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Urban Wastewater Reuse for Citrus Irrigation in Algarve, Portugal—Environmental Benefits and Carbon Fluxes

Manuela Moreira da Silva ^{1,2,3}, Flávia C. Resende ¹, Bárbara Freitas ⁴, Jaime Aníbal ^{1,2}, António Martins ⁵ and Amílcar Duarte ^{4,6,*}

¹ Institute of Engineering, Campus da Penha, Universidade do Algarve, 8005-139 Faro, Portugal

² CIMA—Centre for Marine and Environmental Research, Campus de Gambelas, 8005-139 Faro, Portugal

³ CEiiA—Centre of Engineering and Development, Avenida D. Afonso Henriques 1825, 4450-017 Matosinhos, Portugal

⁴ Faculty of Sciences and Technology, Campus de Gambelas, Universidade do Algarve, 8005-139 Faro, Portugal

⁵ Águas do Algarve, S.A., Águas de Portugal Group, Rua do Repouso, 10, 8000-302 Faro, Portugal

⁶ MED—Mediterranean Institute for Agriculture Environment and Development, 8005-139 Faro, Portugal

* Correspondence: aduarte@ualg.pt

Abstract: Water scarcity is increasing in the Mediterranean and alternative sources of water are needed to meet food production needs, protect the environment and reduce the effects of climate change. Currently, many urban wastewater treatment plants (WWTP) produce high volumes of treated effluents which can be an alternative source of water for agriculture irrigation, since they fulfill the quality requirements for crops and the environment. This work analyzed the quantity and quality of a treated effluent produced by an urban WWTP in Algarve, and the environmental benefits of its use on the irrigation of a citrus orchard, as an alternative to groundwater. Carbon dioxide emissions related to orange production were quantified and the orchard's potential to sequester CO₂ was estimated. The reuse of this urban wastewater is revealed to be technologically feasible and environmentally advantageous, avoiding the overexploitation of the local aquifer and preventing the eutrophication of aquatic ecosystems, contributing to the improvement of soil characteristics and decreasing the carbon emissions in orange production. Furthermore, it was found that during the five-month experimental period, the citrus orchard sequestered 87.5% of the CO₂e emitted by WWTP in the effluent treatment, converting 72,623 kg of sequestered CO₂ into orange biomass.

Keywords: carbon emissions; citrus irrigation; environmental protection; sustainable agriculture; water reuse



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1. Introduction

Global demographic trends, modern societies' consumption patterns and climate change are putting increasing pressure on natural water resources, threatening habitats and biodiversity, particularly in more vulnerable regions such as the Mediterranean [1,2]. Worldwide, agriculture uses around 70% of the total water used in human activities. In addition, the demand for food and animal feed production tends to increase with the growth of the world population [3–6]. Meanwhile, freshwater use has exceeded recharge levels, leading to the desiccation of water streams. Concomitantly, the groundwater over-extraction has promoted saline intrusion phenomena in several coastal areas, posing additional constraints to agricultural irrigation, decreasing production and lowering crop yields [7]. To face this scenario, the agriculture sustainability in more vulnerable regions, such as the south of Portugal, where water scarcity is a common reality, involves the choice of an alternative water supply and more efficient irrigation systems [8,9], as well as crop selection. To ensure the water demands of the human population are met without threatening the ecosystems, it is necessary to reduce the extraction of natural water and the discharge of treated effluents into the environment [10]. The current technological advances in the wastewater

treatment plants (WWTP) often allow the use of reclaimed water as a safe water source for different purposes, such as for the irrigation of some crops [11–13]. Crop irrigation with tertiary treated effluent can preserve the biological and biochemical properties of the soil and provide nutrients for plants. Nitrogen, phosphorus and potassium, present in treated effluents, can reduce the use of synthetic fertilizers [4,8,14], contributing to the decrease in N_2O and CO_2 emissions [15,16]. However, water reuse may pose risks to public health and to the environment, due to the possible existence of pathogenic microorganisms and toxic chemical compounds, such as disinfection products and emergent pollutants [2,4,8]. In recent years, several European countries, including Cyprus, Greece, France, Italy, Spain and Portugal, have been updating the legal framework [17] for water reuse for multiple non-potable purposes, based on risk assessments. Thus, urban water reuse is considered as a safe process, provided that the treated effluents' risk framework management and the quality standards (based on physicochemical and microbiological parameters) are adequate for the proposed use [2,4,18]. The types of crops irrigated with reclaimed urban water and the irrigation method are important aspects for assessing the risk of transmission of human pathogens through the food chain. For fruit trees, such as citrus trees, not in direct contact with irrigation water, the risks of transmission may be lower than for vegetables, which grow in direct contact with the soil and irrigation-reclaimed water [4,19,20]. Citrus trees are native to Southeast Asia, but have been present in the Mediterranean basin for centuries and have become part of the Mediterranean diet, being used as fresh fruit, as well as in various dishes and desserts [21]. Located in southernmost area of Portugal, the Algarve region has a hot-summer Mediterranean climate, according to the Köppen climate classification, and presents a semi-arid coastal zone [22,23]. Citrus fruits are the main Algarve crop, corresponding to a production of 368,000 t in 2020 [24] of which 316,000 t were oranges.

In general, agriculture accounts for 12% of the total greenhouse gas (GHG) emissions by human activities [25], due to diverse field practices, including irrigation and fertilization. The sustainable management of these practices is considered to be the most promising mitigation pathway to reduce GHG emissions from agricultural soils [26,27]. In the Mediterranean, the use of drip-fertigation is increasing, particularly in high-value crops such as orchards [28], constituting an important practice for the efficient water and fertilizer use, and the reduction in production costs. Conversely, traditional irrigation and fertilization practices are responsible for N_2O emissions between 30% and 50% higher than fertigated crops [29,30], due to the excessive application of nitrogen in traditional practices which led to higher nitrification rates [30]. The carbon emissions (CE) related to synthetic fertilizer include the direct and indirect GHG emissions caused by its production, transportation and application. However, agriculture has the potential to remove atmospheric carbon and orchards can function as carbon sinks, contributing to the mitigation of GHG emissions [31,32]. Citrus orchards are considered to have a high carbon sequestration potential [33], and the trees' ages were identified as a major determinant for the carbon potential sink capacity of such systems [34].

The aim of this study was to assess the feasibility and evaluate the environmental advantages of urban wastewater reuse (use of treated urban effluent) in citrus orchard irrigation as an alternative to groundwater.

