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Quality characteristics and hydrogeochemistry of irrigation waters from three major olive groves in Greece

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ABSTRACT

Surface and groundwater samples were collected from three key olive grove regions in Greece in order to assess their overall quality and outline major hydrogeochemical characteristics. The three study areas were selected for their significance to the national olive production as well as for their diverse physiographic characteristics and imposed cultivation practices. Results suggest that quality status in general is acceptable with few exceptions; however, issues related with salinization were identified which in turn could potentially lead to environmental degradation. Hydrogeochemical characteristics are affected by geogenic (natural) factors and anthropogenic influences to some extent. Results were confirmed by PoS index which classified samples according to their quality status. Overall, the controlling factors appear to be the geological setup, the hydrogeological regime, as well as the irrational cultivation practices and groundwater overexploitation. Environmental sustainability in the three examined regions is considered feasible on the grounds of a critical balance between environmental protection and production optimization. This balance may be achieved through the implementation of tailored actions and management measures, designed for each of the three cultivated areas and every plot participating in the study.

Keywords: Hydrogeochemistry; Irrigation water; Environmental assessment; Olive groves; PoS index

1. Introduction

Olives and olive oil are traditional products of Greece that date back a few millennia and mark two of the most characteristic ingredients of the Mediterranean nutrition. Their production is a major element of the overall national agricultural potential and sustains local economies with a high financial profit. Besides that, extensive olive tree groves form characteristic landscapes of high environmental and aesthetic value. Considering the above, olive groves' sustainable cultivation is an issue of major significance

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related both with financial and environmental aspects. Hence, some of the critical factors are related with the hydrogeochemical and environmental characteristics of irrigation water; the latter is related with the yield potential (quantity and quality) and the possible environmental pressures to surface and groundwaters, as well as to soil resources of the regions. The present study examines comparatively the quality characteristics of irrigation waters from three major Greek olive grove areas, and attempts to make an initial assessment of their suitability for irrigation, an identification of the environmental pressures origin and their anticipated impacts. Based on that, specific measures are suggested and remedial actions proposed in order to mitigate the potential adverse environmental effects.

The three case study areas are located in the southern part of the Greek territory (Fig. 1): (a) southeastern Peloponnese, Nileas area (NIL), (b) central Crete, Peza area (PEZ), and (c) eastern Crete, Merambello area (MER). Following the Emberger's bioclimatic classification [1] Nileas is characterized by sub-humid climatic conditions while Peza and Merambello by semi-arid. The geological structure of the three areas is complex and quite diverse, controlled by active fault tectonics, which in all cases affect local hydrogeochemical conditions. Peza area is dominated by quaternary formations that host a heterogeneous aquifer system within the alluvial deposits; the latter covers the eastern part of the study area [2–4]. Merambello, which is located eastern of Peza, is characterized

