optics and rotated during measurement. Samples were measured in triplicate, increasing the amount of sample scanned. The mean spectrum was used for each sample.

Middle IR spectra were recorded in the range of 650 and 4000 cm\(^{-1}\) with a Varian 660 FTIR spectrometer. Samples were placed directly on an attenuated total reflection (ATR, Pike Technologies) accessory equipped with a torque-limited pressure applicator that was used to ensure the contact of the sample with the three-reflection ATR crystal. Each spectrum was mean of 128 accumulations with 2 cm\(^{-1}\) resolution. Background was recorded on the clean and dry ATR crystal. Band interpretation was made following Ben-Dor et al. (1997) and Viscarra Rossel et al. (2011) for NIR region and Changwen et al. (2007) and Madari et al. (2006) for mid-IR region.

Statistical analysis

Statgraphics Centurion XVI software (StatPoint Technologies, Inc.) was employed for basic data analysis that included Pearson’s correlation coefficient and ANOVA. Assumptions of normality were tested with the Saphiro-Wilk test. Normal distributions were studied with F-test ANOVA while Kruskal-Wallis ANOVA was applied for the rest of variables. Difference between means was investigated by the Bonferroni test.

PLS-toolbox from Eigenvector Research Inc. (Wenatchee, USA) was used together with MATLAB 2008R (MathWorks, Natik, USA) to perform principal component analysis (PCA). This allows the detection of natural grouping of the IR spectra of the samples. Different spectra preprocessing were tested using the same software namely derivation, smoothing, detrend, baseline correction and mean centering in order to reduce the noise and increase useful information availability.

Results

Irrigation water analysis

The results of the chemical analysis of the well water used for irrigation are shown in Table 1. Salinity was medium-to-low as indicated by its low EC, as well as its content in total salts. It had a high sodium concentration compared to the rest of the cations, although SAR was not high. The most negative parameter for its use for irrigation was its high pH due to the high concentration of bicarbonates, which causes high RSC. According to water quality recommendations (Ayers & Westcot, 1985), the use of this water should not be restricted, since there is no risk of salinity, chloride or sodium toxicity. Nevertheless, there is a slight to moderate risk of decrease in the infiltration rate due to the combination of high concentration of bicarbonate and high SAR that can affect the crop. With all these data, this water may be said to be suitable for irrigation, however, it should be monitored for any possible effects of the high bicarbonate and the moderate sodium concentration on the soil and the plant in the medium-to-long term. This condition is particularly important when used for fertigation, where salt concentrations are even higher.

Soil physical properties

The results of the soil physical properties studied are shown in Table 2. The dominant texture was sandy clay loam. The homogeneity in terms of clay and sand contents allow us to compare effectively the

| Parameter        | Result  |
|------------------|---------|
| pH               | 8.3     |
| EC, dS m\(^{-1}\) | 0.6     |
| Nitrates, mg L\(^{-1}\) | 2.2 |
| Boron, mg L\(^{-1}\) | 0.6 |
| Total salts, g L\(^{-1}\) | 0.4 |
| Ca, mg L\(^{-1}\) (%) | 29.6 (25) |
| Mg, mg L\(^{-1}\) (%) | 14.6 (21) |
| K, mg L\(^{-1}\) (%) | 9.5 (4) |
| Na, mg L\(^{-1}\) (%) | 66.7 (50) |
| Hardness (dGH)   | 13.4    |
| Chloride, mg L\(^{-1}\) (%) | 29.6 (13) |
| Sulfate, mg L\(^{-1}\) (%) | 23.2 (8) |
| Carbonate, mg L\(^{-1}\) (%) | 0 (0) |
| Bicarbonate, mg L\(^{-1}\) (%) | 297.5 (79) |
| SAR              | 2.3     |
| RSC (%)          | 2.2     |
| ESP (%)          | 2       |
| Ratio Ca/Na      | 0.5     |
| Ratio Ca/Mg      | 1.2     |
| Langier index    | 0.24    |

ESP: exchangeable sodium percentage. RSC: residual sodium carbonate. SAR: sodium adsorption ratio.
Table 2. Mean, SD, t-test and ANOVA of physical properties of samples divided according to parent material, irrigation influence, and material + irrigation influence. Different letters stand for significance differences ($p<0.005$).