2. Materials and Methods

2.1. Study Site

This work was performed in a coastal Mediterranean field at the Algarve region, where agriculture is the biggest water user, and water scarcity is severe during most months of the year. The WWTP, which treated the effluent used in this study, is located in Faro, the capital city of Algarve (7°01'04" N; 7°57'30" W. Figure 1). It was built in 1989 and improved in 2009 to serve between 34,100 and 45,500 equivalent inhabitants, according to population fluctuations, mainly due to the seasonality of tourism. This WWTP is managed by the company responsible for the urban wastewater treatment, Águas do Algarve, S.A. (AdA)—

Águas de Portugal Group, and is located inside the Ria Formosa Natural Park, a shallow coastal lagoon where tourism and shellfish harvesting are important activities for the regional and national economy. The WWTP has a preliminary treatment with an automatic screening system, followed by removal of oil and grease by mechanical separation. There are two lines of biological secondary treatment by activated sludge process (ASP), each one consisting of an anoxic selector followed by an aerobic/anoxic reactor (carrousel type) and a circular decanter. The disinfection is carried out after secondary sedimentation with a UV system, and the treated effluent is discharged into a channel of the Ria Formosa.



Figure 1. Location ($37^{\circ}01'04''$ N; $7^{\circ}57'30''$ W) and details of the study site, with the orchard sectors (I–III) and the WWTP.

The discharge standards and the monitoring results of the treated effluent, reported by AdA, between January 2016 and November 2018 are presented in Table 1.

Considering the existence of an orange (*Citrus × sinensis*) orchard ('Valencia Late' grafted on 'Troyer' citrange) next to the WWTP, with 3397 trees in about 9.5 ha, we evaluated the feasibility of using the treated effluent for irrigation. This is an orchard with drip irrigation (Figure 2), with groundwater from the Campina-Faro aquifer. This aquifer is about 86.4 km² and presents a mean recharge of about 10 hm³ year⁻¹, mostly by precipitation. The water of this aquifer often presents high concentrations of chlorides due to saline intrusion phenomena, and of nitrates resulting from intensive agricultural practices [35,36].

The irrigation system presents two tubes along each row of trees, with dripper spacing of 0.75 m and 2 L h^{-1} discharge rate. The application of synthetic fertilizers is by fertigation and during the experimental period pesticides were not applied.

Table 1. Characteristics of the treated effluent reported by the responsible WWTP management company (AdA) from January 2016 to November 2018.

Parameter	Limit Values Discharge Permit	Min–Max Average \pm SD
Biochemical Oxygen Demand (BOD ₅ , 20 °C) mg L ⁻¹ O ₂	25	<5 ⁽¹⁾ –11 <5 ⁽¹⁾
Chemical Oxygen Demand (COD) mg L ⁻¹ O ₂	125	18–110 34 \pm 11
Total Nitrogen mg L ⁻¹ N	Not Applicable	<3 ⁽¹⁾ –34 11.3 \pm 7.8
Total Phosphorus mg L ⁻¹ P	Not Applicable	<0.50 ⁽¹⁾ –5.3 1.4 \pm 0.9
Total Suspended Solids mg L ⁻¹	35	2–33 5 \pm 4
Fecal coliforms MPN 100 mL ⁻¹	300	3–260 103 \pm 75
Influent Flow Rate m ³ day ⁻¹		4585 \pm 996

⁽¹⁾ Limit of quantification.



Figure 2. General view of the ‘Valencia Late’ orange orchard, where the drip tubes are visible, one on each side of the rows of trees, in the projection of the tree canopy.

2.2. Soil Characterization

This study was performed between March and July 2019. At the beginning of the experimental period, we characterized the chemical properties of the soil, dividing the orchard in three sectors (I–III in Figure 1) and collecting three samples, by sector, of the surface soil (0–10 cm) for further laboratory analysis. In the laboratory, the nine soil samples were air dried, ground on an agate mill and sieved over a 2 mm sieve. For each orchard sector, the texture of the fine earth material (<2 mm) was determined by Bouyoucos method of densimetry [37]. The soil organic matter (OM) was quantified by titrimetry according to the Walkley–Black method [38], and the total nitrogen (TN) by the Kjeldahl method [39]. The water extracts were obtained after the pre-treatment for wet analysis with distilled water. The pH and electric conductivity (EC) were quantified by electrometry, for pH using the Metrohm 780 pH meter in a 1:2.5 suspension of soil in water [40], and for EC using the WTW inolab level 2 with the TetraCon 325 in a 1:2 suspension of soil in water [41]. Chlorides (Cl^-) were quantified by the titration Mohr method [42] in a 1:5 suspension of soil in water. Phosphates (P_2O_5) were determined after Egner–Riehm extraction, by molecular absorption spectrometry [43]. For boron (B), the azomethine-H spectrophotometric method [44] was used after extraction in Morgan’s solution [45]. Calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) were extracted by the ammonium acetate method [46], and for iron (Fe), copper (Cu), manganese (Mn), molybdenum (Mo) and zinc (Zn), the Lakanen–Ervio extraction method was used [47]. After extraction, metals were quantified by atomic absorption spectrometry [43], Ca, Fe, Mg, K, Na and Zn by flame, and Cu, Mn, and Mo by graphite furnace. The sodium adsorption ratio (SAR) was calculated.

To assess whether there were significant differences ($p < 0.05$) in the soil characteristics between the different orchard sectors, a one-way ANOVA test was performed for a 95% confidence interval, using SPSS 26 (IBM, Armonk, NY, USA). After this, was used the Tukey test to check if there was any relationship between the sectors and the detected differences.

2.3. Groundwater and Treated Effluent Characterization

The groundwater (GW) used for orchard irrigation, and the treated effluent (TE) were sampled monthly, between March and July 2019, and three replicates of each sample were collected for further analysis in the laboratory according to Table 2.

Table 2. Analytical methodology used to groundwater (GW) and treated effluent (TE) characterization.