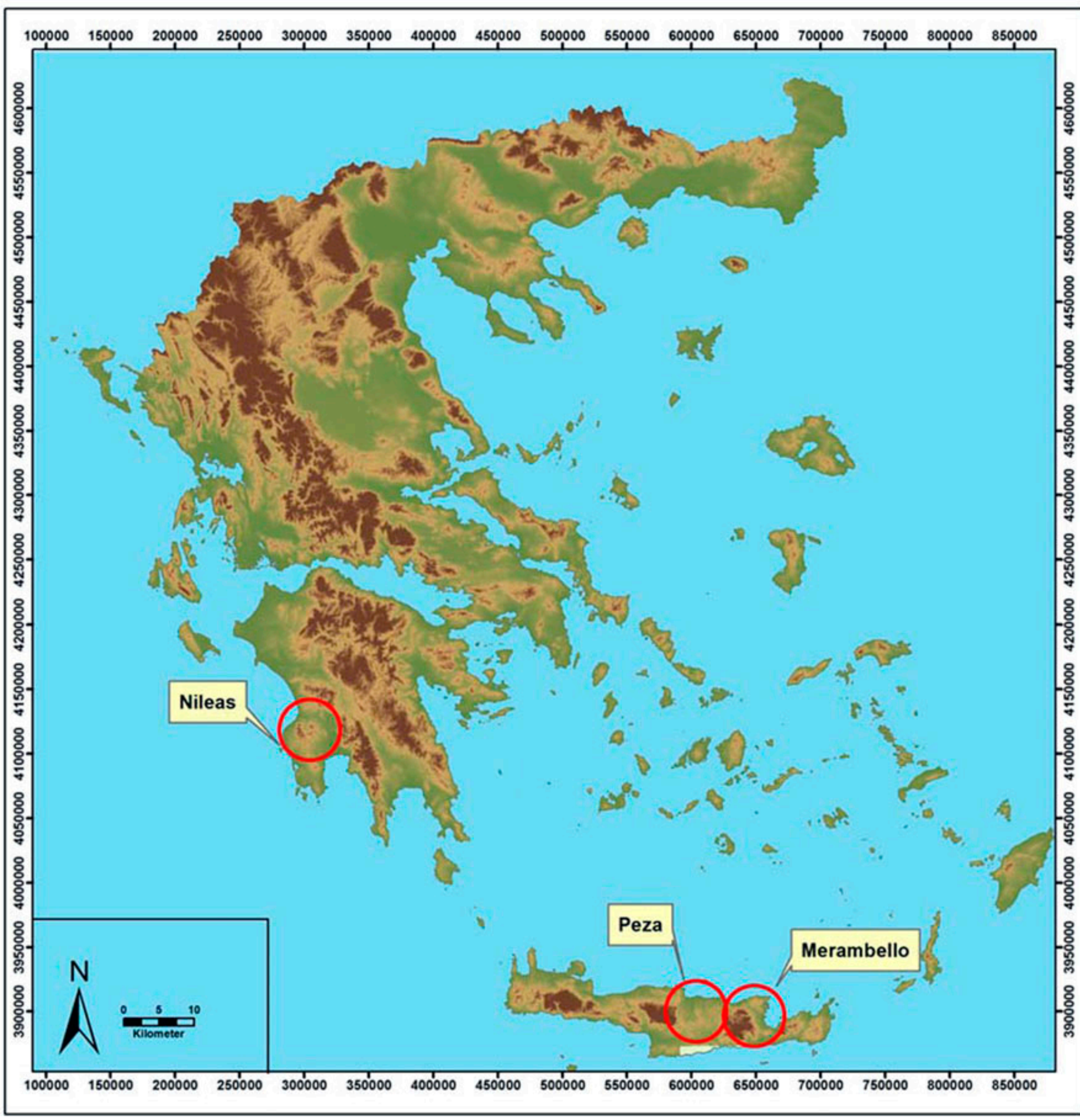

Fig. 1. Geographical location of the three study areas.

mainly by limestones and quaternary formations within which aquifers of variable potential and characteristics are developed [2,5–8]. Finally, Nileas is dominated by a more complex geological structure mainly consisting of limestones, flysch, volcanic formations, and quaternary formations [6,9,10].

2. Sampling and analysis

Totally 97 irrigation water samples (surface and groundwater) were collected from the three study areas during the wet hydrological period of 2011 (November–December) and the dry hydrological period of 2012 (July–August). In situ measurements of pH, electrical conductivity (EC), and temperature (*T*) were performed by means of a portable instrument. Water samples were immediately filtered in the field through 0.45 μm membrane filters and separated into two aliquots of 1 L and 50 mL, respectively. The smaller aliquot was acidified down to pH 2 with ultrapure HNO_3 in order to prevent metal precipitation and complexation, and stored in new polyethylene bottles. Analyses were performed at the accredited laboratory of the Land Reclamation Institute. Samples were analyzed for 15 parameters (Table 1) including major ions, trace elements, and physicochemical parameters. The quality control of the results was validated with the aid of ionic balance ratio [11] which was found to be within the acceptable margins (<10%).

3. Results and discussion

3.1. General hydrogeochemical trends

Based on the analytical results, the samples from the three study areas differ significantly in the concentration range of specific parameters as well as in the dominant water types which are related with the prevalent hydrogeochemical conditions. A general outline of irrigation waters' chemistry is displayed in the Piper diagram of Fig. 2.

A considerable percentage of the examined Merambello water samples is profoundly affected by salinization as documented by the elevated values of Na (up to 1,228 mg/L), Cl (up to 2,256 mg/L), and EC (up to 9,140 μS/cm). The origin of salinization is related with seawater intrusion, as deduced by the spatial distribution of the saline samples (near coastline) and the absence of alternative salinization factors (e.g. evaporates, connate waters, etc). However, irrigation water return flow could probably enhance the recorded salinization but is not considered as the driving factor. In compliance with the above, the dominant water type is Na–Cl which is typical in saline environments of ongoing seawater intrusion [11], whilst some of the samples appear to have Ca–Cl water type which is related with ion-exchange hydrogeochemical processes where the abundant Ca originating from the dominant calcareous substrate replaces Na of seawater [11,12].

