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Effects of Reclaimed Agro-Industrial Wastewater for Long-Term Irrigation of Herbaceous Crops on Soil Chemical Properties

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***Abstract*—**Worldwide, about two-thirds of industrial and domestic wastewater effluent is discharged without treatment, which can cause contamination and eutrophication of the water. In particular, for Mediterranean countries, irrigation with treated wastewater would mitigate the water stress and support the agricultural sector. Changing global weather patterns will make the situation worse, due to increased susceptibility to drought, which can cause major environmental, social, and economic problems. The study was carried out in open field in an intensive agricultural area of the Apulian region in Southern Italy where freshwater resources are often scarce. As well as providing a water resource, irrigation with treated wastewater represents a significant source of nutrients for soil–plant systems. However, the use of wastewater might have further effects on soil. This study thus investigated the long-term impact of irrigation with reclaimed agro-industrial wastewater on the chemical characteristics of the soil. Two crops (processing tomato and broccoli) were cultivated in succession in Stornarella (Foggia) over four years from 2012 to 2016 using two types of irrigation water: groundwater and tertiary treated agro-industrial wastewater that had undergone an activated sludge process, sedimentation filtration, and UV radiation. Chemical analyses were performed on the irrigation waters and soil samples. The treated wastewater was characterised by high levels of several chemical parameters including TSS, EC, COD, BOD_5, Na^+, Ca^{2+}, Mg^{2+}, NH_4-N, PO_4-P, K^+, SAR and $CaCO_3$, as compared with the groundwater. However, despite these higher levels, the mean content of several chemical parameters in the soil did not show relevant differences between the irrigation treatments, in terms of the chemical features of the soil.

***Keywords*—**Agro-industrial wastewater, broccoli, long-term re-use, tomato

I. INTRODUCTION

RE-USE of wastewater in agriculture is being practiced increasingly all over the world, because of increasing scarcity of water resources, especially in arid and semi-arid regions. The Apulia region is a coastal area of south-eastern Italy, and its production system is characterised by numerous agro-food industries, the activities of which include the processing of vegetables, which produces large quantities of wastewater. The re-use in agriculture of these wastewaters offers the opportunity to reduce the costs of their disposal and to minimise their environmental impact [1]. In addition, in several areas of Apulia, very intensive irrigation of horticultural cropping systems is carried out. Among the more frequently cultivated vegetable species, processed tomatoes are particularly diffused, which grow through the spring to summer period, as are broccoli, which are often grown in succession to tomato during the autumn to winter period. The use of non-conventional water resources, such as agro-industrial wastewater, is essential in these areas that suffer from water shortages and from relevant levels of sea-water intrusion into the regional water table, due to excessive and often uncontrolled groundwater withdrawals [2], [3]. Treated agro-industrial wastewater offers not only an alternative to conventional water irrigation sources, but might also provide the opportunity to recycle plant nutrients. Indeed, treated wastewater can contain useful easily biodegradable organic matter and readily absorbable plant nutrients, such as nitrogen (N), phosphorous (P), potassium (K), and magnesium (Mg). On the other hand, irrigation with reclaimed wastewater might have an impact on the quantitative and qualitative traits of crop yields. This might also raise sanitary problems (e.g., risk of microbial infection, both for farmers and consumers), due to residual presence of microorganisms that are pathogenic for human and animals [4]-[6]. In this regard, the effects of the chemical and microbial characteristics of the treated wastewater used in this experimental trial that investigated the quantitative, qualitative and microbiological traits of the tomato fruit and brocoli yields, had been discussed in the previous studies [7]-[9]. These studies reported that soils and plants irrigated with treated agro-industrial wastewater are not contaminated with bacterial indicators that are generally associated with human health risks. Therefore, such treated agro-industrial wastewater appears to represent a valid alternative for irrigation of tomato and broccoli. In addition, the main results of the previous studies showed that irrigation of tomato and broccoli plants with agro-industrial treated wastewater did not negatively affect their main quality parameters.

The main objective of the present study was therefore to determine the possibility of crop irrigation by long-term re-use of agro-industrial wastewater that was originated from a processing vegetable company, and the effects that this might have on the chemical properties of the soil. Two water sources were used: conventional groundwater (GW) and treated agro-industrial wastewater (TW). These provided the irrigation of a test field where tomato and broccoli crops were cultivated in close succession over four years, to evaluate their effects on the main chemical parameters of the soil.

