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The Impact of Wastewater Irrigation on the Vertical transfer of Metals in soils and to Plants

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Abstract

The irrigation with treated wastewater (TW) may affect the vertical mobility of chemical elements both in irrigated soils and crops. This study explores the opportunity of using of enrichment factors (EF), usually calculated to detect pollution levels, to assess the vertical transfers of elements in soils irrigated with TW. Soil samples have been collected along pedological profiles drilled in a field irrigated with treated wastewater for over 15 years and in control area. Olives and olive leaves samples were taken from trees grown near the soil pits. The contents of the major and metal elements were determined on plant and soil samples by AAS and ICP-MS, respectively. The Examining of EF evolution highlights anthropogenic inputs of Cu, Cr and Zn. These metals tend to accumulate mainly in the top layer of the irrigated soil. In the same way, the EF indicates that Cu and Cr have migrated to the top of the olive trees. Thus, the metal contents found in olives and leaves are statistically greater in the trees irrigated with treated wastewater than those not irrigated. Although the low concentrations of metals in the TW and in soils, long-term use of these waters for irrigation has affected the vertical metal mobility. The long-term risks of accumulation of potentially toxic metals (such as Cr) are emphasized by the EF calculation. This last can, in the same way, allow the assessment of risk of sodium transfer to the water table.

Keywords: Calcisol, enrichment factors, olive trees, arid region, El Hajeb-Sfax.

Introduction

The countries from the southern margin of the Mediterranean and especially in the Arab region are known for their semi-arid to arid climate and water scarcity. All of these countries fall below the level of renewable water shortage fixed to 500 m^3 per person per year[1] Therefore, it is crucial to turn to non-conventional water resources to meet the increasing demand for water, especially for irrigation of crops. Various options can be valued for irrigation in order to preserve good quality water for drinking, as the use of drainage water, water of marginal quality with high salinity or treated wastewater[2, 3].

The treated wastewater (TW) can be used for several purpose. Thus, irrigation in the suburbs of cities is the most interesting sector. Indeed, the TW have the advantage of being produced constantly and being already in the pipes at the wastewater treatment plant. This should encourage agricultural use in peri-urban areas located nearby these plants. However, irrigation with treated wastewater can affect the vertical distribution and mobility of potentially toxic elements in irrigated soils and crops. Although the low concentration of metals in TW, it is shown that irrigation may eventually lead to their accumulation in the irrigated soils[4]. Indeed, retention and mobility of metals in soil is governed by various phenomena mechanical, physicochemical and even biological[5]. Metals brought by the TW to the soil are not all in an available or bioavailable form. Their chemical form depends on the intrinsic soil conditions such as pH, Eh, organic matter, the rate of clays, CEC [6].... This is why it would be useful to develop methods and tools to evaluate locally if TW irrigation induces accumulation of metals in soil and crops. The enrichment factor (EF) has proven to be a relevant local and spatial indicator of anthropogenic contamination of soils[7,8]. In addition, some perennial plants such as olive trees are commonly irrigated with treated wastewater in the Mediterranean regions. The metals transfer from soils to the olive leaves may therefore be an indicator for monitoring the long-term, subject to the availability of reference values.

The objective of this study was to evaluate two simple methods based on analyzes of soil and plants: i. the calculation of enrichment factors (EF) of metals in soil, in relation to the deep soil horizon and ii. the calculation of the enrichment levels of irrigated olive trees. To meet this objective, two plots were compared: the first irrigated by treated wastewater for over 15 years and a second non-irrigated neighbouring plot. This study is a part of a research program which aims at evaluating the impact of wastewater application on both soil and crops properties in the arid region of Sfax[9-11]. The overall goals are to aid management of crop irrigation with wastewater, to reduce overexploitation of the local groundwater resources and to improve the water recharge of groundwater.