Parameter	Method	GW	TE
Ammonia $\text{mg L}^{-1} \text{NH}_4^+$	Molecular absorption spectrometry, SMEWW 4500-NH ₃ F [43].	✓	✓
BOD ₅ , 20 °C $\text{mg L}^{-1} \text{O}_2$	Respirometric method, SMEWW 5210 D [43].	X	✓
B mg L^{-1}	Molecular absorption, spectrometry, LAE-7.10.3 [48].	✓	✓
Ca, Fe, Li, Mg, K, Na mg L^{-1}	Flame atomic absorption spectrometry, SMEWW 3111 B [43].	✓ ✓ ✓	✓ ✓ ✓
Chlorides $\text{mg L}^{-1} \text{Cl}^-$	Argentometric method, SMEWW 4500 Cl-B [43].	✓	X
EC, 20 °C $\mu\text{S cm}^{-1}$	Electrometry, SMEWW 2510 B [43].	✓	✓
Phosphates $\text{mg L}^{-1} \text{P}$	Molecular absorption spectrometry, SMEWW 4500-P E [43].	✓	✓
Mn, Mo, Se, V mg L^{-1}	Graphite furnace atomic absorption spectrometry, SMEWW 3113 B [43]	X	✓
Fluorides mg L^{-1}	Electrometry, SMEWW 4500-F ⁻ C [43].	X	✓
Nitrates $\text{mg L}^{-1} \text{NO}_3^-$	Molecular absorption spectrometry, SMEWW 4500-NO ₃ B [43].	✓	✓
Oxidability $\text{mg L}^{-1} \text{O}_2$	Titrimetry, LAE-9.1 [42].	✓	X

Table 2. Cont.

Parameter	Method	GW	TE
pH	Potentiometry, SMEWW 4500-H ⁺ B [43].	✓	✓
Sorenson scale Sulphates mg L ⁻¹ SO ₄ ²⁻	Molecular absorption spectrometry, LAE-7.50.2 [48].	✓	✓
Total Dissolved Solids mg L ⁻¹	Gravimetry, SMEWW 2540 C [43].	✓	✓
Total Suspended Solids mg L ⁻¹	Gravimetry, SMEWW 2540 B [43].	✓	✓
Turbidity (NTU)	Turbidimetry, ISO 7027:2019.	X	✓
<i>Escherichia coli</i> (CFU 100 mL ⁻¹)	Membrane filtration [49].	✓	✓

✓—quantified; X—not quantified.

We performed one-way ANOVA test for a 95% confidence interval, to assess whether there were significant differences ($p < 0.05$) over time for all parameters.

2.4. Carbon Emissions Related to the Urban Wastewater Treatment

During the wastewater treatment there are two types of greenhouse gas emissions (GHG) related to WWTP functioning, the direct and indirect emissions from all processes in the plant. Direct emissions refer mainly to N₂O, CH₄, and CO₂ emissions, usually generated by microbial metabolic activities during wastewater treatment and sludge treatment/disposal processes. Indirect carbon emissions result from the energy in operation and resources [34,50,51]. Previous studies, based on the data reported by EU Member States compliant with the Urban Wastewater Treatment Directive (UWWTD 91/271/EEC) made available by the European Environment Agency, estimated that direct N₂O emissions and indirect electricity emissions are the main contributors in the operation phase, followed by direct CH₄ emissions. Analyzing various scenarios to reduce emissions, it was demonstrated that the efficient use of electricity at the plant and the decarbonization of electricity would significantly help to improve the CO₂e footprint of the WWTP [50]. Similar to most WWTP emission protocols, this study does not include the direct GHG emissions, as these GHG are emitted to the atmosphere through the natural process of decomposition anyway [34,52]. Attending to the specific energy consumption of Faro-Noroeste WWT (KWh/m³), reported by AdA, we calculated the carbon emissions (CE) related to the treatment of the necessary volume of effluent for citrus irrigation, during the experimental period.

2.5. Assessment of Environmental Benefits Related to Urban Wastewater Reuse

To evaluate the impact of treated urban effluent reuse on the CE, we compared the CE related to both sources of water for citrus irrigation.

- (1) Considering the current irrigation dose during the experimental period, the energy consumption to groundwater extraction for irrigation was compared with the energy consumption for transporting the treated effluent from the WWTP to the orchard, assuming the same characteristics of the currently installed pump (submersible with a flow rate of 30 m³ h⁻¹ and 7.5 kW). Then, we calculated the CE related to both energy consumptions, considering the carbon emission factor for electricity in Portugal during 2019, 248.65 g CO_{2eq} kWh⁻¹ (EDP, 2020), including emissions of CO₂, CH₄, and N₂O.
- (2) Attending to the amount of synthetic N and P-fertilizers applied by fertigation during the experimental period (when groundwater was used for irrigation), and to the nutrient concentrations (N and P) in the treated effluent, we calculated the necessary adjustment of synthetic fertilizers, to ensure the same nutrient supply to the citrus trees. The CE related to the different amounts of synthetic fertilizers applied in both irrigation conditions was quantified using the CFP of N and P-fertilizers production in Europe at plant gate, calculated according to ISO 14067 [53] (N-fertilizer

CFP = 1.14 kg CO₂e/kg and P-fertilizer CFP = 0.71 kg CO₂e/kg). The CE related to the transportation of fertilizers was not considered in these calculations.

3. Results and Discussion

3.1. Soil Characterization

The characteristics of the soil are presented in Table 3. The ANOVA test showed significant differences ($p < 0.05$) for all parameters. According to the Tukey test, for levels of pH, Phosphorus, Magnesium, organic matter, Iron, Manganese, Calcium and Molybdenum, sectors II and III do not present significant differences between them, but they present significant differences to sector I. The soil texture in sector I is sandy clay loam and in sectors II and III is loamy sand. As expected, clayey soil is richer in OM and, therefore, in P and N. Higher pH and higher Ca concentrations are associated with lower Fe bioavailability.

Table 3. Chemical soil properties (average \pm standard deviation). Values with different letters (a, b and c) are significantly different at $p < 0.05$.