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II. MATERIAL AND METHODS

A. Wastewater Treatment Plant

This study was conducted within the Fiordelisi Company, which produces processing vegetables (i.e., tomato, broccoli, eggplant, courgette, pepper). The company produces wastewater of on average about 46,500 m^3y^{-1}, which is mainly composed of the process water (used for vegetable processing and cleaning) and water from the bottle-washing line. There is also a relevant proportion that comes from the toilets (5% to 10% of the total).

The wastewater treatment plant function is based on the following steps: screening, oil removal, equalisation, activated sludge processing (anoxic plus aerobic phases), chemically assisted sedimentation, sand filtration (preceded by chlorination), membrane ultrafiltration (nominal pore size, 0.05 µm; Kristal 600ER; Hyflux), and UV radiation (six mercury-vapor lamps; 300 W each). The effluent after the UV radiation is known as the tertiary TW. TW is required for agricultural and landscape irrigation, and recreational and environmental uses, as well as for use as processing water in some industrial applications.

B. Field Experiments Layout

The experimental trials were carried out in an open field over the 5-year period from April 2012 to March 2016, with the close succession of tomato and broccoli each year, in an agricultural area within the Fiordelisi company (Stornarella; 41° 15'N, 15° 44'E; altitude, 154 m a.s.l.). During the study, the two types of water were used for irrigation of both of these crops: GW and tertiary TW. The GW was pumped from a phreatic well that is located near to the experimental field. This represents the irrigation source that would normally be used by the local farmers for their crop irrigation.

The trial was carried out on a clay−loam soil (USDA classification), with: sand, 39.8%; loam, 33.1%; and clay, 28.0%. The soil showed a field capacity (−0.03 MPa) of 30.5% dry weight (dw), a wilting point (−1.5 MPa) of 15.9% dw, and a bulk density of 1.41±0.03 Mg m^{-3}. The experimental field was near to the Fiordelisi wastewater treatment plant, and the study was carried out according to a complete randomised block design with the two irrigation treatments (i.e., GW, TW), each of which was replicated three times. The crops were grown in four identical plots of 450 m^2 (15 m wide × 30 m long), with a sampling area of 20 m^2 (2.5 m wide × 8.0 m long).

The seedlings of the processing tomato (*Lycopersicon esculentum* Mill., cultivar 'Manyla') were transplanted within the first 10 days of April 2012, 2013, 2014 and 2015, in double rows (40 cm apart) spaced at 250 cm, at a distance of 30 cm along each individual row. The final plant density was 2.7 plants m^{-2}. A drip irrigation method was used, with the drip lines placed between each pair of plant rows, under a black plastic mulching film.

The tomato plants were grown vertically, under a net house structure, which was covered with an anti-hail net using nylon threads positioned between the plant collars and iron wires, arranged longitudinally in the direction of the plant rows, and fixed to the upper part of the net house, at 2.5 m from the ground. In each growing cycle for 2012, 2013, 2014, and 2015, the tomato fruit were hand harvested at the full red maturity stage several times between July and September, at approximately 2-week intervals.

The seedlings of the broccoli (*Brassica oleracea* L. var. *italica*, hybrid 'Partenon' F_1) were transplanted in close succession to the tomato within the first 10 days of October 2012, 2013, 2014 and 2015, in single rows spaced at 80 cm apart, at a distance of 35 cm along the rows. The final plant density was 3.6 plants m^{-2}. Also for the broccoli crop, the drip irrigation method was adopted, with the drip lines placed along the plant rows. The broccoli heads with 15 cm of stem and without leaves were harvested in each year in the last 10 days of February 2013, 2014, 2015, and 2016, respectively.

During each cycle of both of these crops, the plants were irrigated whenever the soil water deficit in the effective root zone (i.e., 0-50 cm in depth) was 40% of the total available soil water [10]. This irrigation threshold was assessed through continuous monitoring of the volumetric soil water content using probes that operated under frequency domain reflectometry, and that were installed in each plot prior to crop transplanting at soil depths of 15, 25, 35, and 45 cm. At each irrigation, the water content of the soil of each plot was increased to field capacity with a water volume that varied from 100 m^3 ha^{-1} to 300 m^3 ha^{-1}, depending on the crop growth stage. The seasonal irrigation volumes across the years ranged from 4,500 m^3 ha^{-1} to 5,000 m^3 ha^{-1} for the tomato crops, and from 850 m^3 ha^{-1} to 1,000 m^3 ha^{-1} for the broccoli crops, depending on the crop growth years.