Material and methods

Site presentation: The study was performed at the irrigated perimeter of El Hajeb (Sfax), in the area of the Office of Public Lands (OTD). The study area is settled at ten kilometres in the West next to the sewage treatment plant (figure 1) near to the town of Sfax (approximately with one million of habitants) in crop fields, which are currently irrigated with treated wastewater. The region has an arid climate with monthly air temperature ranging from 11.3°C to 26.7°C, dry summer and annual rainfalls of 200 mm mostly occurring from October to December. The average annual potential evaporation of 1200 mm, combined with the low rainfall and high temperatures makes irrigation essential for crop production.

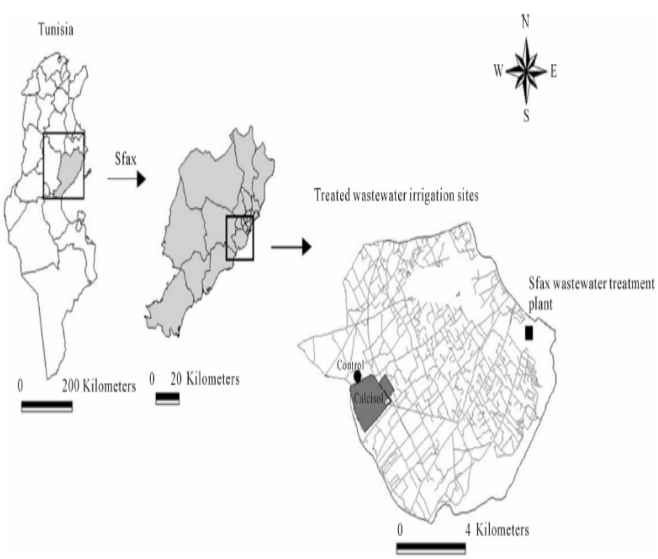

Figure-1
Map of studied area with location of the Sfax water treatment plant and of the calcisol site

The present survey has been carried out in the area of the irrigation perimeter that is covered by a calcisol[12]. This soil presents an isohumic character and shows a homogeneous sandy to sandy loam texture. At this soil, a concrete calcareous crust is present at depth of 60 cm. This crust of sedimentary origin is irregular and has been generally dismantled in the irrigated field in order to help infiltration of irrigation waters. The detailed description of soil profiles is given in Belaid et al[11].

The selected area produces alternate cycles of crops, in association with permanent harvesting of olives, with successive winter and summer harvest of annual crops (oat, sorghum). This kind of cropping system requires irrigation by open surface furrows distributed every 24 m in-between each row of olive trees. The soil has been submitted to wastewater irrigation for 15 years. In order to assess the effects of the wastewater, a nearby field is taken as a control area which produces only olives and has been preserved from any source of irrigation (figure 1)

The TW used for irrigation is characterized by an alkaline pH and a high salinity[10] varying between 3 and 5 gL^{-1}. This TW also contains residual organic pollution expressed in COD and high BOD5 generally exceeding the standards. However, this TW is rich in nutrients, especially phosphorus and nitrogen. However, these waters have a strong alkalizing power (SAR> 12). That's why a periodic monitoring should be ensured during the use of these waters to prevent the degradation of irrigated soils. The contents of metals are generally low with the exception of Cr sometimes exceeds standards[10].

Sampling and characterisation of soils and plants: Two pedological profiles were drilled in the control area (not irrigated) and in the field irrigated with the TW. These profiles were subsequently refreshed in order to identify the structures of different horizon of soil and their characteristics. After the description of the profiles, about 2 kg of soil of each horizon were collected in plastic bags. Sampling for olive has interested both leaves and fruits. Each sample corresponds to a mixture of samples taken within 4 olive trees surrounding soil sampling point.