Parameter	Sector I	Sector II	Sector III	Mean Sectors I, II, III
pH	8.4 ^a \pm 0.1	7.6 ^b \pm 0.1	7.5 ^b \pm 0.1	7.8 \pm 0.5 *
EC, 20 °C dS m ⁻¹	2.90 ^a \pm 0.06	1.99 ^b \pm 0.01	6.62 ^c \pm 0.04	3.84 \pm 2.12 *
TN mg kg ⁻¹ N-NH ₄ ⁺	624 ^a \pm 12	448 ^b \pm 36	520 ^c \pm 28	531 \pm 80 *
Cl ⁻ mg kg ⁻¹	676 ^a \pm 71	193 ^b \pm 183	534 ^a \pm 97	468 \pm 241 *
B mg g ⁻¹	0.60 ^a \pm 0.04	0.57 ^b \pm 0.03	0.67 ^c \pm 0.04	0.61 \pm 0.05 *
P ₂ O ₅ mg kg ⁻¹	689 ^a \pm 71	403 ^b \pm 17	477 ^b \pm 17	523 \pm 134 *
OM% m.m ⁻¹	1.4 ^a \pm 0.1	1.2 ^b \pm 0.1	1.1 ^b \pm 0.1	1.2 \pm 0.2 *
Ca mg kg ⁻¹	560 ^a \pm 8	345 ^b \pm 18	382 ^b \pm 3	429 \pm 100 *
Fe mg kg ⁻¹	39.0 ^a \pm 1.4	78.3 ^b \pm 5.5	78.1 ^b \pm 1.9	65.1 \pm 19.8 *
Cu mg kg ⁻¹	14.1 ^a \pm 0.3	14.2 ^a \pm 0.6	19.1 ^b \pm 0.7	15.8 \pm 2.5 *
Mg mg kg ⁻¹	493 ^a \pm 2	247 ^b \pm 2	250 ^b \pm 2	330 \pm 122 *
K ₂ O mg kg ⁻¹	1092 ^a \pm 7	932 ^b \pm 10	1261 ^c \pm 26	1095 \pm 143 *
Na mg kg ⁻¹	48.3 ^a \pm 2.9	14.2 ^b \pm 0.6	44.5 ^a \pm 1.1	35.7 \pm 16.3 *
Mn mg kg ⁻¹	30.6 ^a \pm 0.9	22.7 ^b \pm 1.5	23.9 ^b \pm 0.6	25.7 \pm 3.8 *
Mo mg kg ⁻¹	1.25 ^a \pm 0.02	2.10 ^b \pm 0.15	2.45 ^b \pm 0.02	1.93 \pm 0.54 *
Zn mg kg ⁻¹	13.8 ^a \pm 0.2	12.4 ^b \pm 0.4	14.4 ^a \pm 0.2	13.4 \pm 0.9 *

* There are significant differences at ANOVA test.

3.2. Climate Conditions and Water Consumption on Irrigation

Between March and July 2019, the local mean atmospheric temperature was 19.3 °C, with a minimum of 12.8 °C (March) and a maximum of 32.0 °C (June). The local precipitation was below 5 mm, and from June the percentage of water in the soil was less than 20% (IPMA, 2019). The total groundwater consumption for orchard irrigation during the experimental period was 27,891 m³. The water consumption per month increased from the coldest month (March) to the warmer months (June and July), according to Figure 3. This figure also shows the consumptions in the same months of the previous two years, as well as the mean per month over the three years.

3.3. Groundwater and Treated Wastewater Characterization

The results of groundwater monitoring during the experimental period, and maximum recommended values (MRV) in Portuguese legislation, are summarized in Table 4. In general, all parameters in groundwater showed lower values than MRV, except for electrical conductivity (1.45 \pm 0.04 dS m⁻¹), chlorides (395 \pm 138 mg L⁻¹ Cl⁻) and TDS (1044 \pm 163 mg L⁻¹). These results seem to confirm the occurrence of saline intrusion phenomena in the Campina-Faro aquifer, as reported before, e.g., by Nunes et al. [36]. During the experimental period, there were significant differences ($p < 0.05$) for all parameters over time, confirming the seasonality effect, except for oxidability and sulphates. The oxidability values were very low (1.3 \pm 0.7 mg L⁻¹ O₂) over all months and sulphate concentrations remained stable throughout the experimental period (217 \pm 18 mg L⁻¹ SO₄²⁻).

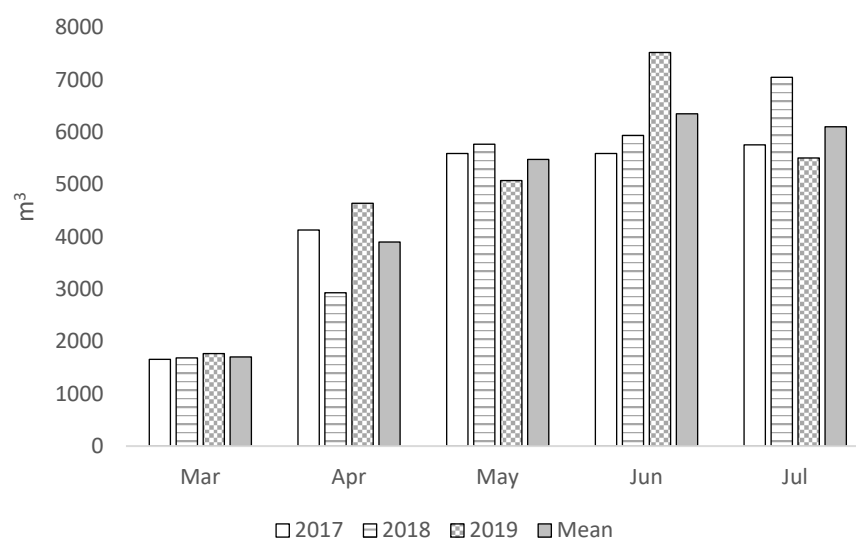


Figure 3. Evolution of groundwater consumption for orchard irrigation during the experimental period, similar months in 2017 and 2018, and mean per month.

Table 4. Chemical characterization of groundwater and treated effluent throughout the experimental period (average \pm standard deviation).

Parameter	Groundwater (GW)	Natural Water for Irrigation MRV ⁽¹⁾	Treated Effluent (TE)	Water Reuse QS ⁽²⁾
Ammonia mg L ⁻¹ NH ₄ ⁺	0.023 \pm 0.020	–	3.92 \pm 1.59	10
BOD ₅ , 20 °C mg L ⁻¹ O ₂	X	–	10.1 \pm 5.3	\leq 25
B mg L ⁻¹	0.08 \pm 0.02	0.3	0.16 \pm 0.03	–
Ca mg L ⁻¹	52.5 \pm 1.1	–	34.1 \pm 1.1	–
Fe mg L ⁻¹	X	5.0	0.44 \pm 0.03	2.0
Li mg L ⁻¹	X	2.5	0.11 \pm 0.01	2.5
Mg mg L ⁻¹	51.2 \pm 11.4	–	34.9 \pm 7.0	–
K mg L ⁻¹	35.6 \pm 19.4	–	23.4 \pm 11.7	–
Na mg L ⁻¹	123 \pm 6	–	142 \pm 25	–
Chlorides mg L ⁻¹ Cl ⁻	395 \pm 138	70	311 \pm 94	–
EC, 20 °C dS m ⁻¹)	1.45 \pm 0.04	1	1.29 \pm 0.23	–
Phosphates mg L ⁻¹ P	<0.125 ⁽³⁾	–	0.5 \pm 0.34	5 (Total Phosphorous)
Mn mg L ⁻¹ Mn	X	0.20	0.02 \pm 0.01	0.2
Mo mg L ⁻¹	X	0.005	0.21 \pm 0.15	0.01
Se mg L ⁻¹	X	0.02	<0.01 ⁽³⁾	0.02
V mg L ⁻¹	X	0.10	<0.01 ⁽³⁾	0.1
Fluorides mg L ⁻¹	X	1.0	0.15 \pm 0.02	2.0
Nitrates mg L ⁻¹ NO ₃ ⁻	<4 ⁽³⁾	50	4 \pm 1	15 (Total Nitrogen)
Oxidability mg L ⁻¹ O ₂	1.3 \pm 0.7	–	X	–
pH Sorenson scale	7.41 \pm 0.17	6.5–8.4	7.87 \pm 0.14	–
SAR	3.6 \pm 0.8	8	4.1 \pm 0.6	–
Sulphates mg L ⁻¹ SO ₄ ²⁻	217 \pm 18	575	171 \pm 15	–
TDS mg L ⁻¹	1044 \pm 163	640	830 \pm 166	–
TSS mg L ⁻¹	1.0 \pm 0.8	60	3.5 \pm 1.8	\leq 35
Turbidity NTU	X	–	7.5 \pm 2.4	–
<i>Escherichia coli</i> CFU/100 mL	0 to 2	100	2 to 100	\leq 100