The agricultural management practices (i.e., fertilisation, weed and pest control) applied to the three crops considered during the experimental trial were those commonly adopted by local farmers.

C. Climate

The study area is characterised by an 'accentuated thermoMediterranean' climate, according to the climate maps of the United Nations Food and Agriculture Organisation, with air temperatures that drop below 0 °C in winter and that can exceed peaks of 40 °C in summer. The long-term mean annual rainfall was 590 mm, which was unevenly distributed through the year, as it was predominantly concentrated in the period from October to April. The mean annual Class 'A' pan-evaporation rate was 1,573 mm.

The mean monthly values of the main climate parameters that were recorded in the course of the growth cycles of the tomato and broccoli crops from April 2012 to February 2016 are reported in Tables I and II, respectively. These were measured by a weather station and stored by a data logger (Campbell Scientific USA), both of which were located near the experimental site.

As the averages over the four years, the monthly mean maximum and mean minimum temperatures during the tomato growth cycle from April to August were 27.5 °C and 14.8 °C, respectively.

The total rainfall was 185.2 mm, while the Class 'A' pan-evaporation was 667.6 mm. As expected, during the broccoli growth cycle (in succession to that of the tomato), for the autumn–winter period from October to February, as the averages over the four years, the monthly mean maximum and mean minimum temperatures were lower, at 15.9 °C and 7.0 °C, respectively. The total rainfall and Class 'A' pan evaporation were 372.4 mm and 138.6 mm, respectively.

TABLE I
CLIMATE DATA FOR THE TOMATO GROWTH SEASONS FROM 2012 TO 2015, AS THE MONTHLY MEAN MAXIMUM AND MINIMUM AIR TEMPERATURES, AND TOTAL RAINFALL AND CLASS 'A' PAN EVAPORATION

Year	Month	Maximum temperature (°C)	Minimum temperature (°C)	Rainfall (mm)	Class 'A' pan-evaporation (mm)
2012-2015 seasons	April	19.8	8.5	63.8	81.5
	May	24.3	10.6	53.8	122.0
	June	29.5	16.4	45.4	148.3
	July	32.6	19.3	18.6	165.6
	August	32.4	19.3	38.6	150.2
Mean		**27.5**	**14.8**	**-**	**-**
Total		**-**	**-**	**185.2**	**667.6**

TABLE II
CLIMATE DATA FOR THE BROCCOLI GROWTH SEASONS FROM 2012 TO 2016, AS THE MONTHLY MEAN MAXIMUM AND MINIMUM AIR TEMPERATURES, AND TOTAL RAINFALL AND CLASS 'A' PAN EVAPORATION

Year	Month	Maximum temperature (°C)	Minimum temperature (°C)	Rainfall (mm)	Class 'A' pan-evaporation (mm)
2012-2016 seasons	October	22.2	12.6	82.8	47.8
	November	17.8	9.0	92.0	25.4
	December	13.2	4.1	66.8	15.0
	January	12.7	4.3	64.9	20.5
	February	13.6	4.8	65.9	29.9
Mean		**15.9**	**7.0**	**-**	**-**
Total		**-**	**-**	**372.4**	**138.6**

D. Water and Soil Sampling

Triplicate samples of the GW and TW were collected each month during the irrigation seasons for the tomato and broccoli crops. Triplicate samples of the soils were collected from the experimental field before the trial started (16 March, 2012) and during the irrigation with each type of water, as four times at the end of each tomato growth cycle (7 September, 2012; 16 September, 2013; 22 September, 2014; 28 September, 2015) and four times at the end of each broccoli growth cycle (1 April, 2013; 6 April, 2014; 14 April, 2015; 28 April, 2016). The water samples were kept in a refrigerator at +4 °C and examined within 24 h of collection. All of the soil samples were taken from a 0 cm to 40 cm layer (i.e., the effective root density zone) from under the drippers, using a soil auger. Before the chemical analysis, these soil samples were air dried and passed through a 2-mm sieve.