After air-drying, the soil samples were sieved at 2 mm. The pH, soil organic matter (SOM) and $CaCO_3$ content were assessed using standard soil analysis methods[13]. For the soil pH measurements, a 1:2.5 soil:water suspension was prepared and left to stand overnight. The SOM was determined by performing the Walkley and Black dichromate oxidation method[14]. The reaction of carbonate with excess hydrochloric acid, so as to produce carbon dioxide, was used to ascertain the soil sample carbonate levels. The accuracy of this method was assessed with Analar grade calcium carbonate. Soil samples CEC were determined at actual soil pH by the cobaltihexamine method[15]. To determine the total contents of heavy metal and major elements in the soil samples, homogenised sub-samples were digested using HF–HNO_3–HCl. A procedure based on acid digestion induced by microwave energy was optimised in order to measure the total elemental contents in soils.
Plant samples were carefully cleaned with de-ionised water as to remove soil particles or dust adhering to the plant surface. All

samples were then oven-dried at 60 ◦C for 48 h to reach dry constant weights. The oven-dried plant tissues were ground by mortar into a fine powder and passed through a 0.5-mm sieve for chemical analysis. About 0.5 g of Tamisa was mineralized in a microwave digestion in the presence of 10 ml of nitric acid (65%) and 2 ml of H_2O_2. All samples were analyzed in three replicas that correspond to repetitions of analyzes and not for sampling repetitions.

The dosage of the major elements and metals (soil and plants) was carried out by atomic absorption spectrometry (AAS) and flame AAS.

Statistical analysis and EF calculations: The enrichment factor (EF) was used to evaluate the effect of irrigation with treated wastewater on the soil properties. This method makes it possible to visualize the variations of a chosen chemical element with depth, relative to a referenced geochemical element considered invariant in the local studied context. Thus, for a given x element corresponding enrichment factor is determined as follows:

$$EF(x) = [(X / i) / (X_0 / i_0)]$$

where i and io are invariant element concentrations, and X and Xo are concentrations of an element respectively in soil horizons and corresponding parent rock (reference horizon).

The determination of this factor is based on the choice of a chemical element reference considered invariant across the profile. During pedogenesis, several items can remain immobile (Sc, Ti, Zr ...) and therefore can be used as invariant element[16-18]. In the case of sediment, elements such as Al, Fe and Si can also be used as invariant elements[19-22]. In this study, Si is considered invariant element because in all the studied profiles (control and irrigated), the level of this element between two successive horizons, is not changed. While the calcareous crust was considered as a reference horizon and the parent material of the soil (C horizon).

Two methods for interpreting the EF values were compared. Profile of enrichment factor was used for the one hand, considering the distribution of chemical elements along the weathering profile. On the other hand, the effect of irrigation was observed by comparing the EF values of chemical elements between them, in each soil pedons.
To evaluate the effect of irrigation with treated wastewater on the enrichment of metallic elements in olive trees (leaves and olives), t-test[9] were performed using the Systat.6 software.

Results and Discussion

Physico-chemical characterization of soils: The studied soil has an alkaline pH which is almost invariable along the profile (table 1). By contrast, carbonate contents increase, from the surface to the lower horizon that corresponds to the partially dismantled calcareous crust (C horizon). The soil cation exchange capacity (CEC) is low and does not exceed the rate of 12% (table 1). In addition, there is a difference between the irrigated profile and the control one, particularly at the depth of organo-mineral horizons (A horizons). The levels of organic matter and total nitrogen are also low. However, values are higher in the irrigated soil than in the non irrigated one, which reveal the effect of irrigation with TW on the soil nutrients as already mentioned by Belaid et al[11].

Relative enhancements of major and metal elements: The determination of the enrichment factors (EF) allows to identify whether a chemical element in the soil is of natural origin or rather came from an anthropogenic source. Thus, if the EF of a given element is between 0.5 and 2, the element is supposed to be of natural origin. By contrast, EF value greater than 2 is likely to indicate an anthropogenic source[16, 19]. The advantage of this method is not only to identify exogenous inputs but also to identify the soil horizons at which chemical elements tend to accumulate, or conversely, to be mobilized, compared to a reference horizon. In this study, the C horizon (i.e. calcareous crust) was taken as the reference horizon. If the information provided by the calculation of EF is quantitative, the results are presented here in the form of vertical variations and used in relative values (qualitatively). Complementary quantitative results can be found in Belaid et al[11] in the form of is volumetric mass balance.