– not referred; X not quantified; ⁽¹⁾ maximum recommended value in Portuguese Law 236/98, Annex XVI; ⁽²⁾ quality standards in Portuguese Law 119/2019 and EU Regulation 2020/741, for fruits not in direct contact with irrigation water [54]; ⁽³⁾ limit of quantification.

The overall volume of treated effluent produced by the WWTP, during the experimental period was about 619,359 m³, 22 times higher than the volume of groundwater consumed for irrigation. The specific energy consumption on the WWTP during the experimental period was 0.77 kWh.m⁻³, meaning that 118,583 kg CO₂e were emitted. Figure 4 presents the monthly variation on treated effluent production during the experimental period and in the same months of the previous two years, as well as the mean per month over the three years.

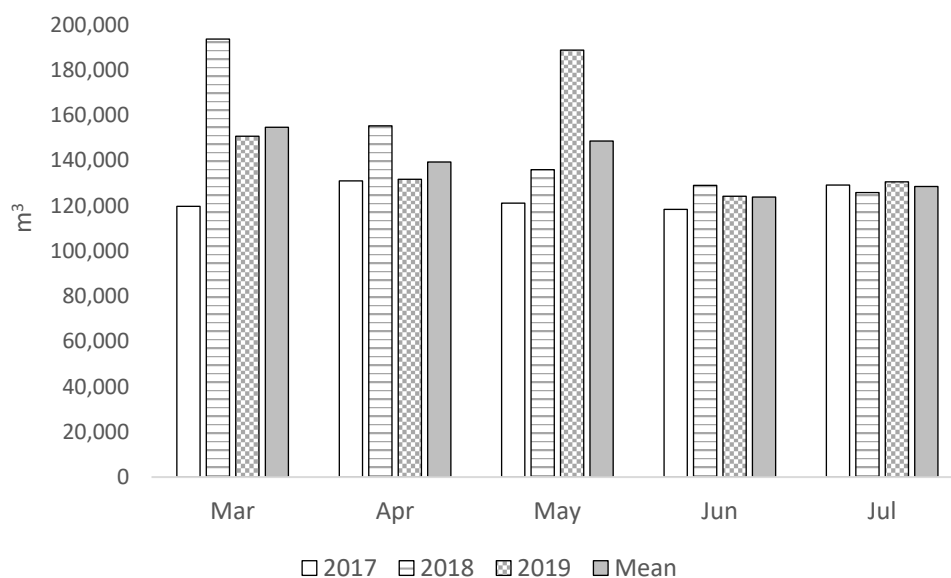


Figure 4. Evolution of treated effluent production during the experimental period, on similar months in 2017 and 2018, and mean per month.

Table 4 also shows the characteristics of the treated effluent and Quality Standards, for water reuse in fruit tree irrigation. All parameters meet the quality standards, except for molybdenum and total dissolved solids. Molybdenum can reach the wastewaters from diverse anthropogenic sources, such as metallurgical processing, coal and petroleum burning or discharges of phosphate detergents. Molybdenum is an essential micronutrient for plants, but toxic if present in high concentrations. The soil properties influence its availability, the molybdenum phytotoxicity being greater in alkaline soils, and in dicotyledonous species [55]. Despite this, under natural conditions there is no reference to the toxicity of molybdenum in citrus trees.

The treated effluent presented a higher organic matter content than the groundwater (in TE: $\text{BOD} = 10.1 \pm 5.3 \text{ mg L}^{-1} \text{ O}_2$ and in GW: oxidability = $1.3 \pm 0.7 \text{ mg L}^{-1} \text{ O}_2$), suggesting that the use of TE can have a positive effect on soil organic carbon and on its water retention [4,56,57]. Attending to the ammonia ($3.92 \pm 1.59 \text{ mg L}^{-1} \text{ NH}_4^+$), nitrate ($4 \pm 2 \text{ mg L}^{-1} \text{ NO}_3^-$) and phosphate ($0.57 \pm 0.34 \text{ mg L}^{-1} \text{ P}$) concentrations, it is expected that the discharge of the treated effluent into Ria Formosa may cause eutrophication phenomena. Alternatively, if this treated effluent is used for irrigation, then it contributes to increasing the N-forms and P-forms in the soil. Efficient irrigation and fertilization practices can be an important contribution to the ecosystem's sustainability and agriculture development [58]. These results confirmed that the use of the treated effluent for irrigation, with higher nutrient levels than groundwater (phosphorous and nitrogen), instead of being discharged into the Ria Formosa lagoon, can be used for supply, at least a part, of the crops requirements, as reported before in other studies [4]. The quantified values for *E. coli* are compatible with the water reuse for the irrigation of fruit trees, and the risk of contamination is even lower when using a drip irrigation system which means that the irrigation water does not come into contact with the aerial part of the plant.