| Physical properties | Material | Irrigation influence |
|---------------------|----------|----------------------|
|                     | Siliceous | Carbonated | Bulb$^1$ | Intercanopy |
| Sand (%)            | 61 ± 12 a | 65 ± 7 a   | 65 ± 10 a | 60 ± 9 a   |
| Silt (%)            | 12 ± 6 a  | 13 ± 4 a   | 13 ± 4 a  | 12 ± 6 a  |
| Clay (%)            | 27 ± 10 a | 22 ± 6 a   | 22 ± 10 a | 27 ± 6 a  |
| Bulk density (g cm$^{-3}$) | 1.62 ± 0.19 a | 1.35 ± 0.15 b | 1.44 ± 0.26 a | 1.53 ± 0.16 a |
| ASI                 | 0.49 ± 0.18 a | 0.42 ± 0.13 a | 0.42 ± 0.19 a | 0.49 ± 0.12 a |
| SDC (%)             | 0.5 ± 1.6 a | 0.2 ± 0.4 a | 0.7 ± 1.6 a | 0 ± 0 a |
| MDC (%)             | 11.5 ± 9.4 a | 3.1 ± 2.3 b | 9 ± 11 a  | 5.6 ± 2.5 a |
| Ks (cm h$^{-1}$)    | 1.35 ± 1.04 a | 1.43 ± 1.71 a | 1.59 ± 1.66 a | 1.19 ± 1.08 a |
| Erodibility K factor (Mg h (MJ mm)$^{-1}$) | 0.018 ± 0.009 a | 0.017 ± 0.002 a | 0.019 ± 0.009 a | 0.016 ± 0.003 a |

| Physical properties$^1$ | Material + Irrigation influence |
|--------------------------|-------------------------------|
|                         | Siliceous bulb | Siliceous intercanopy | Carbonated bulb | Carbonated intercanopy |
| Sand (%)                 | 64 ± 12 a   | 57 ± 11 a      | 67 ± 9 a      | 64 ± 4 a      |
| Silt (%)                 | 13 ± 4 a    | 11 ± 8 a       | 13 ± 5 a      | 13 ± 4 a      |
| Clay (%)                 | 23 ± 12 a   | 31 ± 6 a       | 21 ± 9 a      | 23 ± 2 a      |
| Bulk density (g cm$^{-3}$) | 1.6 ± 0.27 b | 1.63 ± 0.08 b  | 1.28 ± 0.12 a | 1.43 ± 0.15 ab |
| ASI                      | 0.44 ± 0.25 a | 0.55 ± 0.08 a | 0.4 ± 0.14 a  | 0.43 ± 0.13 a |
| SDC (%)                  | 1 ± 2.2 a   | 0 ± 0 a        | 0.4 ± 0.5 a   | 0 ± 0 a       |
| MDC (%)                  | 16 ± 12.1 b | 7 ± 1.6 a      | 2 ± 1.6 a     | 4.2 ± 2.5 a   |
| Ks (cm h$^{-1}$)         | 0.82 ± 0.66 ab | 1.89 ± 1.12 ab | 2.37 ± 2.06 b | 0.49 ± 0.34 a |
| Erodibility K factor (Mg h (MJ mm)$^{-1}$) | 0.023 ± 0.011 b | 0.014 ± 0.002 a | 0.015 ± 0.002 a | 0.018 ± 0.002 ab |

$^1$ASI: aggregate stability index. SDC: spontaneously dispersed clay. MDC: mechanically dispersed clay. Ks: saturated hydraulic conductivity. $^1$Bulb: wetted bulb from drip irrigation system.