Figure 2 shows that all major elements have an EF< 2, thus excluding any anthropogenic input[16] (Both profiles control and irrigated) are comparable in terms of the leaching of Ca and Mg, revealing the dominant pedological process (leaching of carbonates). Similarly, the trends of Fe, Al and K are similar, reflecting the leaching of silicate minerals. At the control profile, except Ti and P showing enrichment in the third horizon (B horizon), all the major elements show losses compared to the calcareous crust (C horizon). On the contrary, at the irrigated Calcisol profile, there is a very high enrichment in P, lighter in Fe, Al, and K in the A horizon. Conversely, P is leached and Ti accumulates to a lesser extent in the B horizon compared to the control soil. Phosphorus enrichment factor reached a value of 2, indicating an anthropogenic effect. In quantitative terms, according to the of isovolumetric masses balance calculated by Belaid et al[11], the profile irrigated with treated wastewater accumulates P (gain= + 66 kg / m²) while the control profile shows a P loss comparable to that of magnesium (-15 kg / m²).

In addition, the loss of Na is greater in the irrigated soil while those of Ca and Mg are comparable with those in the control. In quantitative terms[11], isovolumetric mass balance shows a Na loss amounting to -23 kg / m² for irrigated profile compared to a loss of -6 kg / m² in the control profile.

Table-1
Main properties of irrigated and not irrigated (control) Calcisol profiles

Pedon	Horizon	depth (cm)	pH	CEC (cmol+/Kg)	$CaCO_3$ (%)	OM (%)	Nt (%)	C/N
Irrigated	A1	0-10	8.54	12.05	4.90	1.37	0.033	24.24
	A2	10-30	9.15	11.35	8.51	0.75	0.016	27.18
	B	30-50	8.56	12.45	24.80	0.53	0.010	31.00
	C	50-60	8.5	-	68.41	-	-	-
Not irrigated	A1	0-20	8.55	8.25	5.93	0.27	0.006	25.00
	A2	20-35	8.85	11.45	8.54	0.34	0.007	14.28
	B	35-50	8.83	12.45	11.70	0.42	0.010	25.00
	C	40-70	8.51	-	66.17	-	-	-

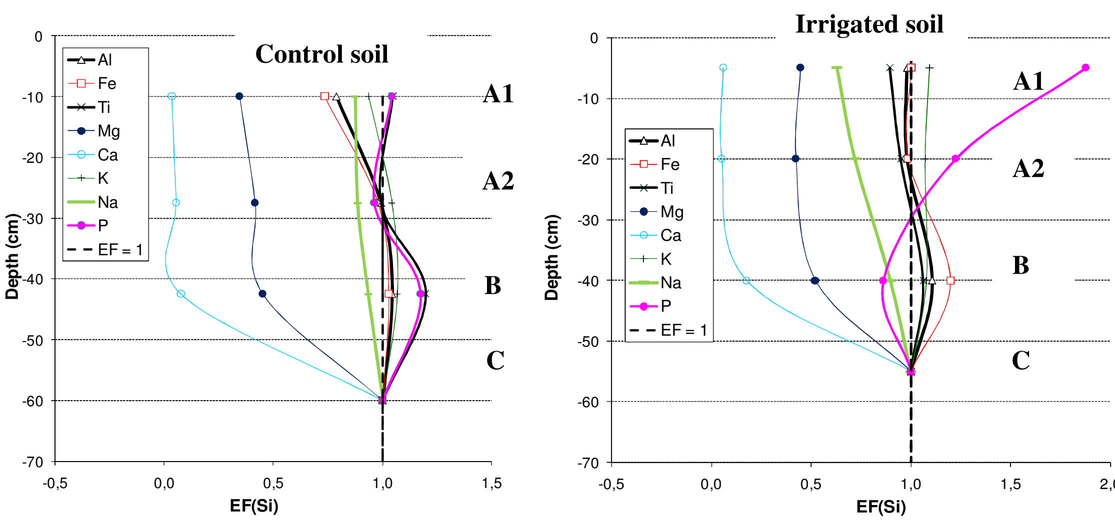

Figure-2
Variation of enrichment factors (Si invariant element) of major elements according to the depth in the two Calcisol profiles

Concerning metallic elements (figure-3), as shown for major elements, there is no enrichment (EF > 2) in the irrigated soil or in the control. At the control profile, all metal elements show relative losses at the top soil layer compared to the calcareous crust (C horizon) with the exception of zinc which remains almost invariant. However, in the irrigated profile, relative enrichments in Zn, Cu and Cr are observed at the surface and at 40 cm of depth (B horizon) for Zn and Cu only. In contrast, the other metallic elements show a loss, except nickel, accumulates relatively at the B horizon.