Although in the Portuguese legal framework *E. coli* is proposed to be the “hazard” indicator as it is the most suitable indicator of fecal contamination, the water quality is not considered the only parameter that can ensure health protection in water reuse projects. The adoption of other preventive measures to reduce hazards and exposure to hazards must be identified, i.e., barriers to minimize contact with reclaimed water and recognized receptors. The irrigation type and schedule, harvest options, and crop characteristics can limit the contact between people and pathogens present in reclaimed water. Previous studies showed that drip irrigation of high-growing crops, 50 cm or more above the ground, allows a $4 \log_{10}$ pathogen reduction meaning 2 equivalent barriers [2]. These studies were

carried out in a vineyard irrigated with reclaimed water from an urban WWTP, where grapes are used exclusively for wine production, therefore in conditions not very different from a citrus orchard.

Regarding the conductivity of the irrigation water, it is recommended not to use water with an electrical conductivity greater than 3 dS/m; the adjusted sodium adsorption ratio should be less than 9 and the chloride ion concentration less than 355 mg L⁻¹. It is also not recommended to use water with boron concentrations above 0.75 mg L⁻¹.

3.4. Orange Production and Carbon Fluxes

The production of oranges was 117.3 t (25 t ha⁻¹), which is considered a relatively low yield for a 30-year-old orchard, but consistent with the relatively small size of the trees.

Orange production is considered to contribute to GHC mainly due to the CO₂ and CH₄ emissions on the production of synthetic fertilizers and to the N₂O emissions from soil denitrification during the agricultural practices [59]. In our work, we calculated the CE per kg of harvested oranges, considering the contribution of synthetic fertilizers production and the energy consumption in pumping water for irrigation, during the experimental period (Table 5).

Table 5. Carbon emissions related to the energy consumption in pumping water for irrigation and orchard fertilization.

Water Source for Irrigation	Energy Consumption in Water Pumping kW	Synthetic Fertilization		Carbon Emissions	
		N-Fertilizer kg	P-Fertilizer kg	kg CO ₂ e	g CO ₂ e. kg ⁻¹ of Oranges
Groundwater	3449	870	733	858.968	7.32
Treated effluent	1734	76.7	683	431.662	3.68

Our results show that the wastewater reuse allows for a significant reduction in CE related to orange production, minus 50% for the water pumping for irrigation, minus 91% for the N-fertilizer and minus 7% for the P-fertilizer, which means minus 3.64 g CO₂e. kg⁻¹ of harvested oranges and a reduction of 427.306 kg CO₂e per total orange production, during the experimental period. These results show that wastewater reuse in citrus orchards irrigation can contribute to more sustainable food production. Previous works [60] presented the carbon footprint of oranges produced in Spain, Italy and Brazil, showing that the values vary considerably from 80 to 330 g CO₂e per kg of harvested oranges. In our work, the carbon emissions per kg of harvested oranges present lower values because we only quantified the CE directly related to the replacement of groundwater by the treated effluent in orchard irrigation. The N₂O emissions due to the agricultural practices, not considered in this study, will be relevant to the carbon footprint and similar in both irrigation conditions.

Previous studies in eastern Spain [33] reported that an adult citrus tree (over 12 years old) is able to fix a net carbon amount higher than 73.29 kg CO₂ tree⁻¹ yr⁻¹ and total biomass of the annual organs accounted for more than 70% of this value, specifically, harvested fruit. According to this reference, we estimated that during the five-month experimental period, the carbon sequestration in biomass was about 30.55 kg CO₂ tree⁻¹, representing about 103,747 kg CO₂ sequestered by the orchard of which 72,623 kg of CO₂ was converted into orange biomass. These results indicate that this orchard has sequestered 87.5% of the carbon emissions related to the energy consumption necessary for the urban wastewater treatment, highlighting its importance in reducing the WWTP impact on GHC emissions.

4. Conclusions

This study shows that treated effluent reuse is technologically feasible for citrus orchards irrigation and can contribute to improving the carbon fluxes, reducing GHC emissions, and promoting carbon sequestration. According to our results, the GHC emis-

sions related to orange production can decrease, mainly due to the reduction in energy consumption of water pumping for irrigation, and the need to apply a smaller amount of synthetic fertilizers, since the treated effluent presents higher concentrations of nitrates and phosphates than groundwater. In addition, although further studies are needed, this alternative source of water for citrus irrigation presents other benefits for natural ecosystem protection. The use of reclaimed water prevents the overexploitation of coastal aquifers, reducing saline intrusion and, at the same time, reducing nutrient discharges into the Ria Formosa, avoiding eutrophication phenomena in this coastal lagoon, classified as a Ramsar site. Since the organic matter content in the treated effluent is higher than in groundwater, it is expected that the use of reclaimed water promotes water retention in soil, improving plant growth and thus carbon sequestration. This improvement in the carbon sequestration by the citrus orchard will increase fruit production and the farmer profits.

Finally, this work highlights the great potential of citrus orchards to sequester GHG emitted by the urban WWTP, and its potential contribution to the carbon neutrality of the urban wastewater treatment.

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References

1. Libutti, A.; Gatta, G.; Gagliardi, A.; Vergine, P.; Pollice, A.; Beneduce, L.; Disciglio, G.; Tarantino, E. Agro-industrial wastewater reuse for irrigation of a vegetable crop succession under Mediterranean conditions. *Agric. Water Manag.* **2018**, *196*, 1–14. [[CrossRef](#)]
2. Rebelo, A.; Quadrado, M.; Franco, A.; Lacasta, N.; Machado, P. Water reuse in Portugal: New legislation trends to support the definition of water quality standards based on risk characterization. *Water Cycle* **2020**, *1*, 41–53. [[CrossRef](#)]
3. Parris, K. *Sustainable Management of Water Resources in Agriculture*; OECD Publishing: Paris, France, 2010.
4. Becerra-Castro, C.; Lopes, A.R.; Vaz-Moreira, I.; Silva, E.F.; Manaia, C.M.; Nunes, O.C. Wastewater reuse in irrigation: A microbiological perspective on implications in soil fertility and human and environmental health. *Environ. Int.* **2015**, *75*, 117–135. [[CrossRef](#)] [[PubMed](#)]
5. Chartzoulakis, K.; Bertaki, M. Sustainable Water Management in Agriculture under Climate Change. *Agric. Agric. Sci. Procedia* **2015**, *4*, 88–98. [[CrossRef](#)]
6. Karandish, F.; Šimůnek, J. A field-modeling study for assessing temporal variations of soil-water-crop interactions under water-saving irrigation strategies. *Agric. Water Manag.* **2016**, *178*, 291–303. [[CrossRef](#)]
7. Jenkins, M.W.; Sugden, S. *Human Development Report 2006*; United Nations Development Programme: New York, NY, USA, 2006; Volume 36.
8. Fatta-Kassinos, D.; Kalavrouziotis, I.K.; Koukoulakis, P.H.; Vasquez, M.I. The risks associated with wastewater reuse and xenobiotics in the agroecological environment. *Sci. Total Environ.* **2011**, *409*, 3555–3563. [[CrossRef](#)]
9. Jiang, Y.; Xu, X.; Huang, Q.; Huo, Z.; Huang, G. Optimizing regional irrigation water use by integrating a two-level optimization model and an agro-hydrological model. *Agric. Water Manag.* **2016**, *178*, 76–88. [[CrossRef](#)]
10. Santana, M.V.E.; Cornejo, P.K.; Rodríguez-Roda, I.; Buttiglieri, G.; Corominas, L. Holistic life cycle assessment of water reuse in a tourist-based community. *J. Clean. Prod.* **2019**, *233*, 743–752. [[CrossRef](#)]
11. Bixio, D.; Thoeye, C.; Wintgens, T.; Ravazzini, A.; Miska, V.; Muston, M.; Chikurel, H.; Aharoni, A.; Joksimovic, D.; Melin, T. Water reclamation and reuse: Implementation and management issues. *Desalination* **2008**, *218*, 13–23. [[CrossRef](#)]
12. Garcia, X.; Pargament, D. Reusing wastewater to cope with water scarcity: Economic, social and environmental considerations for decision-making. *Resour. Conserv. Recycl.* **2015**, *101*, 154–166. [[CrossRef](#)]