samples studied in the carbonated and siliceous soil environment. No significant differences were observed in texture regarding either the parent material or the influence of irrigation (bulb-intercanopy difference). The bulk density values ranged from adequate to incipient compaction problems (Arshad et al., 1996). The bulk density was significantly higher for siliceous soil samples, which could be related to the lower carbonate content. There was also a trend towards higher bulk density in intercanopy soils subjected to the pressure of machinery transit. The mean soil aggregate stability index was 0.5, indicating poor structural stability throughout the farm. Values ranged from medium structural stability (0.4-0.6) to low (0.3-0.4) and very low (<0.3), the latter range most common in the areas affected by the irrigation bulb. No spontaneous clay dispersion was found in any of the studied soils when wetted without mechanical stress, which could be indicative of a high content of illite-like clays. On the contrary, mechanical dispersion of clays was observed in siliceous soils located at the irrigation bulb. Infiltration behavior, analyzed by the saturated hydraulic conductivity (Ks), was very low for all the samples. It is worth noting that water infiltration was generally lower in siliceous samples located at the bulb than in siliceous samples from intercanopy areas. Finally, considering the low soil erodibility (K factor) found for all the samples, there is no high risk of erosion regarding this parameter of the USLE equation, although a significant tendency to greater erodibility appears in the case of siliceous samples at the bulb.

**Soil chemical properties**

The results of the chemical property analyses are shown in Table 3. All soil samples had an alkaline pH, many of them over 8.5, one of the main indicators of salinity and sodicity (Daliakopoulos et al., 2016). In addition, the samples affected by the irrigation bulb, and especially in the case of siliceous soils, had a higher pH than their equivalent intercanopy samples. Electrical conductivity was generally low, and higher for samples affected by the irrigation bulb, but never close enough to cause concern for soil salinization (>4 dS m$^{-1}$). The
soils studied were not very calcareous, with almost total absence of carbonates in the siliceous samples, and relatively low in carbonated soils. OC was very low, being the differences in the amount of OC by sampling area probably related to the presence of olive roots in the bulb samples, as well as the presence of nutrients from fertigation, and the best soil moisture conditions that create an environment more prone to greater microbial activity. Total nitrogen was closely related to OC, and also higher for bulb samples, although the content was generally low in all the samples. This entailed a high C/N ratio for most samples (>12), characteristic of slightly humified OM, and soils with little nitrogen release.

Total cations in the soil solution were low. Sodium was found in an especially larger proportion in siliceous soils, where it had the second highest concentration of cations in carbonated soils. It is also worth mentioning that sodium concentrations were highest in the samples affected by the irrigation bulb, and always significantly higher than those in the intercanopy samples. Calcium appeared as the predominant cation in carbonated soils, as expected, and second in importance in siliceous soils, while magnesium and potassium had lower concentrations. On the contrary, high bicarbonate contents were found in all soils, especially in those affected by the irrigation bulb. This also was also the case of other anions, with relatively high concentrations of chlorides and to a lesser extent, sulfates. All samples showed similar CEC values, although significantly lower in siliceous samples. The SAR was low in most cases, but the mean was significantly higher for the samples located under the irrigation bulb. ESP, on the other hand, was very high in all samples, especially in siliceous samples, and particularly those under the influence of the irrigation bulb. High levels of RSC were also observed in the areas of the irrigation bulb,

### Table 3. Mean, SD, t-test and ANOVA of chemical properties of samples divided according to parent material, irrigation influence, and material + irrigation influence. Different letters stand for significance differences (p<0.005).