The interest of the analysis of EF variations with the depth is to allow the identification of chemical elements that tend to remain associated. This gives a prediction of the fate of elements if the association of metal with major element is translated into a mechanism[8]. Thus, after calculating homothetic factors between EF profiles for major elements (figure-4), it appears three main groups of elements in the non-irrigated control profile: i. Mg, K and Na which behave as Ca and reflect the dominant pedogenetic processes of decarbonation; ii. P and Ti which reflect the organo-mineral complexes influence which accumulate in the horizon B and iii. Fe and Al corresponding to minority alumina silicates in this calcisol profile. In the control profile, it is found that Ti follows Al and Fe and dissociates P. Similarly, Mg, K and Na dissociate Ca. Thus, it can be seen that the irrigation with TW leads to the enrichment in Ca of the B horizon, which is probably related to both leaching and exchange of Na ion brought by the TW.

As regards the metallic elements (figure-5), Pb generally follows the elements assigned to carbonates (i.e. Mg and Ca) in the control profile and mainly Mg in the irrigated profile. The other metals present homothetic follow trends. Thus, applying the same factors, it is possible to compare the two soil profiles. The irrigation with TW resulted in a relative enrichment in these metal elements in the A horizon but also in the B horizon for the most mobile elements (Ni, Cu). Lead, which follows the same pace as calcium and magnesium, reflects a natural origin, while Cr, Cu, Zn and Ni show paces closer to P reflecting an anthropogenic effect.

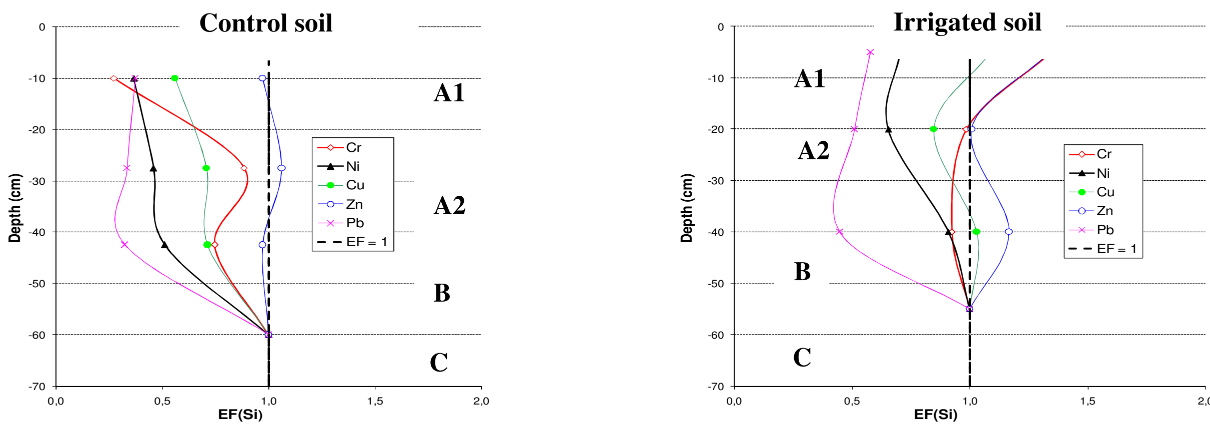

Figure-3
Variation of enrichment factors (Si invariant element) of metals according to the depth in the two Calcisol profiles