The comparison between the analytical results of the two sampling periods (wet and dry) reveals only

Table 1
Analytical results for the two sampling periods of the studied areas

Area		PEZ (*n* = 21)				MER (*n* = 40)				NIL (*n* = 36)			
Parameter	Units	Min	Max	Med	SD	Min	Max	Med	SD	Min	Max	Med	SD
pH	–	6.8	8.4	7.4	0.46	7.4	8.1	7.7	0.16	6.6	8.1	7.2	0.29
EC	μS/cm	763	2,840	1,007	927	525	9,140	2,295	2,246	193	1,706	801	491.4
K	mg/L	1	5	4	1,24	1	40	13	11.36	0	5	2	1.70
Na	mg/L	31	87	54	15.49	15	1,228	313	294.8	10	104	33	25.01
Ca	mg/L	47	700	156	220.9	53	166	93	23.51	24	233	139	41.57
Mg	mg/L	10	45	28	11.47	17	170	44	37.21	5	46	14	10.86
Cl	mg/L	57	143	91	24.25	28	2,256	579	556.3	15	293	40	48.75
HCO_3	mg/L	162	549	348	83.10	159	362	196	47.67	61	500	385	85.80
SO_4	mg/L	33	1,696	149	551	<20	430	116	86.20	<20	350	34	78.1
NO_3	mg/L	<1	63	4	17.9	3	21	5	4.65	1	54	13	14.37
NH_4	mg/L	0.08	0.99	0.22	0.29	<0.1	1.52	0.39	0.35	0.07	1.72	0.60	0.43
B	μg/L	<50	687	119	0.14	<50	620	176	0.14	<50	<50	<50	<50
Fe	μg/L	<5	2,039	15	449.1	<5	6,571	53	1,043	<5	629	22	173.3
Mn	μg/L	<2	108	12	32.32	<2	391	2	85.3	<2	944	7	179.1
Ni	μg/L	<3	59	17	19.16	<3	111	4	22.64	<3	26	6	5.69

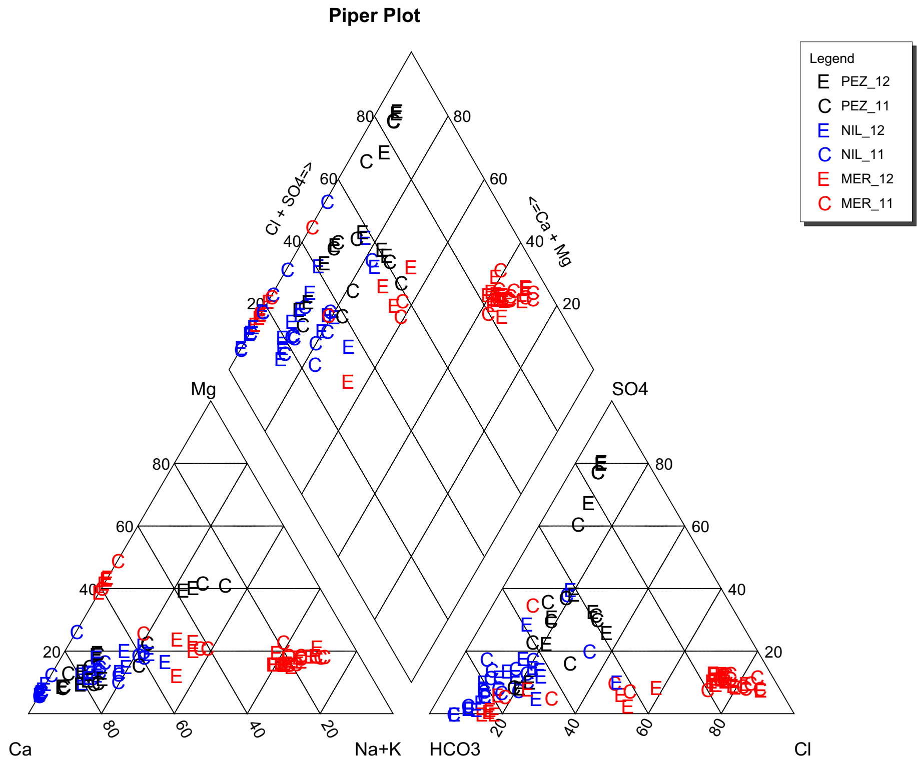

Fig. 2. Piper diagram for the studied water samples (values for 2011 and 2012).