13. Nas, B.; Uyanik, S.; Aygün, A.; Doğan, S.; Erul, G.; Nas, K.B.; Turgut, S.; Cop, M.; Dolu, T. Wastewater reuse in Turkey: From present status to future potential. *Water Supply* **2020**, *20*, 73–82. [[CrossRef](#)]
14. Adrover, M.; Farrús, E.; Moyà, G.; Vadell, J. Chemical properties and biological activity in soils of Mallorca following twenty years of treated wastewater irrigation. *J. Environ. Manag.* **2012**, *95*, S188–S192. [[CrossRef](#)] [[PubMed](#)]
15. Syakila, A.; Kroeze, C.; Slomp, C.P. Neglecting sinks for N₂O at the earth's surface: Does it matter? *J. Integr. Environ. Sci.* **2010**, *7*, 79–87. [[CrossRef](#)]
16. Chojnacka, K.; Kowalski, Z.; Kulczycka, J.; Dmytryk, A.; Górecki, H.; Ligas, B.; Gramza, M. Carbon footprint of fertilizer technologies. *J. Environ. Manag.* **2019**, *231*, 962–967. [[CrossRef](#)]
17. Procuradoria-Geral Distrital de Lisboa. *Decreto Lei 119/2019. Regime Jurídico de Produção de Água Para Reutilização Obtida a Partir do Tratamento de Águas Residuais e Sua Utilização*; Procuradoria-Geral Distrital de Lisboa: Lisbon, Portugal, 2019; pp. 21–44.
18. U.S. Environmental Protection Agency. *Guidelines for Water Reuse*; Environmental Protection Agency (EPA): Washington, DC, USA, 2012.
19. Cirelli, G.L.; Consoli, S.; Licciardello, F.; Aiello, R.; Giuffrida, F.; Leonardi, C. Treated municipal wastewater reuse in vegetable production. *Agric. Water Manag.* **2012**, *104*, 163–170. [[CrossRef](#)]
20. Melloul, A.A.; Hassani, L.; Rafouk, L. Salmonella contamination of vegetables irrigated with untreated wastewater. *World J. Microbiol. Biotechnol.* **2001**, *17*, 207–209. [[CrossRef](#)]
21. Duarte, A.; Fernandes, J.; Bernardes, J.; Miguel, G. Citrus as a Component of the Mediterranean Diet. *J. Spat. Organ. Dyn.* **2016**, *IV*, 289–304.
22. Hugman, R.; Stigter, T.Y.; Monteiro, J.P.; Costa, L.; Nunes, L.M. Modeling the spatial and temporal distribution of coastal groundwater discharge for different water use scenarios under epistemic uncertainty: Case study in South Portugal. *Environ. Earth Sci.* **2015**, *73*, 2657–2669. [[CrossRef](#)]
23. Estrela, T.; Marcuello, C.; Iglesias, A. *Water Resources Problem in Southern EUROPE—An Overview Report*; Office for Official Publications of the European Communities: Luxembourg, 1996.
24. INE. Instituto Nacional de Estatística Bases de Dados. Available online: <https://www.ine.pt> (accessed on 23 May 2022).
25. Edenhofer, O. (Ed.) *Intergovernmental Panel on Climate Change. Climate Change 2014 Mitigation of Climate Change*; Cambridge University Press: Cambridge, UK, 2014; ISBN 9781107654815.
26. Liu, C.; Wang, K.; Meng, S.; Zheng, X.; Zhou, Z.; Han, S.; Chen, D.; Yang, Z. Effects of irrigation, fertilization and crop straw management on nitrous oxide and nitric oxide emissions from a wheat–maize rotation field in northern China. *Agric. Ecosyst. Environ.* **2011**, *140*, 226–233. [[CrossRef](#)]
27. Scheer, C.; Grace, P.R.; Rowlings, D.W.; Payero, J. Nitrous oxide emissions from irrigated wheat in Australia: Impact of irrigation management. *Plant Soil* **2012**, *359*, 351–362. [[CrossRef](#)]
28. Brouwer, C.; Prins, K.; Kay, M.; Heibloem, M. *Irrigation Water Management: Irrigation Methods*; FAO: Rome, Italy, 1989.
29. Kennedy, T.L.; Suddick, E.C.; Six, J. Reduced nitrous oxide emissions and increased yields in California tomato cropping systems under drip irrigation and fertigation. *Agric. Ecosyst. Environ.* **2013**, *170*, 16–27. [[CrossRef](#)]
30. Shcherbak, I.; Millar, N.; Robertson, G.P. Global metaanalysis of the nonlinear response of soil nitrous oxide (N₂O) emissions to fertilizer nitrogen. *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 9199–9204. [[CrossRef](#)] [[PubMed](#)]
31. Sahoo, U.K.; Nath, A.J.; Lalnunpuui, K. Biomass estimation models, biomass storage and ecosystem carbon stock in sweet orange orchards: Implications for land use management. *Acta Ecol. Sin.* **2021**, *41*, 57–63. [[CrossRef](#)]
32. West, T.O.; Marland, G. Net carbon flux from agricultural ecosystems: Methodology for full carbon cycle analyses. *Environ. Pollut.* **2002**, *116*, 439–444. [[CrossRef](#)]
33. Núñez-Florez, R.; Pérez-Gómez, U.; Fernández-Méndez, F. Functional diversity criteria for selecting urban trees. *Urban For. Urban Green.* **2019**, *38*, 251–266. [[CrossRef](#)]
34. Mo, W.; Zhang, Q. Can municipal wastewater treatment systems be carbon neutral? *J. Environ. Manag.* **2012**, *112*, 360–367. [[CrossRef](#)]
35. Almeida, C.; Mendonça, J.J.L.; Jesus, M.R.; Gomes, A.J. *Sistemas aquíferos de Portugal Continental [Aquifer systems in Portugal mainland]*; INAG: Lisbon, Portugal, 2000.
36. Nunes, L.; Monteiro, J.P.; Cunha, M.C.; Vieira, J.; Lucas, H.; Ribeiro, L. The water crisis in southern Portugal: How did we get there and how should we solve it. In *Management of Natural Resources, Sustainable Development and Ecological Hazards*; WIT Press: Southampton, UK, 2006; Volume I, pp. 435–444.
37. Day, P.R. Particle Fractionation and Particle-Size Analysis. *Methods Soil Anal.* **2015**, *9*, 545–567.
38. Schumacher, B.A. *Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments*, EPA/600/R-02/069 (NTIS PB2003-100822); U.S. Environmental Protection Agency: Washington, DC, USA, 2002.
39. Bremner, J.M. Determination of nitrogen in soil by the Kjeldahl method. *J. Agric. Sci.* **1960**, *55*, 11–33. [[CrossRef](#)]
40. *ISO 10390*; Soil Quality Determination of PH. International Organization for Standardization: Genève, Switzerland, 2021.
41. *EN13038*; Soil Improvers and Growing Media—Determination of Electrical Conductivity. CEN, European Committee for Standardization: Brussels, Belgium, 1999.
42. Hesse, P.R. *A Text Book of Soil Chemical Analysis*; Chemical Publishing: New York, NY, USA, 1972.