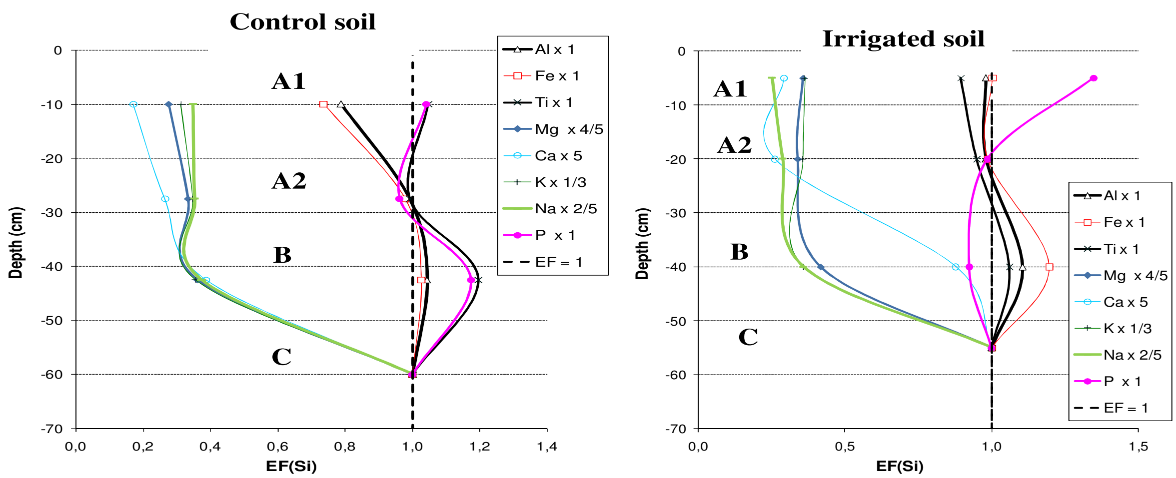

Figure-4
Variation of enrichment factors (with hemothetic factors calculation) of major elements according to the depth in the two Calcisol profiles

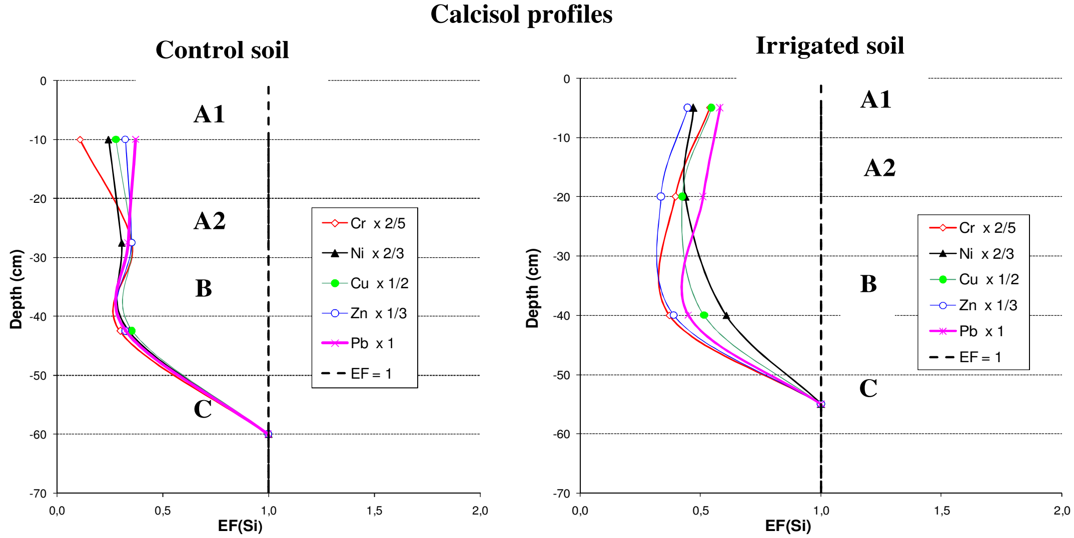

Figure-5
Variation of enrichment factors (with hemothetic factors calculation) of metals according to the depth in the two Calcisol profiles

This result is important because in terms of total contents, the accumulation tendency of Cr, Ni, Zn and Cu associated to irrigation with TW for over 15 years has not been demonstrated by the simple comparison of the total contents of elements in the topsoil (A1 horizon) between the irrigated and the control profile. Belaid et al[10] showed, through spatial analysis along the irrigation direction, that the accumulation of these metals associated to the TW irrigation was only visible on the top 5 cm of the soil horizon.