minor differentiations regarding seawater related parameters; hence salinization is likely to be an established phenomenon which is invariable of any periodical influences. Nevertheless, sulfates do not appear in the expected (elevated) concentrations (median value is 116 mg/L) due to the intrusion of the marine environment; the latter phenomenon should be related with secondary redox processes that affect the concentrations of potential oxidants like SO_4. The presence of organic rich quaternary geological formations creates favorable conditions for oxygen depletion; thus sulfates are possibly reduced to H_2S and cannot be detected in significant concentrations, likewise reported in other Greek areas of similar geological environments [13,14].

Concerning the rest of the analyzed parameters, Ca exhibits slightly elevated values as a result of the aforementioned ion-exchange process and due to calcite dissolution which is in abundance in the karstic environment. Nitrates are practically absent (median value 5 mg/L), and their low concentrations are more likely attributed to the overall redox conditions of aquifer systems (reduced environment) which decreases the initial nitrate loads from the fertilization practices. In support of this, ammonium is enriched in water samples with a median value of 0.39 mg/L which is close to the maximum parametric limit for potable waters [15]. Ammonium is the typical nitrogen ion in reduced environments, so its concentrations are expected to be elevated when compared with NO_3. Finally, heavy metals concentrations are low with few exceptions for Mn (391 μg/L) and Ni (111 μg/L). The statistical population of these parameters reflects no systematic trend approach to the elevated values (e.g. due pollution) but possibly local conditions of geogenic impact.

In respect to Peza area, Ca values chiefly control the hydrogeochemical conditions (up to 700 mg/L) with prevalent water types Ca–HCO_3 and Ca–SO_4. Both types reflect calcium's dominance but refer to different enrichment processes. The former is related with calcite dissolution as a result of limestone's karstification whilst the latter is attributed to evaporitic minerals (e.g. gypsum $CaSO_4{\cdot}2H_20$) which are probably hosted in bedrock formations. In contrast with Merambello area no salinization phenomena occur; hence, EC values fall within the ordinary margins for natural waters [16] except some minor elevations probably related with local conditions of salt dissolution (e.g. halite and/or gypsum). Additionally for Peza area, nitrogen ions (NO_3 and NH_4) have low values denoting practically negligible impact from fertilization. Few exceptions of elevated values over 50 mg/L are related with local individual impacts of effluents in the form of point pollution sources (e.g. manure accumulation or septic tanks) that are noted in wells of small depth (and shallow aquifers) thus characterized by high vulnerability; this can be deduced by the simultaneous increase in NO_3, NH_4, and Cl concentrations which is indicative in similar cases of man-imposed impacts caused by effluents [6,17].

Finally, Nileas' samples are characterized by the strong influence of the karstic substrate which is reflected to the dominant water type of Ca–HCO_3 and the relevant elevated values of Ca (median value 139 mg/L). All parameters are within the margins of natural waters [16] except from NH_4 which are elevated (up to 1.72 mg/L) in some of the analyzed samples (compared with the remaining) and probably denote local influence of redox conditions and fertilization, since Cl concentrations are low thus excluding impact from manure or domestic wastes. Heavy metals concentrations are low, apart from some individual values (e.g. max for Mn 944 μg/L) attributed to the impact from Fe–Mn (hydro) oxides. Compared with the other examined areas, Nileas seems to have the best irrigation water quality.

A comparison of the statistical populations for EC and Na (Fig. 3), both considered as key factors of salinization, concludes that Merambello samples are by far more influenced, having greater median values and outliers (extremes) than the other areas; Peza area is significantly less influenced whilst Nileas exhibits negligible occurrence of saline waters. The origin of salinization in Peza seems to be different than in Merambello due to low Na values that indicate probably an effect from substrate salt dissolution and/or impact from reclaimed irrigation waters rather than seawater intrusion as in Merambello.

3.2. *Assessment of irrigation suitability of water and actions to mitigate identified environmental degradation factors*

The assessment of irrigation suitability identified salinization as the dominant environmental pressure, which characterizes mainly Merambello area and secondarily Peza. Other local factors of minor are the individual elevated concentrations of B (Peza, Merambello), Mn (Nileas), Ni (Peza), and Fe (Peza, Merambello). Despite the fact that some of the examined samples exhibit elevated concentrations of nitrogen compounds, these are not regarded as environmental threats for olive groves, since nitrogen excess may facilitate and supplement the total amount of applied fertilization; hence improving soil fertility and in turn crop yield, whilst directly reducing crop production cost by cutting down on applied fertilizers [17–20].