E. Water and Soil Chemical Analysis

The irrigation water samples were analysed in triplicate, according to the Italian standard methods [11], which refer to the common international methods [12]. The analysis included the physico-chemical parameters of pH, electrical conductivity (EC; dS m^{-1}), total suspended solids (TSS; mg l^{-1}), sodium (Na^+; mg l^{-1}), potassium (K^+; mg l^{-1}), calcium (Ca^{2+}; mg l^{-1}), magnesium (Mg^{2+}; mg l^{-1}), sodium adsorption ratio (SAR), chemical oxygen demand (COD; mg l^{-1}), biological oxygen demand over 5 days (BOD_5; mg l^{-1}), nitrate (NO_3-N; mg l^{-1}), ammonium-nitrogen (NH_4-N; mg l^{-1}), phenols (mg l^{-1}), phosphorus (PO_4-P; mg l^{-1}), carbonates (CO_3^{2-}; mg l^{-1}), bicarbonates (HCO_3^-; mg l^{-1}), sulphate (SO_4^{2-}; mg l^{-1}), chlorides (mg l^{-1}), and fluorides (mg l^{-1}). The pH was measured by using a pH meter (GLP 22+ pH & Ion Meter; Crison Instruments, Spain) and the EC with an EC meter (GLP 31+ EC Meter; Crison Instruments, Spain). The Na^+, K^+, Ca^{2+}, and Mg^{2+} levels were determined by ion-exchange chromatography (Dionex ICS-1100; Dionex Corporation, Sunnyvale, CA, USA). The TSS was determined after filtration of the water samples through 0.45-µm-pore-size (47-mm-diameter) nitrocellulose membranes (Whatman, Maidstone, UK), using a vacuum system. The SAR was calculated according to (1) (concentrations in meq l^{-1}) [13]:

$$SAR = [Na^+] / \{([Ca^{2+}] + [Mg^{2+}]) / 2\}^{1/2} \tag{1}$$

F. Soil Chemical Analysis

The soil subsamples were analysed for pH, Na^+, Ca^{2+}, Mg^{2+}, SAR, EC, NO_3-N, NH_4-N, available phosphorus (P_2O_5), potassium (K_2O), and organic matter (OM). The EC and pH were measured in 1:2 (w/v) and 1:2.5 (w/v) aqueous soil extracts, respectively. The available P_2O_5 was determined using the sodium bicarbonate method [14]. The concentrations of soluble Na, Ca Mg and K were analysed by using an atomic absorption spectrophotometer (model 2380; Perkin-Elmer). The total organic carbon of the soil was determined by oxidation with potassium dichromate titration of $FeSO_4$, according to the Walkley and Black [15] method, and the OM was determined by multiplying the percentage of organic carbon by a factor of 1.724. The soluble NO_3-N and NH_4-N were determined according to [16].

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G. Statistical Analysis

The data for the qualitative parameters of the water during the tomato and broccoli cycles were processed statistically through analysis of variance (ANOVA), and when significant effects were detected ($P \leq 0.05$), mean multiple comparisons were performed according to Tukey's tests. All of the analyses were performed using the JMP software [17].

III. Results and Discussion

A. Physicochemical Characteristics of the Irrigation Waters

Table III gives the mean data for the physico-chemical characteristics of the GW and TW that were used to irrigate the tomato and broccoli crops that were grown in close succession over the 4 years from 2012 to 2016, along with the Italian legal threshold values for wastewater re-use for irrigation [18]. These physicochemical characteristics varied considerably between the GW and TW, with little difference seen between the several crop cycles analysed. In general, the main physico-chemical properties of both the GW and TW sources met the Italian standards for re-use of wastewater for irrigation, except for the TSS, whereby the overall mean TSS for the TW for the whole experimental period was 15.58 mg l^{-1}, which exceeding the legal threshold of 10 mg l^{-1} set by the above-mentioned legislation.

During the crop irrigation periods, the GW and TW were alkaline, with pHs of 7.86 and 7.51, respectively, which were not significantly different. The GW was always characterised by lower N (i.e., as NH_4-N and NO_2-N), P, K, Ca, Mg and TSS, compared to the TW. These chemical components in the TW in particular, represent important nutrients for improved plant growth, soil fertility, and crop yield [19], so they need to be taken into account in crop fertilisation practices.

The GW also had lower OM than the TW (as indicated by the BOD_5 and COD; Table III). However, despite the high values of these OM-related parameters in the TW, they do not appear to be a limiting factor for TW re-use; on the contrary, they are particularly important from the agronomic point of view. This aspect has also been highlighted in several studies relating to the re-use for irrigation of reclaimed urban wastewaters that are derived from simplified tertiary treatments that did not include the biological processes, in order to maintain the agronomic potential of the OM and nutrients that such wastewaters can contain [20]-[22]. In addition, the GW was characterised by significantly lower EC, Na content, and SAR, compared to the TW. If the SAR of the TW is related to the EC [23], it appears that there is no limit to the agricultural application of this TW, and there would be no reduction in its rate of infiltration into the soil.