| Chemical properties¹ | Siliceous | Carbonated | Bulb² | Intercanopy |
|----------------------|----------|------------|-------|-------------|
| pH                   | 8.5 ± 0.6 a | 8.5 ± 0.1 a | 8.8 ± 0.4 a | 8.3 ± 0.3 b |
| EC (dS m⁻¹)          | 0.68 ± 0.33 a | 0.69 ± 0.2 a | 0.88 ± 0.24 a | 0.49 ± 0.09 b |
| OC (%)               | 0.7 ± 0.24 a | 0.88 ± 0.24 a | 0.9 ± 0.26 a | 0.68 ± 0.2 b |
| N (%)                | 0.05 ± 0.01 a | 0.07 ± 0.02 b | 0.07 ± 0.02 a | 0.05 ± 0.01 b |
| C/N                  | 13.7 ± 3.2 a | 13.6 ± 2.6 a | 13.6 ± 2.7 b | 13.7 ± 3.1 a |
| Carbonate (%)        | 0.11 ± 0.22 a | 6.99 ± 4.53 b | 3.03 ± 3.95 a | 4.07 ± 5.54 a |
| Ca²⁺ (mg kg⁻¹)*      | 27 ± 12 a  | 47 ± 13 b  | 35 ± 17 a  | 39 ± 15 a  |
| Mg²⁺ (mg kg⁻¹)*      | 11 ± 5 a   | 12 ± 7 a   | 15 ± 6 a   | 7 ± 1 b    |
| K⁺ (mg kg⁻¹)*        | 17 ± 27 a  | 8 ± 2 a    | 9 ± 2 a    | 16 ± 27 a  |
| Na⁺ (mg kg⁻¹)*       | 87 ± 56 a  | 70 ± 40 a  | 114 ± 44 a | 43 ± 13 b  |
| HCO₃⁻ (mg kg⁻¹)*     | 190 ± 100 a| 205 ± 50 a | 255 ± 63 a | 140 ± 37 b |
| Cl⁻ (mg kg⁻¹)*       | 100 ± 59 a | 91 ± 32 a  | 122 ± 53 a | 68 ± 11 b  |
| SO₄²⁻ (mg kg⁻¹)*     | 29 ± 18 a  | 40 ± 44 a  | 42 ± 46 a  | 27 ± 8 a   |
| SAR*                 | 3.5 ± 1.87 a| 2.46 ± 1.67 a| 4.28 ± 1.69 a| 1.69 ± 0.59 b|
| RSC*                 | 0.97 ± 0.97 a| 0.29 ± 0.51 a| 1.2 ± 0.83 a| 0.06 ± 0.13 b|
| ESP (%)              | 21.9 ± 3.9 a| 14.6 ± 1.4 b| 19.8 ± 5.1 a| 16.7 ± 3.8 a|
| CEC (cmol kg⁻¹)      | 18 ± 4.5 a | 24.4 ± 1.2 b| 21 ± 5 a   | 21.4 ± 4.4 a|
| Base saturation (%)  | 0.79 ± 0.08 a| 0.85 ± 0.05 b| 0.83 ± 0.07 a| 0.81 ± 0.07 a|
| Ca²⁺ ex (cmol kg⁻¹)* | 3.74 ± 1.68 a| 7.39 ± 0.97 b| 4.97 ± 2.27 a| 6.16 ± 2.29 a|
| Ca²⁺ ex. (%)         | 38.9 ± 9.5 a| 59.6 ± 6.9 b| 42.9 ± 11.9 a| 55.6 ± 11.9 b|
| Mg²⁺ ex. (cmol kg⁻¹)*| 1.35 ± 0.65 a| 1.07 ± 0.69 a| 1.68 ± 0.48 a| 0.74 ± 0.47 b|
| Mg²⁺ ex. (%)         | 14.2 ± 4.6 a| 8.4 ± 5.1 b | 15.5 ± 2.8 a| 7.2 ± 4.5 b |
| K⁺ ex. (cmol kg⁻¹)*  | 0.39 ± 0.09 a| 0.39 ± 0.1 a | 0.42 ± 0.1 a| 0.35 ± 0.08 a|
| K⁺ ex. (%)           | 4.2 ± 0.8 a | 3.2 ± 0.9 b | 4 ± 1 a    | 3.5 ± 1 a   |
| Na⁺ ex. (cmol kg⁻¹)* | 3.88 ± 1.17 a| 3.56 ± 0.26 a| 4.02 ± 1.11 a| 3.43 ± 0.26 a|
| Na⁺ ex. (%)          | 42.6 ± 7.8 a| 28.9 ± 2.9 b| 37.7 ± 9.4 a| 33.7 ± 8.8 a|
especially in siliceous samples, indicating an excessive concentration of bicarbonates.

Base saturation over 80% was similar in the various soils studied, although a very strong imbalance was observed in the proportion of each of the cations within the exchange complex. In these soils, a very low proportion of calcium was observed in the exchange complex, whereas sodium was higher. This high proportion of sodium was especially prominent in the samples under the irrigation bulb, and in the siliceous samples, showing serious values for both characteristics, and over 45% for sodium.