43. Baird, R.B.; Eaton, A.D.; Rice, E.W. *Standard Methods for the Examination of Water and Wastewater*, 23rd ed.; Water Environment Federation: Alexandria, VA, USA; American Public Health Association: Washington, DC, USA; American Water Works Association: Denver, CO, USA, 2017.
44. Sarkar, D.; Sheikh, A.A.; Batabyal, K.; Mandal, B. Boron Estimation in Soil, Plant, and Water Samples using Spectrophotometric Methods. *Commun. Soil Sci. Plant Anal.* **2014**, *45*, 1538–1550. [[CrossRef](#)]
45. Sims, J.T. Recommended soil test for boron. *Coop. Bull.* **2011**, *493*, 49–54.
46. Schollenberger, C.J.; Simon, R.H. Determination of exchange capacity and exchangeable bases in soil—Ammonium acetate method. *Soil Sci.* **1945**, *59*, 13–24. [[CrossRef](#)]
47. Lakanen, E.; Erviö, R. A comparison of eight extractants for determination of plant available micronutrients in soil. *Acta Agron. Fenn.* **1971**, *123*, 223–232.
48. Rodier, J.; Legube, B.; Merlet, N. *L'analyse de L'eau*, 10th ed.; Dunod: Paris, France, 2016.
49. *BS EN ISO 9308-1:2014+A1*; Water Quality—Enumeration of Escherichia coli and coliform bacteria Membrane Filtration Method for Waters with Low Bacterial Background Flora. International Organisation for Standardisation (ISO): Geneva, Switzerland, 2017.
50. Parravicini, V.; Nielsen, P.H.; Thornberg, D.; Pistocchi, A. Evaluation of greenhouse gas emissions from the European urban wastewater sector, and options for their reduction. *Sci. Total Environ.* **2022**, *838*, 156322. [[CrossRef](#)]
51. Li, L.; Wang, X.; Miao, J.; Abulimiti, A.; Jing, X.; Ren, N. Carbon neutrality of wastewater treatment—A systematic concept beyond the plant boundary. *Environ. Sci. Ecotechnol.* **2022**, *11*, 100180. [[CrossRef](#)]
52. Crawford, G.G.; Johnson, T.D.; Johnson, B.R.; Krause, T.H.W. *CHEApet Users Manual, OWSO4R07*; Water Environment Research Foundation: Alexandria, VA, USA, 2011.
53. Brentrup, F.; Lammel, J.; Stephani, T.; Christensen, B. Updated carbon footprint values for mineral fertilizer from different world regions. In Proceedings of the 11th International Conference LCA of Food, Bangkok, Thailand, 17–19 October 2018.
54. The European Parliament and the Council Regulation (EU). Minimum requirements for water reuse. *Off. J. Eur. Union* **2020**, *177*, 32–55.
55. McGrath, S.P.; Micó, C.; Zhao, F.J.; Stroud, J.L.; Zhang, H.; Fozard, S. Predicting molybdenum toxicity to higher plants: Estimation of toxicity threshold values. *Environ. Pollut.* **2010**, *158*, 3085–3094. [[CrossRef](#)] [[PubMed](#)]
56. Baldock, J.A.; Nelson, P.N. Soil Organic Matter. In *Handbook of Soil Science*; Sumner, M.E., Ed.; CRC Press: Boca Raton, FL, USA, 2000; pp. B-25–B-84.
57. Sparks, D.L. *Environmental Soil Chemistry*, 2nd ed.; Academic Press: Cambridge, MA, USA, 2003; ISBN 9780126564464.
58. Li, C.; Xiong, Y.; Huang, Q.; Xu, X.; Huang, G. Impact of irrigation and fertilization regimes on greenhouse gas emissions from soil of mulching cultivated maize (*Zea mays* L.) field in the upper reaches of Yellow River, China. *J. Clean. Prod.* **2020**, *259*, 120873. [[CrossRef](#)]
59. Ribal, J.; Sanjuan, N.; Clemente, G.; Fenollosa, M.L. Medición de la ecoeficiencia en procesos productivos en el sector agrario. Caso de estudio sobre producción de cítricos. *Econ. Agrar. Recur. Nat.* **2009**, *9*, 125–148. [[CrossRef](#)]
60. Mordini, M.; Nemecek, T.; Gaillard, G. *Carbon & Water Footprint of Oranges and Strawberries: A Literature Review*; Federal Department of Economic Affairs: Zurich, Switzerland, 2009; Volume 76.