Over the whole experimental period, the GW showed significantly higher NO_3-N than the TW (25.06 mg l^{-1} vs. 2.07 mg l^{-1}; $P \leq 0.05$). This elevated NO_3-N in the GW is due to nitrate contamination of the aquifer in the study area, where the intensive agricultural activity has led to extensive application of nitrogen fertiliser to crops. The resulting nitrogen surplus in the soil is then particularly exposed to the risk of leaching, thus increasing the environmental problem of nitrate pollution. This elevated NO3-N content in the GW represents an important nutrient source for the crops, but unfortunately it is not taken into account by farmers in their crop fertilisation plans.

Finally, the hardness of the water was lower for the GW than the TW, whereas the carbonate, bicarbonate and SO4− contents showed similar levels in the GW and TW.

B. Effects of Irrigation Treatments on Chemical Characteristics of the soil

Table IV shows the main chemical characteristics of the soils for the two irrigation treatments (i.e., GW, TW), as the mean values detected before the experiment started, and at the end of both the tomato and broccoli growth cycles (early in the months of September and April, respectively), over the 4 years. In general, some significant differences between the soils from these tomato and broccoli growth cycles can be noted, whereas there were only minor differences between the soils from the GW and TW irrigation treatments within each crop growth cycle.

For the soils following the GW and TW irrigation treatments for both the tomato and broccoli growth cycles, the mean pHs were not significantly different. However, the soil pH from before the trial started, at 7.9, was slightly increased, with a mean of 8.4 for all of these soil irrigation treatments (Table IV). This appears to be due to the accumulation in the soil of some basic cations as a result of the fertilisation and irrigation being applied over this long period [24]-[26].

In contrast to the mean Na+ concentrations of the GW and TW, those for the soil following the GW and TW irrigation treatments showed no differences. However, significant differences were found for the mean soil Na+ concentrations between the ends of the growth periods for the tomato and broccoli crops. In particular, the mean soil Na+ concentrations at the end of the broccoli growth cycles were significantly lower than for tomato, although these were not different when compared with the initial mean soil Na^+ concentrations before the trial started. This will be due to the rainfall during the broccoli growth cycle, as generally happens during the autumn–winter period in this area, which prevents salt accumulation in the soil (i.e., during the tomato crop cycle) by leaching the excess from the root zone.

Although the Ca^{2+} concentrations in the irrigation waters were significantly lower in the GW than the TW, the mean soil Ca^{2+} content was not different between these two irrigation treatments within each of the tomato and broccoli growth cycles. However, significantly higher values were obtained for both GW and TW at the end of the broccoli growth cycle than for the tomato. Again, this needs to be explained in terms of the relationships between the rainfall conditions and these soluble ions. The high rainfall during the winter enhanced the leaching of Na^+ more than that of Ca^{2+}, in agreement with other studies [27], [28].

TABLE III
Main Physicochemical Parameters Related to the Groundwater and the Tertiary Treated Agro-Industrial Wastewater Used For Irrigation of the Tomato and Broccoli Crops. the Italian Legal Thresholds for Wastewater Re-Use in Irrigation are Also Given (Ministry For The Environmental, Decree N° 152/2006)