### Infrared spectra characterization

The mean NIR spectra calculated after baseline correction for each of the four typologies (5 samples each) included in the study are shown in Figure 1a. The NIR spectra are dominated by absorptions due to the vibration modes (overtones and combination bands) of water molecules and lattice hydroxyl groups. Three main bands are observed. The first at 7065 cm$^{-1}$, can be assigned to the 2$^\text{nd}$ overtone of OH stretching in clays like kaolinite. The second one, at 5230 cm$^{-1}$ is a combination band of the stretching vibration of OH in phyllosilicates and the bending vibration of interlayer water molecules. The 2$^\text{nd}$ overtone of carbonyl stretching (C=O) associated with recalcitrant organic compounds, such as lignins or humic acids, could also contribute to absorption in this spectral region. Finally, the band at 4528 cm$^{-1}$ can be associated with the combination of OH stretching and deformation of Al-OH bonds in clays like kaolinite, illite and montmorillonite. Vibrational bands of NH and OH bonds in OM may also
Figure 1. Mean FT-NIR spectra (a) and mean FTIR spectra (b) of the four soil typologies studied. IC: intercanopy carbonated; BC: bulb carbonated; IS: intercanopy siliceous; BS: bulb siliceous.

Figure 2. Scores for PCA of FTIR and FT-NIR spectra of study samples. BS: bulb siliceous. IS: intercanopy siliceous. BC: bulb carbonated. IC: intercanopy carbonated.
most weight in this PC were those of carbonates like calcite (710, 872 and 1423 cm$^{-1}$) and a band at 1029 cm$^{-1}$ that could be attributed to silicates and little-evolved organic compounds like polysaccharides. On the contrary, siliceous soils, with negative values for this PC, were characterized by the importance of NIR bands of kaolinite and other clays (4528 and 7073 cm$^{-1}$) and illite (4204 cm$^{-1}$). The grouping of samples by a combination of lithology and the influence of the wet bulb was not as clear.

To verify the ability of IR spectroscopy to discriminate between the soils studied, affected by salinity problems to different degrees, and typical soils of the province of Jaen, not suffering from such problems, a PCA was performed on FTIR and FT-NIR spectra of the samples studied along with spectra of a wide database of soil samples from Jaen. An analytical summary of the samples included in this database is shown in Table 4, where basic pH predominates among the samples included, although there is a wide variety for most parameters, with OM ranging from very low to acceptable levels, and ion and cation contents varying over a wide range. In general, no salinity or sodicity problems were detected in these soils, although some of the indicator parameters, such as SAR, ESP and EC were high for some.

The PCA score plot (Fig. 3) shows clear clustering of the samples studied in PC2 (28.08% Variance), indicating a significant difference in the spectral signatures between the samples from this farm and the rest of soil samples in our database. These clusters are also a reasonable match with ESP, which was high in all the samples from the farm in Guarromán, and also high in the two samples from the database in PC2 with similar values. According to the loadings in this PC, this discrimination was based on the greater weight in the Jaen database samples of polysaccharide and silicate bands (1000 cm$^{-1}$) as well as carbonates (711, 871 and 1423 cm$^{-1}$). To a lesser extent, there was a certain influence of bands associated with more evolved organic materials (5227 cm$^{-1}$), illite (3620, 4000 and 4265 cm$^{-1}$) and kaolinite (4440 and 7000 cm$^{-1}$).

**Discussion**

**Effect of irrigation by soil type**

According to the irrigation water analysis results, a priori there should be no risk to the soil. However, the results revealed that its continual application has caused problems of soil sodification due to its relatively high sodium and bicarbonate content.

Furthermore, the results brought to light the huge importance of the type of soil for the effects in response to the application of irrigation water. The higher calcium content of carbonated soils in comparison with siliceous soils, both in the extract and in the exchange complex, due to the influence of the parent