Transfer of metals to the olive trees: The olive trees, as perennials, can be used in long-term assessment, as indicator of the metal transfer from the soil irrigated with treated wastewater to the plants. The contents of Cr, Cu and Ni in the leaves of olive trees irrigated with treated wastewater are statistically higher than those found in the leaves of the non-irrigated control plants (table-2). However, this metal pollution continues its migration and tends to accumulate in the olives. Thus, it was found that the contents of Cu, Cr, Zn and Fe are more important in the olives irrigated with TW than those found in the non-irrigated olives (table-2).

The literature provides few values of metal transfer coefficients from soil to olives. Sappin-Didier et al[23] recently reported accumulations of Pb and Cd in the pulp of olives harvested near an old mine in Tunisia. Compared with other studies (Table 3), metals in the leaves of the olive trees (irrigated and control) lies within the range reported for background areas under Mediterranean conditions[24]. In another study, Belaid et al[10] have reported that the total metal contents measured in aerial parts and roots of forage crops (alfalfa and sorghum) irrigated with TW, lie in the mean average concentration ranges reported in plants for unpolluted sites[25].

Conclusion

The vertical distribution of metals in soils was examined by adopting two approaches, qualitative and quantitative one. On the qualitative level, it is difficult for the studied soil to distinguish the possible metals input by TW irrigation from natural geochemical background by the analysis of the enrichment factor profiles (EF). However, by searching homothetic relationships between elements, it was possible to suggest trends of accumulation of certain metals (Cr, Ni, Cu and Zn) on the surface of irrigated soil, in concordance with phosphorus intake found. However, the absolute values of the enrichment factors are less than one (EF<1) for all these metals. In perspective, it would be interesting to compare the homothetic factors identified in the composition of minerals holders of these metals, to verify that the EF profile can actually give a predictive reading of the evolution of the metallic elements in the soil profile.

Table-2
Effects of treated wastewater irrigation on the transfer of metals to the olive trees (T-test is significant for p <1%)

	Non irrigated olive trees (mg/Kg)	N	Irrigated olive trees means (mg/Kg)	SEM	One-sample T	T-test P (%)
Olive pulp						
Cu	4.90	10	7.25	0.0990	23.7019	0.0000*
Cr	0.01	10	0.15	0.0080	16.8377	0.0000*
Ni	0.13	10	0.08	0.0076	-6.9063	0.0035*
Zn	6.73	10	7.61	0.2580	3.4043	0.3910*
Fe	37.58	10	46.51	0.8588	10.3959	0.0001*
Olive leaves						
Cu	3.70	10	9.45	0.1429	40.2297	0.0000*
Cr	1.17	10	1.61	0.1141	3.8600	0.1923*
Ni	0.88	10	1.66	0.0824	9.4217	0.0003*
Zn	12.16	10	8.92	0.1691	-19.177	0.0000*
Fe	433.33	10	424.17	17.8588	-0.5131	31.0119

Table-3
Metals contents in olive leaves in irrigated and control soil compared to unpolluted soil (mg/Kg)

	Cr	Cu	Fe	Ni	Zn
Irrigated soil	1.61	9.45	424.2	1.65	8.92
Control soil	1.17	3.70	433.3	0.88	12.16
Unpolluted soil[a]	0.55 (0.19-2.04)	7.53 (3.37-19.9)	139 (89-315)	0.54 (0.1-1.15)	22.7 (10.4-30.5)

[a] Bargagli[24]: mean (range)

The quantitative study revealed the long-term effect of irrigation with treated wastewater on the transfer of metals to the olive trees. So, accumulations in some metals were found in the aerial parts of trees (leaves and olives pulp). Importance should be given to this, especially in relation to the pulp (= part consumed) or oil contamination. Thus, we suggest regular monitoring to prevent contamination of the food chain if ever the levels of some metals reached critical thresholds in olives.

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