The quality of irrigation waters may potentially have adverse effects in several compartments, like surface and groundwater bodies, soil horizons, and olive trees. Based on Fig. 4, Nileas' samples are characterized by low sodium hazard (SAR) and medium to high (few samples) salinity hazard, thus classified to categories C_2–S_1 and C_3–S_1.

According to Table 2 that provides the potential yield reduction for olive crops due to irrigation water salinity [21], Nileas' irrigated fields are not expected to present any yield reduction since the maximum measured value of irrigation water EC is below 1,800 μS/cm. Soil salinization hazard from the use of irrigation waters is low, provided total volumes of received water (precipitation and irrigation) are sufficient, and soil drainage is good. In the few cases of saline soils, it is suggested to sustain soil humidity at high levels through frequent irrigation at small doses and salt leaching beyond natural drainage. Regarding plants' toxicity, irrigation water may have significant effects only in few cases (fields irrigated by water originated from three specific boreholes) where Na and Cl concentrations are elevated. Special attention should be given also to remoted cases where elevated concentrations of Mn occur.

Peza samples are characterized by low sodium hazard (SAR) and high (except one which is very high) salinity hazard, hence classified to categories C_3–S_1 and C_4–S_1. According to Table 2, the majority of Peza fields is not expected to experience yield reduction due to high salinity irrigation water (EC median is 1,007 μS/cm), whilst a few of them irrigated with water of EC over 2,600 μS/cm may suffer a yield reduction of 10%. Most of Peza irrigation water sources will not trigger any salinization effects to soils, except from very few cases. In those situations soils should be treated as previously proposed for the cases of Nileas' fields. As these waters may cause reduction of nutrients' assimilation by plants and lead up to 10% of crop reduction, it is suggested to blend them with waters of higher quality. Plants' toxicity is likewise Nileas' area focused only on few samples (one borehole and two wells) and regards elevated values of Na and Cl.

Finally, the majority of Merambello samples is characterized by medium to high sodium hazard (SAR) and very high salinity hazard, hence classified to categories C_4–S_2 and C_4–S_3 and a few of them as C_2–S_1, C_3–S_1, and C_3–S_2. According to Table 2 and based on the median value of EC, the majority of Merambello irrigated fields is expected to present a