**Table 4.** Range and mean ± SD of physical and chemical properties of soil samples in Jaén database. n = 70

| Parameter       | Range     | Mean ± SD |
|-----------------|-----------|-----------|
| Sand (%)        | 30-78     | 50.1 ± 10.7|
| Silt (%)        | 3-25      | 12.2 ± 3.8 |
| Clay (%)        | 12-60     | 37.6 ± 9.6 |
| pH              | 6.8-9.5   | 8.3 ± 0.4  |
| EC (dS m$^{-1}$) | 0.4-3.9   | 1.1 ± 0.8  |
| OM (%)          | 0.2-2.6   | 0.9 ± 0.7  |
| Carbonate (%)   | 0.2-83.8  | 29.2 ± 18.8|
| HCO$_3$ (meq L$^{-1}$)* | 0-376    | 153 ± 62   |
| Chloride (mg kg$^{-1}$)* | 36-379 | 102 ± 69   |
| Sulfate (mg kg$^{-1}$)* | 12-1428 | 288 ± 380  |
| Ca$^{2+}$ (mg kg$^{-1}$)* | 22.8-1114.2 | 146.9 ± 197|
| Mg$^{2+}$ (mg kg$^{-1}$)* | 4.7-203.8 | 24.5 ± 30.5|
| K$^+$ (mg kg$^{-1}$)* | 38.2-598.7 | 125.3 ± 113.5|
| Na$^+$ (mg kg$^{-1}$)* | 0.9-141.9 | 10.2 ± 22.1|
| SAR             | 0.3-8.3   | 1.9 ± 1.5 |
| ESP (%)         | 0-57      | 4.3 ± 9.3  |
| CEC (cmol$^+$ kg$^{-1}$) | 4.1-34.5 | 17.4 ± 6.8 |

EC: electrical conductivity at 25˚C. OM: total organic matter. SAR: sodium adsorption ratio. ESP: exchangeable sodium percentage. CEC: cation exchange capacity. *: soil solution parameters.

**Figure 3.** Scores for PCA of FTIR and FT-NIR spectra of study samples (Guarromán) and Jaen database samples.
material, leads to better maintenance of soil physical properties, with lower bulk density. Thus, calcium played an important role in improving and maintaining the soil structure, as opposed to sodium, in greater concentration in the siliceous samples, which caused degradation of the structure, making the soil more susceptible to compaction (Sumner, 1993). This destruction of structure due to the higher amount of sodium observed in the siliceous samples, led to greater dispersion of clays. The dispersion of the colloidal material of the soil by the presence of sodium could be favoring, among other causes, the access of soil microorganisms to the OM, producing a clear trend towards low OC and nitrogen contents. This seems to indicate that sodium causes greater decomposition of OM (Nelson & Oades, 1998), which is lost over time, reducing fertility in these soils in the mid-to-long term. In addition, high sodium concentrations give rise to very high exchangeable sodium, in both soil typologies, but especially in siliceous soils (over 20%) which causes problems not only for soil, but also plant health (Benlloch et al., 1991). Therefore, prolonged irrigation with this water has caused degradation in both types of soil, but much more evident in siliceous soils than in carbonated soils due to the attenuating effect of the higher calcium concentration in the latter (Li et al., 2013).

**Effect of zone of influence of irrigation**

No significant differences in physical parameters from the effect of the irrigation bulb were found, although there were clear trends in bulk density averages, higher in intercanopy samples, and hydraulic conductivity, higher in the bulb areas. These differences indicate that the soil structure is equally affected throughout the entire farm, although the problems of infiltration are concentrated to a greater extent in the intercanopy areas, probably due to the transit of agricultural machinery, which compacts the soil, increasing soil bulk density, and decreasing infiltration. On the other hand, the prolonged irrigation with water rich in sodium bicarbonate in this farm has entailed very negative consequences on the chemical status of the soil. Thus, the samples affected by the irrigation bulb showed high pH, SAR and RSC. This indicates that these areas are more strongly sodified as a consequence of irrigation, although the entire farm presents this symptomatology, as shown by its high ESP, somewhat higher again in the irrigation bulb samples. In addition, higher EC, chlorides and bicarbonates were observed in the samples directly affected by the irrigation bulb, which indicates that soil salinization is starting, although not yet of concern. It should also be emphasized that in the bulb samples, although there was a higher concentration of sodium due to the more direct influence of irrigation, there was also a higher percentage of magnesium in the exchange complex, replacing calcium to a greater extent in these samples, and thereby increasing all the degradation processes described above, since calcium helps generate and maintain the soil structure. Finally, the higher levels of OC and nitrogen in the bulb area, which may be due to traces of roots present in the soil profile, are interesting.