Water parameter	**Legal threshold**	**Irrigation treatment**		**Significance**
		Ground water	**Tertiary treated water**	
pH	6.0-9.5	7.86 ±0.08	7.51 ±0.08	ns
EC (dS m^{-1})	3	0.79 ±0.03	2.91 ±0.43	*
TSS (mg l^{-1})	10	4.80 ±1.46	15.58 ±2.19	*
NH_4-N (mg l^{-1})	2	0.04 ±0.00	1.10 ±0.24	*
NO_3-N (mg l^{-1})		25.06 ±1.19	2.07 ±1.20	*
NO_2-N (mg l^{-1})		0.08 ±0.05	0.15 ±0.05	*
PO_4-P (mg l^{-1})	10	0.13 ±0.01	0.41 ±0.06	*
BOD_5 (mg l^{-1})	20	8.78 ±0.96	12.45 ±1.07	*
COD (mg l^{-1})	100	16.70 ±2.72	39.78 ±6.39	*
Na^+ (mg l^{-1})		34.70 ±0.58	273.49 ±6.31	*
Ca^{2+} (mg l^{-1})		41.76 ±3.0.4	82.33 ±1.59	*
Mg^{2+} (mg l^{-1})		9.20 ±0.17	10.54 ±0.27	*
K^+ (mg l^{-1})		10.87 ±1.40	45.57 ±1.90	*
CO_3^{2-} (mg l^{-1})		159.63 ±4.44	118.49 ±4.12	ns
HCO_3^- (mg l^{-1})		241.15 ±6.96	187.93 ±23.03	ns
SO_4^- (mg l^{-1})	500	30.89 ±0.94	33.66 ±1.14	ns
SAR	10	1.07 ±0.03	7.62 ±0.20	*
Hardness (mg l^{-1} $CaCO_3$)		202.12 ±7.80	243.38 ±5.70	*

Data are means ±standard errors for each analysed trait (n = 120; 3 replicates × 40 sampling days).
*, $P \leq 0.05$; ns, not significant. For abbreviations, see main text.

TABLE IV
Chemical Parameters Measured for the Soil Samples Collected at 0-40 cm Soil Depth in the Test Field, for the Initial Sample (Taken on 16 March, 2012) and Means of the Four Samples Taken at the End of Each of the of Tomato And Broccoli Growth Cycles Following the Irrigation with Groundwater and Tertiary Treated Agro-Industrial Wastewater

Parameter	**Initial**	**Mean from end of tomato cycles**		**Mean from end of broccoli cycles**	
		Ground water	**Tertiary treated wastewater**	**Ground water**	**Tertiary treated wastewater**
pH (in H_2O)	7.9 ±0.1**b**	8.4 ±0.1 **a**	8.4 ±0.1 **a**	8.3 ±0.1 **a**	8.5 ±0.1 **a**
Na^+(mg kg^{-1})	856 ±10 **b**	1564 ±97 **a**	1623 ±11.5 **a**	815 ±64 **b**	700 ±50 **b**
Ca^{2+} (mg kg^{-1})	4060 ±35 **d**	4799 ±210 **b**	4800 ±20 **b**	5487 ±168 **a**	5755 ±76 **a**
Mg^{2+} (mg kg^{-1})	250 ±25 **b**	270 ±19 **b**	363 ±39 **a**	242 ±29 **b**	218 ±24 **b**
EC (dS m^{-1})	0.49 ±0.11 **b**	0.66 ±0.15 **a**	0.73 ±0.22 **a**	0.38 ±0.03 **b**	0.54 ±0.01 **b**
SAR	3.51 ±0.3 **b**	5.84 ±0.5 **a**	6.1 ±0.3 **a**	2.8 ±0.5 **b**	2.4 ±0.3 **b**
NO_3-N (mg kg^-)	4.70 ±0.4 **c**	8.09 ±1.16 **a**	5.80 ±0.64 **b**	3.28 ±0.32 **d**	3.12 ±0.36 **d**
NH_4-N (mg kg^{-1})	7.50 ±0.6	8.48 ±0.37	7.97 ±0.61	6.88 ±0.32	7.27 ±0.44
P_2O_5 (mg kg^{-1})	80.1 ±5.0 **b**	142.18 ±25.47 **a**	161.36 ±15.76 **a**	104.69 ±12.16 **b**	122.4 ±16.38 **b**
K^+ (mg kg^{-1})	730 ±0.9 **a**	486 ±41 **b**	536 ±40 **b**	658 ±28 **a**	778 ±40 **a**
OM (%)	1.6 ±0.1	1.65 ±0.08	1.68 ±0.12	1.57 ±0.10	1.60 ±0.13

The initial data are means ±standard error for each analysed trait determined on three samples (n =3). The other data are means ±standard errors for each analysed trait determined on 3 samples collected four times at the end of both the tomato and broccoli growth cycles (n = 24). Data across the rows followed by different letters are significantly different at P <0.05 (Tukey's tests). For abbreviations, see main text.

The mean soil Mg^{2+} concentration was significantly lower for the GW irrigation treatment than the TW irrigation treatment, although only at the end of the tomato crop cycles. Here, there were no further specific differences noted for all of the other treatments, and also with respect to the initial soil Mg^{2+} concentration.