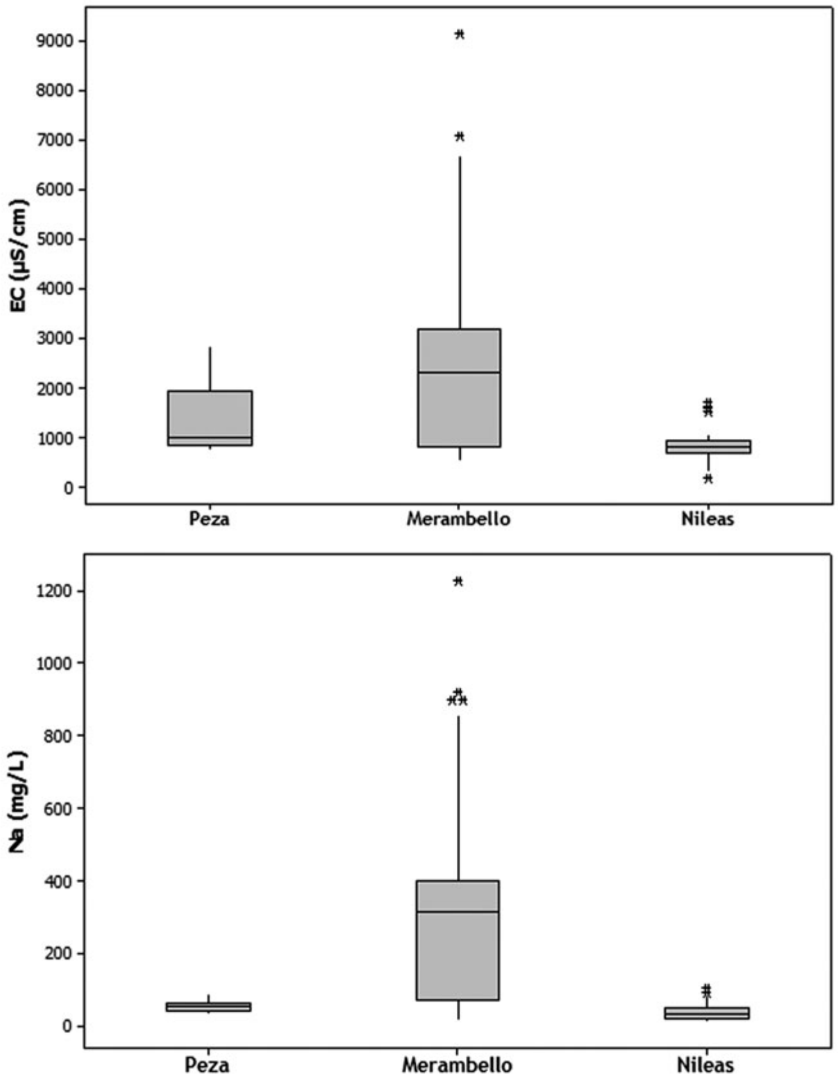

Fig. 3. Box plots of EC and Na with the addition of whiskers (lines) and outliers (dots) for the studied samples.

minor yield reduction up to 10%, whilst some of them (irrigated with waters of EC values over 5,600 μS/cm) may suffer from heavy yield reduction even more than 50% of the total yield potential. The soil salinization hazard in case of Merambello will be increased, if not adopting proper mitigation measures and actions. These may include as mentioned before, maintenance of high soil humidity conditions, salt leaching, good drainage conditions, and blending with waters of higher quality in appropriate ratios in order to achieve acceptable parameters. Failure to take appropriate actions could result in heavy reduction of crop production and soils' degradation that could eventually lead to desertification. Plants' toxicity is related to the elevated values of Na and Cl for the majority of the samples, while Fe and Mn concentration trends should be closely monitored.

3.3. Classification according to PoS index

The overall quality assessment of water samples was performed with the aid of Poseidon (PoS) index [22] which depicts the footprint of a water sample's environmental quality, as a result of its physic–chemical parameters (each of which may have the potential to cause adverse effects to humans and the natural systems) and their potential cumulative effect. It is an alternative approach for the assessment and characterization of water quality that allows temporal comparisons between different periods of time at the same