**Combined effect of irrigation influence zone and soil typology**

Sodification and salinization were more accentuated in siliceous soils located under the influence of the wet bulb. These samples showed the highest physical degradation, also showing the highest pH, EC, bicarbonates, chlorides, sodium (both in the saturation extract and in the exchange complex), and especially SAR and RSC. All these parameters seem to indicate these soils are very alkalinized, severely sodified, and also undergoing salinization, which is clearly affecting soil fertility, reducing production. It is also noteworthy that samples of carbonated soils located within the influence of the bulb have resisted sodification better due to the effect of calcium. Calcium acts as a flocculating agent on one hand, helping the formation of soil structure and improving physical properties, and on the other, decreasing the hazardous effect of sodium cations. Finally, it should be noted that the soils of both materials, although not directly affected by the irrigation bulb, also showed clear signs of sodification, indicating that the high concentration of sodium, over time, is affecting the entire farm, turning soils sodic in the medium-to-long term. However, in these samples there were no signs of salinization, since they were lower in chlorides, EC and bicarbonates, indicating that the salinization process, at least for the moment, is only concentrated in the area affected by the irrigation bulb.

**Infrared spectra for assessing the state of salinity and sodicity**

The strong influence of the bands associated with inorganic parent material in the IR spectra must be considered first. There, the NIR spectra are dominated by inorganic bands associated with clays like illite and kaolinite, with higher contribution from siliceous soils, whereas in carbonated samples the characteristic bands of carbonate in the form of calcite are clearly visible in the mid-IR region. The ability of IR spectroscopy to discriminate soils with low fertility due to salinity and sodicity from soils with similar parent material,
but without such problems (like most of the soils included in the Jaén database) was also proven. The spectral signatures responsible for this discrimination revealed the important role of calcium carbonate in the maintenance of soil structure with bands assigned to calcite (710, 872 and 1423 cm\(^{-1}\)) as the most distinctive features. Regarding OM, little evolved OM bands (~1000 cm\(^{-1}\)) predominate in soil less affected by sodicity problems, and particularly in carbonated soils. Less evolution of OM in carbonated soils could be attributed to more total OM in these soils due to the lower rate of decomposition of fresh OM, which may be associated with the protective effect exerted by calcium (Duchaufour, 1976). As described by Duchaufour, this could be related to the retention of particulate OM from a substrate particularly rich in carbonates. In soils affected by sodicity, and particularly in siliceous soils, the higher amount of sodium may have caused more intense destruction of fresh OM, causing a relative accumulation of the most recalcitrant fraction. Although the IR spectra was not directly sensitive to the presence of salinity and sodicity, it did seem to be able to detect the problem by its correlation with other compounds and possibly by changes in the soil structure reflected in slight changes in band position and intensity of the silicate clay fraction. This is manifested in mid-IR spectra as a broadening and shifting of Si-O stretching modes observed mainly in the 900-1100 cm\(^{-1}\).

In conclusion, irrigation generates significant increases in agricultural production, especially in semi-arid areas where water is usually a limiting factor. However, in the long run, the use of low-quality water can cause soil degradation and decrease productivity. In our study, it was demonstrated that the use of medium-to-low quality irrigation water affected soil physical properties, generating infiltration and structural problems. However, we lack sufficient information on the water chemical properties along the irrigation years, in which, different drought and rainy periods could have changed its composition. Chemical characteristics of the soil were especially affected, leading to salinization and sodification which decreased fertility. In the comparison of two contrasting soil types, it was found that soils developed on siliceous materials are much more vulnerable to this effect, while carbonated soils attenuate it due to the protective effect of the higher calcium concentration. In addition, sodicity problems were very noticeable in the area directly affected by the irrigation bulb, although over time, the pernicious effect extended throughout the farm. This problem could be solved by reducing the daily fertigation, and using calcium as part of the fertilization program or adding it as an amendment directly to the soil. We also demonstrated that infrared spectroscopy can be a useful technique to characterize soils and detect degradation. Thus, infrared spectroscopy can be regarded as a quick and economical technique to discriminate soils with decreased fertility due to incipient salinity and sodicity.

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