The EC is often used to define the water and soil salinity. In agreement with the soluble ion concentrations of the soil, higher soil EC was recorded at the end of the tomato cycles, with respect to the broccoli cycles, with the broccoli data not showing any significant difference from the initial soil condition. Nevertheless, the soil EC for all of the irrigation treatments remained generally well below (i.e., <0.8 dS m^{-1}) the threshold salinity of 4.00 dS m^{-1} that is considered to be dangerous for plants [29].

The SAR is widely accepted as an evaluation of the potential soil degradation caused by a relatively high Na content of a soil profile [30].

For the soil SAR, there was no significant difference between the GW and TW irrigation treatments within each of the crops, whereas the SAR was significantly higher at the end of the tomato cycles.

The higher SAR for the irrigated soil of the tomato crop was probably due to Na^+ accumulation in the root zone and reduced water infiltration rates that will have negatively affected the Na transport to the deeper soil layers [28].

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However, in the present study, all of the SAR values were well below the limit of 15 where a soil is considered sodic [31].

For the soil concentrations of NO_3-N, in agreement with the high levels in the GW, the mean soil NO_3-N was significantly higher for the GW treatment than for TW, at least at the end of the tomato crop cycles. However, there was no difference at the end of the broccoli crop cycles, where for both the GW and TW irrigation treatments the soil NO_3-N was particularly low. This might be due to the water movement pattern along the soil profile following the high rainfall during the winter crop of broccoli, which might have caused NO_3-N leaching out of the upper 0 cm to 40 cm soil layer sampled here. Indeed, the decreased nitrate concentration from the plant uptake and also from the leaching during the rainy season indicates a long-term risk of contamination of the shallow groundwater environment.

No differences were noted for the soil NH_4-N concentrations across any of the treatments and the crops.

According to the two irrigation waters, the soil concentrations of P_2O_5 and K^+ were slightly lower with the GW than the TW irrigation treatment, although these differences did not reach statistical significance. This suggests that some fertilising effects of the wastewater were possible, as already reported in prevision studies of field experiments with irrigation with treated [32], [33]. Moreover, for both the GW and TW irrigation treatments, higher soil P_2O_5 was noted for the end of the tomato crop cycle, and higher soil K^+ for the end of the broccoli crop cycle.

Finally, although the TW showed higher BOD, COD and TSS, there were no differences in the mean soil OM levels between the GW and TW irrigation treatments, nor between the crops. Any increase in OM will probably have been only temporary, as the abundant microbial activity on the organic material supplied by the TW is rapidly mineralised [34], [35].

IV. CONCLUSIONS

Irrigation water is the main source for the addition of salts to the soil, and the magnitude of this effect will depend on the total water salinity and composition, the leaching and climate characteristics, the management practices, and the consumption by the crops to be cultivated. In the present study, the long-term re-use of TW for irrigation was compared with conventional GW for tomato and broccoli crops that were cultivated in close succession over a period of four years.

The TW was characterised by higher levels of several of the chemical parameters compared to the GW, including NH_4-N, NO_2-N, PO_4-P, K^+, Ca^{2+}, Mg^{2+}, BOD_5, COD, EC, Na^+, SAR, hardness, carbonates, bicarbonates and TSS.

Soil irrigation with both the GW and the TW slightly increased the soil pH, which is mainly attributed to the concentrations of the basic cations in these irrigation waters when applied over long periods, such as Na^+, Ca^{2+}, and Mg^{2+}. The behaviour of the Na in the soil depends mainly on the balance between precipitation and evaporation, as well as on the sorption and desorption processes with the solid soil phase. In southern Italy, due to the high rainfall in the autumn–winter period, the balance between precipitation and evapotranspiration favours precipitation, which also promotes the migration of Na into and through the soil.

Irrigation with the TW compared to the GW slightly increased the cation concentrations in the soil, for Ca, Mg, P_2O_5, and K; these are also considered as potential sources of plant nutrients. Consequently, the slight increase in the EC will be mainly due to the original high levels of TSS of the TW that will accumulate in the soil with this long-term wastewater application. In the end, though, there was no increase in the OM content in the soil irrigated with TW.

Overall, the long-term irrigation with the TW compared to the conventional GW did not show relevant differences in terms of the chemical characteristics of the soil. This indicates that the re-use of TW in semi-arid areas represents a real alternative to the use of fresh water, which will also serve to reduce environmental pollution.

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