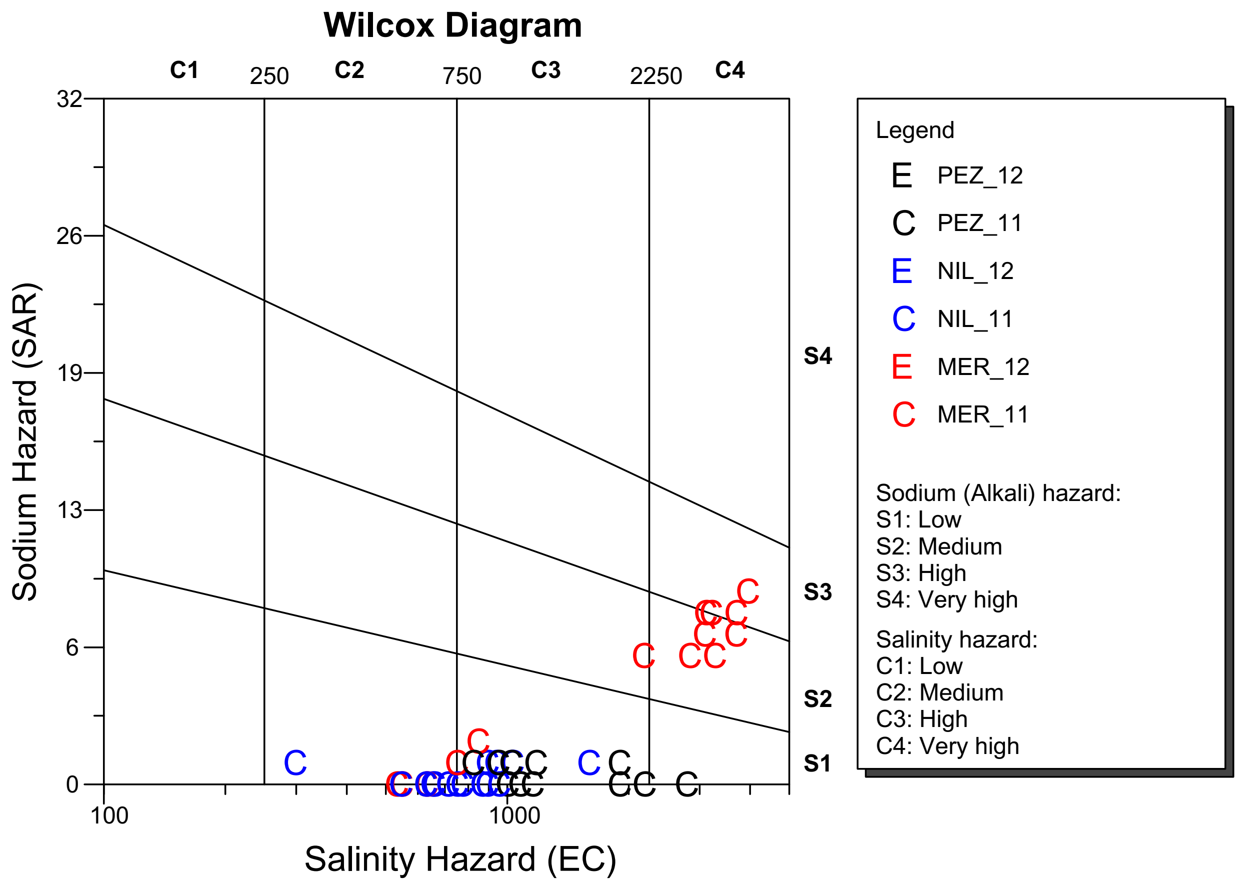

Fig. 4. Wilcox diagram for the studied water samples (values for 2011 and 2012).

Table 2
Irrigation water salinity tolerances for olive crops and estimated yield reduction (adapted from [21])

Yield potential	100%	90%	75%	50%
Irrigation water EC	1,800 μS/cm	2,600 μS/cm	3,700 μS/cm	5,600 μS/cm

basin, but also enables assessments between basins that are subject to different pressures and controlled by diverse mechanisms. Classification according to PoS index includes the initial sample characterization through a common ranking system of six classes referring to quality degradation level (Table 3).

The detailed description of PoS index may be found on relative literature (e.g. [22]). Below follows a brief description of the methodology. Initially, the 13 parameters (Ni, NH_4^+, NO_3^-, Mn, B, Ca, Cl^-, Fe, K, Na, Mg, SO_4^{2+}, and EC) which had concentrations above the detection limit were chosen for further processing. Subsequently, they were classified (Table 4) according to their toxicity and overall environmental adverse effects which is related with the "P-class", based on the original PoS method. The basis of their classification was found on the "Priority List of Hazardous

Table 3
Characterization of PoS index classes according to their quality degradation level

Class	Quality degradation level
1	None–minimum
2	Low
3	Medium
4	High
5	Very high
6	Severe

Substances" [23] but it was further modified so as to consider also additional aspects of water quality (e.g. ecosystem functioning).

In the next step, the influence of each parameter to the overall assessment of sample's quality is assigned by means of the individual quality contribution factors (Qf), calculated by Eq. (1):

$$Qf_i = \left[(C_i * W_i)/MAC_i\right] * 1{,}000 \quad (1)$$

where Qf_i: the quality contribution factor of i-th parameter; C_i: the concentration of i-th parameter (units according to the studied parameter); W_i: the weight factor of i-th parameter; MACi: the maximum parametric value of i-th parameter.

The weight factor, which is considered as critical in Eq. (1), reflects the magnitude of impact for each parameter in terms of human toxicity. It is based on previously mentioned "P-class" classifications following a trial-and-error approach in order to obtain the optimal results, which were verified in terms of environmental significance. The reliability of the final extracted weight factors was validated with multivariate techniques (item analysis) by calculating the Cronbach's alpha (a) which accounts for the internal consistency of the examined values.

The maximum admissible concentration (MAC) is introduced solely to normalize the concentration of a parameter against a well-established threshold or trigger value, and does not by any means relate the concluded water quality assessment to a particular use, nor does it create any dependency to use specific characterizations. The MAC values used in this case followed the thresholds imposed by the potable water directive [24].

The final step of PoS index calculation consists of summing up all the individual Qf factors (Eq. (2)). The derived score is a dimensionless number which may be used for the qualitative assessment of a sample.

$$PoS = \Sigma Qf \quad (2)$$

For the final evaluation, a reference water sample (R-sample) is assumed which reflects the mean typical concentrations of the focal parameters as expected in natural groundwaters [25], according to the original PoS method. Based on this, collected samples were classified accordingly into the categories of Table 3. According to the graphical visualization of PoS results (Fig. 5), Merambello (MER) area appears to have the lowest quality of irrigation waters with the majority of samples belonging to class 3 that corresponds to high quality degradation and in parallel the widest distribution of quality classes. Accordingly follows Peza area (PEZ) with the majority of samples belonging both to classes 2 and 3, which correspond to low–medium quality degradation. Finally, Nileas' (NIL) samples exhibit the best quality when compared with rest, with the majority of samples belonging to class 2 (low quality degradation).

Table 4
Characterization of PoS index classes according to their quality degradation level

Parameter	P-class	Toxicity characterization
As	VI	Severely toxic
Pb	V	Highly toxic
F	V	
NH_4^+	IV	Moderately toxic
NO_2^-	IV	
Cr tot	III	Non toxic
NO_3^-	III	
B	II	Non toxic
Ca	I	Non toxic
Cl^-	I	
Mg	I	
SO_4^{2+}	I	
EC	I	

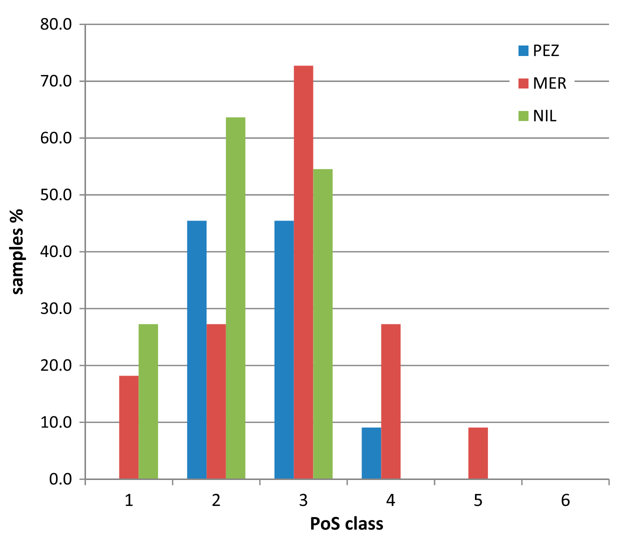

Fig. 5. Comparative classification of irrigation water samples according to PoS classes for the three study areas.

4. Conclusions

Surface and groundwater samples were collected from three key olive growing regions in Greece in order to assess their overall quality and outline major hydrogeochemical characteristics. Results identified salinization as the major environmental issue affecting mainly Merambello area and secondarily Peza. The magnitude of salinization differs between these areas, probably reflecting their different origin; Merambello suffers a more extended salinization of irrigation waters due to seawater intrusion related with aquifer overexploitation and hydrodynamic evolution, while Peza seems to be affected by natural salinization processes related with evaporitic mineral dissolution. Nileas, on the other hand, is characterized by irrigation waters of good quality and signs of deterioration were identified only in few individual cases.

Quality assessment with PoS index classified samples according to their quality degradation; Merambello samples appear to be of lower quality when compared with rest. The comparative study between surface and groundwater samples showed little differences as expected, due to the fact that artificial surface reservoirs are regularly fed by groundwater exploitation. Minor deviations were noticed to the redox sensitive elements of Fe and Mn that were significantly lower at surface waters as a result of the developed oxidizing conditions.

Despite the identified quality deterioration issues, examined water resources may be used for irrigation even in the more affected areas, provided appropriate measures are taken. These measures include but are not restricted to the reduction and control of soil salinization hazard through appropriate irrigation volumes applied, careful blending of saline with higher quality water, salt leaching in the form of frequent and small doses, maintenance of optimal soil humidity, and good soil drainage. Following these general guidelines, crop production is expected to sustain its optimal quality and quantity without any further impacts to the soil resources, the end product, and local economies.

Based on nominal irrigation needs and water quality of specific sources, considerable reduction in crop yields would be expected and also desertification phenomena should have been triggered, at least locally. However, such phenomena are spatially restricted and when they occur are of low intensity. Analysis of the reasons and conditions that have shaped the "paradox" of limited impacts despite the strong influences from deteriorated water resources, suggests that precipitation, insufficient irrigation due to water shortage and the soil texture play a crucial role in restricting the adverse effects of deteriorated irrigation water on crops and soil resources.

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